Kinetic Studies of the Oxidation Pathways of Gaseous Elemental Mercury

Deanna L. Donohoue

University of Miami, ddonohoue@gi.alaska.edu

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KINETIC STUDIES OF THE OXIDATION PATHWAYS OF GASEOUS ELEMENTAL MERCURY

By

Deanna L. Donohoue

A DISSERTATION

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the requirements for the degree of
Doctor of Philosophy

KINETIC STUDIES OF THE OXIDATION PATHWAYS OF GASEOUS
ELEMENTAL MERCURY

Deanna L. Donohoue

Approved:

________________                    _________________
Dr. Anthony Hynes  Dr. Terri A. Scandura
Professor of Marine and  Dean of the Graduate School
Atmospheric Chemistry

________________                    _________________
Dr. Daniel D. Riemer  Dr. Jose Rodriguez
Research Assistant Professor of  Branch Head Atmospheric
Marine and Atmospheric Chemistry  Chemistry and Dynamics

________________
Dr. Matthew Landis
Senior Research Environmental
Health Scientist
US EPA Office of Research and
Development
Over the last decade our understanding of mercury cycling has dramatically changed. Evidence of rapid atmospheric oxidation has been observed in the Arctic, Antarctic, the MBL, coastal environments, saline lakes, and the upper troposphere/lower stratosphere. These results show that, $\text{Hg}^0$, can undergo rapid gas-phase oxidation under standard atmospheric conditions. However, the mechanism and importance of this transformation is still unclear. The goal of this work was two-fold: to investigate the kinetics of potential pathway for the gas phase oxidation of atmospheric mercury and to develop new laser based techniques, which can be employed for both laboratory and field studies of $\text{Hg}^0$ and the products of mercury oxidation.

First and foremost, this work determined kinetic rate coefficients for the potentially important mercury reactions. Rate coefficients were determined using a Pulse Laser Photolysis – Laser Induced Fluorescence (PLP-LIF) technique monitoring one or more of the following species, $\text{Hg}^0$, Cl, Br, HgCl, and HgBr. The concentrations of these species were measured by LIF as the reaction occurred and a concentration vs. time profile was generated. From these profiles a rate coefficient for the reaction can be obtained. In the course of this work kinetic rate coefficients for the following mercury reactions were measured.
\[ \text{Hg}^0 + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M} \]
\[ \text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \]
\[ \text{HgBr} + \text{M} \rightarrow \text{Hg}^0 + \text{Br} + \text{M} \]
\[ \text{HgBr} + \text{Br} \rightarrow \text{products} \]
\[ \text{HgCl} + \text{O}_2 \rightarrow \text{products} \]

This work is the first direct measurement of a kinetic rate coefficient for these reactions, and the first work which employed one photon LIF to monitor the HgCl and HgBr products.

The second aspect of this work was the development of new laser based techniques to detect atmospheric mercury and its oxidation products for both laboratory and field application. In this work a LIF technique was develop to detect HgCl and HgBr. In addition, a two photon LIF technique initially developed by Bauer et al., 2002 was verified and expanded. The two photon LIF technique was used to directly monitor Hg$^0$ atoms in-situ, to monitor Hg$^0$ evolving form a gold tube, and to monitor the Hg$^0$ evolving from the thermal decomposition of reactive gaseous mercury collected on a KCl coated or uncoated denuder. This work represents a significant advance in the development of a viable method the detect mercury and the mercury oxidation products in the laboratory and in the field and is the first study to observe clear differences in the characteristic desorption profiles of HgO and HgX$_2$.

This work has broad implications, it enhanced our current knowledge concerning the biogeochemical cycling of mercury, broadened our understanding of the mercury chemistry in high halogen environment, and provided new techniques which can be applied in future field and laboratory studies.
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Hg + BrCl $\rightarrow$ BrHgCl ................................................................. R1.51
Hg + BrO $\rightarrow$ BrHgO ................................................................. R1.52
Hg + ClO $\rightarrow$ ClHgO ................................................................. R1.53
Hg + O$_3$ $\rightarrow$ OOHand ............................................................. R1.54

CHAPTER II
A + B $\rightarrow$ AB* ............................................................................... R2.1
AB* $\rightarrow$ A + B ............................................................................... R2.2
AB* + M $\rightarrow$ AB + M ..................................................................... R2.3
B + B + M $\rightarrow$ B$_2$ + M ................................................................. R2.4
A + X $\rightarrow$ products ....................................................................... R2.5
B + X $\rightarrow$ products ....................................................................... R2.6
Cl$_2$ + h$_\nu$ $\rightarrow$ Cl + Cl ................................................................. R2.7
Br$_2$ + h$_\nu$ $\rightarrow$ Br + Br ................................................................. R2.8
CF$_3$Br + h$_\nu$ $\rightarrow$ CF$_3$ + Br ........................................................... R2.9

CHAPTER III
Cl + Cl + M $\rightarrow$ Cl$_2$ + M ............................................................. R3.1
Cl + O$_2$ + M $\leftrightarrow$ ClO$_2$ + M .................................................... R3.2
Cl + ClO$_2$ $\rightarrow$ Cl$_2$ + O$_2$ ............................................................ R3.3
Cl + C$_2$H$_6$ $\rightarrow$ C$_2$H$_5$ + HCl .................................................... R3.5
Hg + Cl $\rightarrow$ HgCl* ................................................................. R3.6
HgCl* $\rightarrow$ Hg + Cl ................................................................. R3.7
HgCl* + M $\rightarrow$ HgCl + M ............................................................. R3.8

CHAPTER IV
Br + Br + M $\rightarrow$ Br$_2$ + M ............................................................. R4.1
O$_3$ + X $\rightarrow$ products ................................................................. R4.2
Hg + X $\rightarrow$ products ................................................................. R4.3
Hg + Br $\rightarrow$ HgBr* ................................................................. R4.4
HgBr* $\rightarrow$ Hg + Br ................................................................. R4.5
HgBr* + M $\rightarrow$ HgBr + M ............................................................ R4.6

CHAPTER V
HgCl$_2$ + h$_\nu$ $\rightarrow$ Hg + 2 Cl .......................................................... R5.1
HgCl$_2$ + h$_\nu$ $\rightarrow$ HgCl + Cl ........................................................ R5.2
\[ \text{HgCl} + \text{Cl}_2 \rightarrow \text{products} \]  \hspace{1cm} \text{R5.3}

\[ \text{HgBr}_2 + \text{h} \nu \rightarrow \text{Hg} + 2 \text{Br} \]  \hspace{1cm} \text{R5.4}

\[ \text{HgBr}_2 + \text{h} \nu \rightarrow \text{HgBr} + \text{Br} \]  \hspace{1cm} \text{R5.5}

\[ \text{HgBr} + \text{Br}_2 \rightarrow \text{products} \]  \hspace{1cm} \text{R5.6}

\section*{CHAPTER VI}

\[ \text{HgBr} + \text{M} \rightarrow \text{Hg}^0 + \text{Br} + \text{M} \]  \hspace{1cm} \text{R6.1}

\[ \text{Br} + \text{CF}_3 \rightarrow \text{CF}_3\text{Br} \]  \hspace{1cm} \text{R6.2}

\[ \text{Br} \rightarrow \text{loss} \]  \hspace{1cm} \text{R6.3}

\[ \text{CF}_3 + \text{Br} \rightarrow \text{CF}_3\text{Br} \]  \hspace{1cm} \text{R6.4}

\[ \text{HgBr} + \text{HgBr} \rightarrow \text{products} \]  \hspace{1cm} \text{R6.5}

\[ \text{HgBr} + \text{Br}_2 \rightarrow \text{products} \]  \hspace{1cm} \text{R6.6}
CHAPTER I
Flux = \( V_d \times C_{\text{Air}} \) .................................................................E1.1

\[ V_d = R_d + R_b + R_c \] ..............................................................E1.2

\[ \text{slope} = \frac{\Delta \text{RMG}}{\Delta \text{Hg}^0} = \frac{\text{RMG}_{\text{obs}} - \text{RMG}_{\text{Bkgd}}}{\text{Hg}^0_{\text{obs}} - \text{Hg}^0_{\text{Bkgd}}} = \frac{\text{RMG}_{\text{obs}}}{\text{RMG}_{\text{obs}} - \text{MF}} \] ........................................E1.3

\[ \tau = k_{R1.14} + k_{R1.16}[\text{Br}] / k_{R1.10} k_{R1.16} [\text{Br}]^2 \] .....................................................E1.4

CHAPTER II

\[ k_{\text{obs}} = k[A]^y [B]^z [C]^v \] ..................................................E2.1

\[ k_{\text{obs}} = \frac{k_{R2.1} k_{R2.3} [M][A][B]}{k_{R2.2}} + \frac{k_{R2.1} k_{R2.3} [M][A][B]}{k_{R2.3} [M]} \] ........................................E2.2

\[ k_{\text{obs}} = \frac{k_{R2.1} k_{R2.3} [M][A][B]}{k_{R2.2}} \] ........................................E2.3

\[ k_{\text{obs}} = k_{R2.1} [A][B] \] .............................................................E2.4

\[ \frac{d[A]}{dt} = -k_{\text{obs}} ' [A] \] .....................................................E2.5

\[ \frac{d[A]}{dt} = -k_{\text{Hg}} [B][\text{Hg}][M] \] ..............................................E2.6

\[ \frac{d[B]}{dt} = -2 k_{R2.4} [B]^2 [M] \] ................................................E2.7

\[ \frac{1}{[B]} = 2 \times k_{R2.4} ' t + \frac{1}{[B]_0} \] ............................................E2.8

\[ \frac{d[\text{Hg}]}{dt} = -k_{\text{Hg}} ' [\text{Hg} \left( \frac{1}{2 k_{R2.4} ' t \times (1/[B]_0)} \right) \] ......................................................E2.9

\[ \ln \frac{[B]}{[B]_0} = \frac{k_{R2.6}}{k_{R2.5}} \ln \frac{[A]}{[A]_0} \] ............................................E2.10
\[
[X] = [X_{\text{prec}}}]*QY \left(1 - \exp \left(\frac{P_l}{h} \left(\frac{\sigma_{\text{prec}}}{A_l}\right)\right)\right)
\]

.................................................E2.11

CHAPTER III

\[
[\text{Cl}] = [\text{Cl}_2] * QY \left(1 - \exp \left(\frac{P_l}{h} \left(\frac{\sigma_{\text{Cl}_2}}{A_l}\right)\right)\right)
\]

.................................................E3.1

\[
\frac{d[Hg]}{dt} = -k_{R1.1} [\text{Cl}][Hg][M].
\]

.................................................E3.2

\[
\frac{d[\text{Cl}]}{dt} = -2k_{R3.1} [\text{Cl}]^2 [M] - k_{R1.11} [\text{Cl}][Hg][M].
\]

.................................................E3.3

\[
\frac{d[\text{Cl}]}{dt} = -2k_{R3.1} [\text{Cl}]^2 [M].
\]

.................................................E3.4

\[
\frac{1}{[\text{Cl}]} = 2k_{R3.1} t + \frac{1}{[\text{Cl}]_0}
\]

.................................................E3.5

\[
\frac{d[Hg]}{dt} = -k_{R1.11} [Hg] \left(\frac{1}{2k_{R3.1} t + (1/[\text{Cl}]_0)}\right).
\]

.................................................E3.6

\[
k_{R1.11,N_2} (243 - 298K) = (2.2 \pm 0.5) \times 10^{-32} \exp \left[680 \pm 400 \left(\frac{1}{T} - \frac{1}{298}\right)\right].
\]

.................................................E3.7

\[
[\text{Cl}]_r = [\text{Cl}]_0 \times \exp^{-k't}.
\]

.................................................E3.8

\[
\frac{1}{[\text{Cl}]} = 2k_{R3.1} t + \frac{1}{[\text{Cl}]_0}.
\]

.................................................E3.9

\[
k_{R3.1,N_2} (243 - 298K) = (8.4 \pm 2.3) \times 10^{-33} \exp \left[850 \pm 470 \left(\frac{1}{T} - \frac{1}{298}\right)\right].
\]

.................................................E3.10

\[
[\text{Cl}]_r = [\text{Cl}]_0 \times \exp^{-k_{R3.1,N_2}t}.
\]

.................................................E3.11

CHAPTER IV

\[
[\text{Br}] = [\text{Br}_2] * QY \left(1 - \exp \left(\frac{P_l}{h} \left(\frac{\sigma_{\text{Br}_2}}{A_l}\right)\right)\right)
\]

.................................................E4.1
\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Br][Hg][M]. \quad \text{E4.2}
\]

\[
\frac{d[Br]}{dt} = -2k_{R4.1} [Br]^2 [M] - k_{R1.10} [Br][Hg][M]. \quad \text{E4.3}
\]

\[
\frac{d[Br]}{dt} = -2k_{R4.1} [Br]^2 [M]. \quad \text{E4.4}
\]

\[
\frac{1}{[Br]} = 2 \times k_{R4.1} \text{'t} + \frac{1}{[Br]_0}. \quad \text{E4.5}
\]

\[
\frac{d[Hg]}{dt} = -k_{R1.10} \text{'[Hg]} \left( \frac{1}{2k_{R4.1} \text{'t} + (1/[Br])} \right)^{(1.86 \pm 1.49)} \quad \text{E4.6}
\]

\[
k_{R1.10, N_2} (243 - 298K) = (1.46 \pm 0.34) \times 10^{-32} \times \left( \frac{T}{298} \right)^{(1.86 \pm 1.49)}. \quad \text{E4.7}
\]

\[
\frac{1}{[Br]} = 2 \times k_{R4.1} \text{'t} + \frac{1}{[Br]_0}. \quad \text{E4.8}
\]

\[
k_{2, N_2} (243 - 298K) = (4.31 \pm 0.21) \times 10^{-33} \times \left( \frac{T}{298} \right)^{(2.77 \pm 0.30)}. \quad \text{E4.9}
\]

\[
\frac{d[Br]}{dt} = k_{R4.1} [Br]^2 [M]. \quad \text{E4.10}
\]

\[
\frac{d[Br]}{dt} = -k_{R4.1} [Br]^2 [M]. \quad \text{E4.11}
\]

\section*{CHAPTER V}

\[
\frac{d[HgCl]}{dt} = -k_{R1.24 \text{'}} [HgCl]. \quad \text{E5.1}
\]

\[
k_{R1.24 \text{'}} = k_{R1.24} \times [O_2]. \quad \text{E5.2}
\]

\[
k_{1.24 N_2} = 2.7 \pm 0.6 \times 10^{-17} \text{ molecules}^{-1} \text{ cm}^3. \quad \text{E5.3}
\]

\[
k_{1.24 He} = 3.2 \pm 0.2 \times 10^{-17} \text{ molecules}^{-1} \text{ cm}^3. \quad \text{E5.4}
\]

xvi
CHAPTER VI

\[
\frac{d[Br]}{dt} = -k_{R1.2} [Br][CF_3] - k_{R1.10} [Br][Hg] - k_{R1.29} [HgBr][Br] + k_{R6.1} [HgBr]. \quad \text{E6.1}
\]

\[
\frac{d[HgBr]}{dt} = k_{R1.10} [Br][Hg] - k_{R1.29} [HgBr][Br] - k_{R6.1} [HgBr]. \quad \text{E6.2}
\]

\[
k_{R1.10.29} = (243 - 420K) = (1.49 \pm 0.12) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-1.76 \pm 0.5} \quad \text{E6.3}
\]

\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Br][Hg] + k_{R6.1} [HgBr]. \quad \text{E6.4}
\]

\[
[HgBr] = \frac{k_{R1.10} [Br][Hg]}{k_{R6.1} + k_{R1.29} [Br]}. \quad \text{E6.5}
\]

\[
\tau_{Hg} = \frac{k_{R6.1} + [Br]}{k_{R1.29} [Br]^2}. \quad \text{E6.6}
\]

\[
\tau_{Hg @ 260 K} = \frac{0.0128}{4.85 \times 10^{-10} + 1 \times 10^8} = 6.6 \text{ hours} \quad \text{E6.7}
\]

\[
\tau_{Hg @ 260 K} = \frac{0.0128}{4.85 \times 10^{-10} + 1 \times 10^7} = 7.9 \text{ days} \quad \text{E6.8}
\]

CHAPTER VII

LIF_{total} = LIF_{blank} + LIF_{inject}. \quad \text{E7.1}

LIF_{blank} = Hg_{blank} \times X_{LIF}. \quad \text{E7.2}

LIF_{inject} = Hg_{inject} \times X_{LIF}. \quad \text{E7.3}

X_{LIF} = \frac{LIF_{total} - LIF_{blank}}{Hg_{inject}}. \quad \text{E7.4}
\[
\text{% Hg} = \frac{\text{Hg}_{\text{step}}}{\text{Hg}_{\text{total}}} \times 100 
\]

\[
\text{Hg}_{\text{Norm}} = \frac{\text{Hg}_{\text{measured}}}{\text{Hg}_{\text{total}}} (\text{pg Hg}^\circ) 
\]
CHAPTER I
INTRODUCTION

(1.1) Mercury as a Global Pollutant

Mercury is a known neurotoxin. Over the last decade, concern over mercury pollution has surfaced as a growing international issue. One reason for the emergence of mercury pollution onto the international arena is the recognition of mercury as a global pollutant that affects all countries and global commons (Selin, 2005). Traditionally, it was asserted that the unique physical properties of mercury result in a long atmospheric lifetime, on the order of a year. However, evidence of unexpectedly high levels of mercury in the Arctic (Lindberg et al., 2002; Lu et al., 2001; Schroeder et al., 1998; Steffen et al., 2002), the Antarctic (Ebinghaus et al., 2002; Sprovieri et al., 2002; Temme et al., 2003), the marine boundary layer (MBL) (Laurier and Mason, 2007; Laurier et al., 2003; Malcolm et al., 2003; Mason, 2005; Peleg et al., 2007; Sprovieri et al., 2003; Weiss-Penzias et al., 2003), and in the upper troposphere/lower stratosphere (Landis et al., 2005; Murphy et al., 2006a; Murphy et al., 2006b; Murphy et al., 2003; Swartzendruber et al., 2006; Weiss-Penzias et al., 2007; Weiss-Penzias et al., 2006) has lead scientists to re-evaluate this previous understanding of mercury biogeochemistry. Many of these locations are considered “clean” environments, with no known local or regional sources and no known physical or chemical processes can produce the observed mercury distributions. This shifted our understanding of mercury cycle, as now it must include an unknown mechanism where by elemental mercury (Hg⁰) is rapidly oxidized.
(1.2)  Speciation and Distribution

To better understand how this discovery significantly changed the framework of the biogeochemical cycling of mercury, the specific properties of each mercury species must be considered. Mercury exists in three oxidation states: elemental (Hg$^{0}$), divalent (Hg(II)), and monovalent (Hg(I)). The monovalent species is unstable and believed to undergo rapid oxidation or reduction to one of the two primary species, Hg(II) or Hg$^{0}$; hence, Hg(I) is not a major atmospheric mercury species.

Hg$^{0}$, the most abundant atmospheric species (>95%), is relatively unreactive, insoluble in water, and has a low deposition rate. This low solubility and reactivity account for the long atmospheric lifetime, estimated at 6 months to one year (Lin and Pehkonen, 1999), resulting in a global background concentration for Hg$^{0}$ of 1-4 ng m$^{-3}$ (Lin and Pehkonen, 1999). There must be a distinction between Hg$^{0}$, gaseous elemental mercury (GEM), and total gaseous mercury (TGM). Hg$^{0}$ and GEM refer to only gas phase mercury in the elemental form and are interchangeable terms. TGM is an operationally defined term that refers to all mercury, which collects on gold tube during a sampling period. If sampling is performed without removing oxidized mercury species before gold tube sampling, some of the oxidize species may be collected on the gold tube resulting in an over-estimate of Hg$^{0}$. Therefore, TGM is equal to Hg$^{0}$ + a portion of Hg(II) compounds. As Hg(II) usually account for only 3% TGM (Lin and Pehkonen, 1999), [TGM] is often employed as a proxy for [Hg$^{0}$].

Hg(II) compounds are readily soluble in water and have a short atmospheric lifetime, minutes to weeks, due to rapid wet and dry deposition (Mason and Sheu, 2002). These Hg(II) compounds tend to have deposition velocity in the range of 1 - 5 cm s$^{-1}$
(Malcolm et al., 2003). As this is a rapid deposition velocity, Hg(II) compounds tend to deposit within 100 km of the production source depending on the meteorology and height of the source (Schroeder and Munthe, 1998). Hg(II) is often referred to as reactive gaseous mercury (RGM). However, RGM is an operational defined term that includes all mercury species that collect on a KCl denuder, are observed using a refluxing mist chamber/mist chamber, or collected on ion exchange membranes. RGM is also considered water soluble because all Hg(II) species are significantly more soluble than Hg\(^0\). It is important to note that while RGM is used as a proxy for Hg(II), RGM and Hg(II) species are not interchangeable terms.

Mercury can be incorporated into particles producing particulate-phase mercury (Hg\(_P\)), which usually accounts for 0.3 to 0.9% of mercury in the unpolluted air, but can increase to 40% near production sources (Lin and Pehkonen, 1999). As in the case of Hg(II), Hg\(_P\) is easily removed from the gases phase by wet and dry deposition. The lifetime of Hg\(_P\) in the range of minutes to weeks and is highly dependent on the size distribution (Mason and Sheu, 2002).

The primary method of distributing mercury globally is via atmospheric processes (Schroeder and Munthe, 1998), understanding the gas-phase chemistry of mercury is essential to evaluating the effects of mercury on human health and the environment on a global scale.

(1.3) **Toxicity**

In its oxidized form, mercury is a “class C” hazardous chemical, a possible human carcinogen. It acts as a neurotoxin, which can cross the blood/brain barrier and penetrate
into the placenta. The health effects of exposure can include abdominal pain, excessive salivation and thirst, diarrhea, kidney damage, vomiting, ataxia, anuria and headache. The primary health effect is damage to the central nervous system, via reactions of mercury atoms with sulfur atoms present in brain proteins, resulting in reduced brain function (Jitaru and Adams, 2004). Human exposure to mercury is primarily through ingestion of methylmercury. Methylmercury is highly toxic as a result of its increased lipophilic nature due to the addition of an organic methyl group.

The source of methylmercury in food begins with the deposition of inorganic mercury into aquatic and terrestrial environments (Orihel et al., 2007). Through a series of biotic and/or abiotic transformations, inorganic mercury can be transformed into highly lipophilic methylmercury. As mentioned previously, methylmercury is easily absorbed into the tissues of an organism, where it is retained in the fatty tissues. This means that methylmercury present in a prey organism will be transferred to a predator's fatty tissue and hence propagate through the food web (Morel et al., 1998). This cumulative effect is termed biomagnification. Large predators can have mercury levels, which are $10^6$ times greater than the concentrations found in lower level taxa (Schroeder and Munthe, 1998).

Methylmercury can act as an acute or cumulative toxin. The most widely publicized incident of mass mercury poisoning occurred in 1953, following the dumping of tons of mercury-enriched chemical wastes from a plastics processing plant in Minamata Bay, Japan. The local waters were poisoned, directly leading to increased mercury levels in the fish within the bay. Over the next decade, thousands of people were poisoned, some fatally, from eating the contaminated fish (Olmez and Ames, 1997).
Another incident, in Iraq, in 1971 resulted from the ingestion of bread made from seed grain that had been treated with a mercuric fungicide and was not for human consumption. The consumption of this seed grain resulted in the death of over 600 people and the poisoning of many more (Clarkson, 1997). From these and other incidents, mercury is recognized as a major public health issue, and needs both regulation and research in order to truly understand the best way to prevent additional disasters.

Both of these examples were acute exposure events, however over the last decades an increasing amount of evidence for cumulative chronic exposure events has been recorded. The most dramatic of these is the exposure in the Arctic region. Observations of increased mercury levels have been documented in Arctic lake waters (Lockhart et al., 1998), Arctic animal populations (Wagemann et al., 1996), and Arctic indigenous human populations (Wheatley and Wheatley, 2000). The alarming rise in mercury levels for top level predators, such as seal, whales and humans, has catalyzed mercury science forcing the scientific community to re-evaluate the current understanding of the biogeochemical cycling of mercury.

(1.4) Biogeochemical Cycling of Mercury

(1.4.1) Sources

The biogeochemical cycle of mercury involves complex interactions of chemical, biological and geological forces, figure 1.1. Inputs into the atmosphere have tripled since pre-industrial times (Shotyk et al., 2003). The sources of mercury range from episodic natural injections to long-term anthropogenic releases. Natural sources of mercury to the atmosphere include the outgasing from mantle and crustal material, release from wind
blown dust, and evasion from surface soils, water bodies, and vegetation. More episodic natural sources include volcanic eruptions and other geothermal sources as well as wildfires, although wildfires emissions have been enhanced by anthropogenic mercury sources. Anthropogenic sources include fossil fuel combustion, waste incineration, biomass burning, and the release of mercury from industrial applications such as fluorescent light bulbs, fungicides, pesticides, paints, batteries and catalysts. Additionally, metal mining and smelting, as well as chlor-alkali plants can be sources of atmospheric mercury (Schroeder and Munthe, 1998). Global mercury emissions estimates for 1995 are included in table 1.1.

Figure 1.1: The biogeochemical cycling of mercury adapted from (Schroeder, 2004).
Table 1.1: Anthropogenic emissions of mercury in 1995 adapted from Pacyna and Pacyna, 2002.

<table>
<thead>
<tr>
<th>Continent</th>
<th>Stationary Fossil Fuel Combustion</th>
<th>Non-ferrous Metal Production</th>
<th>Pig Iron and Steel Production</th>
<th>Cement Production</th>
<th>Waste Disposal</th>
<th>TOTAL</th>
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<tbody>
<tr>
<td></td>
<td>Error: ± 25%</td>
<td>Error: ± 30%</td>
<td>Error: ± 30%</td>
<td>Error: Up to 5x</td>
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<td>Elemental Hg(^e) (Mg Hg/year)</td>
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<td>1.1</td>
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<td>0.2</td>
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<td>---</td>
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<tr>
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<td>6.4</td>
<td>22.2</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Europe</td>
<td>185.5</td>
<td></td>
<td>10.2</td>
<td>26.2</td>
<td>12.4</td>
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<td>5.2</td>
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<tr>
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<td>81.8</td>
<td>32.6</td>
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<tr>
<td>North America</td>
<td>104.8</td>
<td></td>
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<td>12.9</td>
<td>66.1</td>
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<td>5.5</td>
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<tr>
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<td>29.1</td>
<td>132.4</td>
<td>111.2</td>
<td>1912.8</td>
</tr>
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</table>
Emissions are divided into categories based on emission processes, location of emission, and speciation of emitted mercury. From this estimate, it is obvious that fossil fuel combustion sources, i.e. gas, coal, and oil combustion, are the primary source of mercury into the atmosphere, accounting for 77% of anthropogenic emissions in 1995. This is a dramatic shift in source strength. Before the 1970’s the strongest anthropogenic source of mercury was attributed to emissions from chlor-alkali plants; however, increased regulations have dramatically reduced the overall number of plants and the emissions from active plants. Concurrently, global emissions from fossil fuel combustion have increased over the last three decades and are likely to continue to increase in the future. An example of this increase is can be seen in mercury emissions from Asia. China and India are the fastest growing sources of atmospheric mercury in the world. Overall, these emissions accounted for 56% of anthropogenic emissions in 1995, 80% of which are attributed to combustion sources. This means that 45% of global emissions can be attributed to fossil fuel combustion in Asia.

The emission study of Pacyna et al. did not consider the mercury emitted from artisanal gold mining. The reason for this exclusion was that the emission estimates from this source are highly variable and speculative. However, a rough calculation places this source at 325 Mg of mercury per year (Pacyna and Pacyna, 2002), increasing the global mercury inventory for 1995 to 2238 Mg mercury, in this scenario emissions from artisanal gold mining account for 15% of the total anthropogenic emissions. The Pacyna et al. study also classified mercury emissions according to mercury species, \( \text{Hg}^0 \), \( \text{Hg}^{\text{II}} \), and \( \text{Hg}_p \). Overall 53% of global mercury emissions are in the elemental form, \( \text{Hg}^0 \), 37% in the divalent form, \( \text{Hg}^{\text{II}} \), and 10% in the particulate phase \( \text{Hg}_p \).
Biogenic sources are also significant sources of mercury into the atmosphere. Natural emissions play an essential role in the biogeochemical cycling of mercury. Table 1.2 presents a series of recent global flux estimates for both mercury emission and deposition processes. Despite the significant variation observed between all studies, it is evident that emission from “natural” sources are estimated to be in the same range as direct anthropogenic emissions, with the relative source strength between ocean and land based emission ranging from 1:2 to 3:1. New studies using isotopically labeled mercury species may provide some insight into the relative source strengths in the future.

Table 1.2:  Emission and Deposition fluxes from various studies adapted from Mason and Sheu, 2002.

<table>
<thead>
<tr>
<th>Type</th>
<th>Mason et al., 1994</th>
<th>Bergan et al., 1999</th>
<th>Shia et al., 1999</th>
<th>Lamborg et al., 2002</th>
<th>Mason and Sheu, 2002</th>
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<tr>
<td>Land</td>
<td>1003</td>
<td>501</td>
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<tr>
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<td>602</td>
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<td>2006</td>
<td>802</td>
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</tr>
<tr>
<td>Total</td>
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<tr>
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<td>---</td>
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<td>---</td>
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<tr>
<td>Deposition to Ocean</td>
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<tr>
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<td>---</td>
<td>---</td>
<td>1926</td>
</tr>
<tr>
<td>Dry</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1163</td>
</tr>
<tr>
<td>Total</td>
<td>2006</td>
<td>---</td>
<td>2006</td>
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<tr>
<td>Deposition to Land</td>
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<td>---</td>
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<td>Total Dep (Land+</td>
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<td></td>
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<td></td>
</tr>
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<td>---</td>
<td>3932</td>
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<td>---</td>
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<td>---</td>
<td>2106</td>
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<tr>
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<td>4212</td>
<td>6619</td>
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<td>6178</td>
<td>4413</td>
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<tr>
<td>Total Sinks</td>
<td>7021</td>
<td>---</td>
<td>6178</td>
<td>4212</td>
<td>6619</td>
</tr>
</tbody>
</table>
(1.4.2) **Sinks**

After mercury is released into the atmosphere, it can be deposited on land or in water bodies by wet or dry deposition. Mercury deposition is difficult to characterize as it is highly variable and direct measurements are problematic. Despite these difficulties, extensive efforts have been made to measure and model the deposition of mercury. Mercury deposition occurs as dry deposition, the direct transport of a species to the earth’s surface, or wet deposition, the uptake of a soluble species into a water droplet or ice crystal.

(1.4.2a) **Wet Deposition**

Wet deposition is a major sink for mercury species in the environment. During wet deposition a molecule/particle can be incorporated into cloud droplets during formation, in-cloud scavenging, or it can be scavenged as the precipitation droplet falls through the atmosphere. In general, a precipitation drop is assumed to be in equilibrium between the phases using Henry’s Law coefficients. Hence, a more soluble species, such as the oxidized mercury species, will be more effected by wet deposition process than a less soluble species, such as Hg\(_0\).

In addition, wet deposition is rather episodic as it can occur only during precipitation events. This results in an uneven distribution of the effects of wet deposition, i.e. wet deposition is of higher significance in a region with higher precipitation. The episodic nature of wet deposition, results in pulses of mercury being input into the ecosystem rather than a constant deposition rate. Both in-situ measurements and Model studies have shown that RGM and Hg\(_P\) will build in the atmosphere until a
precipitation event and then be almost completely washed-out by wet deposition. Figure 1.2 is a map of the wet deposition pattern observed in the United States from the National Atmospheric Deposition Program Mercury Deposition Network. Notice that the largest wet deposition fluxes occur in areas of high precipitation.

**Figure 1.2:** Wet Deposition Patterns for the continental US from the National Atmospheric Deposition Program Mercury Deposition Network.

(1.4.2b) **Dry Deposition**

Dry deposition is a difficult parameter to quantify in the biogeochemical cycling of mercury, although recent advances have been made (Lyman et al., 2007). The difficulty in quantifying dry deposition rates is due to the simultaneous emission of mercury from surfaces and the slow response time of mercury detectors. In general, the loss rate of a species due to dry deposition is expressed as a flux, \( E_{1.1} \),

\[
\text{Flux} = V_d \times C_{\text{Air}} \tag{E1.1}
\]
where $V_d$ is the deposition velocity and $C_{Air}$ is the concentration of the species in air. The deposition velocity is in fact the sum of all the resistances that influence the molecule/particle or surface. The sum of these resistances results in the following expression, E1.2, where $R_a$ is the aerodynamic resistance, $R_b$ is the quasi-laminar sub-layer resistance, and $R_c$ is the total surface resistance of the gas.

$$V_d = R_a + R_b + R_c \quad \text{(E1.2)}$$

$R_c$ is highly variable and depends on the deposition surface. This variability makes it difficult to apply a deposition rate under one set of condition to another environment or set of conditions. The dry deposition rates have been estimated for all mercury species; $\text{Hg}^0 = 0.06 \text{ cm s}^{-1}$ (Seigneur et al., 2004), RGM ranges from 0.1 to 7.6 cm s$^{-1}$ (Lindberg and Stratton, 1998; Poissant et al., 2004; Rea et al., 2000), $\text{Hg}_p$ deposition will depend primarily on size distributions and as mercury tend to be in the fine mode ($<2.5 \mu m$) deposition velocities should be in the range of 0.1 to 1.0 cm s$^{-1}$ (Keeler et al., 1995; Zhang et al., 2001).

(1.4.3) \quad \textbf{Recycling}

Understanding the relationship between natural and anthropogenic sources of mercury is wrought with challenges. The most significant of these challenges is the recycling of mercury. Due to its volatility once emitted from a source, natural or anthropogenic, mercury species are transported and then deposited. Once deposited, a large fraction of this mercury can be re-emitted as $\text{Hg}^0$ into the atmosphere. This cycle of emission, deposition, volatilization and re-deposition makes determining the anthropogenic contribution of current mercury cycle difficult to define. To elucidate the
cumulative anthropogenic component of mercury emissions, both the direct emission and re-emission must be considered. Direct anthropogenic emissions include all the mercury emissions from anthropogenic sources. Indirect emission or the anthropogenic component of re-emission must be separated from the natural component of re-emission.

The studies outlined in table 1.2 aimed at distinguishing the natural and anthropogenic component of re-emission. Each study employs a slightly different technique; however all techniques can be generalized as follows. Direct anthropogenic sources were calculated from emission inventories. Most studies extrapolated available experimentally determined flux measurements, but in some cases the fluxes themselves are determined by mass balance constraints. In Mason et al. (Mason and Sheu, 2002), all fluxes were taken from within the error limits of the measured fluxes using an overall mass balance to further constrain each flux. As each flux has large errors, the resulting mass balance should be considered in terms of relative strength rather than an absolute value for each flux.

This data can be used to assess the relative source strengths of the three types of mercury sources: direct anthropogenic, natural, and re-emission, and further distinguish the anthropogenic component of re-emission sources. Mason et al. (Mason and Sheu, 2002) made estimates of both the current and pre-industrial biogeochemical mercury cycle. Figure 1.3 is an illustration adapted from Selin et al. (Selin, 2005), which includes both estimates. By assuming that the pre-industrial emission sources are equivalent to the natural emissions component of the current mercury cycle, the remainder can be attributed to enhancement of these natural processes due to human activity. Therefore, the contribution from natural cycling and anthropogenic enhancement are approximately
equivalent at \( \sim 2000 \text{ Mg yr}^{-1} \). The direct anthropogenic contribution is also on the same order of magnitude as these two sources. Therefore, anthropogenic emissions, direct and indirect, account for \( \sim 70\% \) of total mercury emissions.

![Figure 1.3: Global Budget estimates for industrial and pre-industrial regimes (Figure adapted from (Selin, 2005), Budget data from (Mason and Sheu, 2002)).](image)

To understand the effects of the large input of mercury from anthropogenic sources on the overall biogeochemical cycle of mercury, all processes that impact the speciation of mercury must be considered. As atmospheric processes are the primary method of distributing mercury, understanding the atmospheric transformations of mercury is essential. The focus of this work will be to elucidate these atmospheric transformations and evaluate their implications.

(1.5) Field Studies

In 1998, our understanding of atmospheric mercury oxidation was challenged by new observations in the Arctic. Schroeder et al. (Schroeder et al., 1998) measured 6 hr averages of both surface-level [TGM] and [O\(_3\)] from January 1995 to December 1995. This data revealed that for the three month period following polar sunrise there were
frequent episodic depletions of TGM from the atmosphere. These episodes were strongly correlated with tropospheric ozone depletion events. During these events [TGM] would drop from background levels of 1 – 2 ng m\(^{-3}\) to below the detection limit of 0.1 ng m\(^{-3}\), while [O\(_3\)] would drop from 30-50 ppb to below 10 ppb. Schroeder et al. concluded that an unidentified chemical oxidation converted Hg\(^0\) to a mercury species with shorter atmospheric lifetime. In order to quantify how important these Atmospheric Mercury Depletion Events (AMDEs) are for mercury transfer to the biosphere, Schroeder estimated a flux due to AMDEs. Assuming that the boundary layer (500 ± 100 m) is emptied five times each spring and a mean background [Hg\(^0\)] is 1.84 ng m\(^{-3}\) and the calculated flux is 2.5 ± 0.5 ng m\(^{-2}\) hr\(^{-1}\). This flux is two times larger than the flux estimated for a site in northern Wisconsin. Schroeder concluded that AMDEs could be introducing high levels of mercury into the Arctic environment at a time when primary production is at peak. The Alert study also observed a peak in total particulate mercury (TPM) in the summer. Some of this TPM data was prone to error due to the collection of RGM on the quartz filter used to collect particulates. Thus the TPM measurement may, in fact, be the sum of TPM and a portion of RGM that collects on the filter. This peak in TPM or RGM might be indicative of a photolytic loss of mercury species from the snow. A loss of mercury from the snow would slightly offset any deposition due to Springtime AMDEs.

In a follow-up study Lu et al. (Lu et al., 2001) monitored Hg\(^0\) and TPM concentration in Alert, Canada and in Ny-Ålesund, Spitsbergen. Again their “TPM”, may have been prone to an RGM artifact. Once again AMDEs were observed in the spring after polar sunrise. In addition, their “TPM” concentration demonstrate a strong anti-
correlation to both O$_3$ and Hg$^0$ increasing from 0.002 ng m$^{-3}$ to 0.45 ng m$^{-3}$ in Alert and 0.002 ng m$^{-3}$ to 0.16 ng m$^{-3}$ in Ny-Ålesund. Lu et al. propose that this anti-correlation indicates that the product of the AMDE mechanism is particulate. As HgO tends to form particles, Lu et al. proposes HgO as the primary oxidation product. Assuming that HgO is the primary reaction product and recognizing the strong correlation of AMDE to tropospheric ozone depletion, BrO maybe the primary oxidant. Potential reaction pathways and their energetics will be discussed later in this work. However, as the TPM measured in this study contains a RGM artifact it is difficult to unambiguously identify the changing “TPM” as true particulate and not as a RGM artifact.

In Barrow, Alaska Lindberg et al. (Lindberg et al., 2002) began monitoring Hg$^0$ in September 1998 and RGM the following year, with full speciation beginning in 2001. A strong Hg$^0$/O$_3$ correlation was observed, figure 1.4. By evaluating the temporal profiles of the mercury species and evaluating the relationships between the species, mechanistic information can be inferred. For example, the fact that is little to no temporal offset between the formation of RGM and appearance of UV radiation indicates that the oxidation is likely occurring in the gas phase or on outer surfaces of aerosols, figure 1.5. This data is not in conflict with the Lu et al. data for two reasons. First, the “TPM” observed in the Lu et al. study was influenced by an RGM artifact, thus the identification of the Hg$^0$ as a mixed phase reaction is not definitive. Second, even if the oxidation occurs purely in the gas phase, the RGM formed will rapidly adhere to particles resulting in an increase TPM signal over time.
Figure 1.4: Trends in Hg\(^0\) and ozone in Barrow, Alaska during 1999 adapted from (Lindberg et al., 2002).

Figure 1.5: Temporal profiles of UV-B, Hg\(^0\), and RGM from Barrow March 17, 2000 adapted from (Lindberg et al., 2002).
In addition, Lindberg et al. evaluated the observed AMDEs to see if the Barrow data demonstrated a bromine oxide (BrO) correlation similar to that observed with O$_3$ depletion events. GOME satellite data of total column [BrO] were strongly anti-correlated with to [Hg$^0$] indicating significant AMDEs occur during high BrO periods. Lindberg et al. proposed the following reaction mechanism to account for the loss of both Hg$^0$ and O$_3$, and the instantaneous production of RGM.

$$\text{Br}/\text{Cl} + \text{O}_3 \rightarrow \text{BrO}/\text{ClO} + \text{O}_2$$  \hspace{1cm} (R1.1)

$$\text{BrO}/\text{ClO} + \text{Hg}^0 \rightarrow \text{HgO} + \text{Br}/\text{Cl}$$  \hspace{1cm} (R1.2)

$$\text{Br}/\text{Cl} + \text{Hg}^0 \rightarrow \text{HgBr}_2/\text{HgCl}_2$$  \hspace{1cm} (R1.3)

The source of the Br and Cl is the heterogeneous production of Br$_2$, Cl$_2$ and BrCl from sea salt. The sudden onset of depletion events at polar sunrise is due to the fact that the initiation reaction for the “bromine explosion” (Wennberg, 1999) in Polar Regions is photolytic. The sudden end of AMDEs can be attributed to the loss of the snow surface, because the heterogeneous production of halogen radical requires a frozen surface.

(1.5.1)  Additional Field Studies in the Polar Regions

Since that time, numerous additional observations of AMDEs have been observed in the Arctic and in the northern latitudes (Berg et al., 2003; Lu and Schroeder, 2004; Poissant et al., 2005; Skov et al., 2004; Steffen et al., 2002), as well as in Antarctic sites (Ebinghaus et al., 2002; Sprovieri et al., 2002; Temme et al., 2003). Table 1.3 includes each polar site, the species collected, the method of detection, and any resulting publications.
### Table 1.3: Mercury sampling sites in Polar Regions.

<table>
<thead>
<tr>
<th>Site</th>
<th>Long./Lat.</th>
<th>Date</th>
<th>Species</th>
<th>Methods</th>
<th>Reference</th>
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<td>Alert, Canada</td>
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<td>1995 – 2002</td>
<td>Hg&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Tekran 2537A • CRPU • AE-TPM Traps</td>
<td>Schroeder et al., 1998 Lu et al., 2001 Steffen et al., 2002</td>
</tr>
<tr>
<td>Barrow, Alaska</td>
<td>71°19’ N 156°37’ W</td>
<td>1999 – 2003</td>
<td>Hg&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Tekran 2537A • Tekran 1130 w/ KCl denuders</td>
<td>Lindberg et al., 2002 Landis, 2006</td>
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<td>Station Nord, Greenland</td>
<td>81°30’ N 16°40’ W</td>
<td>1998 – 2002</td>
<td>Hg&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Tekran 2537A</td>
<td>Skov et al., 2006</td>
</tr>
<tr>
<td>Ny-Ålesund, Svalbard</td>
<td>78°54’ N 11°53’ E</td>
<td>2000 – 2003</td>
<td>Hg&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Tekran 2537A • Tekran 1130 w/ KCl denuders</td>
<td>Berg et al., 2003 Sprovieri et al., 2005a Sprovieri et al., 2005b Aspmo et al., 2005 Gauchard et al., 2005</td>
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<tr>
<td>Amderma, Russia</td>
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<td>Ebinghaus et al., 2002 Temme et al., 2003</td>
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<td>2000 – 2001</td>
<td>Hg&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Tekran 2537A • Tekran 1130 w/ KCl denuders</td>
<td>Sprovieri et al., 2002</td>
</tr>
</tbody>
</table>

(1.5.1a)  **Field Studies in the Arctic or in High Northern Latitudes**

AMDEs have been observed in the Arctic and the sub-arctic. The longest continuous record is from Alert, Canada where observation began in 1995. Although there is significant variation in the timing, number, and magnitude of events; the seasonal cycle is evident, figure 1.6 from (Steffen et al., 2005). While this is the longest Hg<sub>0</sub> record, it is limited in that Hg<sub>0</sub> was the only species measured, thus it is difficult if not impossible to make conclusion concerning transport patterns and the mechanism of mercury oxidation.
Ny-Ålesund in Svalbard has been the site of multiple mercury campaigns that include speciated data (Berg et al., 2003; Gauchard et al., 2005; Sprovieri et al., 2005a, b); as well as, an inter-comparison study (Aspmo et al., 2005). The Svalbard data behaves similar to the Alert data with the onset of a period where $\text{[Hg}^0\text{]}$ are highly variable and include AMDEs in spring with recovery to stable background level in the fall.

An extensive speciation and inter-comparison study was conducted at Ny-Ålesund between April and May of 2003. Five groups participated in the Hg$^0$ inter-comparison, while four groups participated in the RGM and Hg$_p$ inter-comparison. Mercury species were sampled at three locations within Ny-Ålesund; two coastal sites the Ny-FID'sund site and the Italian station. The third site, the Zeppelin station, is located on the Ridge of Zeppelin Mountain. Hg$^0$ measurements agreed within 5% of each other.
during non-AMDE periods and 10% for the entire campaign. RGM and Hg\textsubscript{P} levels were below detection limit for non-AMDE sampling periods and demonstrated inverse proportionality to Hg\textsuperscript{0} during the five AMDEs observed during the campaign. There was significant variation in [RGM] and [Hg\textsubscript{P}], at times over 100% between different groups, methods and replicates. The author cites that some of the variation maybe due to small scale changes in meteorological conditions between the coastal sites and the Zeppelin sites. However, this cannot fully account for the variability observed between groups, methods and replicates. Much of the variation can be attributed to the non-standard implementation of the sampling procedure. As in any trace species detection, a standardized sampling procedure is essential to ensuring the quality of the data. Therefore, during an inter-comparison campaign it is essential that all groups implement the same sampling procedure. This was not the case for the Ny-Ålesund study, each group operated under slightly different conditions. These variations change what was sampled as RGM. For example, changing the flow rate can change the Hg\textsubscript{P} cut size thus influencing the partitioning between RGM and Hg\textsubscript{P}. Changes in cleaning, coating and conditioning procedure could effect the collection efficiency and the background Hg levels in the denuder. Although the paper suggests the need for calibration techniques for RGM and Hg\textsubscript{P}, much of the variation could be solved by adopting a standard operation procedure (SOP) that can be uniformly applied between groups. This need for a SOP for KCl denuder sampling does not preclude the need for some type of calibration technique. As new techniques for RGM sampling are developed, these techniques can be compared and some of the ambiguity associated with sampling an operational defined species can be limited.
The implementation of an SOP is essential in the development and application of mercury speciation monitoring equipment to ensure all data is comparable; the general trend in the behavior of Hg\(^0\), RGM, and Hg\(_P\) was evaluated at Ny-Ålesund by Gauchard et al. (Gauchard et al., 2005). From April 17\(^{th}\), 2003 to May 3\(^{rd}\), 2003 five AMDE were characterized. Each AMDE was evaluated considering: the meteorological data (wind speed, wind direction, air temperature), the ratio between RGM and Hg\(_P\), BrO data from the GOME satellite and a simple back trajectory analysis, apparent O\(_3\) destruction rates (\(\Delta\text{O}_3/\Delta t\)) (Tuckermann et al., 1997), and relative increases/decreases in Hg\(^0\), O\(_3\), and particle concentrations. By using all five of these criteria to evaluate the AMDE, each event can be classified as primarily influence by local chemistry or as depleted air masses advected into the region. Air masses are influence not only by the current environmental conditions, but all the conditions that the air mass has been exposed to over time. Hence, advection influences are present in all air masses. In addition the RGM/Hg\(_P\) ratio has been cited as an indicator of the time since the depletion event occurred (Landis, 2006).

In 2004, Skov et al. (Skov et al., 2004) monitored O\(_3\), filterable Br, and Hg\(^0\) at Station Nord, in NE Greenland from 1999 to Aug 2002. They observed the typical AMDE seasonality with the initial onset of high variability occurring in Feb–March with stable [Hg\(^0\)] returning in July. Concentrations were in the ranges O\(_3\) = 40 to 0 ppbv, Hg\(^0\) = 1.5 to 0 ng/m\(^3\), while filter Br increased to a maximum of 10 ng/m\(^3\). Skov et al. estimated the rate coefficient for the reaction of mercury and halogen atoms; details of this estimate will be discussed in Chapter 4.
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(1.5.2)  *Field Studies in Antarctic*

AMDEs were first reported in the Antarctic by Ebinghaus et al. (Ebinghaus et al., 2002; Temme et al., 2003). They monitored the three Hg species (Hg\textsuperscript{0}, RGM and Hg\textsubscript{P}) and O\textsubscript{3} at Neumayer from January 2000 to February 2001. Three modes were observed in the annual data Springtime Depletions (Aug – Nov), summertime depletions (Dec – Feb), and then a period of stability (March – July). Springtime depletions were similar to those observed in the Arctic and sub-arctic. AMDEs occur upon polar sunrise and are highly correlated to O\textsubscript{3}. The depleted air mass monitored in the Ebinghaus et al. study appeared to be air masses that were advected to the region. A simple back trajectory analysis indicated that the air masses that exhibited signs of mercury depletion seemed to spend significant time over ocean with at least 40% ice cover. The Spring AMDEs also appeared to end with the melting of the sea ice. From this, somewhat anecdotal evidence, the authors postulate that a halogen initiated mechanism similar to the mechanism proposed for AMDEs observed in Arctic Regions was responsible for the Springtime depletion as sea ice is a significant source of the halogen species.

Beginning in December and stretching to February there was a period in which [Hg\textsuperscript{0}] are highly variable and anti-correlated to [O\textsubscript{3}]. Significant increases in [RGM] (5-300 pg m\textsuperscript{-3}) and [TPM] (15-120 pg m\textsuperscript{-3}) were observed. The Summertime depletions begin with snow melt and are postulated to be related to the potential oxidants, OH, HO\textsubscript{2}, O, or NO, related to photo-denitrification in the snow pack (Domine and Shepson, 2002; Grannas et al., 2007).

Sprovieri et al. (Sprovieri et al., 2002) monitored [Hg\textsuperscript{0}] and [RGM] at Terra Nova Bay located on Gulf of the Ross Sea in western Antarctic from November to December
The Hg\textsuperscript{0} measurements confirmed the lower concentration of mercury expected in the southern hemisphere but observed no AMDEs. This is not in conflict with the Ebinghaus et al. data as the sampling period was short and between the height of the springtime and summertime depletion seasons. However, the Sprovieri et al. study did observed elevated concentrations of RGM. The observed RGM levels were comparable to sites directly effected by anthropogenic sources. These results indicate that Hg is undergoing a dynamic oxidation cycle in Polar Regions, independent of large scale depletion events.

(1.5.3) **Field Studies in the Marine Boundary Layer**

Although the focus of the discussion surrounding the atmospheric oxidation of mercury is centered on observations of AMDEs in Polar Regions; evidence from mercury campaigns at coastal sites and on-board research vessels reveal that the atmospheric oxidation of mercury may influence the chemical cycling of mercury throughout the Marine Boundary Layer (MBL). In order to capture the dynamic nature of mercury cycling in the MBL it is necessary to monitor both elemental and oxidized mercury species; as the dynamic process of oxidation, deposition and re-emission discussed previously can result in little to no observable change in the overall atmospheric Hg\textsuperscript{0} reservoir.

Table 1.4 highlights studies conducted in the ocean environment aboard research vessels and measurement conducted at coastal sites. In general, these studies observed elevated concentrations of RGM. The ship bases studies tend to observe higher concentration of RGM than land based studies.
### Table 1.4: Mercury sampling sites in coastal sites and ocean environments.

<table>
<thead>
<tr>
<th>Site</th>
<th>Method</th>
<th>[Hg] (ng m(^{-3}))</th>
<th>[RGM] (pg m(^{-3}))</th>
<th>[Hg(_0)] (pg m(^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LAND BASED OBSERVATIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cheeka Peak, Washington (Spring 2002)</td>
<td>Tekran 2537A</td>
<td>1.54 ± 0.16</td>
<td>1.6</td>
<td>0.5</td>
<td>Weiss-Penzias et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>1.3</td>
<td>&gt;MDL = 1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pompano Beach, Florida (June 2000)</td>
<td>Tekran 2537A</td>
<td>1.6 ± 0.06</td>
<td>1.6 ± 1.5</td>
<td>6.3 ± 4.4</td>
<td>Malcolm et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>1.8</td>
<td>7</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>1.5</td>
<td>&gt;MDL = 6</td>
<td>&gt;MDL = 4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>2.5</td>
<td>113</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>1.3</td>
<td>&lt;MDL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ein Bokek, Dead Sea, Israel</td>
<td>*Tekran 2537A</td>
<td>1.97 ± 0.39</td>
<td></td>
<td></td>
<td>Peleg et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SHIP BASED OBSERVATIONS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mediterranean</td>
<td>Tekran 2537A</td>
<td>1.9 ± 1.02</td>
<td>7.9</td>
<td></td>
<td>Sprovieri et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>11.2</td>
<td>30.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.4</td>
<td>&lt;MDL = 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N. Pacific, Japan → Hawaii</td>
<td>Tekran 2537A</td>
<td>2.5</td>
<td>9.5</td>
<td></td>
<td>Laurier et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>4.7</td>
<td>92.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>1.6</td>
<td>&lt;MDL = 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N. Atlantic, Bermuda → Barbados</td>
<td>Tekran 2537A</td>
<td>1.63 ± 0.8</td>
<td>5.9</td>
<td></td>
<td>Laurier and Mason, 2007</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>1.9</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>1.5</td>
<td>&lt;MDL = 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†Reported concentrations are from marine air masses if identified by the authors

* TGM is reported, this will have a positive artifact due to RGM sampled on gold tube hence this is an upper limit for Hg\(_0\)

However, it is difficult to evaluate the validity of these absolute differences as RGM level are near or below reported MDL and significant discrepancies have been observed during inter-comparison studies (Aspmo et al., 2005). Another limitation on the shipboard studies of mercury is the absence of collocated sampling of tracer gases, such
as SO₂, NO, O₃, PM, or trace metal. Collocated data is needed to ensure that the air masses sampled are, in fact, background marine air masses. Without this data it is impossible to attribute the observed mercury solely to in-situ production as the air mass could have been contaminated by a local pollution source, such as a passing ship, or the result of longer range transport of a near shore pollution source. So while all of these studies find that the highest levels of RGM were observed under high UV conditions, without collocated trace gas data it is impossible to unambiguously identify the source as photochemical production.

In addition, the studies on the coastal sites indicate that due the dynamic processing of Hg species within the mercury environment any RGM produced will be rapidly deposited or reduced back into Hg⁰, hence oxidation in the MBL is not a significant source to coastal communities (Malcolm et al., 2003). This hypothesis is further supported by ship based measurement that measure higher RGM concentration at low wind speeds and in the absence of precipitation (Laurier and Mason, 2007).

Influences on mercury chemistry in unique marine environments have been observed. Most recently Peleg et al. reported the observation of mercury depletion in the area surrounding the Dead Sea at [BrO] as low as 10 ppt (Peleg et al., 2007). This observation is not unexpected as ozone depletion has been observed before these measurements in the Dead Sea (Matveev et al., 2001) and BrO levels can reach up to 70 ppt. This observation highlights the influence atmospheric mercury oxidation can have in areas that build high halogen radical concentrations even without the snow surfaces. This indicates that the ice surface is not a pre-requisite for mercury depletion. Other site of
interest would include the Great Salt Lake (BrO = 6ppt) (Stutz et al., 2002) and Salar de Uyuni in Bolivia (BrO = 20ppt) (Honninger et al., 2004).

(1.5.4) **Gaseous Elemental Mercury in the free troposphere and at the Tropopause**

Current data sets that monitored mercury species in the free troposphere are limited. Most measurements on background mercury concentrations were conducted at ground level. The few aircraft studies conducted have either focused on local emission sources and/or only characterized TGM, which will include a positive sampling artifact due to the collection of some oxidized mercury species on the gold tube. Studies, which monitor mercury species at different altitudes, are further complicated by the fact that the standard instrument used to monitor TGM (Tekran 2573A) shows a decreasing sensitivity as pressure decrease, i.e. sensitivity of the instrument is reduced with increasing altitude (Landis and Stevens, 2001).

(1.5.4a) **Aircraft measurements in the free troposphere**

Early flights in the former Soviet Union at altitudes up to 3.5 km (Ionov et al., 1976; Kvietkus, 1995; Kvietkus et al., 1985), in the sea west of Göteborg at altitudes up to 3.0 km (Brosset, 1987), and in Lithuania (Kvietkus, 1995) revealed a vertical gradient in TGM concentration that demonstrated a strong proportionality to the pressure at the sampling altitudes. None of these studies discussed a possible dependence of the detector response on the ambient pressure.

In 1985, Slemr et al. (Slemr et al., 1985) monitored [TGM] at 6 – 12 km above central Europe. They found [TGM] ranging from 1.2 to 3.1 ng standard m$^{-3}$ after the
detector was corrected for sensitivity variations. Although the data demonstrated high variability, the author stated that no vertical gradient was observed. An additional study conducted by the same group over Germany in 1996 (Ebinghaus and Slemr, 2000). This flight included an outbound flight at 0.9 km, a return flight at 2.5 km, and two measurements made at 0.3 km at the end of the return flight. The average [TGM] were 1.774 ± 0.101 ng m⁻³, 1.635 ± 0.094 ng m⁻³, and 2.2 ± 0.2 ng m⁻³, respectively. The authors attribute this, not to a vertical gradient, but to differences in air masses at the different altitudes.

Figure 1.7: Plot of altitude versus [TGM] observed in remote regions throughout Canada from (Banic et al., 2003).

Banic et al. (Banic et al., 2003) monitored [TGM] from 0.1 to 7.0 km in several sites throughout Canada during Summer, Winter, and Spring. The resulting vertical
profiles with average [TGM] of 1.5 ng standard m$^{-3}$ for the summer, 1.7 ng standard m$^{-3}$ for the Winter, and 1.7 ng standard m$^{-3}$ for the Spring. The spring data was only averaged from 1.0–7.0 km as AMDEs resulted in low [TGM] levels below 1 km. Most data demonstrated little to no vertical gradient. However, a small trend was observed as sites were influenced from anthropogenic sources. The anthropogenic influence was observed as an enhancement of [TGM] above the 1.7 ng standard m$^{-3}$ typically observed in the troposphere. Figure 1.7 is all [TGM], this data was corrected for detector sensitivity however it is not clear that correction factors used were appropriate. Assuming this correction factor is appropriate, no dramatic trend was observed. However any trend could be obscured by an inappropriate pressure correction factor and the general scatter of the data.

Three groups have reported measurements in the free troposphere or tropopause of oxidized Hg species (Landis et al., 2005; Murphy et al., 2006a; Murphy et al., 2006b; Murphy et al., 2003; Radke et al., 2007). Landis monitored both Hg$^0$ and RGM in a series of flights in southern Florida in January and June 2000. During the flights, they monitored [Hg$^0$], [RGM], and [Hg$_P$] between 0.06 and 3.5 km. The resulting plots are shown in figure 1.8. Landis et al. observed a small negative trend with altitude in [Hg$^0$] and a more pronounced positive trend between [RGM] and increasing altitude. The Landis et al. data set is the only aircraft data, which monitors both [Hg$^0$], [RGM], and [Hg$_P$]. The negative correlation between Hg$^0$ and altitude is reported as $-0.15 \times \text{Altitude} + 1.68$ (ng standard m$^{-3}$). If a similar analysis is applied to the limited data set reported by Ebinghaus and Slemr (Ebinghaus and Slemr, 2000) not including the two data points collected at 0.3 km, the TGM/altitude correlation is $-0.094 \times \text{Altitude} + 1.88$ (ng
standard m$^{-3}$). In addition, both the Ebinghaus et al. and Banic et al. (Banic et al., 2003) data monitor TGM, while Landis et al. monitors Hg$^0$. As the trend is not strong and the scatter with in the data is on the same order of magnitude, it is possible that the collection of oxidized mercury species as Hg$^0$ in TGM sampling buffered the vertical profile.

![Figure 1.8: Plot of [Hg$^0$] vs. altitude, [RGM] vs. altitude observed in Southern Florida, June 2000 from (Landis et al., 2005).](image)

Another possible explanation in the conflict in conclusions on the vertical profile of Hg$^0$ is that the Landis data was impacted by a local or regional mercury source at lower altitudes. The presence of this additional source is unlikely as [Hg$^0$] observed within the mixed layer had low levels of Hg (1.9 – 1.3 ng standard m$^{-3}$), which is indicative of clean MBL air with limited local or regional mercury sources. The Hg$^0$ vertical profiles were further confirmed by the RGM vertical profiles that resulted in a positive RGM/altitude correlation of 26.94 × Altitude -3.08. This increase in RGM concentration in the upper troposphere could be due to the subsidence and subsequent
volatilization of \( \text{Hg}_P \) from the stratosphere/tropopause, this will be discussed below, or the result of in-situ oxidation the \( \text{Hg}^0 \).

The Murphy group has obtained and analyzed the mass spectra of \(~1,000,000\) individual particles using a Particle Analysis by Laser Mass Spectroscopy (PALMS) instrument (Murphy et al., 2006a; Murphy et al., 2006b; Murphy et al., 2003). A single sample was collected in the lower stratosphere for analysis by Scanning Transmission Electron Microscopy (STEM) (Murphy et al., 2006a). The extensive PALMS data set revealed that at the tropopause a large fraction of the observed particles in both the tropics and mid-latitudes during multiple seasons contain \( \text{Hg} \). The presence of \( \text{Hg} \) in upper tropospheric/lower stratospheric aerosols confirmed by both the PALM and STEM data. The distribution of \( \text{Hg} \) onto up to \( 70\% \) of sampled particles, even small (20nm) particles is indicative of a local \( \text{Hg}_P \) source rather than transport of \( \text{Hg} \)-rich aerosols from surface sites. The peak in aerosols containing \( \text{Hg} \) is centered at the tropopause with almost none of the particles sampled below 5 km containing \( \text{Hg} \). This rapid decline could be due the re-volatilization of \( \text{Hg} \) or RGM from the aerosol once in the warmer troposphere or the rapid washout of \( \text{Hg}_P \) and RGM during precipitation events. As the PALMS instrument measures both positive and negative ions it is of interest that \( \text{Hg} \) ions and \( \text{Br}^- \) follow a similar profile, indicating that they are present in the same aerosol species even if they are not chemical bound to each other. This trend is also observed, although less dramatically, between \( \text{Hg} \) ion and \( \Gamma^- \) or \( \Gamma^+ \).

Radke et al. (Radke et al., 2007) sampled \( \text{Hg}^0 \), along with important co tracers, such as \( \text{CO}, \text{O}_3 \), and VOCs as part of the Intercontinental Transport and Chemical Transformation Experiment – 2002 (ITCT2K2). They observed a significant vertical
gradient in [Hg\(^0\)] and depleted [Hg\(^0\)] in the upper troposphere indicating a possible sink of Hg\(^0\) in the upper troposphere/\lower stratosphere with reduces the lifetime of mercury in the atmosphere to 100 days. The data collected in this work was corrected to eliminate the pressure dependence of the Tekran detection system, however at the highest altitudes the pump was found to be insufficient to draw the required 1.5 SLPM. In addition, Radke et al. conclude that the integration interval for Hg\(^0\) detection may smear together distinct air masses if the flight path encounters short lived pollution plumes.

(1.5.4b) Measurements from Land Based sites in the Free Troposphere

Aircraft time is expensive and access is limited. In addition, it is difficult to collect speciated mercury data from an aircrafts as the measurements require long sampling times. To overcome these challenges, measurements were made at two sites, which are impacted by air from the free troposphere. The first site is 3.4 km above sea level at Mauna Loa, Hawaii. Figure 1.9 depicts some initial observations. These initial results confirm the observations made during aircraft campaigns in South Florida in 2000, with periods where Hg\(^0\) appears depleted concurrent with elevated RGM and Hg\(_P\) levels (Landis et al., 2005).
Figure 1.9: Temporal profiles of $[\text{Hg}^0]$, [RGM], and [Hg(p)] from Mauna Loa, Hawaii from (Landis et al., 2005).

Mount Bachelor Observatory (MBO) is a site that is characterized by a nighttime shallowing of the mixed layer, this shallowed mixed layer falls below the MBO site allowing for the sampling of free tropospheric air during the night. TGM measurements conducted before 2006 reveal a dynamic Hg system, which can be influenced by local, regional and global pollution sources, changes in the synoptic wind patterns, and potential local oxidation chemistry. Weiss-Penzias et al. (Weiss-Penzias et al., 2007; Weiss-Penzias et al., 2006) have identified several interesting mercury events by evaluating the relationship between TGM and co-tracers, such as CO, O$_3$ and H$_2$O. Anthropogenic plumes have been identified from long-range transport from Asia, biomass burning plumes from Alaska, and biomass burning plumes from fires in the Pacific Northwest. Speciated mercury data was obtained at MBO from May 2005 to
August 2005. During this time a strong diurnal variation in RGM, Hg$^\circ$, O$_3$ and H$_2$O was observed, figure 1.10.

![Figure 1.10: Temporal profiles of [Hg$^\circ$], [RGM], [O$_3$], and [H$_2$O] from Mount Bachelor Observatory in Oregon from (Swartzendruber et al., 2006).](image)

Nighttime data was averaged for 3 hours and correlation coefficients were reported between all species. The strongest correlations were anti-correlations between RGM/Hg$^\circ$ and RGM/H$_2$O and the correlation between Hg$^\circ$/H$_2$O. There was a significant correlation between Hg$^\circ$/CO and RGM/CO however, it was weaker than expected if the [Hg$^\circ$] and [RGM] were solely driven by anthropogenic influences. The authors conclude that the observe Hg$^\circ$ depletion/RGM enhancement was a mixture of subsiding air from the free troposphere and air from the mixed layer.

As [RGM] were highly variable during the campaign, the authors took a sub-set of the data during which [RGM] > 50 pg m$^{-3}$ for at least two sequential measurements. The average [RGM] was 194 ± 154 pg m$^{-3}$ while the average [Hg$^\circ$] was 1.32 ± 0.212 ng m$^{-3}$. If this Hg$^\circ$ depletion/RGM enhancement were due to local oxidation, a plot of the
RGM deviation from background levels ($\Delta \text{RGM}$) versus Hg$^0$ deviation from background levels ($\Delta \text{Hg}^0$) should be unity. However, as some RGM will be lost to mixing and potential to deposition the overall equation can be expressed as E1.3, where MF is the mixing factor.

$$\text{slope} = \frac{\Delta \text{RGM}}{\Delta \text{Hg}^0} = \frac{\text{RGM}_{\text{obs}} - \text{RGM}_{\text{bkgd}}}{\text{Hg}^0_{\text{obs}} - \text{Hg}^0_{\text{bkgd}}} = -\frac{\text{RGM}_{\text{obs}}}{\text{RGM}_{\text{obs}} - \text{MF}}$$  \hspace{1cm} (E1.3)

The authors assigned a MF of 0.075 ng m$^{-3}$, which resulted in a slope of 0.87 independent of RGM loss by deposition, which would decrease the slope, or transport of anthropogenically produced RGM into the air mass, which would increase the slope. A plot of the $\Delta \text{RGM}/\Delta \text{Hg}^0$ results in a slope of 0.89 and indicates that the observed RGM was produced by in-situ oxidation of Hg$^0$.

(1.6) Oxidation of Gaseous Elemental Mercury

The oxidation of mercury in the atmosphere can occur both in the gas phase and in the aqueous phase. Studies, which evaluate important mercury reactions, are limited and divergent with discrepancies between measured rates are orders of magnitude. Some potentially important reactions and the corresponding kinetic information are outlined in Table 1.5. However, it must be recognized that mercury chemistry, particularly in the gas phase, is still relative uncharacterized. For this discussion we will highlight those reactions which are most often include in regional and global modeling studies.

| Table 1.5: Potential oxidation reactions of Hg$^0$. |
Gas phase mercury chemistry includes reaction with oxidants such as ozone, NO₃, OH, molecular halogens and H₂O₂. Due to the low vapor pressure of mercury, slow rate coefficients, and complications with secondary and heterogeneous chemistry, rate coefficients for gas phase mercury reactions are challenging to measure. This inherent difficulty is reflected in the large discrepancy of published rate coefficients outlined in Table 1.5. These four rate coefficients are relatively slow and cannot account for the field observations detailed in the previous section.

Aqueous phase reactions of mercury are slightly faster and believed to play a vital role in the oxidation of mercury, particularly in polluted environments. The aqueous oxidation of mercury in fog or cloud droplets is believed to be the primary sink for Hg⁰ in the troposphere.
Reaction (R1.4), the aqueous oxidation of mercury by ozone, is most likely the primary oxidation pathway.

\[
\text{Hg}^0 + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{OH}^- + \text{Hg}^{2+} \tag{R1.4}
\]

The aqueous phase reaction of mercury with hydroxide (OH) and hypochlorite (ClO\(^-\)) radicals are also believed to be a sink of \(\text{Hg}^0\), depending on the conditions that are present in the atmosphere. The aqueous reaction with OH is a two step addition shown in reactions (R1.5) and (R1.6).

\[
\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^+ + \text{OH}^- \tag{R1.5}
\]

\[
\text{Hg}^+ + \text{OH} \rightarrow \text{Hg}^{2+} + \text{OH}^- \tag{R1.6}
\]

The rate coefficients for R1.5 (Lin and Pehkonen, 1997) and R1.6 (Buxton et al., 1988) are \(2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) and \(10^{10} \text{ M}^{-1}\text{s}^{-1}\), respectively. Therefore, the overall reaction rate depends only on the addition of the first OH, because once the \(\text{Hg}^+\) ion is formed the second addition will occur at the rate of diffusion.

The last major pathway of mercury oxidation, proposed by Kobayashi (Kobayashi, 1987) is the aqueous oxidation of mercury by hypochlorite species. This reaction pathway has a 1:2 mercury to hypochlorite stoichiometry. The proposed mechanism and the resulting rate coefficients are reported in Table 1.5.

(1.7) **Potential Mechanisms for the Gas Phase Oxidation of Elemental Mercury**

None of the known gas-phase or aqueous phase reaction discussed in the previous section can account for the \(\text{Hg}^0\) depletion/RGM enhancement observed in numerous locations throughout the world. One potential mechanism that could produce the observed concentration of mercury is an unidentified gas-phase oxidation by a radial
species such as Cl, Br, I, ClO, BrO, or IO. Another possible explanation for the discrepancy between the known chemistry and the observation could be an underestimate of the gas phase reaction of Hg$^0$ with OH or O$_3$.

Experimental difficulties have lead to a limited kinetic data base on the gas phase chemistry of Hg$^0$. This is exacerbated by the fact that for many of the potential reactants are highly variable and the global distribution of these species is unknown. This makes the evaluation of their relative importance difficult. Despite these difficulties, a series of potentially important reactions for the oxidation of Hg$^0$ will be outlined below.

(1.7.1) Radical Addition Reaction

One of the most likely reaction mechanism is radical addition reaction, where a single radical species is added to the Hg$^0$ to form an HgX species, reaction (R1.7), where X = Cl, Br, I, ClO, BrO, IO, or OH radical.

\[
\text{Hg} + X + M \rightarrow \text{HgX} + M \quad \text{(R1.7)}
\]

An evaluation of thermochemistry, using thermodynamic data from the NIST-JANAF tables (Chase, 1998) and theoretical data from Balabanov et al. (Balabanov and Peterson, 2003), is included for each potential reaction below, all paths are exothermic.

\[
\begin{align*}
\text{Hg} + \text{BrO} & \rightarrow \text{HgBrO} \quad \Delta H_{Rx} = -84.6 \text{ kJ/mole} \quad \text{(R1.8)} \\
\text{Hg} + \text{ClO} & \rightarrow \text{HgClO} \quad \Delta H_{Rx} = -90.4 \text{ kJ/mole} \quad \text{(R1.9)} \\
\text{Hg} + \text{Br} & \rightarrow \text{HgBr} \quad \Delta H_{Rx} = -69 \text{ kJ/mole} \quad \text{(R1.10)} \\
\text{Hg} + \text{Cl} & \rightarrow \text{HgCl} \quad \Delta H_{Rx} = -104 \text{ kJ/mole} \quad \text{(R1.11)} \\
\text{Hg} + \text{I} & \rightarrow \text{HgI} \quad \Delta H_{Rx} = -35 \text{ kJ/mole} \quad \text{(R1.12)} \\
\text{Hg} + \text{OH} & \rightarrow \text{HgOH} \quad \Delta H_{Rx} = -30 \text{ to } -60 \text{ kJ/mole} \quad \text{(R1.13)}
\end{align*}
\]
However, the actual loss of mercury will depend on the stability and reactivity of the product. In most of the addition reactions the HgX is unstable and will either decompose, (R1.14), or undergo further reaction, (R1.15)

$$\text{HgX} \rightarrow \text{Hg} + \text{X} \quad \text{(R1.14)}$$

$$\text{HgX} + \text{Y} + \text{M} \rightarrow \text{YHgX} + \text{M} \quad \text{(R1.15)}$$

where Y could be Cl, Br, O₂, ClO, BrO, IO, OH, or I. Thus, the HgX intermediate must have a sufficient lifetime to react with species Y. In a theoretical study, Goodsite et al. calculated a dissociation lifetime of < 1s at temperatures above 200 K for both HgI and HgOH. This means that these addition reactions should not play a significant role in atmospheric mercury chemistry. On the other hand, the reaction of Hg⁰ with Br radicals was identified as a potential reaction pathway.

Observations of the co-variance of gas-phase Hg⁰ and BrO and Hg ion and Br ion within mercury containing aerosols along with the finding from theoretical studies has led many researchers to identify the gas-phase oxidation of Hg⁰ by Br or Cl atoms as a potentially important atmosphere oxidation pathway, (R1.10 and R1.11). The low steady state concentration of Cl atoms means it is unlikely to be the primary pathway for extensive mercury depletion, however understanding this rate is essential to understanding how halogen species affect mercury concentrations globally. Br atoms concentrations are estimated to reach concentrations on the order of 10⁷ molecules cm⁻³, during polar sunrise (Boudries and Bottenheim, 2000). In addition, elevated concentrations of reactive bromine species, Br and BrO, have been observed in over highly saline bodies of water such as the Dead Sea (Matveev et al., 2001) and the Great Salt Lake (Stutz et al., 2002). At these high concentrations a relatively slow ($5 \times 10^{-13}$
cm³ molecules⁻¹ s⁻¹) Br atom initiated reaction sequence could account for the rapid losses of mercury observed. This mechanism has been proposed as the major pathway for mercury oxidation in numerous experimental and theoretical studies (Ariya et al., 2002; Balabanov et al., 2003; Calvert and Lindberg, 2003, 2004; Goodsite et al., 2004; Khalizov et al., 2003; Skov et al., 2004; Tossell, 2003).

If R1.10 and R1.11 are pathways for mercury depletion, it is essential to characterize the rate coefficients. Currently, little kinetic data is available for rate coefficients of elemental mercury with halogen radicals. In tables 1.6 and 1.7 the observed rate coefficients for R1.10 and R1.11 are outlined, respectively.

**Table 1.6:** Second order rate coefficients for the recombination of mercury and bromine atoms, k₉R₁.10.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (K)</th>
<th>Pressure (Torr)</th>
<th>k₉R₁.10 (a) cm³ molecule⁻¹ s⁻¹</th>
<th>k₉R₁.10 (b) cm⁶ molecule⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>298</td>
<td>760</td>
<td>3.0×10⁻¹³</td>
<td>Spicer et al., 2002</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>9.7×10⁻¹³</td>
<td>Spicer et al., 2002</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>(3.2+/−0.3)×10⁻¹²</td>
<td>Ariya et al., 2002</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>200-600</td>
<td>(1.46±0.34)×10⁻³²×\left(\frac{T}{298}\right)^{−1.8±1.49}</td>
<td>Donohoue et al., 2006</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>1.01×10⁻¹²×\exp^{(200.03/T)}</td>
<td>Khalizov et al., 2003</td>
</tr>
<tr>
<td></td>
<td>180-400</td>
<td>760</td>
<td>1.1×10⁻¹²×(T/298)^⁻².3⁷</td>
<td>Goodsite et al., 2004</td>
</tr>
<tr>
<td>He</td>
<td>243-293</td>
<td>200-600</td>
<td>(4.2±0.2)×10⁻³⁸</td>
<td>Donohoue et al., 2006</td>
</tr>
<tr>
<td>Air</td>
<td>233-263</td>
<td>760</td>
<td>1×10⁻¹²</td>
<td>Skov et al., 2004</td>
</tr>
<tr>
<td>CF₃Br</td>
<td>393-448</td>
<td>200</td>
<td>2.82×10⁻¹³</td>
<td>Greig et al., 1970</td>
</tr>
</tbody>
</table>

**Table 1.7:** Second order rate coefficients for the recombination of mercury and chlorine atoms, k₉R₁.11.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (K)</th>
<th>Pressure (Torr)</th>
<th>k₉R₁.11 (a) cm³ molecule⁻¹ s⁻¹</th>
<th>k₉R₁.11 (b) cm⁶ molecule⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>298</td>
<td>760</td>
<td>6.4×10⁻¹¹</td>
<td>Spicer et al., 2002</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>(1.0±0.2)×10⁻¹¹</td>
<td>Ariya et al., 2002</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>760</td>
<td>(2.2±0.5)×10⁻³²×\exp^{(680±400)(\frac{1}{T}\frac{T}{298})}</td>
<td>Donohoue et al., 2005</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>1.38×10⁻¹²×\exp^{(208.02/T)}</td>
<td>Khalizov et al., 2003</td>
</tr>
<tr>
<td>He</td>
<td>243-293</td>
<td>760</td>
<td>(9.37±0.95)×10⁻³³</td>
<td>Donohoue et al., 2005</td>
</tr>
<tr>
<td>CF₃Cl</td>
<td>383-443</td>
<td>720</td>
<td>5.0×10⁻¹¹</td>
<td>Horne et al., 1968</td>
</tr>
<tr>
<td>Ar</td>
<td>383-443</td>
<td>720</td>
<td>1.5×10⁻¹¹</td>
<td>Horne et al., 1968</td>
</tr>
</tbody>
</table>
These rates will be discussed in subsequent chapters; however it is important to note the discrepancies between the relative rate determinations (Ariya et al., 2002; Spicer et al., 2002), the theoretical determinations of the rate coefficients (Goodsite et al., 2004; Khalizov et al., 2003; Skov et al., 2004) and the direct determinations (Donohoue et al., 2006; Donohoue et al., 2005; Greig et al., 1970; Horne et al., 1968). This large discrepancy and the fact that the rate coefficient observed by the relative rate method seem to have been influenced by secondary or heterogeneous chemistry highlights the need for the determination of the rate coefficient for R1.10 and R1.11 via a direct technique.

\[(1.7.2) \quad \text{HgX reactions - HgX} + Y \rightarrow \text{YHgX}\]

A Br initiated reaction has been suggested as a primary reaction in AMDEs. Specifically, R1.10 has been proposed as the initiation reaction, resulting in the HgBr species. However, this species contains mercury in the unstable monovalent state. Therefore, the question becomes what is the fate of HgBr molecule? Goodsite et al. (Goodsite et al., 2004) proposed that HgBr would rapidly undergo decomposition, R1.14 or react to produce an YHgBr species, R1.16:

\[\text{HgBr} + Y \rightarrow \text{YHgBr} \quad \text{(R1.16)}\]

where Y is Br, I, OH, O₂. By assuming that species Y was Br atoms, Goodsite et al. evaluated a rate coefficient using the RRKM theory and a master equation formulation, determining a value of \(2.5 \times 10^{-10} \times (T/298)^{-0.57} \text{ cm}^3 \text{ molecules}^{-1} \text{s}^{-1}\), close to the collision frequency of a gas phase reaction. Additionally, the rate of decomposition of the HgBr radical, R1.14 where X = Br atoms, was determined to be \(1.2 \times 10^{10} \times (8357/T) \text{ s}^{-1}\).
Using these two rate coefficients and the rate coefficient for the recombination of mercury and bromine, \( R1.10 \), the atmospheric lifetime for mercury with respect to \( \text{Br} \) atoms can be determined by the following expression, (E1.4).

\[
\tau = \frac{(k_{R1.14} + k_{R1.16}[\text{Br}])}{k_{R1.10} k_{R1.16}[\text{Br}]}^2
\]

(E1.4)

From the theoretical rate coefficients for these reactions Goodsite et al. determined that the lifetime of mercury during an AMDE with respect to bromine varied from 0.7 hours to 60 hours depending on exact temperature conditions and bromine concentrations. This work clearly demonstrates that the lifetime of mercury during an AMDE depends not only on the first addition of the halogen species, \( R1.10 \) and \( R1.11 \), but the subsequent reactions of the resulting species.

Therefore, to evaluate the potential influence of \( \text{Br} \) atom initiated oxidation of mercury it is essential to determine rate coefficients for possible \( \text{HgX} \) reactions. The heat of formation at 0 K for each reaction is calculated from the thermodynamic data in the NIST-JANAF tables (Chase, 1998), as well as, theoretical estimates by Balabanov et al. (Balabanov and Peterson, 2003) for \( \text{ClHgBr}, \text{OHgBr}, \text{and OHgCl} \) because no experimental data is available for these molecules. Additionally, the heat of formation could not be calculated for all potential species because there is no estimate for the product of the reaction. Potential reactions of \( \text{HgX} \) reactions include:

\( \text{HgCl Reactions} \)

\[
\begin{align*}
\text{HgCl} + \text{Cl} & \rightarrow \text{ClHgCl} & \Delta H_{\text{Rx}} = -344 \text{ kJ/mole} & \quad \text{(R1.17)} \\
\text{HgCl} + \text{Cl} & \rightarrow \text{Hg} + \text{Cl}_2 & \Delta H_{\text{Rx}} = -138 \text{ kJ/mole} & \quad \text{(R1.18)} \\
\text{HgCl} + \text{Br} & \rightarrow \text{ClHgBr} & \Delta H_{\text{Rx}} = -303 \text{ kJ/mole} & \quad \text{(R1.19)} \\
\text{HgCl} + \text{ClO} & \rightarrow \text{ClOHgCl} & & \quad \text{(R1.20)}
\end{align*}
\]
HgCl + ClO $\rightarrow$ Cl + OHgCl \hspace{1cm} \Delta H_{Rx} = 50 \text{ kJ/mole} \hspace{1cm} (R1.21)

HgCl + ClO $\rightarrow$ O + ClHgCl \hspace{1cm} \Delta H_{Rx} = -79 \text{ kJ/mole} \hspace{1cm} (R1.22)

HgCl + BrO $\rightarrow$ BrOHgCl \hspace{1cm} (R1.23)

HgCl + BrO $\rightarrow$ Br + OHgCl \hspace{1cm} \Delta H_{Rx} = 15 \text{ kJ/mole} \hspace{1cm} (R1.24)

HgCl + BrO $\rightarrow$ O + ClHgBr \hspace{1cm} \Delta H_{Rx} = -72 \text{ kJ/mole} \hspace{1cm} (R1.25)

HgCl + OH $\rightarrow$ HOHgCl \hspace{1cm} (R1.26)

HgCl + O$_2$ $\rightarrow$ OOHgCl \hspace{1cm} (R1.27)

\textit{HgBr Reactions}

HgBr + Cl $\rightarrow$ ClHgBr \hspace{1cm} \Delta H_{Rx} = -338.1 \text{ kJ/mole} \hspace{1cm} (R1.28)

HgBr + Br $\rightarrow$ BrHgBr \hspace{1cm} \Delta H_{Rx} = -300.7 \text{ kJ/mole} \hspace{1cm} (R1.29)

HgBr + Br $\rightarrow$ Hg + Br$_2$ \hspace{1cm} \Delta H_{Rx} = -123 \text{ kJ/mole} \hspace{1cm} (R1.30)

HgBr + ClO $\rightarrow$ ClOHgBr \hspace{1cm} (R1.31)

HgBr + ClO $\rightarrow$ Cl + OHgBr \hspace{1cm} \Delta H_{Rx} = 16.9 \text{ kJ/mole} \hspace{1cm} (R1.32)

HgBr + ClO $\rightarrow$ O + ClHgBr \hspace{1cm} \Delta H_{Rx} = -72.8 \text{ kJ/mole} \hspace{1cm} (R1.33)

HgBr + BrO $\rightarrow$ BrOHgBr \hspace{1cm} (R1.34)

HgBr + BrO $\rightarrow$ Br + OHgBr \hspace{1cm} \Delta H_{Rx} = -17.0 \text{ kJ/mole} \hspace{1cm} (R1.35)

HgBr + BrO $\rightarrow$ O + BrHgBr \hspace{1cm} \Delta H_{Rx} = -69.3 \text{ kJ/mole} \hspace{1cm} (R1.36)

HgBr + OH $\rightarrow$ HOHgBr \hspace{1cm} (R1.37)

HgBr + O$_2$ $\rightarrow$ OOHgBr \hspace{1cm} (R1.38)

From the thermodynamics, R1.17, R1.18, R1.19, R1.22, R1.25, R1.28, R1.29, R1.30, R1.33 and R1.36 are exothermic and are potentially important reactions. Therefore, in
order to evaluate the rate coefficients for HgX radical reactions the focus of this work will be to develop a viable PLIF detection method for both HgCl and HgBr radicals.

(1.7.3) Other Potential Mechanisms

Although there is mounting evidence that at least some gas-phase oxidation of mercury occurs via a halogen atom initiated reaction channel, this does not preclude addition reaction pathways. Additional pathways include but are not limited to gas phase abstraction reactions and gas phase insertion reactions. Abstraction reactions are reactions in which the Hg atom abstracts one of the atoms from a molecule forming a new mercury species and a radical. A thermochemical evaluation of this data shows that many of these reactions are endothermic, and thus not significant to the overall atmospheric cycling of mercury. For all calculations, $\Delta H_{Rx}$ was taken from the Balabanov et al. (Balabanov and Peterson, 2003) calculation and the references there in. These calculations use the $\Delta H_{HgO} = 295\text{kJ mole}^{-1}$ predicted by Shepler et al. (Shepler et al., 2003).

\[
\begin{align*}
\text{Hg} + \text{Br}_2 & \rightarrow \text{HgBr} + \text{Br} \quad \Delta H_{Rx} = 128 \text{kJ/mole} \quad (\text{R1.39}) \\
\text{Hg} + \text{Cl}_2 & \rightarrow \text{HgCl} + \text{Cl} \quad \Delta H_{Rx} = 147 \text{kJ/mole} \quad (\text{R1.40}) \\
\text{Hg} + \text{BrCl} & \rightarrow \text{HgBr} + \text{Cl} \quad \Delta H_{Rx} = 153 \text{kJ/mole} \quad (\text{R1.41}) \\
\text{Hg} + \text{BrCl} & \rightarrow \text{HgCl} + \text{Br} \quad \Delta H_{Rx} = 124 \text{kJ/mole} \quad (\text{R1.42}) \\
\text{Hg} + \text{BrO} & \rightarrow \text{HgBr} + \text{O} \quad \Delta H_{Rx} = 165 \text{kJ/mole} \quad (\text{R1.43}) \\
\quad & \rightarrow \text{HgO} + \text{Br} \quad \Delta H_{Rx} = 210 \text{kJ/mole} \quad (\text{R1.44}) \\
\text{Hg} + \text{ClO} & \rightarrow \text{HgCl} + \text{O} \quad \Delta H_{Rx} = 170 \text{kJ/mole} \quad (\text{R1.45}) \\
\quad & \rightarrow \text{HgO} + \text{Cl} \quad \Delta H_{Rx} = 243 \text{kJ/mole} \quad (\text{R1.46})
\end{align*}
\]
\[
\begin{align*}
\text{Hg} + \text{OH} & \rightarrow \text{HgO} + \text{H} \quad \Delta H_{\text{Rx}} = 90 \text{ kJ/mole} \quad (R1.47) \\
\text{Hg} + \text{O}_3 & \rightarrow \text{HgO} + \text{O}_2 \quad \Delta H_{\text{Rx}} = 86 \text{ kJ/mole} \quad (R1.48)
\end{align*}
\]

Gas phase mercury reactions can also proceed via insertion channels. These are reactions in which the Hg molecule will be added into a molecule. Potential reaction and there calculated \(\Delta H_{\text{Rx}}\) are listed below. These heats of formation are calculated using heats of formation at 0 K from the JANAF table and Balabanov values when no experimental data was available.

\[
\begin{align*}
\text{Hg} + \text{Br}_2 & \rightarrow \text{BrHgBr} \quad \Delta H_{\text{Rx}} = -68 \text{ kJ/mole} \quad (R1.49) \\
\text{Hg} + \text{Cl}_2 & \rightarrow \text{ClHgCl} \quad \Delta H_{\text{Rx}} = -139 \text{ kJ/mole} \quad (R1.50) \\
\text{Hg} + \text{BrCl} & \rightarrow \text{BrHgCl} \quad \Delta H_{\text{Rx}} = -103 \text{ kJ/mole} \quad (R1.51) \\
\text{Hg} + \text{BrO} & \rightarrow \text{BrHgO} \quad \Delta H_{\text{Rx}} = 114 \text{ kJ/mole} \quad (R1.52) \\
\text{Hg} + \text{ClO} & \rightarrow \text{ClHgO} \quad \Delta H_{\text{Rx}} = 75 \text{ kJ/mole} \quad (R1.53) \\
\text{Hg} + \text{O}_3 & \rightarrow \text{OOHgO} \quad \Delta H_{\text{Rx}} = 114 \text{ kJ/mole} \quad (R1.54)
\end{align*}
\]

The reactions with molecular halogen species are exothermic and may play a role in oxidation of Hg\(^0\) in environments with high halogen concentration, such as flue stacks. The reactions with the halogen oxide species are endothermic and will not be a significant reaction pathway. Reaction (R1.54) was proposed by Calvert et al. as a potential pathway for the formation of the HgO species. Calvert suggests that the formation of the OOHgO intermediate may decompose into HgO and O\(_2\) molecules, thus accounting for the HgO product formation observed in laboratory studies.
(1.8) Goal of Research

The goal of this work is to evaluate potential pathways of atmospheric mercury oxidation. Specifically, this will be accomplished by: determining the kinetic rate coefficients for reactions of $\text{Hg}^0$ with $\text{Br}$ and $\text{Cl}$, evaluating the stability and reactivity of $\text{HgCl}$ and $\text{HgBr}$ intermediate species, and developing new methods to monitor mercury species in both laboratory and field scenarios. The direct determination of the rate coefficient for the reaction of mercury and halogen atoms is essential to understand the biogeochemical cycling of mercury. The results obtained in this study will be vital to the modeling community and provide rate coefficient data to be used in both global and regional mercury models, which can then be used to evaluate the impacts of mercury emissions and develop effective mercury pollution control strategies.
CHAPTER II
EXPERIMENTAL TECHNIQUES FOR KINETIC STUDIES
MONITORING HG$^0$, BR, AND CL ATOMS

(2.1) Background

A detailed understanding of the reactions that control the transformation from elemental mercury to its more reactive counterpart, Hg(II), in the atmosphere is essential to unraveling the effects of mercury on the environment, how the mercury cycle will respond to climate change, and the development of effective environmental policy. To evaluate these complex environmental processes, the identification and determination of kinetic rate coefficients for reactions, which oxidize elemental mercury in the atmosphere is crucial.

Kinetic theory is the study of the fundamental properties of a chemical reaction. Often it is thought of as a study of how fast, the kinetic rate coefficient, and by what pathway, the mechanism, a reaction proceeds. This information can clarify the significance and implications of a reaction in the global biogeochemical system. To understand kinetics, there must be a distinction between the observed rate and the fundamental rate coefficient. The observed rate will be influenced by the how the reaction is observed; the concentration, temperature, pressure and bath gas. It is important to note that it is impossible to “prove” a kinetic rate coefficient, as the observations are always of the observed rate coefficient. However, by observing the reaction under a series of conditions expected behavior are observed and a fundamental rate coefficient
can be determined. It is possible to design an experiment, which tests the mechanistic assumptions made, resulting in an accurate measure of the kinetic rate coefficient.

(2.2) Rate Laws

In order to determine a kinetic rate coefficient, we must define a kinetic rate law. A rate law is the equation, which governs the observe rate coefficients. Rate laws usually take the form,

$$k_{obs} = k[A]^x[B]^y[C]^z \ldots$$  \hspace{1cm} (E2.1)

where $k$ is the "kinetic rate coefficient" and sum of exponents is the "order" of the reaction. Some common rate laws are first, and second order reactions. Although higher order rates are possible, these first two orders are the most commonly employed because the resulting integrated rate law has a simple solution for the kinetic rate coefficient. Table 2.1 contains the order, the reaction, rate equation, the rate law, the integrated rate law, and the plot necessary to solve the integrate rate law for $k$.

<table>
<thead>
<tr>
<th>Order</th>
<th>Reactions</th>
<th>Rate Equation</th>
<th>Rate Law</th>
<th>Integrated Rate Law</th>
<th>Plot Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>A $\rightarrow$ P</td>
<td>$k_{obs} = k[A]$</td>
<td>$\frac{d[A]}{dt} = -k [A]$</td>
<td>$\ln[A] = -kt + \ln[A_0]$</td>
<td>$x = $ time, $y = \ln[A]$</td>
</tr>
<tr>
<td>Second</td>
<td>A + A $\rightarrow$ P</td>
<td>$k_{obs} = k[A]^2$</td>
<td>$\frac{d[A]}{dt} = -k [A]^2$</td>
<td>$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$</td>
<td>$x = $ time, $y = 1/[A]$</td>
</tr>
</tbody>
</table>

(2.3) Three-Body Recombination Reaction Mechanism

The reactions studied in this work are three-body recombination reactions. A three-body recombination reaction consists of an initial collision that generates an excited complex, reaction (R2.1). A portion of the excited complex will directly decompose back
into reactants, reaction (R2.2); while the other portion undergoes an collision and is stabilized, reaction (R2.3)

\[
A + B \rightarrow AB^* \quad \text{(R2.1)}
\]
\[
AB^* \rightarrow A + B \quad \text{(R2.2)}
\]
\[
AB^* + M \rightarrow AB + M \quad \text{(R2.3)}
\]

The derived rate law can be defined as:

\[
k_{\text{obs}} = \frac{k_{R2.1}k_{R2.3}[M][A][B]}{k_{R2.2}} + \frac{k_{R2.1}k_{R2.3}[M][A][B]}{k_{R2.3}[M]} \quad \text{(E2.2)}
\]

In equation (E2.2) it is observed that as \([M] \rightarrow 0\); \(k_{R2.3} \times [M] \rightarrow 0\) so the second term in equation (E2.2) becomes 0 and the expression becomes:

\[
k_{\text{obs}} = \frac{k_{R2.1}k_{R2.3}[M][A][B]}{k_{R2.2}} \quad \text{(E2.3)}
\]

Hence in the low pressure regime we should observe a linear dependence of \(k_{\text{obs}}\).

On the other hand, as that as \([M] \rightarrow \infty\); \(k_{R2.3} \times [M] \rightarrow \infty\) so the first term in equation (E2.2) becomes insignificant and the expression becomes independent of pressure, (E2.4).

\[
k_{\text{obs}} = k_{R2.1}[A][B] \quad \text{(E2.4)}
\]

This behavior results the roll-off curve shown in Figure 2.1.

From the mechanism expressed in equations (R2.1-R2.3) an assessment can be made concerning the expected temperature and bath gas dependencies. In a three body recombination, the excited AB* complex formed in the initial reaction (R2.1) must undergo collisional deactivation. This means that conditions that influence either the energy in the complex or the ability for that transfer to occur will effect the observe rate coefficient.
Figure 2.1: Theoretical plot of the pressure dependent three-body mechanism.

In the case of temperature, we would expect to observe a negative temperature dependence; as the species would be expected to have increasing excess energy as the temperature is increased. In this scenario although the number of collisions maybe increased due to the temperature, fewer of those collisions will result in the transfer of sufficient energy to stabilize the AB* complex to AB.

Bath gases can also influence the observed rate coefficient. The bath gas of a system will be the primary species that collides with the AB* complex. Hence, if the bath gas can readily accept excess energy, like SF$_6$, then we would expect the observed rate coefficient to be higher. Whereas, if the bath gas is a simple molecule like He, which has limited ability to accept excess energy for the AB* species, the observed rate coefficient will be slower.
Pseudo First Order Approximation and Numerical Integration

In an experiment, conditions can be designed so that a second order reaction appears to be first order, i.e. a pseudo first order approximation. The pseudo first order approximation is achieved when the concentration of \([A] \ll [B]\). Under these conditions any change in \([B]\) due to reaction with \([A]\) is insignificant; thus \([B]\) can be considered a constant. The rate law can then be defined as equation (E2.5) where \(k_{\text{obs}}' = k_{\text{obs}}[B]\).

\[
\frac{d[A]}{dt} = -k_{\text{obs}}'[A] \tag{E2.5}
\]

\(k_{\text{obs}}'\) can be observed under a series of conditions, during which \([B]\) is varied. The slope of a plot of \(k_{\text{obs}}'\) vs. \([B]\) results in the kinetic rate coefficient for the reaction.

In general, the pseudo first order approximation requires that the loss of \([B]\) is negligible on the time scale of the observed decays. However, in this work the observed rate coefficients are slow and the mercury concentration is limited by the vapor pressure. This means that the experiment must be run with the radical species in excess to drive the loss of the stable species. Under these conditions the radical concentration is not constant over the time scale of the experiment due the radical self reaction,

\[
B + B + M \rightarrow B_2 + M \tag{R2.4}
\]

where \(B = \text{Cl or Br}\). Here, a simple pseudo first order rate coefficient is not be observed. Instead, the temporal profiles of the stable species, \(A\), and the radical species, \(B\), will be characterized by the following equations,

\[
\frac{d[A]}{dt} = -k_{\text{Hg}}[B][Hg][M] \tag{E2.6}
\]

\[
\frac{d[B]}{dt} = -2k_{R2.4}[B]^2[M] \tag{E2.7}
\]
where $B = \text{Cl or Br}$. In order to obtain a rate coefficient, temporal profiles of both the radical and stable species will be measured using LIF. Effective second order rate coefficients, $k_{R2.4}'$, for the recombination of the radical species will be determined using equation (E2.8), which assumes that first order losses by diffusion and reaction with impurities are negligible, and the observed temporal profiles of the radical species.

$$\frac{1}{[B]} = 2 \times k_{R2.4}' t + \frac{1}{[B]_0}$$

(E2.8)

A linear fit of a plot of $1/[B]$ vs. time gives $k_{R2.4}'$. In addition, the $1/[B]$ plot provides an indication of the precision of the data, as all data under the same temperature and pressure conditions should have the same slope irrespective of initial radical concentration. Substituting the $[B]$ from equation (E2.8) into equation (E2.6), yields equation (E2.9),

$$\frac{d[Hg]}{dt} = -k_{Hg}' [Hg]\left(\frac{1}{2k_{R2.4}' t \times (1/[B]_0)}\right)$$

(E2.9)

and from this equation an effective second order rate coefficient for the oxidation reaction of mercury, $k_{Hg}'$, can be determined.

(2.5) Experimental Approaches for Kinetic Studies

Experimental techniques can be grouped into two approaches: direct and indirect. A direct technique will directly observed the temporal profile of a species over time. An indirect technique will observe the loss of two species; the species of interest and a reference species, from the relationship between these species a kinetic rate will be derived. The oxidation of mercury by halogens has been studied by both a direct and indirect approach; these studies have produced significantly different results.
(2.5.1) \textit{Indirect Techniques}

Determination of kinetic rate coefficients via the relative rate method involves the comparison of two rates:

\begin{align*}
A + X & \rightarrow \text{products}; \quad \text{known, well characterized rate} \quad (R2.5) \\
B + X & \rightarrow \text{products}; \quad \text{unknown, uncharacterized rate} \quad (R2.6)
\end{align*}

where X is a radical species of interest, for mercury reaction this can be Cl, Br, OH, O\textsubscript{3}, ClO and BrO. The reactants will be put in a gas chamber, which has a relatively constant source of X, reaction products are monitored by MS, GC, or FT-IR. From this the amount of A lost to X can be determined. This can then be compared to the loss processes of B and the rate can be determined by relating the two losses, equation (E2.10)

\[
\ln \left( \frac{[B]_t}{[B]_0} \right) = \frac{k_{R2.6}}{k_{R2.5}} \ln \left( \frac{[A]_t}{[A]_0} \right)
\]  \hspace{1cm} (E2.10)

Hence, a plot of the $\ln \left( \frac{[B]_t}{[B]_0} \right)$ vs. $\ln \left( \frac{[A]_t}{[A]_0} \right)$ should result in a straight line with the slope equal to $\frac{k_{R2.6}}{k_{R2.5}}$. The relative rate technique works especially well for hydrocarbon chemistry, and especially poorly for uncharacterized reactions with significant secondary chemistry.

The major advantages of this system are:

1) The kinetic rate coefficients obtained by this approach are under atmospheric conditions.

2) Losses of the radical species, X, by secondary chemistry or due to reaction with impurities are not important because reactants are analyzed by FTIR or GC.
3) The system has no inherent pressure limits, can easily go to high pressures.

4) The system is rapid, relatively simple, and cost effective.

The major disadvantages:

1) It is a relative rate, not absolute; the resulting rate can only be as accurate as the reference rate. Meaning the relative rate technique can only be employed when there is a direct determination of a reaction rate coefficient for a suitable reference reaction.

2) The system can be influenced by secondary chemistry, if that chemistry consumes or produces the stable species or reference species.

3) The system is a static system that is prone to heterogeneous loss of reactant on the walls.

(2.5.2) Direct Techniques

The Laser Induced Fluorescence technique employed to study the mercury/halogen system will be detailed in section 2.5, here will be a brief overview of the basic principle, advantages and disadvantages of the approach.

To perform LIF, first the radicals of interest are generated by photolysis, a laser tuned to a specific transition of the precursor molecule. This initial photolysis will result in a pulse of the radical that can be monitored over time. Traditionally, the stable species, i.e. the species that reacts with the generated radical, will be in pseudo first order excess; so the species whose concentration changes over the time scale of the experiment is the
radical. The stable species can also be monitored by LIF with few complications to the experiment or data analysis.

The species of interest is monitored by introducing another laser, tuned to a specific rovibronic transition of the radical, atom or molecule. The molecule will be excited to an upper electronic state. Once in this excited state the molecule will relax to the ground state; however, this relaxation can occur to several rovibronic levels and the observed fluorescence can occur at multiple wavelengths depending on the molecule. An example of the laser excitation and the resulting fluorescence can be seen in Figure 2.2.

![Principles of LIF detection](image)

**Figure 2.2:** Principles of LIF detection.

The major advantages of this approach are:

1) The slow flow system limits heterogeneous reactions, as there is little contact and limited time for the reactions to occur.

2) The system has no inherent pressure limits.
3) The time is limited only by electronics and laser, so this technique is good for very fast reactions.

4) The laser is monochromatic and results in quantitative radical generation.

5) The laser has a narrow band so the photolysis and probe lasers can be tuned to specific rovibronic transitions increasing sensitivity and selectivity.

The major disadvantages:

1) The reaction must include a species with a photolytic source.

2) The concentrations must be measured in real time.

3) The system can be influence by secondary chemistry if that chemistry, consumes or produces the species of interest.

4) The technique is limited to the species that have accessible excitation wavelengths and observable fluorescence

5) The system has increased operational cost and complexity over other experimental approaches.

(2.6) Principles of Operation: PLP-LIF Schemes

Due to the complex unknown chemistry of the mercury/halogen system, a direct PLP-LIF system, shown in Figure 2.3, was selected as the method to determine kinetic rate coefficients. The system consists of:

1) **Photolytic source of radicals** – a precursor will be photolyzed by Nd:YAG laser at 532nm, 355 nm, 266nm, or 212nm
2) **The Probe Laser** – will be the initial excitation source. This tunable laser will be produced from a dye laser pumped by an Nd:YAG laser.

3) **The Detector** – the resulting fluorescence from the probe laser excitation is detected on a photomultiplier tube, PMT, with appropriate filter pack.

![Diagram of experimental set-up](image)

**Figure 2.3:** General experimental set-up for the PLP-PLIF system, including optical and flow system configurations.

### (2.6.1) PLP-LIF Scheme for the Observation of Chlorine Atoms

Chlorine atoms were produced by photolysis of molecular chlorine using the 355 nm, third harmonic of a Nd:YAG laser.

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \]  

(\text{R2.7})

An output power of approximately 350 mJ per pulse resulted in chlorine concentrations ranging from 2.5 - 13 \times 10^{15} molecules cm^{-3}. The photolysis of molecular chlorine at 355 nm from the ground state, \(^1\Sigma_g^+\), to the repulsive exited state, \(^1\Pi_{1u}\), generates chlorine
atoms almost exclusively in the $^2P^0_{3/2}$ ground state (Busch et al., 1969). This results in a quantum yield for the photolysis of molecular chlorine (Burkholder and Bair, 1983) of 2.

The resulting Cl atoms were monitored by a two-photon LIF excitation scheme described previously in the literature (Sappey and Jeffries, 1989). This excitation scheme involves the two-photon excitation of the spin forbidden $4p\,^4S^0_{3/2} - 3p\,^2P^0_{3/2}$ transition near 233 nm with subsequent fluorescence detection near 755 nm from the $4p\,^4S^0_{3/2} - 4s\,^4P_1$ transition as shown in Figure 2.4. The 233 nm probe laser, with a typical output power of 400 μJ, was generated by mixing the frequency doubled output from a dye laser (Spectra Physics PDL3) with the 1064 nm fundamental from a Nd:YAG laser. The fluorescence was detected by a PMT with both an interference filter centered at 755 nm and a 700 nm cut-off filter to eliminate laser stray light. A 60 cm focal length lens was used to focus the laser beam into the detection volume, resulting in a detection limit of $4.0 \times 10^9$ molecules cm$^{-3}$ for measurements in 200 Torr of nitrogen.

Figure 2.4: The two-photon excitation scheme for the two-photon LIF of Cl atoms. The excitation transition is at 2×233 nm with subsequent fluorescence transition near 755 nm.
(2.6.2) **PLP-LIF Scheme for Br Radicals**

Bromine atoms were produced by photolysis in one of two ways. First, by the photolysis of molecular bromine using the 532 nm, third harmonic of a Nd:YAG laser (R2.8).

\[
\text{Br}_2 + h\nu \rightarrow \text{Br} + \text{Br} \quad \text{(R2.8)}
\]

An output power of approximately 500 mJ per pulse resulted in bromine atom concentrations ranging from \(2.5 - 40 \times 10^{15}\) molecules cm\(^{-3}\). The photolysis of molecular bromine at 532 nm from the \(^3\Pi_{1u}\) and \(^2\Pi_{0u^+}\) bonding states to the \(^1\Pi_{1u}\) repulsive exited state leads to the formation of two bromine atoms. Some of the resulting bromine atoms were electronically excited, however, these excited species were rapidly deactivated to the \(^2\Pi_{3/2}\) ground state (Oldman et al., 1975), resulting in a quantum yield for the photolysis of molecular bromine (Hippler et al., 1984) of 2.

The second method of generation Br atoms is the photolysis of CF\(_3\)Br using 212 nm, fifth harmonic of a Nd:YAG laser (R2.9).

\[
\text{CF}_3\text{Br} + h\nu \rightarrow \text{CF}_3 + \text{Br} \quad \text{(R2.9)}
\]

An output power of approximately 7 mJ per pulse resulted in bromine atom concentrations ranging from \(1 - 100 \times 10^{13}\) molecules cm\(^{-3}\). Some of the resulting bromine atoms were electronically excited, however, these excited species were rapidly deactivated to the \(^2\Pi_{3/2}\) ground state (Oldman et al., 1975) with the addition of H\(_2\), resulting in a quantum yield for the photolysis of CF\(_3\)Br of 1.

The relative Br atom concentration was monitored by a two-photon LIF excitation scheme described previously in the literature (Simeonsson and Sausa, 1994). This excitation scheme involves the two-photon excitation of the spin forbidden 5p \(^4\)D\(_{3/2}\) –
4p$^5$ 2p$^0_{3/2}$ transition near 261 nm with subsequent fluorescence detection near 844 nm from the 5p $^4$D$^0_{3/2}$ – 5s $^4$P$_{3/2}$ transition as shown in Figure 2.5. The 261 nm probe laser, with a typical output powers in the range of 85 - 300 μJ, was generated by frequency doubling the 522 nm output from a tunable dye laser (Spectra Physics PDL3). The fluorescence was detected by a PMT with both an interference filter centered at 850 nm and a 750 nm cut-off filter to eliminate laser stray light. A 60 cm focal length lens was used to focus the laser beam into the detection volume, resulting in a detection limit of $2.0 \times 10^{13}$ molecules cm$^{-3}$ for measurements in high pressures of nitrogen.

![Diagram of two-photon excitation scheme](attachment:image.png)

**Figure 2.5:** The two-photon excitation scheme for the two-photon LIF of Br atoms. The excitation transition is at 2×261 nm with subsequent fluorescence transition near 845 nm.

(2.6.3) **PLP-LIF Scheme for Hg**

The relative Hg concentration was monitored by exciting the 6p $^3$P$_1$ – 6s $^2$S$_0$ transition at 253.7 nm. The excitation beam was generated by frequency doubling the 507
nm output of a dye laser (Spectra Physics PDL3) that was passed through a variable attenuator and reduced to a laser power of approximately 5 μJ, to avoid saturation of the $6p^3P^0_1 – 6s^2^1S_0$ transition, reducing stray light. Resonance fluorescence was observed by a PMT with an interference filter centered at 254 nm. A lens was used to adjust the diameter of the probe beam to about 0.3 cm, approximately half the size of the photolysis laser. This size was found to give best results for the detection of mercury while minimizing diffusion related problems. For the mercury LIF, the detection limit was less than $4 \times 10^{10}$ molecules cm$^{-3}$ for low-pressure helium measurements and $2 \times 10^{11}$ molecules cm$^{-3}$ for measurements conducted in high pressures of nitrogen.

(2.7) Data Acquisition and Signal Processing

Kinetic information was obtained by varying the time between the photolysis and probe lasers. A four channel digital delay generator (Stanford Research Systems, DG535) produced trigger pulses that were used to overlap the lasers and then vary the time between the photolysis and the probe lasers. The fluorescence signal was detected in the system by the appropriate PMT with a filter pack, optimized to reduce Raman and Rayleigh scattering. The LIF detection apparatus is outlined in Table 2.2 for each species.

<table>
<thead>
<tr>
<th>Table 2.2:</th>
<th>Fluorescence detection for relevant species.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>λ</td>
</tr>
<tr>
<td>Hg</td>
<td>254 nm</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>726, 755, 775 nm</td>
</tr>
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<td></td>
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</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>845 nm</td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>

The PMT output was amplified (Sonoma, 310) and processed by a 500MHz scope (Tektronix, TDS 520), terminated at 50Ω. The LIF signal was averaged in the scope,
usually 50 pulses, to limit data loss during transfer. The average LIF signal was transferred to a PC via a GPIB interface. Each temporal profile consisted of 21 data points, 3 normalization points and 6 background measurements.

(2.8) Reaction Cell

All experiments were conducted in a temperature controlled Pyrex reaction vessel. Four mutually perpendicular side arms with quartz windows were attached to the center of the vessel. The photolysis and the probe lasers were overlapped using dichroic mirrors and then propagated through two of the cell’s side arms, perpendicular to the gas flow. The temperature of the reaction vessel was controlled by a circulating bath. During low temperature measurements, windows were constantly flushed with dry air to prevent condensation. A thermocouple was inserted into the reaction zone through a vacuum seal, allowing measurement of the gas temperature under the precise pressure and flow conditions of the experiment. The thermocouple calibration was checked by testing each thermocouple at 100°C (water at the boiling point) and 0°C (a water/ice slurry), all thermocouple were within 2°C of the expected value at both temperatures.

(2.9) Gas Flow System

Reagent gases, such as N₂, Air, He, O₂, H₂ and CH₄, were introduced directly from high pressure storage gas cylinders. Mixtures of halogen molecules and the bath gas were made in Pyrex bulbs by volume addition and then introduced directly into the system from the bulb. All flows were monitored using calibrated mass flow controllers or meters and passed through shut off valves and needle valves as needed. The mass flow
controllers or meters were often calibrated in-situ, using a Gilian Gilibrator 2. The pressure in the reaction cell was monitored with a capacitance manometer. The capacitance manometers were calibrated in the lab by inter-comparison of multiple manometers under vacuum and atmospheric pressure.

Experiments were carried out under “slow-flow” conditions. The gas velocities ranged from 10 - 30 cm s\(^{-1}\) and completely replace the gas mixture in the reaction zone between the laser pulses. Flows were mixed immediately before introduction into the cell to minimize the “dark” reaction.

(2.10) **Concentration Determination of Reagent Gases**

Concentrations of the bath gases (N\(_2\), Air, O\(_2\), He) and the H\(_2\) and CH\(_4\) quenchers were calculated from mass flow rates monitored during experiments by calibrated flow mass flow meters or controllers. Halogen radical precursors (Cl\(_2\), Br\(_2\), CF\(_3\)Br) were introduced from bulb mixture and concentrations were determined in two ways to ensure accurate determination, by mass flow ratios and \textit{in situ} UV photometry at 365 nm using a 1 m cell. The literature cross-section of molecular chlorine (Maric et al., 1993) at 365 nm used was \(1.06 \times 10^{-19}\) cm\(^2\), while for molecular bromine the literature cross-section (Maric et al., 1994) at 365 nm used was \(1.258 \times 10^{-19}\) cm\(^2\). The concentration of CF\(_3\)Br was only determined by flow due to the low concentration and low cross-section of the molecule.

Initial halogen radical concentrations were determined by employing equation (E2.11)
\[
[X] = [X_{\text{precursor}}] \times QY \times \left(1 - \exp \left(\frac{P_L}{h} \left(\frac{c}{\lambda} \left(\frac{\sigma_{\text{Xprecursor}}}{A_L}\right)\right)\right)\right) \tag{E2.11}
\]

where QY is the quantum yield of photolysis reaction, \( P_L \) is the in laser power in joules, \( h \) is Planck’s constant, \( c \) is the speed of light in cm s\(^{-1}\), \( \sigma_{\text{Xprecursor}} \) is the absorbance cross-section for the precursor molecule at the photolysis wavelength in cm\(^2\), \( \lambda \) is the photolysis wavelength in cm, and \( A_L \) is the area of the laser in cm\(^2\). The photolysis laser has a nominally Gaussian profile.

Mercury was introduced into the cell via a calibrated permeation tube, a mercury bubbler, or a high temperature mercury oven. The buffer gas flowed over a mercury permeation tube with a permeation rate between 120 – 7000 ng min\(^{-1}\) depending on temperature. This produced stable mercury concentrations, which ranged from 1 – 60 × 10\(^{12}\) molecules cm\(^{-3}\) under our flow conditions. The second method of producing stable mercury concentrates was to flow the bath gas through a mercury bubbler at room temperature. This produced stable mercury concentrations, which ranged from 5 – 20 × 10\(^{11}\) molecules cm\(^{-3}\) under our flow conditions. Mercury was produced a third way. Mercury was introduced into a heated oven. This oven varied in temperature from room temperature to 120°C, resulting in mercury concentrations ranging from 0.05-20.0 × 10\(^{15}\) molecules cm\(^3\). All lines, running to the oven and from the oven to the cell, were heated to at least 10°C higher than the saturated mercury flow. In this set-up, mercury concentrations were determined by flow. This calculation was confirmed by offline absorption measurement, after the saturated flow was diluted, all [Hg] calculated by were within 25% of [Hg] observed by absorption after dilution.
Elemental mercury could be monitored *in situ* by UV photometry using the 253.7 lines from a mercury lamp. The reaction mixture was flowed through a 1 cm absorption cell and detected by a PMT assembly. However, as the line width of the mercury absorption line, is narrower than the broadened output of the mercury lamp, the effective cross-section depends on the line width of the lamp, requiring a determination of the effective absorption cross-section. The effective cross-section was determined by monitoring absorbance as a function of path length and Hg concentration. Mercury concentrations were generated using a calibrated permeation tube at 100°C and were confirmed by analysis with a Tekran 2537A mercury analyzer. Figure 2.6 shows a plot of absorbance verses mercury concentration ([Hg]) × path length (L) illustrating the deviation from the Beer-Lambert law. For absorbances less than 0.7, the Beer-Lambert law held and the effective cross-section was $1.36 \times 10^{-14}$ cm$^2$. For absorbances greater than 0.7, there was a significant deviation from the Beer-Lambert law and a third order polynomial fit was used to calculate the mercury concentration.

![Observed Data, Linear Fit, Third-order Polynomial Fit](image)

**Figure 2.6:** Absorbance vs. mercury concentration ([Hg]) × path length (L) illustrating the deviation from the Beer-Lambert law.
(2.11) **Chemicals**

N₂, He, H₂, and CH₄ were all UHP grade from either Praxair or Airgas. The Air used in these experiments was Medical Grade USP from Praxair with a N₂/O₂ ratio of 79.0/21.0%. Flow of the bath gas was diverted directly over the mercury source either a Dynacal Permeation Device, Mercury H.E.-SR or a pool of Mallinckrodt Redistilled Purified Mercury. Cl₂ gas was stored a high pressure cylinder, Mathson Cl₂ gas HP grade. For use during the experiment, the Cl₂ gas was transferred into a high pressure bulb and mixed with He. Br₂ (Aldrich) was stored in the liquid form at a temperature of ~5°C. The liquid Br₂ was transferred to a small cold finger with a syringe. This cold finger was then flushed and pumped to remove all lab air. Br₂ gas was then transferred from this cold finger to a high pressure bulb where it was mixed with appropriate bath gas, He or N₂. Solid phase RGM compounds; HgCl₂, HgBr₂, and HgO compounds were stored at room temperature in gas bubblers flushed with N₂ to prevent oxidation during storage.
CHAPTER III
TEMPERATURE AND PRESSURE DEPENDENT RATE COEFFICIENTS FOR THE REACTION OF Hg\(^0\) WITH CHLORINE ATOMS AND THE CHLORINE ATOM SELF REACTION

(3.1) Background

Historically, a major cornerstone of global mercury cycling centered on the relative inertness of Hg\(^0\). This cornerstone has come into question due to observation of rapid atmospheric mercury depletion episodes (AMDEs) in the Arctic (Lindberg et al., 2002; Lu et al., 2001; Schroeder et al., 1998), Antarctic (Ebinghaus et al., 2002; Temme et al., 2003), Greenland (Skov et al., 2004), and Norway (Berg et al., 2001). Disproportionately high levels of oxidized mercury species have been observed in the upper troposphere (Jaffe et al., 2005; Landis et al., 2005; Murphy et al., 2006b; Murphy et al., 2003) and marine boundary layer (MBL) (Hedgecock and Pirrone, 2004; Hedgecock et al., 2003); and a number of studies have reported increased mercury concentrations in remote environments (Lockhart et al., 1998), animal populations (Wagemann et al., 1996) and human populations (Wheatley and Wheatley, 2000). Although these measurements indicate that there is an atmospheric transformation occurring, the exact mechanism has yet to be identified.

To understand the biogeochemical cycling of mercury in terrestrial and aquatic systems and the potential affects of mercury on human and ecological health it is essential to identify this transformation. Mercury events correlate well with tropospheric ozone depletion events, which are known to be triggered by the photolysis of labile halogen species, released from snow pack at polar sunrise (Vogt et al., 1996). It has been
suggested that the mercury transformation mechanism is driven by halogen chemistry. The implications of a mercury halogen reaction for atmospheric mercury chemistry on a global scale are unclear because the precise mechanism of this transformation is not known and very little data is available on rate coefficients for reactions of elemental mercury with halogen radicals.

In this work we report direct measurements of the rate coefficient for the reaction of elemental mercury with chlorine atoms, as a function of temperature and pressure in nitrogen and helium buffer gases.

\[ \text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M} \]  \hspace{1cm} (R1.11)

Kinetic measurements were performed with each of the reactants in excess concentration, with temporal profiles of both reactants being monitored by LIF. Measurements made under conditions in which Cl atoms were the reactant in excess concentration required an accurate concentration calibration and must account for the chlorine atom recombination. Consequently, we also measured the rate coefficient for the recombination of chlorine atoms, under similar experimental conditions.

\[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \]  \hspace{1cm} (R3.1)

(3.2) Experimental

The reaction between gaseous elemental mercury and chlorine atoms was studied by Pulsed Laser Photolysis – Pulsed Laser Induced Fluorescence (PLP-PLIF) as a function of pressure and temperature in nitrogen, helium and air buffer gas. Experiments were conducted at three temperatures 293, 263 and 243 K, and three pressures, 200, 400 and 600 Torr.
Chlorine atoms were produced by pulsed laser photolysis of molecular chlorine. The temporal profiles of both chlorine atoms and mercury atoms were monitored by two and one photon Laser Induced Fluorescence (LIF) respectively. The experimental configuration is extensively detailed in Chapter 2 and Figure 3.1. is an illustration of the experimental set-up employed for this study.

**Figure 3.1:** Experimental set-up for the PLP-PLIF system to detect Hg$^0$ by one photon LIF and Cl atom by two photon LIF, including optical and flow system configurations.

Experiments were carried out under “slow-flow” conditions. The gas velocity was maintained at approximately 13 cm s$^{-1}$, to completely replace the gas mixture in the reaction zone between the laser pulses. All flows were monitored using calibrated mass flow controllers. The pressure was monitored with a capacitance manometer.
Chlorine atoms were produced by photolysis of molecular chlorine by the 355 nm, third harmonic of a Nd:YAG laser.

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \]  

(R2.7)

The photolysis is from the ground state, \(^1\Sigma^+_g\), to the repulsive excited state, \(^1\Pi_{1u}\), generating chlorine atoms almost exclusively in the \(^2P_{3/2}\) ground state (Busch et al., 1969). This results in a quantum yield of 2 for the photolysis of molecular chlorine (Burkholder and Bair, 1983).

The initial chlorine atom concentration produced by photolysis was determined from equation (E3.1) (Rodgers et al., 1980):

\[
[\text{Cl}] = [\text{Cl}_2] \cdot QY \cdot \left(1 - \exp\left(-\frac{P_L}{\pi} \left(\frac{\sigma_{\text{Cl}_2}}{2\lambda A_L}\right)^2\right)\right)
\]

(E3.1)

where QY is the quantum yield of reaction (R2.7), \(P_L\) is the in laser power in joules, \(h\) is Planck’s constant, \(c\) is the speed of light in cm s\(^{-1}\), \(\sigma_{\text{Cl}_2}\) is the absorbance cross-section at 355 nm in cm\(^2\), \(\lambda\) is the laser wavelength in cm, and \(A_L\) is the area of the laser in cm\(^2\). The laser diameter was determined by passing a 0.5 mm pinhole ceramic aperture across the width of the photolysis laser. The transmitted photolysis laser power was recorded in 0.05 cm steps. From the observed beam profile the laser diameter in the reaction volume was determined to be 0.8 ± 0.1 cm. During these experiments an output power of approximately 350 mJ per pulse resulted in chlorine concentrations ranging from 2.5 - 13 \(\times 10^{15}\) molecules cm\(^{-3}\).

The buffer gas flowed over a mercury permeation tube with a permeation rate between 120 – 7000 ng min\(^{-1}\) depending on temperature. This produced stable mercury
concentrations, which ranged from $1 - 60 \times 10^{12}$ molecules cm$^{-3}$ under our flow conditions.

Elemental mercury and molecular chlorine concentrations were monitored \textit{in situ} by UV photometry using the 253.7 and 365 nm lines from a mercury lamp, respectively. After passage through the absorption cell the lamp output was split with a dichroic beamsplitter and detected by two interference filter/photomultiplier (PMT) combinations and each absorbance was recorded. Since the line width of the mercury absorption line, is narrower than the broadened output of the mercury lamp, the effective cross-section depends on the line width of the lamp, the effective cross-section of $1.36 \times 10^{-14}$ cm$^2$ which was determined by monitoring absorbance as a function of path length and Hg concentration. During kinetic measurements an absorption path length between 1 and 100 cm was used, depending on the mercury concentration, in order to maintain an absorption in the range of our calibration curve. The molecular chlorine concentration was also determined by \textit{in situ} UV photometry at 365 nm using a 1 m cell and the literature cross-section of molecular chlorine (Maric et al., 1993) at 365 nm, $1.06 \times 10^{-19}$ cm$^2$.

(3.3) \textbf{Results}

(3.3.1) \textit{Measurements of Hg + Cl + M $\rightarrow$ HgCl + M with Cl in Excess}

Direct determination of rate coefficients for the reactions of gaseous elemental mercury presents a significant experimental challenge due to the low vapor pressure of mercury. This low vapor pressure makes it difficult to study the kinetics of this system using a traditional approach with the stable reactant in pseudo-first order excess for anything other than reactions with very fast rate coefficients. To overcome this difficulty
we made kinetic measurements under conditions in which chlorine atoms were the reactant in pseudo-first order excess whilst simultaneously monitoring the concentration of both reactants.

The rate coefficient for the recombination of mercury and chlorine atoms, $R_{1.11}$, was determined with the Cl atom concentrations typically 1000 times larger than the mercury concentration, $[\text{Cl}] \sim 1000 \times [\text{Hg}]$. Both mercury and chlorine atom concentrations were monitored by LIF. The Cl atom concentration was varied between $1.75 - 13 \times 10^{15}$ molecules cm$^{-3}$, and Hg concentrations were in the range of $0.4 - 15 \times 10^{11}$ molecules cm$^{-3}$.

At the Cl atom concentrations required to observe a significant loss of mercury atoms, the chlorine atom recombination reaction, $R_{3.1}$, resulted in a significant decrease in Cl atom concentration on the timescale of the mercury atom decays. Since the Cl atom concentration was not constant, a simple pseudo-first order decay, i.e. an exponential decay, of the mercury atoms was not observed. Instead, the mercury temporal profiles were fit by numerical integration, and the observed chlorine temporal profiles were analyzed assuming simple second order kinetics.

The temporal profiles of the chlorine and mercury atoms were characterized by equations (E3.2) and (E3.3):

$$\frac{d[Hg]}{dt} = -k_{r_{1.11}} [\text{Cl}][Hg][M]$$  \hspace{1cm} (E3.2)

$$\frac{d[Cl]}{dt} = -2k_{r_{3.1}} [\text{Cl}]^2 [M] - k_{r_{1.11}} [\text{Cl}][Hg][M]$$  \hspace{1cm} (E3.3)
Since the concentration of mercury was at least two orders of magnitude smaller than the initial Cl atom concentration, the second term in equation (E3.3) two is negligible and results in a simplified equation, Equation (E3.4).

$$\frac{d[Cl]}{dt} = -2k_{R3.1}[Cl]^2[M]$$  \hspace{1cm} (E3.4)

For each experimental condition, temporal profiles of chlorine and mercury atoms were measured using LIF. Typical sets of temporal profiles of each atom are shown in Figures 3.2 and 3.3. Under each set of conditions, i.e. a fixed pressure, temperature and initial chlorine atom concentration, the effective second order rate coefficient, $k_{R3.1}'$, for the recombination of chlorine atoms was calculated from equation (E3.5) which assumes that first order losses by diffusion and reaction with impurities are negligible.

$$\frac{1}{[Cl]_0} = 2\times k_{R3.1}'t + \frac{1}{[Cl]_0}$$  \hspace{1cm} (E3.5)

Substituting for [Cl] into equation (E3.2) gives equation (E3.6):

$$\frac{d[Hg]}{dt} = -k_{R1.11}'[Hg]\left(\frac{1}{2k_{R3.1}'t + (1/[Cl]_0)}\right)$$  \hspace{1cm} (E3.6)

This equation was numerically integrated to give the best fit to the measured mercury profiles and hence a value for $k_{R1.11}'$, the effective second order rate coefficient for the recombination of Hg with Cl. The numerical integration procedure was checked by simulating the measured decays using the derived values of $k_{R1.11}'$ and $k_{R3.1}'$ in the ACUCHEM program (Braun et al., 1986). The numerically integrated fits to the observed mercury temporal profiles are shown as lines in Figure 3.3 and the second order rate coefficients, $k_{R1.11}'$, obtained in He and N$_2$ are listed in Table 3.1. Molecular nitrogen quenched the mercury fluorescence efficiently, therefore, the fluorescence yield and thus
the S/N ratio degraded with increasing pressure. This accuracy of the pressure dependent rate data should not have been significantly affected by this reduction of the S/N ratio.

Table 3.1: Second order rate coefficients for the recombination of mercury and chlorine atoms, $k_{R1.11}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T$ (K)</th>
<th>$P$ (Torr)</th>
<th>$k_{R1.11}^r ± 2\sigma$ error (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
<td></td>
<td>$(1.91 ± 0.69) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td></td>
<td>$(4.68 ± 1.33) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>$(9.35 ± 2.44) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>200</td>
<td></td>
<td>$(1.73 ± 0.57) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td></td>
<td>$(4.96 ± 0.46) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>$(7.18 ± 0.93) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td></td>
<td>$(1.18 ± 0.43) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>$(3.01 ± 0.36) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td>$(4.42 ± 0.90) \times 10^{-13}$</td>
</tr>
<tr>
<td>$He$</td>
<td>293</td>
<td></td>
<td>$(0.48 ± 0.12) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
<td>$(1.19 ± 0.35) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td>$(1.93 ± 0.42) \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Figure 3.2: Typical chlorine atom temporal profiles, shown for measurements conducted in 600 Torr N2 at 293 K.
The third order recombination rate coefficients were then determined from linear fits of the plots of the second order rate coefficients, $k_{R1.11'}$, versus the concentration of $\text{N}_2$ or He as shown in Figure 3.4. The plots show the expected linear dependence of rate coefficient versus concentration indicating that the reaction was in the low pressure, third order regime as might be expected for an atom-atom recombination. However, the plots show a slight negative offset, the magnitude of which increases with temperature. Assuming that the recombination rate coefficients are in the low pressure limit, the effective second order rate coefficient should be zero at zero pressure. Consequently the third order recombination rate coefficients, $k_{R1.11}$, have been calculated by forcing the plots through the origin. The difference between the forced and unforced slopes varied between 10% for the $\text{N}_2$ data at 293 K to 25% for the $\text{N}_2$ data at 243 K. As we show
below, similar behavior was observed in the Cl atom recombination data. The third order recombination rate coefficients, $k_{R1.11}$, are listed in Table 3.2 and plotted in Arrhenius form in Figure 3.5. The Arrhenius expression for R1.11 is given by equation (E3.7) reported with $2\sigma$ errors of precision only.

$$k_{R1.11,N_2}(243-298K) = (2.2 \pm 0.5) \times 10^{-32} \exp\left[(680 \pm 400) \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

(E3.7)

However, due to uncertainty in the calculation of absolute Cl atom concentrations, which are discussed below; we conservatively estimate the error in the rate coefficient to be $\pm 50\%$. The observed behavior is consistent with a three-body recombination, demonstrating a positive pressure dependence, an inverse temperature dependence, and a slower rate coefficient in helium than in nitrogen.

Figure 3.4: Variation of the effective second order rate coefficients for the recombination Hg and Cl atoms, $k_{R1.11}'$, with pressure.
Table 3.2: Third order rate coefficients for the recombination of mercury and chlorine atoms, $k_{R1.11}$, determined in this work at 293 K in He and 243, 263, and 293 K in N$_2$, with the resulting Arrhenius expression for N$_2$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>$k_{R1.11} \pm 2\sigma$ error (cm$^6$ molecule$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>293</td>
<td>$(9.37 \pm 0.95) \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>$(35.3 \pm 7.6) \times 10^{-33}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>263</td>
<td>$(32.4 \pm 3.5) \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>$(22.2 \pm 1.7) \times 10^{-33}$</td>
</tr>
</tbody>
</table>

Arrhenius Expression

$(2.2 \pm 0.5) \times 10^{-32} \exp \left( \frac{680 \pm 400}{T} \left( \frac{1}{T} - \frac{1}{298} \right) \right)$

Figure 3.5: Arrhenius plot of the third order rate coefficients for the recombination of Hg and Cl atoms, $k_{R1.11}$, in N$_2$ and He.

(3.3.2) Measurements with Mercury in Excess

To confirm the reported mercury chlorine recombination rate coefficient, $k_{R1.11}$, measurements were done with mercury in pseudo-first order excess over chlorine atoms, [Hg] $\sim 60 \times$ [Cl]. Experiments were conducted at 298 K and 200 Torr. A heated permeation tube generated Hg concentrations close to the vapor pressure of mercury at
298 K. Mercury atom and molecular chlorine concentrations were monitored photometrically. The initial Cl atom concentration was kept below $1.0 \times 10^{12}$ molecules cm$^{-3}$. The chlorine atom profiles are shown in Figure 3.6. Under these conditions chlorine atom temporal profiles should follow the simple first order exponential behavior given by equation (E3.8).

$$[\text{Cl}]_t = [\text{Cl}]_0 \times \exp(-k't) \quad \text{(E3.8)}$$

In the third order low pressure limit, $k'$ is equal to $k_{R1.11} [\text{Hg}][\text{M}] + k_d$, where $k_d$ was the background loss of chlorine atoms by self-reaction, reaction with impurities, and loss due to diffusion. The average of three experiments with no mercury in the cell gave a background chlorine decay rate, $k_d$, of $79 \pm 14 \text{ s}^{-1}$. Four measurements were then made with an Hg concentration of $5.3 \times 10^{13}$ molecules cm$^{-3}$, for which the decay rate increased to $87 \pm 20 \text{ s}^{-1}$. In each case the error represents a $2\sigma$ measure of precision only. The difference between the pseudo-first order decay rates obtained in the two determinations was $8 \pm 24 \text{ s}^{-1}$. Based on our measured rate coefficient at 293 K and 200 Torr in N$_2$ and the measured Hg concentration we would expect an increase in the pseudo-first order rate of $7.6 \text{ s}^{-1}$ ($k'[\text{M}] \times [\text{Hg}] = 1.43 \times 10^{-13} \times 5.3\times10^{13}$). Hence this measurement, which does not depend on a calculated chlorine atom concentration, is in excellent agreement with the value obtained with chlorine atoms in excess.
Figure 3.6: Temporal profile of Cl atoms with mercury in excess concentration. Profiles of Cl in the presence and absence of mercury have been shifted for clarity. The dotted line shows the best fit to the Hg + Cl decay. The thick solid line shows the calculated temporal profile derived from the Arrhenius expression determined from measurements with Cl in excess. Other lines show the calculated temporal profiles based on rate coefficients reported by Ariya et al., 2002 and Spicer et al., 2002.

(3.3.3) Measurements of Cl + Cl + M → Cl₂ + M (M = He, N₂)

The determination of temporal profiles of Cl atom concentration was a critical component in measuring the rate coefficient for the mercury and chlorine recombination reaction. The relative concentration profile was determined with good precision, ±10%, using LIF. However, the initial Cl atom concentration was calculated and was, we believe, the largest source of systematic error in the reported rate coefficient for R1.11. We can, however, make some assessment of the accuracy of this calculation by comparing our measured chlorine atom recombination rate coefficients, which also
depends on the accuracy of the Cl atom concentration calibration, with literature values. As shown in Figure 3.2, chlorine atom temporal profiles were monitored by LIF with the concentration typically followed to 5-20% of the original chlorine atom signal. Under each set of experimental conditions, i.e. a fixed pressure, temperature and initial chlorine atom concentration, the effective second order rate coefficient, $k'_{R3.1}$, for the recombination of Cl atoms was calculated from the Cl temporal profile using equation (E3.9), again assuming a negligible first order loss due to reaction with impurities or diffusion.

$$\frac{1}{[Cl]} = 2 \times k'_{R3.1} t + \frac{1}{[Cl]_0}$$  \hspace{1cm} (E3.9)

Linear fits of plots of $1/[Cl]$ vs. time give the effective second order recombination rate coefficient, $k'_{R3.1}$. Figure 3.7 shows a series of plots for the reciprocal of absolute chlorine atom concentration versus time. This plot provides an indication of the precision of the data, since all data series under the same temperature and pressure conditions should have the same slope irrespective of initial Cl atom concentration. The data shown in Figure 3.7 were taken at 293 K in 600 Torr nitrogen buffer gas with initial Cl atom concentrations ranging from $1.8 - 9.9 \times 10^{15}$. The plots demonstrated excellent linearity and gave an average second order recombination rate coefficient of $(1.71 \pm 0.17) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ where the uncertainty is a 2σ error of precision. To ensure that the addition of mercury did not affect the observed Cl atom decay, experiments were conducted in the presence and absence of mercury. The temporal profiles and derived rate coefficients were identical, within the precision of the measurements. This was expected since the Hg concentration was at least two orders of magnitude smaller than the initial
Cl atom concentration. The values of the effective second order rate coefficients together with $2\sigma$ errors are summarized in Table 3.3.

![Figure 3.7](image.png)

**Figure 3.7:** Second order rate coefficient plot for Cl atom, shown for measurements conducted in 600 Torr N$_2$ at 293 K.

![Figure 3.8](image.png)

**Figure 3.8:** Second order rate coefficient plot for Cl atom, shown for measurements conducted in 600 Torr N$_2$ at 293 K.
Table 3.3: Second order rate coefficients for the recombination of chlorine atoms, $k_{R3.1}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R3.1}$ ± 2σ error (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>243</td>
<td>200</td>
<td>$(9.30 \pm 1.97) \times 10^{-14}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>200</td>
<td>200</td>
<td>$(6.20 \pm 1.22) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>200</td>
<td>$(6.00 \pm 1.00) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>200</td>
<td>$(4.41 \pm 0.85) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>200</td>
<td>$(4.41 \pm 0.85) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>200</td>
<td>$(4.41 \pm 0.85) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>200</td>
<td>$(4.41 \pm 0.85) \times 10^{-14}$</td>
</tr>
<tr>
<td>He</td>
<td>293</td>
<td>200</td>
<td>$(2.65 \pm 1.32) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>200</td>
<td>$(2.65 \pm 1.32) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>200</td>
<td>$(2.65 \pm 1.32) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>200</td>
<td>$(2.65 \pm 1.32) \times 10^{-14}$</td>
</tr>
</tbody>
</table>

The third order recombination rate coefficients were then determined from linear fits of the plot of second order rate coefficients, $k_{R3.1}'$, versus concentration of N$_2$ or He as shown in Figure 3.8. As is the case for the Hg + Cl recombination, the data show a good linear dependence of the effective second order rate coefficient on pressure. However, we again see a consistent, negative offset. As for R1.11, the third order rate coefficients were obtained by forcing all fits through the origin. The forced plots pass through most of the error bars associated with each data point while the difference in the slopes of the forced and unforced fits varies from 12% to 17%. The third order recombination rate coefficients, $k_{R3.1}$, are listed in Table 3.4 and plotted in Arrhenius form in Figure 3.9. For the data in nitrogen the resulting Arrhenius expression is given by (E3.10).

$$ k_{R3.1,N_2}(243 - 298K) = (8.4 \pm 2.3) \times 10^{-33} \exp\left(850 \pm 470\left(\frac{1}{T} - \frac{1}{298}\right)\right) \quad (E3.10) $$
Figure 3.9: Arrhenius plot of the third order rate coefficients for the recombination of Cl atoms, $k_{R3.1}$, in $N_2$ and He. Literature values are shown for comparison.

In equation (E3.10) the uncertainties are measures of $2\sigma$ error of precision only. As we discuss in detail below we estimate an uncertainty of $\pm 50\%$ in the accuracy of the rate coefficient, due principally to the uncertainty in the calculation of absolute Cl atom concentrations. Overall the data showed the expected behavior for a three-body recombination, a positive pressure dependence, an inverse temperature dependence, and a higher deactivation efficiency for nitrogen relative to helium.

Table 3.4: Third order rate coefficients for the recombination of chlorine atoms, $k_{R3.1}$, determined in this work at 293 K in He and 243, 263, and 293 K in $N_2$, with the resulting Arrhenius expression for $N_2$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>$k_{R3.1} \pm 2\sigma$ error (cm$^6$ molecule$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>293</td>
<td>$(5.17 \pm 0.49) \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>$(15.2 \pm 2.0) \times 10^{-33}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>263</td>
<td>$(13.5 \pm 2.0) \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>$(8.48 \pm 0.71) \times 10^{-33}$</td>
</tr>
</tbody>
</table>

**Arrhenius Expression**

$$k_{R3.1} = \frac{(8.4 \pm 2.3) \times 10^{-33} \exp \left[ -\frac{850 \pm 470}{T} \left( \frac{1}{298} \right) \right]}{T}$$
(3.3.4) Measurements in Air

We observed a large increase in the chlorine atom decay rate in air buffer gas as compared with measurements in N₂. If this loss were solely due to Cl atom recombination it would have resulted in an increase in the recombination rate coefficient by a factor of 25 implying a two order of magnitude increase in the deactivation efficiency of O₂ relative to N₂. This is not consistent with the expected relative three body efficiencies of nitrogen and oxygen suggesting an additional loss of Cl atoms due to secondary chemistry.

One possible explanation of the observed increase in the recombination rate coefficient in air is the following reaction sequence (R3.2-R3.4):

\[
\begin{align*}
\text{Cl} + \text{O}_2 + \text{M} & \leftrightarrow \text{ClO}_2 + \text{M} \quad \text{(R3.2)} \\
\text{Cl} + \text{ClO}_2 & \rightarrow \text{Cl}_2 + \text{O}_2 \quad \text{(R3.3)} \\
\text{Cl} + \text{ClO}_2 & \rightarrow 2\text{ClO} \quad \text{(R3.4)}
\end{align*}
\]

To determine if this additional ClOx chemistry could account for the observed increased loss of Cl atoms, we performed simulations in ACUCHEM (Braun et al., 1986) using a simplified reaction system consisting of reactions (R3.1-R3.4). The JPL panel recommended rate coefficients (Sander et al., 2003) were used for reactions (R3.2-R3.4), and the rate coefficient determined in nitrogen during this work was used for R3.1. Simulations were also performed using a more complex reaction system, which included the secondary reactions of the products, ClO and ClO₂. However, these reactions were not fast enough to influence the chlorine atom decay and the simplified system was an adequate mechanism. The fits were able to reproduce the increased decay rate within the error range of the rate coefficients and equilibrium constant for reaction (R3.2).
Therefore, the proposed ClOx chemistry can account for the observed increased loss of chlorine atoms.

A significant enhancement in the apparent recombination rate coefficient of mercury and chlorine atoms was also observed in the presence of air. If this loss were solely due to the mercury chlorine recombination reaction it would have resulted in an increase in the recombination rate coefficient by a factor of 4 relative to the rate coefficient obtained in N₂. Again this is not consistent with the expected relative three body efficiencies of nitrogen and oxygen and we have chosen not to report a recombination rate coefficient for M = O₂. This observation suggests an additional loss of mercury atoms due to the secondary chemistry described above. Based on this chemistry the only plausible candidates are ClO or ClO₂ and we plan to investigate the reactivity of elemental Hg with these species.

(3.3.5)  **Measurement of the Rate Coefficient for the Reaction Cl + C₂H₆ → Products**

Two photon LIF has not been used in this laboratory to monitor Cl atom temporal profiles in kinetics experiments. Therefore, the experimental configuration was tested by measuring the rate coefficient for the reaction of chlorine atoms with ethane.

\[ \text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl} \]  \hspace{1cm} (R3.5)

The rate coefficient, \( k_{R3.5} \), was determined at 298 K and 200 Torr, using two-photon LIF detection of chlorine atoms with ethane molecules in pseudo-first order excess concentration, \([\text{C}_2\text{H}_6] > 500 \times [\text{Cl}]\).
Chlorine atom temporal profiles were analyzed assuming simple first order exponential behavior, where $k_{R3.5}$, the rate coefficient for reaction (R3.5), is determined by Equation (E3.11).

\[
[CI]_t = [CI]_0 \times \exp(-k_{R3.5}t)
\]  
(E3.11)

Where $k'_{R3.5} = k_{R3.5} \times [C_2H_6] + k_d$, and $k_d$ was the background loss of chlorine atoms by diffusion, self-reaction, and reaction with impurities. The pseudo-first order rate coefficient for reaction (R3.5) was determined at five ethane concentrations ranging from $5 \times 10^{13}$ to $11 \times 10^{13}$. We determined a rate coefficient with a $2\sigma$ error of $(5.2 \pm 0.6) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ which is in good agreement with the literature value (Sander et al., 2003) of $(5.7 \pm 1.1) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. The good agreement of the rate coefficient determined for reaction (R3.5) by this work and the reference value confirms the viability of the two photon PLP-PLIF system employed in this work to measure CI atom temporal profiles.

(3.3.6) Potential Sources of Systematic Error

As we have noted above the variation of effective second order rate coefficients with pressure should show a linear dependence which passes through the origin. In fact the data consistently show slight negative offsets which may be indicative of a systematic error in the calculation of the chlorine atom concentration. It should be noted that these offsets were relatively small, in the case of the N$_2$ data all the intercepts lay within a $4\sigma$ error of the origin. The fits also passed within the $2\sigma$ errors of precision associated with each data point in most cases.
To calculate the initial chlorine atom concentration equation (E3.1) was employed using the absorption cross-section of chlorine molecules at 355 nm, the molecular chlorine concentration, the average laser power, and the laser diameter. The error associated with the first two parameters in equation (E3.1) should be less than 5%. There was some uncertainty in the laser diameter because the laser beam has a nominally Gaussian intensity profile. As discussed previously the laser diameter was determined by measuring the laser power through a pinhole across the width of the beam. We estimate the maximum error in the diameter determination to be less then 15%. Finally, we have the error associated with the calibration of the laser power meter, homogeneity within the beam profile and shot to shot variability which we estimate gives an uncertainty in the fluence in the range of 25%. We believe that ± 50% represents a conservative overall estimate of the uncertainty in the initial Cl atom concentration. As we discuss below, a comparison of our measured Cl atom recombination rates in He, with literature values, suggests that this estimate is reasonable.

(3.4) Discussion and Comparison with Previous Work

(3.4.1) Chlorine Atom Recombination

The chlorine atom recombination reaction rate coefficient, $k_{R3.1}$, has been determined in both helium and nitrogen in several studies (Bader and Ogryzlo, 1964; Hippler and Troe, 1973, 1976; Weng et al., 1987; Widman and DeGraff, 1973). The results of these studies, including the specific pressure and temperature regimes used are outlined in Table 3.5 and Figure 3.9. The agreement between the rate coefficients obtained in this experiment and previous measurements in helium is good. Our reported
rates lie between the most recently reported measurements but agree within the respective error limits. The difference between our rate coefficient and the most recent rate coefficient reported by Hippler et al. (Hippler and Troe, 1976) is less than 10%, while our results are about 20% lower than the value reported by Widman et al. (Widman and DeGraff, 1973). The good agreement between the measurements suggests that our calculation of the initial Cl atom concentration is accurate and the uncertainty estimate is conservative.

The discrepancy between the rate coefficients determined in this work and the previous results in nitrogen is greater. In nitrogen, all data agrees within a factor of three, with the rate coefficient determined in this work being the slowest rate coefficient. The most recently reported data from Weng et al. (Weng et al., 1987) is 60% faster than our determination; this is within the combined error limits.

We can identify one possible complication in our rate coefficient determination that might account for a systematic discrepancy between the results in He and N₂. A significant impurity in the N₂ might result in additional loss of chlorine atoms by reaction. However, any additional reaction, which resulted in the loss of chlorine atoms, would increase the observed rate coefficient. Since the rate coefficient that we observed is slower than the previous studies it seems unlikely that our system was influenced by this complication. Any other systematic errors should influence the results in He and N₂ in a similar manner.
### Table 3.5: Comparison of literature data for third order rate coefficients for the recombination of chlorine atoms, $k_{R3.1}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R3.1}$ (cm$^6$ molecule$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>(a)</strong></td>
</tr>
<tr>
<td>N$_2$</td>
<td>296</td>
<td>450-1280</td>
<td>$(1.38 \pm 0.28) \times 10^{-32}$</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760-1520</td>
<td>$(2.21 \pm 0.55) \times 10^{-32}$</td>
</tr>
<tr>
<td></td>
<td>293-373</td>
<td>760</td>
<td>$1.6 \times 10^{-33}$ exp$^{(1.6 \pm 1987/RT)}$</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>200-600</td>
<td>$(8.4 \pm 2.3) \times 10^{-33}$ exp$^{(850 \pm 470) \left(\frac{1}{T} - \frac{1}{298}\right)}$</td>
</tr>
<tr>
<td>He</td>
<td>298</td>
<td>760-1520</td>
<td>$(4.68 \pm 0.55) \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$4.05 \times 10^{-33}$ exp$^{(0.26 \pm 9.94(kcal/mole)/RT)}$</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.6 - 0.4</td>
<td>$8.27 \times 10^{-33}$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>200-600</td>
<td>$(5.17 \pm 0.49) \times 10^{-33}$</td>
</tr>
</tbody>
</table>

(a) Weng et al., 1987; (b) Hippler and Troe, 1976; (c) Widman and DeGraff, 1973; (d) Bader and Ogryzlo, 1964; (e) This work

#### (3.4.2) Mercury and Chlorine Atom Recombination

Three previous experimental determinations (Ariya et al., 2002; Horne et al., 1968; Spicer et al., 2002) and one theoretical study (Khalizov et al., 2003) have reported values for $R1.11$ and these results are compared with the current work in Table 3.6. Horne et al. (Horne et al., 1968) used flash photolysis combined with absorption spectroscopy to study $R1.11$ at temperatures 383-443 K and 720 Torr. The Horne study reported a rate coefficient for the mercury chlorine recombination of $5.0 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ in CF$_3$Cl and $1.5 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ in Ar, with a reported error of a factor of 3.

The rate coefficients obtained are not directly comparable to those reported here, due to temperature and buffer gas differences. However, the large difference in the rate coefficients cannot be reasonably explained by the differences in experimental conditions. Amongst the potential problems associated with this experiment, two appear to be particularly significant. First, the system was a static system where a gas mixture...
undergoes repeated flashes. This experimental approach increases the possibility of secondary chemistry, product photolysis and interfering species. Second, to determine the rate coefficient for R1.11 it was necessary to determine the absolute mercury chloride (HgCl) concentration. Horne et al. determined mercury chloride concentrations by determining the loss of mercury and assuming that all the mercury that is lost in the system is converted to mercury chloride. This determination could have a large uncertainty and could be influenced by secondary loss processes of mercury. These complications could lead to significant errors in the calculation of the absolute concentration.

Table 3.6: Reported rate coefficients for the recombination of mercury and chlorine atoms, $k_{R1.11}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R1.11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(cm$^3$ molecule$^{-1}$ s$^{-1}$) (a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(cm$^3$ molecule$^{-1}$ s$^{-1}$) (b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(cm$^3$ molecule$^{-1}$ s$^{-1}$) (c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(cm$^3$ molecule$^{-1}$ s$^{-1}$) (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(cm$^3$ molecule$^{-1}$ s$^{-1}$) (e)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>298</td>
<td>760</td>
<td>$6.4 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$(1.0 \pm 0.2) \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>383-443</td>
<td>720</td>
<td>$1.38 \times 10^{-12} \exp^{208.02/T}$</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>200-600</td>
<td>$(2.2 \pm 0.5) \times 10^{-32} \exp^{\left[\frac{(680\pm 400)}{T} \frac{1}{298}\right]}$</td>
</tr>
<tr>
<td>He</td>
<td>243-293</td>
<td>200-600</td>
<td>$(9.37 \pm 0.95) \times 10^{-33}$</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>383-443</td>
<td>720</td>
<td>$5.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>Ar</td>
<td>383-443</td>
<td>720</td>
<td>$1.5 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

(a) Spicer et al., 2002; (b) Ariya et al., 2002; (c) Khalizov et al., 2003; (d) This work; (e) Horne et al., 1968

Two more recent studies have utilized relative rate techniques at pressures of one atmosphere and at room temperature. Ariya et al. (Ariya et al., 2002) reported a rate coefficient of $(1.0 \pm 0.2) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. This study was conducted in a static 2 L or 3 L Pyrex flask. Five different reference molecules were used obtaining results, which differed by a factor of 270 in the measured relative rates together with a strong non-linearity of the relative rate plot when determined in a bath gas of air. They
concluded that the variation was caused by the presence of a secondary reaction between the reference molecules and OH. The buffer gas was switched from air to nitrogen to eliminate oxygen chemistry, giving an overall reduction in the observed rate. However, the variation in the measured relative rate between the reference molecules was still a factor of 30 and the non-linearity remained. Ultimately, a series of 8 measurements were made using 1,3-dichloropropane as the reference molecule, and the addition of 835 ppm of benzene, as an OH scavenger. The reported rate coefficient was determined from this small sub-set of the data.

The second relative rate study, Spicer et al. (Spicer et al., 2002), was performed on much more limited set of experiments monitoring mercury loss relative to that of dimethylsulfide (DMS) in air. This work was performed in a 17.3 m$^3$ environmental chamber. Ultimately, Spicer et al. reported a value of $6.4 \times 10^{-11}$ cm$^3$molecules$^{-1}$s$^{-1}$.

The large dependence of the measured relative rate coefficient on the identity of the reference compound demonstrates clearly that the study of Ariya et al. was influenced by secondary chemistry. The large discrepancy observed between measurement in air and nitrogen, and the non-linearity observed in the relative rate plots in both bath gases are further confirmation of this. Ariya et al. attributes the secondary chemistry to the formation of OH but offer no mechanism for OH formation in nitrogen buffer. It should also be noted that an enhanced removal of the reference compound by secondary chemistry would produce an under-estimate of the rate coefficient. However, the rate coefficients obtained in both competitive rate studies exceed any reasonable theoretical estimate of the rate coefficient. We feel that a more plausible explanation would be additional loss of mercury, either by heterogeneous reaction or possibly by a gas phase
reaction with an oxygenated species, like ClO. An additional process that removed mercury would generate the observed faster rate coefficient.

Figure 3.6 shows the experimental temporal profiles of chlorine atoms in the presence and absence of mercury at its saturation vapor pressure. As we show above the difference between the pseudo-first order decay rate, $8 \pm 24$ s$^{-1}$, agrees well with that calculated from our measured rate coefficient with Cl atoms in excess, 7.6 s$^{-1}$. However the calculated pseudo-first order decay rates using the rate coefficients reported in the competitive rate studies would be much larger. Assuming a linear dependence on pressure the rate coefficient reported by Ariya et al. would produce an increase in the pseudo-first order decay rate of 139 s$^{-1}$ ($2.63 \times 10^{-12} \times 5.3 \times 10^{13}$) in the presence of mercury. As shown in Figure 3.6, this would lead to an overall pseudo-first order decay rate of 218 s$^{-1}$, which would be clearly distinguishable from the decay in the absence of mercury. The increase in pseudo-first order decay rate calculated from the rate coefficient of Spicer et al. would be even larger, 893 s$^{-1}$ ($1.68 \times 10^{-11} \times 5.3 \times 10^{13}$). The temporal profiles calculated using these rate coefficients are shown in Figure 3.6 and it is clear that they are not compatible with our experimental data.

Khalizov et al. (Khalizov et al., 2003) determined the recombination rate coefficient for R1.11 using electronic structure calculations to obtain both molecular parameters and the capture rate or high-pressure limit. Once this high pressure limit was obtained, Khalizov et al. determined a pressure dependent rate coefficient by assuming a strong collisional deactivation. In order to compare this with the observed data it is essential to consider the mechanism of a three-body recombination. A three-body recombination consists of an initial collision that generates an excited complex, reaction
A portion of the excited complex will directly decompose back into reactants, reaction (R3.7); while the other portion undergoes an collision and is stabilized, reaction (R3.8)

\[
\begin{align*}
  \text{Hg} + \text{Cl} & \rightarrow \text{HgCl}^* \quad \text{(R3.6)} \\
  \text{HgCl}^* & \rightarrow \text{Hg} + \text{Cl} \quad \text{(R3.7)} \\
  \text{HgCl}^* + \text{M} & \rightarrow \text{HgCl} + \text{M} \quad \text{(R3.8)}
\end{align*}
\]

The calculated pressure dependent rate coefficient reported by Khalizov et al. assumed that every collision of the buffer gas with the initially formed energized HgCl* complex deactivated the complex to produce a stable HgCl molecule that cannot dissociate to products. This typically unrealistic assumption should produce the maximum possible recombination rate coefficient at any particular pressure. The value they obtained, \(2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}\) at 298 K, 760 Torr, is a factor of three smaller than the rate coefficient reported by Ariya et al. and a factor of twenty smaller than that reported by Spicer et al.

On the other hand, this rate coefficient is a factor of five faster than the rate coefficient report in this work. This difference can be attributed to the fact that not all collisions with the buffer gas will transfer sufficient energy to stabilize the molecule, resulting in a slower rate coefficient.

In this work the measurement of \(k_{R1.11}\), was performed under two experimental configurations at room temperature. First, the rate coefficients were obtained with chlorine in excess, where an absolute determination of the chlorine atom concentration was necessary. For confirmation a limited set of experiments were performed in a second configuration with mercury in excess, where it was not necessary to determine the
absolute chlorine atom concentration. There is good agreement between these two rate coefficient determinations. This agreement suggests that the determination of the initial chlorine atom concentration is not a source of significant error for either R1.11 or R3.1. We would also note that this is the first study of R1.11 that has systematically varied the temperature, pressure and buffer gases. The observed behavior was entirely consistent with the behavior expected for a three-body recombination.

(3.5) Summary

We have reported recombination rate coefficients for the reaction of mercury and chlorine atoms, \( k_{R1.11} \), together with the self-reaction of chlorine atoms, \( k_{R3.1} \). In both cases the rate coefficients show pressure, temperature and third body deactivation efficiencies, which are consistent with three-body recombination. For R1.11, the recombination of chlorine with mercury we obtain rate coefficients that are much smaller than previously reported results. For this reaction measurements were conducted in two experimental configurations with either mercury or chlorine atoms in excess, both methods obtained similar results. The large discrepancy observed between this work and the previous studies questions the viability of using the relative rate method to determine kinetic rate coefficients for mercury halogen reactions. For R3.1, the self-reaction of chlorine atoms, we obtain results, which are in good agreement with literature values in helium buffer gas. The rate coefficient obtained in nitrogen is smaller than those obtained in prior studies.

To evaluate the importance of the recombination of elemental mercury and chlorine atoms, an effective second order rate coefficient of \( 8.7 \times 10^{-13} \) cm\(^3\) molecules\(^{-1}\)s\(^{-1}\)
was calculated from the reported Arrehenius expression for Arctic conditions, 260 K and 760 Torr. Assuming a peak concentration (Boudries and Bottenheim, 2000) of chlorine atoms of $10^4$-$10^5$ cm$^{-3}$ the lifetime of mercury due to reaction with chlorine atoms is between 3.7 years – 134 days. This suggests that the recombination reaction of mercury with chlorine atoms does not contribute significantly to the chemistry of mercury depletion events.
CHAPTER IV
TEMPERATURE AND PRESSURE DEPENDENT RATE COEFFICIENTS FOR THE REACTION OF Hg\(^0\) WITH BROMINE ATOMS AND THE BROMINE ATOM SELF REACTION

(4.1) Background

In the atmosphere mercury exists primarily in its elemental form, Hg\(^0\), which, until recently, was thought to be relatively unreactive in the gas phase. Hg\(^0\) is relatively insoluble, 0.303 \(\mu\)M (Lin and Pehkonen, 1999), in water and has a low deposition rate. Estimates of the atmospheric lifetime of Hg\(^0\) vary, but it is believed to be in the range of six months to one year. Mercury is a known toxin, and over the last decade there have been observations of increased mercury levels in Arctic lake waters (Lockhart et al., 1998), Arctic animal populations (Wagemann et al., 1996), and Arctic indigenous human populations (Wheatley and Wheatley, 2000). With no known local sources of mercury and no known physical or chemical process that could concentrate mercury in the Arctic, these high levels of mercury were an enigma and a significant health concern.

In addition, observations have shown that there is a fast atmospheric transformation of Hg\(^0\) in Polar Regions; these have become known as atmospheric mercury depletion episodes (AMDEs). Mercury depletion events demonstrate a strong correlation to tropospheric ozone depletion. Early measurements in the Arctic (Barrie et al., 1988) revealed a large increase in the levels of filterable bromine compounds which coincided with the ozone depletion events. Direct spectroscopic observations have shown that large increases in bromine monoxide, BrO, concentrations also coincide with these...
depletion events; it seems clear that a catalytic cycle involving BrO plays a role in ozone depletion episodes (Sander et al., 1997). It is then reasonable to suspect that similar halogen chemistry is driving AMDEs. The reactions of Hg\(^0\) with BrO and Br have been suggested as potential mechanism. However, there is little kinetic data available for rate coefficients of elemental mercury with halogen radicals, making it difficult to model AMDEs.

Evidence in recent years have also suggested the halogen initiated oxidation of mercury may be influencing concentrations of mercury in the marine boundary layer (Hedgecock and Pirrone, 2004; Hedgecock et al., 2003) and the upper troposphere. In a recent modeling study, Hedgecock and coworkers (Hedgecock et al., 2003) suggested that Br atoms are the primary oxidant of Hg\(^0\) in the marine boundary layer and they calculate a typical lifetime of about 10 days. The implications of this for chemistry on a global scale are unclear; because the precise mechanism of mercury transformation is unknown. While in the upper troposphere evidence of elevated levels of reactive gaseous mercury has been observe by several groups (Jaffé et al., 2005; Landis, 2006; Landis et al., 2005; Murphy et al., 2006b; Murphy et al., 2003; Sillman et al., 2007).

If an effort to elucidate the role of Br atoms in AMDEs, MBL and the upper troposphere we have made direct measurements of the rate coefficient for the reaction of elemental mercury with bromine atoms, reaction (R1.10), as a function of temperature and pressure in nitrogen and helium buffer gases.

\[
\text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \quad (\text{R1.10})
\]

Kinetic measurements were performed with bromine as the reactant in excess concentration, while temporal profiles of both reactants were monitored by LIF. These
measurements require an accurate determination of the Br atom concentration; thus we must account for the loss of Br atoms by the bromine atom recombination. Consequently, we also measured the rate coefficient for the recombination of bromine atoms, reaction (R4.1), under similar experimental conditions.

\[ \text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} \]  

(R4.1)

(4.2) Experimental

The reaction between gaseous elemental mercury and bromine atoms was studied by pulsed laser photolysis – pulsed laser induced fluorescence (PLP-PLIF) as a function of pressure and temperature in nitrogen or helium buffer gas. Experiments were conducted at three temperatures, 293, 263 and 243 K, and three pressures, 200, 400 and 600 Torr. The experimental design is similar to the apparatus employed in the previously reported determination of the rate coefficient for mercury with chlorine atoms (Donohoue et al., 2005).

Bromine atoms were produced by pulsed laser photolysis (PLP) of molecular bromine. The temporal profiles of both bromine atoms and mercury atoms were monitored by two and one photon laser induced fluorescence (LIF) respectively. The experimental configuration is detailed in Chapter 2 and illustrated in Figure 4.1.

Experiments were carried out under “slow-flow” conditions. The gas velocity was maintained at approximately 26 cm s\(^{-1}\), to completely replace the gas mixture in the reaction zone between the laser pulses. All flows were monitored using calibrated mass flow controllers. The pressure in the reaction cell was monitored with a capacitance manometer.
Figure 4.1: Experimental set-up for the PLP-PLIF system to detect Hg atoms by one photon LIF and Br atoms by two photon LIF, including optical and flow system configurations.

Bromine atoms were produced by photolysis of molecular bromine using the 532 nm, third harmonic of a Nd:YAG laser.

\[ \text{Br}_2 + h\nu \rightarrow \text{Br} + \text{Br} \quad \text{(R2.8)} \]

An output power of approximately 500 mJ per pulse resulted in bromine atom concentrations ranging from $2.5 - 40 \times 10^{15}$ molecules cm$^{-3}$. The photolysis of molecular bromine at 532 nm from the $^3\Pi_{1u}$ and $^2\Pi_{0u^+}$ bonding states to the $^1\Pi_{1u}$ repulsive exited state leads to the formation of two bromine atoms. Some of the resulting bromine atoms were electronically excited, however, these excited species were rapidly deactivated to the $^2p^0_{3/2}$ ground state (Oldman et al., 1975), resulting in a quantum yield for the photolysis of molecular bromine (Hippler et al., 1984) of 2.
The buffer gas flowed through a mercury bubbler at room temperature. This produced stable mercury concentrations, which ranged from $5 - 20 \times 10^{11}$ molecules cm$^{-3}$ under our flow conditions.

Elemental mercury and molecular bromine concentrations were monitored *in situ* by UV photometry using the 253.7 and 365 nm lines from a mercury lamp, respectively. The reaction mixture was passed through an absorption cell and the lamp output was split with a dichroic beamsplitter and detected by two interference filter/photomultiplier (PMT) combinations and each absorbance was recorded. The molecular bromine concentrations were determined using a 1 m cell and the literature cross-section of molecular bromine (Maric et al., 1994) at 365 nm of $1.258 \times 10^{-19}$ cm$^2$. As the line width of the mercury absorption line is narrower than the broadened output of the mercury lamp; we employed the effective absorption cross-section determined of $1.36 \times 10^{-14}$ cm$^2$ for absorbencies less than 0.7, while a polynomial relationship was used for absorbencies greater than 0.7. The methods used to determine this cross-section and the relevant plot is reported in Chapter 2. During kinetic measurements an absorption path length of 1 cm was used.

When both mercury and bromine were passed through the absorption cell, a significant reduction of the mercury concentration was observed, while the bromine concentration was left unchanged. This observation was expected because the bromine concentration was three orders of magnitude larger than the mercury concentration. These observations indicate that there is a heterogeneous reaction occurring within the system, most likely on the walls of the cell. Therefore, in order to reduce the effects of this heterogeneous chemistry, the absorption cell was placed after the LIF cell and the
mercury and bromine gases were mixed immediately before the LIF cell. By reducing the mixing time and cell wall surface area before the detection zone, this loss of mercury before reaction zone was minimized.

The initial bromine atom concentration produced by photolysis was determined from equation (E4.1) (Rodgers et al., 1980):

\[
[Br] = [Br_2] * QY * \left(1 - \exp \left(\frac{P}{\pi} \sqrt{\frac{c}{\lambda}} \sigma_{Br_2} A_L \right)\right)
\]  

(E4.1)

where \(QY\) is the quantum yield of reaction (R2.8), \(P_L\) is the in laser power in joules, \(h\) is Planck’s constant, \(c\) is the speed of light in cm s\(^{-1}\), \(\sigma_{Br_2}\) is the absorbance cross-section at 532 nm in cm\(^2\), \(\lambda\) is the laser wavelength in cm, and \(A_L\) is the area of the laser in cm\(^2\). The photolysis laser has a nominally Gaussian profile, hence the beam passed through a ceramic aperture, located 2 m from the reaction zone, to cut off the edges of the beam. The variation in the fluence across the beam profile at the reaction zone was determined by measuring the power passing through a 0.05 cm pinhole ceramic aperture. The power meter/aperture combination was placed on a linear translation stage and the transmitted photolysis laser power was recorded in 0.05 cm steps giving the power variation across the horizontal diameter of the beam. From the observed beam profile the effective laser diameter in the reaction volume was determined to be 0.6 ± 0.05 cm. Over this diameter the beam profile has an approximately homogeneous or “top hat” power profile with a maximum deviation of ± 20% from the mean. The homogeneity of the beam was confirmed by evaluating the difference between laser power measurements conducted with and without an additional 0.487 cm aperture, which was located approximately 40 cm from the reaction zone. The ratio of the powers was in good agreement with that
calculated from the ratio of the areas suggesting that there are no significant hot spots in the center of the beam. The laser power was measured before and after the LIF cell for each decay. This was done to account for reflection loss on the windows, the small absorption of the laser before reaching the detection volume, and any variation in the laser power. The averaged laser power was used for the calculation of the bromine atom production.

(4.3) Results

(4.3.1) Measurements of \( \text{Hg} + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \) with \( \text{Br} \) atoms in Excess

Direct determination of rate coefficients for the reactions of gaseous elemental mercury presents a significant experimental challenge due to the low vapor pressure of mercury. To overcome these difficulties we made kinetic measurements under conditions in which bromine atoms were the reactant in excess while simultaneously monitoring the concentration of both reactants.

The rate coefficient for the recombination of mercury and bromine atoms, reaction (R1.10), was determined with Br atom concentrations typically 5000 times larger than the mercury concentration. Both mercury and bromine atom concentrations were monitored by LIF. The Br atom concentration was varied between \( 2.5 - 40 \times 10^{15} \) molecules cm\(^{-3}\), and Hg concentrations were in the range of \( 5 - 20 \times 10^{11} \) molecules cm\(^{-3}\).

At the Br atom concentrations required to observe a significant loss of mercury atoms, the bromine atom recombination reaction, (R4.1), resulted in a significant decrease in Br atom concentration on the timescale of the mercury atom decays. Since the Br atom concentration was not constant, a simple pseudo-first order decay, i.e. an
exponential decay, of mercury atoms was not observed. Instead, the mercury temporal profiles were fit by numerical integration, and the observed bromine temporal profiles were analyzed assuming simple second order kinetics.

The temporal profiles of the bromine and mercury atoms were characterized by equations (E4.2) and (E4.3):

\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Br][Hg][M] \tag{E4.2}
\]

\[
\frac{d[Br]}{dt} = -2 k_{R4.1} [Br]^2 [M] - k_{R1.10} [Br][Hg][M] \tag{E4.3}
\]

Since the concentration of mercury was at least three orders of magnitude smaller than the initial Br atom concentration, \(k_{R1.10} \times [Hg]\) should be at least an order of magnitude smaller than \(k_{R4.1} \times [Br]\); therefore, the second term in equation (E4.3) is negligible and results in the simplified equation:

\[
\frac{d[Br]}{dt} = -2 k_{R4.1} [Br]^2 [M] \tag{E4.4}
\]

For each experimental condition, temporal profiles of bromine and mercury atoms were measured using LIF. Typical sets of temporal profiles of each atom are shown in Figures 4.2 and 4.3. Under each set of conditions, i.e. a fixed pressure, temperature and initial bromine atom concentration, the effective second order rate coefficient, \(k_{R4.1}'\), for the recombination of bromine atoms was calculated from equation (E4.5),

\[
\frac{1}{[Br]} = 2 \times k_{R4.1}' t + \frac{1}{[Br]_0} \tag{E4.5}
\]

which assumes that first order losses by diffusion and reaction with impurities are negligible. Substituting [Br] into equation (E4.2) gives equation (E4.6):
**Figure 4.2:** Typical bromine atom temporal profiles, shown for measurements conducted in 400 Torr N\textsubscript{2} at 243 K.

**Figure 4.3:** Typical mercury atom temporal profiles, shown for measurements conducted in 400 Torr N\textsubscript{2} at 243 K.
\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Hg] \left( \frac{1}{2k_{R4.1} t + (1/|Br|)} \right)
\]  
(E4.6)  

This equation was numerically integrated to give the best fit to the measured mercury profiles and hence a value for \(k_{R1.10}'\), the effective second order rate coefficient for the recombination of Hg with Br. The numerical integration procedure was checked by simulating the measured decays using the derived values of \(k_{R1.10}'\) and \(k_{R4.1}'\) in the ACUCHEM program (Braun et al., 1986).  

**Table 4.1:** Second order rate coefficients for the recombination of mercury and chlorine atoms, \(k_{R1.10}').

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>(k_{R1.10}' \pm 2\sigma) error (cm(^3) molecule(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>243</td>
<td>200</td>
<td>((1.63 \pm 0.17) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((2.96 \pm 0.52) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((5.12 \pm 1.77) \times 10^{-13})</td>
</tr>
<tr>
<td>(N_2)</td>
<td>263</td>
<td>200</td>
<td>((1.32 \pm 0.05) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((2.95 \pm 0.20) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((4.37 \pm 1.15) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>200</td>
<td>((1.04 \pm 0.15) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((1.70 \pm 0.34) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((2.92 \pm 0.67) \times 10^{-13})</td>
</tr>
<tr>
<td>(He)</td>
<td>293</td>
<td>200</td>
<td>((0.30 \pm 0.03) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((0.55 \pm 0.03) \times 10^{-13})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((0.81 \pm 0.19) \times 10^{-13})</td>
</tr>
</tbody>
</table>

The numerically integrated fits to the observed mercury temporal profiles are shown as lines in Figure 4.3 and the second order rate coefficients, \(k_{R1.10}'\), obtained in He and \(N_2\) are listed in Table 4.1. Molecular nitrogen quenched the mercury fluorescence signal efficiently, therefore, the fluorescence yield and thus the S/N ratio degraded with increasing pressure. This was most noticeable in the 243 K dataset; however, the overall accuracy of the pressure dependent rate data should not have been significantly affected by this reduction of the S/N ratio.
The third order recombination rate coefficients were then determined from linear fits of the plots of the second order rate coefficients, $k_{R1.10}$, versus the concentration of N$_2$ or He as shown in Figure 4.4. The plots show the expected linear dependence of rate coefficient versus concentration indicating that the reaction was in the low pressure, third order regime as might be expected for an atom-atom recombination. Assuming that the recombination rate coefficients are in the low pressure limit, the effective second order rate coefficient should be zero at zero pressure. Consequently the third order recombination rate coefficients, $k_{R1.10}$, have been calculated by forcing the plots through the origin. The difference between the forced and unforced slopes was under 7% and within the precision of the fit. The third order recombination rate coefficients, $k_{R1.10}$, are listed in Table 4.2 and plotted in Arrhenius form in Figure 4.5. The Arrhenius expression for reaction (R1.10) in nitrogen is given by equation (E4.7) reported with 2σ errors of precision only.

$$k_{R1.10,N_2}(243 - 298 K) = (1.46 \pm 0.34) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-1.86 \pm 1.49}$$  \hspace{1cm} (E4.7)

However, due to uncertainty in the calculation of absolute Br atom concentrations, which is discussed below; and other unidentified systematic error we conservatively estimate the error in the rate coefficient to be ± 50%. The observed behavior is consistent with a three-body recombination, demonstrating a positive pressure dependence, an inverse temperature dependence, and a slower rate coefficient in helium than in nitrogen.
Figure 4.4: Variation of the effective second order rate coefficients for the recombination Hg and Br atoms, $k_{R1.10}$, with pressure.

Figure 4.5: Arrhenius plot of the third order rate coefficients for the recombination of Hg and Br atoms, $k_{R1.10}$, in N$_2$ and He.
Table 4.2: Third order rate coefficients for the recombination of mercury and bromine atoms, $k_{R1.10}$, determined in this work at 293 K in He and 243, 263, and 293 K in N$_2$, with the resulting third order expression for N$_2$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>$k_{R1.10} \pm 2\sigma$ error (cm$^4$ molecule$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>293</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>2.06 ± 0.18</td>
</tr>
<tr>
<td>N$_2$</td>
<td>263</td>
<td>1.98 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>1.43 ± 0.13</td>
</tr>
</tbody>
</table>

Third Order Expression

$(1.46 \pm 0.34) \times 10^{-32} \times \left(\frac{T}{298}\right)^{(0.86 \pm 0.40)}$

(4.3.2) Measurements of Br + Br + M $\rightarrow$ Br$_2$ + M

The determination of temporal profiles of Br atom concentration was a critical component in measuring the rate coefficient for the mercury and bromine recombination reaction. The relative concentration profile was determined with good precision using LIF. However, the initial Br atom concentration was calculated and was, we believe, the largest source of systematic error in the reported rate coefficient for reaction (R1.10). We can, however, make some assessment of the accuracy of this calculation by comparing our measured bromine atom recombination rate coefficients, which also depend on the accuracy of the calculation of the initial Br atom concentration, with literature values. As shown in Figure 4.2, bromine atom temporal profiles were monitored by LIF with the concentration typically followed to 5 – 20% of the initial bromine atom signal. Under each set of experimental conditions, i.e. a fixed pressure, temperature and initial bromine atom concentration, the effective second order rate coefficient, $k_{R4.1}'$, for the recombination of Br atoms was calculated from the Br temporal profile using equation (E4.8), again assuming a negligible first order loss due to reaction with impurities or diffusion.
Linear fits of plots of \( \frac{1}{[Br]} \) vs. time give the effective second order recombination rate coefficient, \( k_{R4.1}' \). Figure 4.6 shows a series of plots for the reciprocal of absolute bromine atom concentration versus time. This provides an indication of the precision of the data sets, which were obtained at the same temperature and pressure. Each plot should have the same slope independent of initial Br atom concentration. The data shown in Figure 4.6 were taken at 243 K in 400 Torr nitrogen buffer gas with initial Br atom concentrations ranging from \( 1.8 - 3.8 \times 10^{16} \). The plots demonstrated good linearity and gave an average second order recombination rate coefficient of \((1.08 \pm 0.17) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) where the uncertainty is a 2\(\sigma\) error of precision. To ensure that the addition of mercury did not affect the observed Br atom decay, experiments were conducted in the presence and absence of mercury. The temporal profiles and derived rate coefficients were identical, within the precision of the measurements. This was expected since the Hg concentration was at least three orders of magnitude smaller than the initial Br atom concentration. The values of the effective second order rate coefficients together with 2\(\sigma\) errors are summarized in Table 4.3.

The third order recombination rate coefficients were then determined from linear fits of the plot of second order rate coefficients, \( k_{R4.1}' \), versus concentration of N\(_2\) or He as shown in Figure 4.7. As is the case for the Hg + Br recombination, the data show a good linear dependence of the effective second order rate coefficient on pressure. However, we see a consistent, negative offset. As for reaction (R1.10), the third order rate coefficients were obtained by forcing all fits through the origin. The forced plots pass
Table 4.3: Second order rate coefficients for the recombination of chlorine atoms, $k_{R4.1}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R4.1} \pm 2\sigma$ error (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>N$_2$</td>
<td>243</td>
<td></td>
<td>$(4.66 \pm 0.87) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td></td>
<td>$(3.06 \pm 0.25) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td></td>
<td>$(2.44 \pm 0.71) \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td></td>
<td>$(0.96 \pm 0.22) \times 10^{-14}$</td>
</tr>
<tr>
<td>He</td>
<td>293</td>
<td></td>
<td>$(3.00 \pm 0.70) \times 10^{-14}$</td>
</tr>
</tbody>
</table>

Figure 4.6: Second order rate coefficient plot for Br atom, shown for measurements conducted in 400 Torr N$_2$ at 243 K.
Figure 4.7: Variation of the effective second order rate coefficients for the recombination of Br atoms, $k_{R4.1}'$, with pressure.

Figure 4.8: Arrhenius plot of the third order rate coefficients for the recombination of Br atoms, $k_{R4.1}$, in $N_2$ and He. Literature values are shown for comparison.
through most of the error bars associated with each data point while the difference in the slopes of the forced and unforced fits varied from 8% to 25%. The third order recombination rate coefficients, $k_{R4.1}$, are listed in Table 4.4 and plotted in Arrhenius form in Figure 4.8. For the data in nitrogen, the resulting Arrhenius expression is given by equation (E4.9).

$$k_{2,N_2}(243-298K) = (4.31 \pm 0.21) \times 10^{-33} \times \left( \frac{T}{298} \right)^{-2.77 \pm 0.30}$$  \hspace{1cm} (E4.9)

In equation (E4.9) the uncertainties are measures of 2σ error of precision only. As we discuss in detail below we estimate an uncertainty of ± 50% in the accuracy of the rate coefficient, due principally to the uncertainty in the calculation of absolute Br atom concentrations. Overall the data showed the expected behavior for a three-body recombination, a positive pressure dependence, an inverse temperature dependence, and a higher deactivation efficiency for nitrogen relative to helium.

**Table 4.4:** Third order rate coefficients for the recombination of bromine atoms, $k_{R4.1}$, determined in this work at 293 K in He and 243, 263, and 293 K in N$_2$, with the resulting third order expression for N$_2$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>$k_{R4.1} \pm 2\sigma$ error ($\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>293</td>
<td>$1.43 \pm 0.17$</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>$7.53 \pm 1.03$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>263</td>
<td>$6.18 \pm 0.89$</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>$4.46 \pm 0.86$</td>
</tr>
</tbody>
</table>

(4.3.3) **Potential Sources of Systematic Error**

As we have noted above the variation of the effective second order rate coefficients with pressure should show a linear dependence which passes through the...
origin. In fact the bromine atom recombination reaction data consistently show slight negative offset which may be indicative of a systematic error in the calculation of the bromine atom concentration. It should be noted that these offsets were relatively small, and in most cases the fits that were forced through the origin passed within the $2\sigma$ errors of precision associated with each data point.

To calculate the initial bromine atom concentration, equation (E4.1) was employed using the absorption cross-section of bromine molecules at 355 nm, the molecular bromine concentration, the average laser power, and the laser diameter. The error associated with the first two parameters in equation (E4.1) should be less than 5%. As discussed previously there is some uncertainty in the calculation of the effective diameter and homogeneity of the laser beam and hence the fluence. This was assessed by measuring the variation in the fluence across the width of the beam. We estimate the error in the diameter determination to be less then 10%. However, the error associated with the calibration of the laser power meter, homogeneity within the beam profile and shot to shot variability increase the uncertainty and result in an estimated error of ± 20% in the fluence. Therefore, we believe that ± 30% represents a conservative overall estimate of the uncertainty in the Br atom concentrations.

A second source of systematic error could be the influence of secondary chemistry on the bromine atom temporal profiles. Molecular bromine does not thermally dissociate at the temperatures in this study. HgBr and we expect it to react with both Br and Br$_2$, however its concentration is much lower than that of [Br] and it should not affect Br atom profiles. Therefore, we believe that ± 30% represents a conservative overall estimate of the uncertainty in the Br atom concentrations.
A third source of systematic error could be the influence of reaction (R1.30) on the Hg$^0$ temporal profiles.

\[ \text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2 \]  \hspace{1cm} (R1.29)

\[ \text{HgBr} + \text{Br} \rightarrow \text{Hg} + \text{Br}_2 \]  \hspace{1cm} (R1.30)

If the major products of reaction (R1.26) are molecular bromine species and a mercury atom, than the mercury temporal profiles will underestimate the loss of mercury due to reaction (R1.10). To evaluate the potential regeneration of mercury for reaction (R1.30), a limited number of Hg temporal profile were obtained after the photolysis of HgBr$_2$. If the reaction of HgBr and a Br atom regenerated Hg atoms then the Hg profiles will demonstrate a strong non-linearity on short time scales. Our observed temporal profile did not demonstrate any non-linearity outside of the precision of the data. Hence we calculate that the branching ratio for the (R1.30) channel of the reaction of HgBr molecules and Br atoms must be less than 0.2. If this reaction is included in a numerical integration simulation of the reaction system, we find that the maximum effect on $k_{R1.10}$ is 20% increase in the rate coefficient.

Considering the typical errors of precision in the data and the possibility of other small, systematic errors, we believe that ±50% represents a reasonable estimate of the overall uncertainty in the measured rate coefficients.

(4.4) Discussion and Comparison with Previous Work

(4.4.1) Bromine Atom Recombination

The bromine atom recombination reaction, $k_{R4.1}$, has been determined in both helium and nitrogen in several studies (Clarke and Burns, 1972; Clyne and Woon-Fat,
The results of these studies, including the specific pressure and temperature regimes used are outlined in Table 4.5.

<table>
<thead>
<tr>
<th>gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>( k_{R4.1} ) (cm(^6)molecule(^{-2})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>~500</td>
<td></td>
<td>((9.46 \pm 0.94) \times 10^{-33})</td>
</tr>
<tr>
<td>300-1225</td>
<td>~100</td>
<td></td>
<td>((4.55 \pm 0.55) \times 10^{-33})‡</td>
</tr>
<tr>
<td>298-373</td>
<td>2.2-3.2</td>
<td></td>
<td>((9.1 \pm 0.83) \times 10^{-33})</td>
</tr>
<tr>
<td>N(_2)</td>
<td>298</td>
<td>~2.25</td>
<td>((8.3 \pm 0.30) \times 10^{-33})</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>750-5250000</td>
<td>((1.1 \pm 0.11) \times 10^{-32})</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>200-600</td>
<td>((4.31 \pm 0.21) \times 10^{-33} \times \left(\frac{T}{298}\right)^{-2.77 \pm 0.30})</td>
</tr>
<tr>
<td>300-1225</td>
<td>100-300</td>
<td></td>
<td>(1.6 \times 10^{-33} \times (T/298)^{-1.26 \pm 0.04})‡</td>
</tr>
<tr>
<td>298-373</td>
<td>2.2-3.2</td>
<td></td>
<td>((3.31 \pm 0.27) \times 10^{-33})</td>
</tr>
<tr>
<td></td>
<td>300-1500</td>
<td>760</td>
<td>(1.725 \times 10^{-33} \times (T/298)^{-0.68} \times \exp(-0.21(kcal/mole)/RT))‡</td>
</tr>
<tr>
<td>He</td>
<td>298</td>
<td>~2.25</td>
<td>((2.81 \pm 0.50) \times 10^{-33})</td>
</tr>
<tr>
<td>293</td>
<td>750-5250000</td>
<td></td>
<td>((4.25 \pm 0.41) \times 10^{-33})</td>
</tr>
<tr>
<td>293</td>
<td>750-5250000</td>
<td></td>
<td>((3.31 \pm 0.78) \times 10^{-33})</td>
</tr>
<tr>
<td>293</td>
<td>200-600</td>
<td></td>
<td>((1.43 \pm 0.17) \times 10^{-33})</td>
</tr>
</tbody>
</table>

‡ Rate Coefficients were corrected to include factor of 2 for second order rates

When evaluating these studies it is essential to determine identify the relationship used to determine the rate coefficient. In the review of literature we found that three relationships were used to evaluate \( k_{R4.1} \), equations (E4.4), (E4.10), and (E4.11).

\[
\frac{d[Br_2]}{dt} = k_{R4.1} [Br]^2 [M] \quad (E4.10)
\]

\[
\frac{d[Br]}{dt} = -k_{R4.1} [Br]^2 [M] \quad (E4.11)
\]

Equation (E4.4) and equation (E4.10) should result in an equivalent \( k_{R4.1} \) rate coefficient, whereas equation (E4.11) will result in an expression of the \( k_{R4.1} \) rate coefficient which is
a factor of 2 too fast. Therefore two studies (Clarke and Burns, 1972; Ip and Burns, 1969) had to be corrected for this factor of 2 in order to be comparable to our second order rate coefficients. Once corrected these two rate coefficient agree, within error limits, with our rate determination for the Br atom self reaction in both helium and nitrogen.

On the other hand the rates determined by Strong et al. (Strong et al., 1957), DeGraff et al. (DeGraff and Lang, 1970), Clyne et al. (Clyne and Woon-Fat, 1973), and Hippler et al. (Baer et al., 1991; Hippler et al., 1978) are consistently a factor of 2 – 3 faster than our rate determination. All of these studies reported agreement with the earlier Ip et al. study (Ip and Burns, 1969), without accounting for the difference of a factor of 2 in the defined second order rate coefficient. When, in fact the reported rate coefficients for the later studies are a factor of 2 – 3 faster than the Ip et al. study.

In assessing potential sources of systematic error we can identify two possible complications in our experimental approach. The first is additional loss of bromine atoms by reaction with impurities. However, any additional reaction, which resulted in the loss of bromine atoms, would increase the observed rate. Since the rate that we observed is slower than the previous studies this cannot account for the observed discrepancy. The second possible complication in our system is the over or under estimation of the Br atom concentration. Since we must determine absolute Br atom concentrations, an error in this determination could affect the resulting rate coefficient. However, the errors associated with our determination were previously discussed and resulted in a maximum estimated error of ± 30%; therefore this should not account for the discrepancy. We therefore agree with the earlier work of Ip et al. (Ip and Burns, 1969) and Clarke et al. (Clarke and Burns, 1972).
(4.4.2)  Mercury and Bromine Atom Recombination

Four previous experimental (Ariya et al., 2002; Greig et al., 1970; Spicer et al., 2002) (Summer, 1998), a field study (Skov et al., 2004) and two theoretical determinations (Goodsite et al., 2004; Khalizov et al., 2003) have reported values for reaction (R1.10) and these results are compared with the current work in Table 4.6 and in Figure 4.9.

Table 4.6: Comparison of literature data for third order rate coefficients for the reaction of Hg0 with Br atoms with, $k_{R1.10}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R1.10}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$(3.2 \pm 0.3) \times 10^{-12}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Ariya et al., 2002</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$3.0 \times 10^{-13}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Spicer et al., 2002</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$9.7 \times 10^{-13}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Spicer et al., 2002</td>
</tr>
<tr>
<td>N$_2$</td>
<td>298</td>
<td>760</td>
<td>$(2.8 \pm 0.8) \times 10^{-12}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Sommar et al., 1998</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>$1.01 \times 10^{-12} \exp^{(209.03/T)}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Khalizov et al., 2003</td>
</tr>
<tr>
<td></td>
<td>180-400</td>
<td>760</td>
<td>$1.1 \times 10^{-12} \times (T/298)^{-2.37}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Goodsite et al., 2004</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>760</td>
<td>$(1.46 \pm 0.34) \times 10^{-12} \times \left(\frac{T}{298}\right)^{-0.86 \pm 0.49}$ (cm$^6$ molecule$^{-2}$ s$^{-1}$)</td>
<td>This work</td>
</tr>
<tr>
<td>He</td>
<td>243-293</td>
<td>760</td>
<td>$(4.2 \pm 0.2) \times 10^{-13}$ (cm$^6$ molecule$^{-2}$ s$^{-1}$)</td>
<td>This work</td>
</tr>
<tr>
<td>Air</td>
<td>233-263</td>
<td>760</td>
<td>$1 \times 10^{-12}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Skov et al., 2004</td>
</tr>
<tr>
<td>CF$_3$Br</td>
<td>393-448</td>
<td>200</td>
<td>$2.8 \times 10^{-13}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</td>
<td>Greig et al., 1970</td>
</tr>
</tbody>
</table>

Greig et al. (Greig et al., 1970) used flash photolysis combined with absorption spectroscopy to study reaction (R1.10) at temperatures 393 - 448 K in 200 Torr CF$_3$Br resulting in a rate coefficient of $2.82 \times 10^{-13}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, with a reported error of a factor of 3. The rate coefficient obtained is not directly comparable to those reported here, due to temperature and buffer gas differences; however, using the Arrhenius
expression reported in this work we predict a recombination rate coefficient in 200 Torr nitrogen and 393 K of $6.15.7 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This is approximately a factor of 4.5 slower than the rate coefficient reported by Greig et al. This difference in the rate coefficients might be explained by the difference in the third body efficiencies of CF$_3$Br versus N$_2$. Hippler et al. found C$_3$F$_8$ to be a factor of 6.5 more efficient as a third body than N$_2$ in a study of Br atom recombination (Hippler et al., 1984).

Additionally, we would identify two particularly significant sources of systematic error in the Greig et al. study. First, the system was a static system where a gas mixture undergoes repeated flashes. This experimental approach increases the possibility of secondary chemistry, product photolysis and interfering species. Second, to determine the
rate coefficient for reaction (R1.10) it was necessary to determine the absolute mercury bromide (HgBr) concentration. Mercury bromide concentrations were determined by monitoring the C\textsubscript{2}F\textsubscript{6} concentration as a proxy for bromine atom concentrations and assuming that all the bromine atoms are converted to mercury bromide. The C\textsubscript{2}F\textsubscript{6} is formed via the self reaction of CF\textsubscript{3}, a product of the that is formed in the flash photolysis of CF\textsubscript{3}Br. By using C\textsubscript{2}F\textsubscript{6} concentrations as a proxy for HgBr concentrations, the Greig study assumes that all the Br atoms which formed in the initial photolysis of the CF\textsubscript{3}Br species, react with an Hg atom. This determination does not account for the formation of mercury (II) bromide (HgBr\textsubscript{2}) via reaction (R1.29).

\begin{equation}
\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2
\end{equation}

(R1.29)

However, if the rate coefficient calculated by Goodsite et al. (Goodsite et al., 2004) for reaction (R1.29) is correct, than reaction (R1.29) could be a significant sink for bromine atoms. Thus the estimate of the [HgBr] could be too large and this would result in the overestimation of the rate coefficient for reaction (R1.10) in the Greig et al. determination.

Three more recent studies have utilized relative rate techniques to study reaction (R1.10) at 1 ATM and at room temperature. First Summer et al. reported a conference report at the 5th International Conference on Mercury as a Global Pollutant, Rio de Janeiro, 1999 The \(k_{\text{R1.10}}\) for 1 ATM and at room temperature was (2.8 ± 0.8) \(\times 10^{-13}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. The second relative rate study by Ariya et al. reported rate coefficient for the reactions of Hg\textsuperscript{0} with Cl\textsubscript{2}, Cl, Br\textsubscript{2} and Br (Ariya et al., 2002). We have discussed the rate coefficient obtained for the Hg\textsuperscript{0} + Cl reaction previously (Donohoue et al., 2005) and in Chapter 3. Ariya et al. (Ariya et al., 2002) reported a rate coefficient of (3.2 ± 0.3)
$10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for reaction (R1.10), which is a factor of 9 faster than the rate determined in this work. In contrast to their Cl atom work, Ariya et al. used a single reference reaction, Hg$^0$ with 1-butene, to measure the relative rate of reaction (R1.10). Kinetic studies on the reaction of Hg$^0$ and 1-butene are limited, with only one study referenced (Barnes et al., 1989). This study was also a relative rate study and noted that the observed rate coefficient depended on the O$_2$ partial pressure, indicating a complex reaction mechanism. In the Ariya et al. study the rate observed depended on the concentration of the reference molecule, the concentration of the OH scavenger, and the identity of the buffer gas. The observed reaction coefficient for reaction (R1.10) varied by a factor of 3 as the buffer gas was varied between nitrogen and air. In order to obtain linear relative rate plots in the Ariya et al. study, they added large amounts of an OH scavenger (cyclohexane) leading to an enhancement in the absorption of reactant on the cell walls. Ariya et al. reported that the primary complication to their system was enhanced removal of the reference compound by reaction with OH or loss on the cell walls. Any additional loss of the reference compound would produce an under-estimate of the rate coefficient. However, the rate coefficient obtained in that work exceeds both our directly measured rate coefficient and two theoretical estimates of the rate coefficient. We feel that a more plausible explanation would be additional loss of mercury, either by heterogeneous reaction or possibly by gas phase reaction with an oxygenated species; since any additional process that removed mercury would generate the observed over-estimate.

The third relative rate study, a technical report by Spicer et al. (Spicer et al., 2002), was performed in a 17.3 m$^3$ environmental chamber using two reference
molecules dimethylsulfide (DMS) and propene (C\textsubscript{3}H\textsubscript{6}) in a buffer gas of air. Spicer et al. reported values of $3.0 \times 10^{-13}$ cm\textsuperscript{3} molecules\textsuperscript{-1} s\textsuperscript{-1} for the rate coefficient relative to DMS and $9.7 \times 10^{-13}$ cm\textsuperscript{3} molecules\textsuperscript{-1} s\textsuperscript{-1} for the rate coefficient relative to propene. They gave greater weight to the higher value since the results obtained using the DMS reference were more variable. Again the factor of 3 variation of the measured relative rate on the identity of the reference compound implies that the measured rates were influenced by secondary or heterogeneous chemistry.

Skov et al. reported a value for the kinetic rate coefficient of reaction (R1.10) of $1.0 \times 10^{-12}$ cm\textsuperscript{3} molecules\textsuperscript{-1} s\textsuperscript{-1}. This study was an in field relative rate study. The reference reaction was reaction (R4.2) where X is either Br or Cl.

\[
\begin{align*}
O_3 + X & \rightarrow \text{products} \quad \text{(R4.2)} \\
\text{Hg} + X & \rightarrow \text{products} \quad \text{(R4.3)}
\end{align*}
\]

The reaction rate coefficients for the reaction of ozone with Br and Cl atoms are well characterized, due to this importance in stratospheric ozone depletion. This technique will also assume that reaction (R4.2) is the only loss process for ozone and reaction (R4.3) is the only loss process for Hg. [Hg] and [O\textsubscript{3}] from station Nord in Greenland was limited to three concurrent O\textsubscript{3} and Hg depletion events. A plot of ln([Hg]/[Hg]\textsubscript{i}) against ln([O\textsubscript{3}]/[O\textsubscript{3}]\textsubscript{i}) resulted in a straight line with a slope of 0.039, an intercept of -0.095, and a R value of 0.8. By multiplying the slope with the appropriate rate coefficient for the reference reaction the rate coefficient was obtained for reaction (R1.10). This type of determination is extremely limited and must inherently be influenced by secondary chemistry. However, it does agree within the error limits of the study with the rate coefficient determined in this work.
In addition to the experimental work described above there have been two theoretical determinations of the rate coefficient. Khalizov et al. (Khalizov et al., 2003) determined the recombination rate coefficient for reaction (R1.10) using electronic structure calculations to obtain both molecular parameters and the capture rate or high-pressure limit. Once this high pressure limit was obtained, Khalizov et al. determined a pressure dependent rate coefficient by assuming a strong collisional deactivation. In order to compare this with the observed data it is essential to consider the mechanism of a three-body recombination. A three-body recombination consists of an initial collision that generates an excited complex, reaction (R4.4). A portion of the excited complex will directly decompose back into reactants, reaction (R4.5); while the other portion undergoes a collision and is stabilized, reaction (R4.6).

\[ \text{Hg} + \text{Br} \rightarrow \text{HgBr}^* \quad (\text{R4.4}) \]

\[ \text{HgBr}^* \rightarrow \text{Hg} + \text{Br} \quad (\text{R4.5}) \]

\[ \text{HgBr}^* + \text{M} \rightarrow \text{HgBr} + \text{M} \quad (\text{R4.6}) \]

The calculated pressure dependent rate coefficient reported by Khalizov et al. made the physically unrealistic assumption that every collision of the buffer gas with the initially formed energized HgBr* complex deactivated the complex to produce a stable HgBr molecule that cannot dissociate to products. If the initial calculation of the capture rate coefficient, reaction (R4.4), is accurate, this assumption should produce the maximum possible recombination rate coefficient under each set of conditions. They obtained a rate coefficient of \( 2.07 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \) at 298 K, 760 Torr.

The second theoretical study of reaction (R1.10) was carried out by Goodsite et al. (Goodsite et al., 2004). This study employed the RRKM theory using a master
equation formulation to predict the rate coefficient for several mercury reactions of interest. In this work the rate of deactivation of HgBr* is calculated by assigning the energy of HgBr* into a series of energy grains and assuming that the average energy removed by each collision with N₂ was 400 cm⁻¹. The rate coefficient obtained using this approach was $1.1 \times 10^{-12}$ cm³ molecules⁻¹ s⁻¹. This more physically realistic energy transfer model produces a rate coefficient that is a factor of 2 slower than the study of Khalizov et al. However both studies reported rate coefficients that were slower than the experimental rate coefficient reported in the Ariya study. Goodsite et al. addressed the large discrepancy with the Ariya et al. measurement and found that in order to obtain the experimental rate coefficient the bond energy in HgBr had to be increased by 30 kJ mole⁻¹ over the current experimental data of 74.9 kJ mole⁻¹. Since the error limits of the experimental determination of the bond energy is only ± 4 kJ mole⁻¹, the authors concluded that the Ariya et al. rate coefficient was over-estimated.

The determination of the reaction coefficient for reaction (R1.10) at 298 K and 760 Torr of $3.456 \times 10^{-13}$ cm³ molecules⁻¹ s⁻¹ from this work reflects a rate coefficient that is a factor of 3 and factor of 6 slower than the two theoretical studies. As noted above the strong collision assumption is normally physically unrealistic and should give an upper limit to the rate coefficient. Our results suggest that the 400 cm⁻¹ energy removal parameter of Goodsite et al. is a little too large. Incorporation of a slightly smaller value would produce a result in good agreement with our experimental value.

We should note that this is the first study of reaction (R1.10) that has systematically varied the temperature, pressure and buffer gas. As we note above our
observations are entirely consistent with the behavior expected for a three body recombination and our rate agrees well with the two theoretical determinations.

(4.5) Summary

We have reported recombination rate coefficients for the reaction of mercury and bromine atoms, \( k_{R1.10} \), together with the self-reaction of bromine atoms, \( k_{R4.1} \). In both cases the rate coefficients show pressure and temperature dependencies, as well as, third body deactivation efficiencies, which are consistent with a three-body recombination. For reaction (R1.10), the recombination of bromine with mercury, we obtain rate coefficients that are slower than previously reported rate coefficients. The discrepancy observed between this work and the relative rate studies together with the variability in those studies questions the viability of using the relative rate method to determine kinetic rate coefficients for mercury halogen reactions. For reaction (R4.1), the self-reaction of bromine atoms, we obtain results, which are in agreement with the early experimental determination of Ip et al. (Ip and Burns, 1969) and the theoretical determination of Clarke et al. (Clarke and Burns, 1972) but are somewhat slower than more recent studies.

To evaluate the importance of the recombination of elemental mercury and bromine atoms, an effective second order rate coefficient of \( 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \) was calculated from the reported Arrhenius expression for Arctic conditions, 260 K and 760 Torr. Assuming a peak concentration (Boudries and Bottenheim, 2000) of bromine atoms of \( 10^7 - 10^8 \text{ cm}^3 \) the lifetime of mercury due to bromine is between 2.5 days and 6 hours. This means reaction (R1.10) could play a significant role in AMDEs. However, the importance of the recombination of mercury and bromine atoms, reaction (R1.10),
will depend on the stability and reactivity of the HgBr species. Further studies into the reactivity of HgBr are discussed in Chapter 6 along with the lifetime of mercury due to reaction with bromine in the free troposphere. In a low Br environment, such as the free troposphere, subsequent reactions of the HgBr species will be essential in calculating an effective lifetime, as the lifetime due to solely to reaction with bromine atoms will be slow.

Finally, Hedgecock et al. (Hedgecock and Pirrone, 2004) reported a lifetime of mercury in the MBL of 10.5 days. This lifetime assumes that removal by reaction (R1.10) is the dominant process in the conversion of elemental mercury to reactive gaseous mercury, with reaction with OH and ozone playing an important, but lesser role. To calculate this lifetime, Hedgecock et al. assumed a steady state Br concentration of [Br] = 3.1 × 10^5 molecules cm^{-3} and used the rate coefficient reported by Ariya et al. (Ariya et al., 2002), this results in a lifetime of elemental mercury due to reaction with bromine atoms of 11.5 days. If we perform the same calculation using the rate coefficient for reaction (R1.10) determined in this work at 760 Torr and 298 K, we find the lifetime of mercury due to the reaction with bromine increases to 104 days. Using the Hedgecock et al. lifetimes of 133 days for reaction with OH and 578 days for reaction with O_3 we obtain an overall lifetime of 53 days for mercury in the MBL. The factor of 5 increase in the lifetime of Hg^0 using our rate coefficient for reaction (R1.10) highlights the need for direct determination of rate coefficients for Hg^0 reactions in order to elucidate the overall biogeochemical cycling of mercury.
CHAPTER V

DEVELOPMENT OF LIF DETECTION FOR PRODUCTS OF THE REACTION OF HG\(^0\) WITH CHLORINE AND BROMINE ATOMS

(5.1) Background

In order to monitor the reaction products of mercury halogen reactions, it was necessary to develop a method to monitor HgX species under the same conditions that mercury, chlorine, and bromine atoms were monitored. Ideally, this system would allow the back to back determination of the kinetic temporal profiles of each species. In obtaining this data, a detailed understanding of the gas phase oxidation of Hg\(^0\) by halogen atoms will be gained. The development of an LIF detection system involves three steps:

1) The development of the photolytic source for the radical of interest, HgCl and HgBr
2) The determination of an appropriate excitation wavelength
3) The determination of an appropriate wavelength region for the fluorescence detection

In this system, the detection wavelength region for the fluorescence must not be significantly influenced by Raman or Raleigh scatter from the excitation laser. Minimization of the excitation laser stray light will increase the sensitivity of the detection. In this work, we developed a LIF detection scheme for both the HgCl and HgBr molecules.
(5.2) Experimental

Experiments were conducted in one of three configurations; the excitation spectra configuration, resolved fluorescence spectra configuration and kinetic rate coefficient determination configuration. All configurations employed a Pyrex cell with four mutually perpendicular side arms at the reaction vessel. The photolysis and the probe lasers were overlapped using dichroic mirrors and then propagated through two of the cell’s side arms through quartz windows. The fluorescence was detected perpendicular to the direction of the photolysis and probe lasers to minimize Raleigh and Raman scattering. Flows were monitored using calibrated mass flow controllers and passed through shut off valves and needle valves as needed. The pressure in the reaction cell was monitored with a capacitance manometer.

During excitation spectra experiments, the fluorescence signal was detected on a filter pack/PMT assembly. The filter packs used for each species are outlined in Table 5.1. The PMT output was amplified (Sonoma, 310) and processed by a 500MHz scope (Tektronix, TDS 520), terminated at 50Ω. The LIF signal was transferred to a PC via a GPIB interface. The grating of a tunable dye laser was scanned across a select wavelength range using a stepper motor driven by a function generator.

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>Band</th>
<th>PMT</th>
<th>Filter Pack</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl</td>
<td>245&lt;(\lambda&lt;265)</td>
<td>(D^2P_{3/2} - X^2S)</td>
<td>Hamamatsu, 1P28</td>
<td>Interference filter 262±10 nm &lt;300 nm cutoff filter</td>
</tr>
<tr>
<td>HgBr</td>
<td>250&lt;(\lambda&lt;265)</td>
<td>(D^2P_{3/2} - X^2S)</td>
<td>Hamamatsu, 1P28</td>
<td>Interference filter 262±10 nm &lt;300 nm cutoff filter</td>
</tr>
<tr>
<td></td>
<td>460&lt;(\lambda&lt;510)</td>
<td>(X^2S_{1/2} - B^2S_{1/2}^+)</td>
<td>Hamamatsu, 1P28</td>
<td>Interference filter 500±8 nm Interference filter 445±70 nm</td>
</tr>
</tbody>
</table>
Resolved fluorescence was detected by propagating the fluorescence signal from the center of the cell through a focusing lens and into the slit of a monochromator (600 line grating or 150 line grating). A gated diode array detector was attached to the exit of the monochromator. The gate on the diode array was set to 1 μs and the signal was averaged for $1 \times 10^5$ laser pulses. The wavelength scale on the diode array was calibrated using multiple lines from Hg penray lamp and the small stray light signal from the photolysis laser pulse. The resolved fluorescence spectra were not corrected for variations in sensitivity across the diode array.

A four channel digital delay generator (Stanford Research Systems, DG535) was used to temporally overlap the lasers and then vary the time between the photolysis and LIF detection. Both excitation spectra and resolved fluorescence spectra were determined at fixed delays between the lasers. This delay was optimized for each method of radical production. For HgCl experiments, the optimal delay was 3 μs for HgCl$_2$ photolysis and 45 μs for production via reaction (R1.11). The delays between the lasers for HgBr detection were longer, 500 μs for HgBr$_2$ photolysis. 100 μs and 2000 μs delays were used for production of HgBr via reaction (R1.11) with Br$_2$ and CF$_3$Br acting as the Br atom precursor. Temporal profiles for kinetic studies of the HgX species were obtained by varying the timing between the photolysis pulse and the probe laser. The data acquisition method is described in detail in Section 2.7.

(5.3) HgCl Spectroscopy

HgCl was monitored previously in a flash photolysis – absorption spectroscopy system (Horne et al., 1968). They detected two major bands, the $D^2\Pi_{3/2} - X^2\Sigma$ at 245.0 –
255.0 nm and the $C^2 \Pi_{3/2} - X^2 \Sigma$ at 271.0 – 280.0 nm. The observed transitions agreed with previous studies (Cornell, 1938; Howell, 1943; Wieland, 1929). The Horne determination identified seven transitions in the $D^2 \Pi_{3/2} - X^2 \Sigma$ band. They noted two interference sources that obscured some transitions. A strong Si transition at 251.61 nm from the flash lamp obscured the (0,0) transition at 251.66 nm; while the pressure broadened 253.65 nm Hg transition obscured the (0,1) transition at 253.50 nm. The wavelengths reported for the $D^2 \Pi_{3/2} - X^2 \Sigma$ transitions of HgCl are listed in Table 5.2.

**Table 5.2:** $D^2 \Pi_{3/2} - X^2 \Sigma$ transitions of HgCl report by Horne et al., 1968 and Wieland, 1929.

<table>
<thead>
<tr>
<th>$v''/v'$</th>
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<th>2</th>
<th>3</th>
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<tr>
<td>2</td>
<td>255.35</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>246.96</td>
</tr>
</tbody>
</table>

(5.3.1) Photolytic HgCl Production

HgCl was produced via two methods, via photolysis of HgCl$_2$ and the in-situ production of HgCl via Reaction (R1.11).

\[
Hg + Cl + M \rightarrow HgCl + M \quad (\text{R1.11})
\]

The photolysis of HgCl$_2$ produced Hg atoms, Cl atoms, and the HgCl radical.

\[
\text{HgCl}_2 + h\nu \rightarrow \text{Hg} + 2 \text{Cl} \quad (\text{R5.1})
\]

\[
\text{HgCl}_2 + h\nu \rightarrow \text{HgCl} + \text{Cl} \quad (\text{R5.2})
\]

Experiments were performed by photolyzing the HgCl$_2$ with both the 4$^{th}$ (266 nm) and 5$^{th}$ (213 nm) harmonic of an Nd:YAG laser. Gas phase HgCl$_2$ was introduced into the cell by passing N$_2$ or He over a heated reservoir of HgCl$_2$ solid. All lines were heated to prevent the deposition of the HgCl$_2$ species in the lines or on the entry port. This method of
formation has the benefit of resulting in the instantaneous production of the HgCl radical. However, the LIF signals can only show relative loss as no absolute HgCl concentration was obtained.

The second source of HgCl was photolysis of a Cl atom precursor with the subsequent formation of the HgCl radical via reaction (R1.11). Chlorine atoms were produced by photolysis of molecular chlorine by the 355 nm, third harmonic of an Nd:YAG laser. A detailed discussion of the photolysis and concentration determination for Cl atoms can be found earlier in this work, Section 3.2.

(5.3.2) *HgCl Excitation Spectra*

Excitation spectra were obtained for the wavelength range 246.3 nm – 251.8 nm with the HgCl produced by the photolysis of HgCl$_2$ at 266 nm. Figure 5.1 illustrates a scan from 246.3 nm – 250.3 nm with the HgCl produced by the photolysis of HgCl$_2$ at 266 nm with all major vibrational transitions labeled. The scanning rate is 2 pm s$^{-1}$, the resolution is 0.0002 nm for the scan and 0.05 nm for the 250 point averaged data. The agreement between the observed scan and the expected HgCl excitation wavelengths positively identifies that the observed fluorescence is from the HgCl radical. The relative intensities of the fluorescence will be characterized by both absorption efficiency at the excitation wavelength and the fluorescence efficiency at the detection wavelength. For these scans, the filter pack has a detection range of 255 nm – 275 nm with maximum transmittance at 260 nm.
**Figure 5.1:** Excitation Spectrum of HgCl from the photolysis of HgCl$_2$ at 266 nm with fluorescence detection at 265 ± 10 nm.

**Figure 5.2:** Excitation Spectrum of HgCl from the photolysis of HgCl$_2$ at 266 nm (black and red lines) and at 213 nm (blue and green)
In addition, a series of scans were conducted to compare the different HgCl production methods. Consecutive scans of HgCl excitation lines were done to compare the efficiency of the 4th and 5th harmonic photolysis of HgCl₂. The scans were conducted over 246.7 nm – 247.9 nm with ~10 μJ of probe power and the maximum photolysis power for each wavelength, 50 mJ for the 4th harmonic and 2 mJ for the 5th harmonic. There was a 2:1 ratio between the 4th and 5th harmonic photolysis, indicating that the 266 photolysis of HgCl₂ resulted in higher concentrations of HgCl in our system. Figure 5.2 illustrates these two scans.

A series of scans were done to monitor the formation of HgCl via reaction (R1.11). In these experiments, the initial molecular chlorine concentration was varied from 45 – 0.03 × 10¹⁵ molecules cm⁻³ with Hg atom concentration stable at 5 × 10¹³ molecules cm⁻³. The delay between the probe and photolysis laser was optimized to produce maximum HgCl LIF. It was determined that with increasing Cl atom concentration the HgCl LIF signal was reduced. At the highest Cl atom concentrations little to no HgCl LIF was observed. Figure 5.3 illustrates the reduced signal for the two scans with the lowest Cl atom concentration, 1.0 – 0.3 ×10¹⁴ molecules cm⁻³. The observed reduction in LIF signal is due to the loss of HgCl via the following reactions;

\[
\text{HgCl} + \text{Cl} \rightarrow \text{HgCl}_2 \quad \text{(R1.17)}
\]

\[
\text{HgCl} + \text{Cl} \rightarrow \text{Hg} + 2 \text{Cl} \quad \text{(R1.18)}
\]

\[
\text{HgCl} + \text{Cl}_2 \rightarrow \text{products} \quad \text{(R5.3)}
\]

Therefore at high Cl₂/Cl atom concentration there is little to no LIF signal because upon formation each HgCl radical reacts with an additional Cl atom to form products.
Resolved fluorescence spectra for the HgCl radical were obtained by tuning the grating of dye laser to a specific excitation line. An LIF signal was then produced and passed through a monochromator (600 line grating) with a gated diode array detector. The source of HgCl in all the HgCl resolved fluorescence spectra experiments was the photolysis of HgCl\textsubscript{2} at 266 nm.

The wavelength scale for the 600 line monochromator/diode array assembly was calibrated using the 253.65 nm Hg line from the penray lamp and scatter from the 266 nm photolysis. The resolution of the monochromator was 0.5 nm, while the overall resolution was 0.8 nm. Resolved fluorescence spectra was collected for six excitation lines, (0,1) at 253.50 nm, (0,0) at 251.66 nm, (1,0) at 249.54 nm, (2,1) at 249.26 nm, (2,0) at 247.47 nm.
nm, and (3,0) at 245.46 nm. Figure 5.4 shows the resolved fluorescence spectrum obtained for each excitation wavelength. In addition, figure 5.4 shows the transmission spectra for the filter pack/PMT assembly during the HgCl excitation spectra scans.

**Figure 5.4:** Resolved Fluorescence Spectra for six HgCl excitation lines and the transmission of the filter/PMT assembly for LIF detection.
The detection region for the LIF during excitation scans does not cover the entire range of the observed fluorescence. This offset is intentional as by detecting the LIF in a wavelength range that is shifted from the excitation line the scatter light from the probe laser will be minimized increasing the overall sensitive of the detection scheme. Table 5.2 lists the wavelength of the transition observed in the resolved LIF spectra, all values have an error of ± 0.8 nm calculated from the fwhm of the observed fluorescence peaks.

Table 5.3: Observed fluorescence transitions for the D$^3\Pi_{3/2}$ – $X^2\Sigma$ band from 245 nm – 265 nm, all values are in nm and have error of ± 0.8 nm.

<table>
<thead>
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</tr>
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<td>7</td>
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<td>10</td>
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<td>---</td>
<td>---</td>
<td>263.3</td>
</tr>
</tbody>
</table>

Overall, it was determined that LIF detection of HgCl was possible under several configurations and conditions. For the instantaneous generation of HgCl, the 266 nm photolysis of HgCl$_2$ resulted in the highest HgCl signal in our experiment. However, by increasing the power of the 213 nm photolysis above 2 mJ a similar yield was obtained while eliminating the scattered light form the photolysis beam detected by the PMT. For production of HgCl via the reaction of mercury atoms and Cl atom, the 355 nm third harmonic of an Nd:YAG laser was the photolytic source of Cl atoms. In these experiments it is necessary to keep the Cl atom concentration below $1 \times 10^{14}$ as at higher
concentrations the reactions (R1.15) and (R5.3) are rapid and the [HgCl] is reduced below detection limits.

The (1,0) transition at 249.5 nm was selected as the best HgCl excitation wavelength. This transition is the strongest line observed in our excitation spectra. In addition, it is shifted from the 252 – 272 nm LIF detection region, so scatter from the probe beam should be blocked by the filter pack. Figure 5.5 is a schematic of the final experimental set-up for the LIF detection of HgCl.

**Figure 5.5:** Experimental configuration for the detection of HgCl radicals, including optical and flow system configurations.

(5.3.4) **Kinetics Studies of the HgCl radical using LIF**

Kinetic profiles of the [HgCl] were collected over 0.02 s. The HgCl radical was generated via the 355 nm photolysis of Cl₂ with subsequent reaction with mercury atoms. Figure 5.6 is a plot of the relative [HgCl] versus time. The observed loss of HgCl is due
to reaction with the Cl₂, Cl atoms generated in the photolysis, impurities, and diffusional and wall losses.

![Graph showing HgCl LIF Signal versus Time (s)](image)

**Figure 5.6:** HgCl decays in N₂ with [Hg] and [Cl₂] varying; (points) measured LIF, (lines) linear fit of the natural log of the LIF signal.

Reaction (R1.24) was studied in both He and N₂ bath gases at 25 °C and total pressures of 300 Torr.

\[
\text{HgCl + O₂} \rightarrow \text{products} \quad \text{(R1.24)}
\]

O₂ concentrations were varied from 0 to 200 Torr partial pressures with all other conditions held constant. The HgCl₂ was introduced into the cell via gas flow over solid HgCl₂. N₂, O₂, and He were introduced into the cell through calibrated flow mass flow meters or controllers with shutoff valves and needle valves as needed. Absolute concentrations of the gases were calculated from mass flow rates monitored during experiments. Pressure was monitored by a capacitance monometer and ambient room temperature was monitored with a thermocouple. Figures 5.7 and 5.8 show the observed HgCl LIF signal versus time for experiments conducted in N₂ and He, respectively.
Figure 5.7: HgCl decays in N$_2$ with varying partial pressures of O$_2$; (points) measured LIF, (lines) linear fit the natural log of the LIF signal.

Figure 5.8: HgCl decays in He with varying partial pressures of O$_2$; (points) measured LIF, (lines) linear fit the natural log of the LIF signal.
As \([\text{HgCl}] \ll [\text{O}_2]\), a simple pseudo first order approximation, described in detail in Chapter 2, can be employed;

\[
\frac{d[\text{HgCl}]}{dt} = -k_{R_1.24}' [\text{HgCl}]
\]  \hspace{1cm} (E5.1)

where,

\[
k_{R_1.24}' = k_{R_1.24} \times [\text{O}_2]
\]  \hspace{1cm} (E5.2)

The resulting first order decays, \(k_{R_1.24}'\), are reported in the figures along with partial pressure of \(\text{O}_2\).

The S/N ratio for \(\text{HgCl}\) in the absence of \(\text{O}_2\) was 50:1 for experiments conducted in He and 6:1 for experiments conducted in \(\text{N}_2\). The reduction is the S/N ratio can account for the increased uncertainty in measurements conducted in \(\text{N}_2\). In addition, the \(\text{O}_2\) molecule acts as a quencher of the LIF signal so the S/N ratio does slightly degrade with increasing \([\text{O}_2]\).

A second order rate loss for \((R_1.24)\) was determined by plotting the \(k_{R_1.24}'\) versus the partial pressure of \(\text{O}_2\), Figure 5.9.

![First order rate coefficients for the reaction of Hg atoms and O₂](image)

**Figure 5.9:** First order rate coefficients for the reaction of Hg atoms and \(\text{O}_2\), \(k_{R_1.24}'\), as \(\text{O}_2\) partial pressure is varied.
The slope of a linear regression from this plot will be $k_{R1.24}$, while the offset observed in the regression is the first order loss of HgCl due to reaction with impurities, Cl atoms from the photolysis of HgCl$_2$, and potentially other unidentified loss processes. The observed $k_{1.24}$ for He and N$_2$ gas at 300 Torr and 25 °C were:

$$k_{1.24(N_2)} = (2.7 \pm 0.6) \times 10^{-17} \text{ (molecules}^{-1} \text{ cm}^3)$$ (E5.3)

$$k_{1.24(He)} = (3.2 \pm 0.2) \times 10^{-17} \text{ (molecules}^{-1} \text{ cm}^3)$$ (E5.4)

The observed rates agree with each other within the error of the measurement, indicating that the bath gas may not significantly influence the kinetic rate for reaction (R1.24).

### (5.4) HgBr Spectroscopy

The HgBr radical was monitored previously in a flash photolysis – absorption spectroscopy system by the same group as the HgCl radical (Greig et al., 1970). They detected two major bands the D$_2^2\Pi_{3/2} - X^2\Sigma$ at 254.0 – 263.0 nm and the C$_2^2\Pi_{3/2} - X^2\Sigma$ at 277.0 – 293.0 nm. The transitions reported by Greig et al. for the D$_2^2\Pi_{3/2} - X^2\Sigma$ transitions of HgBr are listed in Table 5.4. The Greig study reports good agreement with a previous study and with values calculated from based on a Boltzman distribution for the D$_2^2\Pi_{3/2} - X^2\Sigma$ transition band. They also reported that the relative absorption intensities did not change as the timing was shifted, indicating that the HgBr species was in thermal equilibrium with the surroundings.

The B$_2^2\Sigma - X^2\Sigma$ transition in the visible wavelength region, has been studied in the development of HgBr lasers (Greene et al., 1986a, b; Parks, 1977; Schimitschek et al., 1977; Tellinghuisen and Ashmore, 1982). This excited band is observed at 435 nm – 505 nm. The fluorescence is primarily characterized by transitions from a highly excited B$_2^2\Sigma$
level to the ground state of the $X^2\Sigma$ level (Parks, 1977). The maximum fluorescence was observed at ~502 nm, this is often attributed to the (22,0) transition. However, the observed peak contains fluorescence from all transitions, which have a $\Delta \nu = 22$ such as (22,0), (23,1), and (24,2).

The HgBr fluorescence spectrum is further complicated by the multiple isotopes of Br atoms ($\text{Br}^{79}$, $\text{Br}^{81}$) and Hg atoms ($\text{Hg}^{198}$, $\text{Hg}^{199}$, $\text{Hg}^{200}$, $\text{Hg}^{201}$, $\text{Hg}^{202}$, $\text{Hg}^{204}$). This results in twelve isotopomers for the HgBr radical, all of which occur in natural HgBr$_2$.

The wavelength of three $\Delta \nu = 22$ transitions for all 12 isotopomers and their natural abundance are listed in table 5.5.

**Table 5.4:** $D^2\Pi_{3/2} - X^2\Sigma$ transitions of HgBr report by Greig et al., 1970 all transition are reported in nm.

<table>
<thead>
<tr>
<th>$\nu''/\nu'$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>259.02</td>
<td>257.51</td>
<td>256.02</td>
<td>254.54</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>260.28</td>
<td>258.76</td>
<td>255.75</td>
<td>254.28</td>
<td>254.28</td>
</tr>
<tr>
<td>2</td>
<td>261.54</td>
<td>---</td>
<td>258.47</td>
<td>---</td>
<td>255.41</td>
</tr>
<tr>
<td>3</td>
<td>262.76</td>
<td>261.27</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

**Table 5.5:** The natural abundance and wavelength for $\Delta \nu = 22$ transitions of the 12 isotopomers of HgBr from Tellinghuisen and Ashmore, 1982.

<table>
<thead>
<tr>
<th></th>
<th>Br$^{79}$</th>
<th>Br$^{81}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abud. %</td>
<td>(22,0) nm</td>
</tr>
<tr>
<td>Hg$^{198}$</td>
<td>5.1 %</td>
<td>502.05</td>
</tr>
<tr>
<td>Hg$^{199}$</td>
<td>8.5 %</td>
<td>502.00</td>
</tr>
<tr>
<td>Hg$^{200}$</td>
<td>11.7 %</td>
<td>501.95</td>
</tr>
<tr>
<td>Hg$^{201}$</td>
<td>6.7 %</td>
<td>501.90</td>
</tr>
<tr>
<td>Hg$^{202}$</td>
<td>15.1 %</td>
<td>501.85</td>
</tr>
<tr>
<td>Hg$^{204}$</td>
<td>3.5 %</td>
<td>501.75</td>
</tr>
</tbody>
</table>
(5.4.1) Photolytic HgBr Production

The HgBr radical was produced using similar methods to the HgCl experiments, via photolysis of HgBr$_2$ or the in-situ production of HgBr via Reaction (R1.10)

$$\text{Hg} + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \quad \text{(R1.10)}$$

The photolysis of HgBr$_2$ produced Hg atoms, Br atoms, and the HgBr radical.

$$\text{HgBr}_2 + h\nu \rightarrow \text{Hg} + 2\ \text{Br} \quad \text{(R5.4)}$$

$$\text{HgBr}_2 + h\nu \rightarrow \text{HgBr} + \text{Br} \quad \text{(R5.5)}$$

HgBr$_2$ photolysis was done using either the 4$^{\text{th}}$ or 5$^{\text{th}}$ harmonics of an Nd:YAG laser. Gas phase HgBr$_2$ was introduced into the cell by passing N$_2$ or He over a heated reservoir of HgBr$_2$ solid. The gas flow system was slightly heated before the cell to prevent the deposition of the HgBr$_2$ species in the lines or on the entry port. As in the case of the photolysis of HgCl$_2$, this was an instantaneous production of the HgBr radical, but the absolute [HgBr] was unknown.

HgBr radicals were also produced via reaction (R1.10) Br atoms were generated by the photolysis of Br$_2$ or CF$_3$Br. Photolysis of molecular bromine occurred at 532 nm; the cross-section of the Br$_2$ species at 532 is $1.475 \times 10^{-19}$ (Maric et al., 1994). The photolysis of the CF$_3$Br, bromine atom precursor, was conducted at 213 nm. The cross-section of CF$_3$Br at 213 is $1.095 \times 10^{-19}$ (Sander et al., 2002). The calculation for the determination of the absolute concentration of Br atoms was outline earlier in this work, Section 4.2. Kinetic profiles of HgBr generated by reaction (R.10) will be characterized by an initial rise time with a subsequent decay.
(5.4.2) HgBr Excitation Spectra

Excitation spectra were obtained for HgBr in the wavelength range of 252.9 nm – 260.7 nm. Figure 5.10 illustrates a typical scan; from 252.9 nm – 260.0 nm. The HgBr source for this scan was the photolysis of HgBr$_2$ at 213 nm. The scanning rate is 2 pm s$^{-1}$, the resolution is 0.0002 nm for the scan and 0.05 nm for the 250 point averaged data.

![Excitation Spectrum of HgBr](image)

**Figure 5.10:** Excitation Spectrum of HgBr from the photolysis of HgBr$_2$ at 213 nm with fluorescence detection at 262 nm.

For these scans, the filter pack has a detection range of 252 nm – 272 nm with maximum transmittance at 262 nm. The agreement between this work and previous work (Greig et al., 1970) positively identifies observed fluorescence as HgBr LIF. The relative intensities of the fluorescence will be characterized by both absorption efficiency at the excitation wavelength and the fluorescence efficiency at the detection wavelength.
The excitation spectra were collected using each of the three methods of HgBr production. These scans had similar scan speeds and probe laser power, 10 μJ. HgBr₂ was photolyzed at 213 nm (3mJ) with a delay time of 500 μs and a total pressure of 13.5 Torr. HgBr was produced via reaction (R1.10) at 120 Torr using Br₂ and CF₃Br as precursor molecules. Photolysis of the Br₂ precursor was conducted at 532 nm (150mJ) with a delay of 100 μs, generating initial Br atom concentrations of 6 × 10¹⁴ molecules cm⁻³, while CF₃Br was photolyzed at and at 213 nm (1.0mJ) with a delay of 2000 μs producing [Br] = 7 × 10¹² molecules cm⁻³. In Figure 5.11, the LIF signal and a 250 point sliding average for each scan is shown; the LIF signal is slightly offset to ensure each scan is visible. The gray lines in figure 5.11 designate major HgBr transitions in the scan range. From this experiment it was observed that little to no HgBr product was observed when the Br₂ photolysis method was employed; whereas, HgBr was observed after the photolysis of CF₃Br in the presence on mercury. This rapid loss of the HgBr radical indicates that the radical undergoes immediate reaction with Br atoms (R1.26) and/or molecular bromine (R5.6)

\[
\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2 \quad \text{(R1.29)}
\]

\[
\text{HgBr} + \text{Br} \rightarrow \text{Hg} + 2 \text{Br} \quad \text{(R1.30)}
\]

\[
\text{HgBr} + \text{Br}_2 \rightarrow \text{products} \quad \text{(R5.6)}
\]

In the high Br₂/Br system, each HgBr radical will react with Br₂ or Br upon formation. As the HgBr radical does have a significant lifetime in the CF₃Br/Br system, it is reasonable to infer that reaction of HgBr + Br₂ does play a role in the loss of the mercury halide radical.
(5.4.3) **Resolved Fluorescence Spectra of HgBr**

Resolved fluorescence spectra for the HgBr radical was obtained using the same procedure employed to obtain HgCl resolved spectra. A dye laser was fixed at a specific excitation wavelength, while the resulting fluorescence was monitored by a (150 line or 600 line grating) monochromator/gated diode array assembly. The HgBr source was the photolysis of HgBr$_2$ at 213 nm or 266 nm. The 600 line monochromator/diode array assembly was calibrated for the range, 230 nm – 730 nm using the 253.65 nm from an Hg lamp and its second harmonic line at 507.30 nm. The resolution of the monochromator
was 4.1 nm; it was calculated from the full width half maximum (fwhm) of the 253.65 nm mercury line.

Resolved HgBr spectra were collected in four configurations, photolysis of HgBr$_2$ at 213 nm with HgBr excitation on the (2,0) line at 256.08 nm and the (4,0) line at 253.17 nm and photolysis of HgBr$_2$ at 266 nm with excitation on the (2,0) and (4,0) lines. Figure 5.12 shows the resolved spectrum for each of these configurations; as well as, the transmission spectra for the filter pack/PMT assembly for LIF detection of the D$^2\Pi_{3/2}$ – X$^2\Sigma$ and B$^2\Sigma$ – X$^2\Sigma$ bands. Each configuration has two spectra, blue line is the LIF directly observed by the diode array. The red line is a spectrum collected under the same condition with the addition of a Pyrex filter to cut off UV fluorescence. Comparison of the full and UV blocked spectra will distinguish between the contribution of a second harmonic of UV lines and the B$^2\Sigma$ – X$^2\Sigma$ band.

It was determined that maximum fluorescence signal was obtained with photolysis at 266 nm and excitation at the (2,0) line. This LIF scheme was further studied for pressure dependences at 80 Torr, 200 Torr, and 400 Torr. Figure 5.13 is a plot of the spectra obtained at each pressure corrected for variation in [HgBr] due to pressure. A significant reduction of the D$^2\Pi_{3/2}$ – X$^2\Sigma$ band intensity was observed with increasing pressure while the B$^2\Sigma$ – X$^2\Sigma$ band in the visible is virtually unchanged. This indicates that the D$^2\Pi_{3/2}$ – X$^2\Sigma$ band fluorescence is quenched by the buffer gas and fluorescence detection of the B$^2\Sigma$ – X$^2\Sigma$ band centered at 500 is the preferred detection region for HgBr LIF.
Figure 5.12: Resolved Fluorescence Spectra for four HgBr LIF configurations with the transmission of the filter/PMT assembly for both UV and visible LIF detection of HgBr. Full wavelength spectrum (blue lines); UV blocked spectrum (red lines).
**Figure 5.13:** Pressure dependence of the resolved fluorescence spectra with excitation on the (2,0) line at 256.08 nm and photolysis of HgBr$_2$ at 266 nm along with the transmission spectrum for the filter/PMT assembly for the LIF detection of HgBr at 262 nm and 500 nm. Full wavelength spectrum (blue lines); UV block spectrum (red lines).

To better characterize the 500 nm band, the monochromator was reconfigured to the use the 600 line grating. The 600 line monochromator/diode assay assembly was calibrated using the 2nd harmonic of the 253.65 mercury line and the 546.07 mercury line. A resolved spectrum for HgBr in the wavelength region, 455 nm to 590 nm, was obtained with a resolution of 0.8 nm. The observed resolved fluorescence spectrum is shown in Figure 5.14. The resulting spectrum is similar to that reported in Parks et al. (Parks, 1977)
with a broad peak structure, which can be attributed primarily to transitions from a highly excited \( B^2\Sigma \) state (12 < \( \nu'' \) < 23) to the ground \( X^2\Sigma \) state. However, this peak is not only due to this transition as the 0.8 nm resolution is inadequate to resolve peak with the same \( \Delta\nu \).

Additionally, there is the complication of the isotopomers of HgBr. The upper portion of Figure 5.14 is a blow up of the \( \Delta\nu = 22 \) peak. The wavelengths reported by Tellinghuisen et al are represented on the plot as lines. Here we see that there is a \(~0.5\) nm shift as a Br\(^{79}\) is replaced with a Br\(^{81}\), this shift can be observed in the dual peak structure observed in the higher resolution resolved fluorescence spectra. However, this shift is actually smaller than the resolution of the monochromator and these two sets of peaks are not fully resolved. The even smaller isotope shifts for the mercury species, \(~0.05\) nm with every 1 g increase in the Hg atomic weight are not observable. Tellinghuisen states;

It should be noted that th[e] overlap [of the \( \nu'' - \nu' \) bands of the 12 isotopomers] is so extensive that most of the band heads … cannot possible be discerned in the spectrum of “natural” HgBr and can only be accounted for through the analysis of a single isotopic species.

However, in this work, full band identification is not necessary to continue with the LIF detection as the fluorescence from the \( B^2\Sigma - X^2\Sigma \) band is detected over a broad range, 492 nm – 507 nm.
Figure 5.14: The Fluorescence spectra from the 600 line monochromator with excitation on the (2,0) line at 256.08 nm and photolysis of HgBr\textsubscript{2} at 266 nm. The black line is the observed spectra with a resolution 0.8 nm, the wavelengths for the (22,0) transition for the two primary isotopomers are shown, Hg\textsuperscript{202}Br\textsuperscript{79} (green) and Hg\textsuperscript{202}Br\textsuperscript{81} (blue). The inlay shows the complex HgBr due to the 12 isotopomers, the wavelengths for each isotopomer for the (22,0) (23,1) and (24,2) transitions are from (Tellinghuisen and Ashmore, 1982).
Figure 5.15 is a plot showing two scans. A scan from 255.0 nm – 256.2 nm employing the original system (HgBr$_2$ photolysis at 213 nm and detection centered at 262 nm) and the new system (HgBr$_2$ photolysis at 266 nm and detection centered at 500 nm). The laser powers, scan speeds, and flow conditions are comparable for both scans. This new system provides a 10 fold improvement of the detection of the HgBr LIF signal. Therefore, this new configuration was identified as the ideal detection scheme for HgBr LIF, figure 15.16.

![Graph showing compare LIF configurations](image-url)

**Figure 5.15:** Scan over the 2,0 line from 255.0 nm – 256.9 nm to compare LIF configurations. (Red line) the original system with HgBr$_2$ photolysis at 213 nm and detection centered at 262 nm. (Black line) the new system with HgBr$_2$ photolysis at 266 nm and detection centered at 500 nm; laser powers, scan speeds, and flow conditions are comparable.
**Figure 5.16:** Experimental configuration for the detection of HgBr radicals, including optical and flow system configurations.

*(5.4.4) Kinetics Studies of the HgBr radical using LIF*

Kinetic profiles of the HgBr were obtained by varying the time delay between the photolysis and probe lasers. The HgBr radical was generated via the 213 nm photolysis of HgBr$_2$. Figure 5.17 is a plot of the relative [HgBr] versus time. The observed loss of HgBr can be attributed to reaction with Br atoms generated in the photolysis, impurities, and diffusional and wall losses. In this experiment the laser power was increased by 25%, this resulted in a 50% increase in the loss of HgBr. This increase is what would be expected as both the [HgBr] and [Br] depend of laser power. Specifically, the overall concentration of both will increase with increasing laser power, hence the observed decay rate should also increase.
Figure 5.17: Temporal profiles of HgBr in N\textsubscript{2} at different 213 nm photolysis powers. (red and blue) photolysis laser power = 2.4 mJ; (black) photolysis laser power = 3.0 mJ; (points) measured LIF; (lines) linear fit of natural log of the LIF signal.

Figure 5.17 demonstrated the feasibility of using LIF to detect HgBr radicals under the same conditions as Hg atom, and X atoms. Further investigations of the kinetic rate coefficients of mercury halogen reaction employing this LIF technique will be discussed in the following chapter.

(5.5) Summary

In this work, we have developed and validated LIF techniques to detect HgCl and HgBr radicals.

The HgCl LIF detection system consists of the initial generation of HgCl radical via the photolysis of HgCl\textsubscript{2} at 213 nm or the photolysis of a Cl\textsubscript{2} at 355 nm in the presence of Hg atoms. These photolytically produced HgCl species are then excited at the (1,0)
transition of the $D^2\Pi_{3/2} - X^2\Sigma$ band at 249.5 nm. The resulting fluorescence was detected by a filter pack/PMT assembly, which detects fluorescence centered at 262 nm.

The HgBr LIF detection scheme employs a photolysis laser pulse to generate HgBr radicals via the photolysis of HgBr$\textsubscript{2}$ at 266 nm or the initial photolysis of a Br atom precursor in the presence of Hg atoms. HgBr created by photolysis are then excited by a probe laser pulse tuned to the (2,0) transition of the $D^2\Pi_{3/2} - X^2\Sigma$ band at 256.08 nm. The resulting fluorescence was detected by a filter pack/PMT assembly, which detects the $B^2\Sigma - X^2\Sigma$ fluorescence band at 500 nm.

The ability to monitor the HgCl and HgBr radical species during kinetic measurements will provide new insights into the reaction mechanism and rates of reaction for important mercury halogen reactions.
(6.1) Background

In chapter IV, the rate coefficient for the recombination of Hg\(^0\) and Br atoms was studied with Br radicals in excess. This was done to overcome limitations due to the low vapor pressure of mercury. Another approach that overcomes the challenge of mercury’s low vapor pressure is to perform measurement at higher temperatures with mercury in excess. The vapor pressure of mercury increases by a factor of 40 as the temperature is raised from 25 °C to 80 °C; at 80 °C the vapor pressure is \(2.5 \times 10^{15}\) molecules cm\(^{-3}\). At this concentration it is possible to perform measurements where Hg\(^0\) is the reactant in excess, monitoring the Br atom and HgBr molecule temporal profiles. In this system, the Br and HgBr profiles will be characterized by the following reaction system.

\[
\begin{align*}
\text{Hg}^0 + \text{Br} + \text{M} & \rightarrow \text{HgBr} + \text{M} \quad \text{(R1.10)} \\
\text{HgBr} + \text{M} & \rightarrow \text{Hg}^0 + \text{Br} + \text{M} \quad \text{(R6.1)} \\
\text{HgBr} + \text{Br} & \rightarrow \text{HgBr}_2 \quad \text{(R1.29)} \\
\text{Br} + \text{CF}_3 & \rightarrow \text{CF}_3\text{Br} \quad \text{(R6.2)} \\
\text{Br} & \rightarrow \text{loss} \quad \text{(R6.3)}
\end{align*}
\]

By monitoring both the Br atom and the HgBr molecule temporal profiles under a series of conditions, it was possible to determine the rate coefficient for the mercury reactions R1.10, R1.29, and R6.1.
(6.2) **Experimental**

Kinetic measurements for the reaction of Hg\(^0\) with Br atoms, R1.10, and the two HgBr loss processes, thermal decomposition, R6.1, and reaction with Br atoms, R1.29, were performed in pulsed laser photolysis – pulsed laser induced fluorescence (PLP-PLIF) system with Hg\(^0\) as the reactant in excess concentration. The LIF signals for both Br atoms and the HgBr product were monitored at two temperatures (420 K and 360 K), three pressures (200, 400 and 600 Torr), and \([\text{Hg}^0]\) ranging from \((0.5 – 28.5) \times 10^{14}\) molecules cm\(^{-3}\).

The general experimental approach has been described earlier in this work, and has been employed here with few alterations. Bromine atoms were produced by the photolysis CF\(_3\)Br at 213 nm.

\[
\text{CF}_3\text{Br} + \text{hv} \rightarrow \text{CF}_3 + \text{Br} \quad (\text{R2.9})
\]

An output power of approximately 2 mJ per pulse resulted in bromine atom concentrations in the range of \((0.05 – 40) \times 10^{13}\) molecules cm\(^{-3}\). The photolysis of CF\(_3\)Br leads to the formation of a Br radical and a relatively inert CF\(_3\) radical. Some of the resulting bromine atoms were electronically excited; however, these excited species were rapidly deactivated to the \(^2\text{P}_{3/2}\) ground state with the addition of approximately 5 Torr H\(_2\) quencher. The initial bromine atom concentration produced by photolysis was determined from equation (E4.1) described in chapter IV. The only change in this calculation stems from a switch in the precursor molecule from Br\(_2\) to CF\(_3\)Br; thus \(\sigma_{\text{Br}_2}\) should be \(\sigma_{\text{CF}_3\text{Br}}\) at 213 nm, \(1.10 \times 10^{-19}\) cm\(^2\).

The photolysis laser did not demonstrate a Gaussian profile, so the beam was passed through a 0.41 cm ceramic aperture located 0.5 m from the reaction zone.
Variations in the laser power across the beam profile at the reaction zone were determined by measuring the power passing through a 0.05 cm pinhole ceramic aperture. The power meter/aperture combination was placed on a linear translation stage and the transmitted photolysis laser power was recorded in 0.05 cm steps, giving the power variation across the horizontal diameter of the beam. The aperture was centered around the strongest laser output blocking cold spots in the laser profile. The resulting beam had a diameter of 0.41 cm and was fairly uniform with variations in the power of up to 25%.

Mercury atoms were introduced into the cell from a mercury oven. The oven was a 32 cm brass cylinder with four 8 cm long heaters and a 1.0 cm channel drilled in the block. Inlet and outlet holes were drilled perpendicular to the channel so that gas could be passed over the channel. The channel was filled with approximately 2 g Hg$^0$ and maintained at a constant temperature with a constant flow of N$_2$ to prevent the build up of Hg$^0$ within the system. The oven temperature could be varied from room temperature to 120°C. For this work the oven was maintain at 80 ± 5 °C. All lines, running to the oven and from the oven to the cell, were heated to at least 10°C higher than the oven temperature to prevent condensation of Hg$^0$ within the system.

Mercury concentrations were determined by flow and ranged from (0.5 – 28.5) × 10$^{14}$ molecules cm$^{-3}$. The flow calculation assumes that the gas passed through the oven reaches saturation. This assumption was tested by performing a series of dilution experiments. For each flow setting the saturated flow was diluted until the calculated [Hg$^0$] was less than 5 × 10$^{13}$ molecules cm$^3$. The actual [Hg$^0$] was then determined by absorption on the 253.7 Hg$^0$ line using the cross-section reported earlier in this work. Absorbencies were kept below 0.7 so that the Beer Lambert law would be valid and a
linear cross-section of $1.36 \times 10^{-14} \text{ cm}^2$ was used. All $[\text{Hg}^0]$ calculated by flow were within 25% of $[\text{Hg}^0]$ observed by absorption.

Kinetic experiments were carried in a temperature controlled Pyrex reaction vessel under “slow-flow” conditions to minimize secondary and heterogeneous chemistry. The gas velocity was maintained at approximately 11 cm s$^{-1}$, to completely replace the gas mixture in the reaction zone between the laser pulses. All flows were monitored using calibrated mass flow controllers. A small $\text{N}_2$ flow, <10% of the total flow, was passed through the side arms to ensure that no product build up occurred in the side arms. The pressure in the reaction cell was monitored with a capacitance manometer.

The temporal profiles of Br atoms and HgBr molecules were monitored by two and one photon LIF, respectively. The experimental configuration for the two photon LIF for Br atoms is detailed in Chapter 2 and details concerning the one photon LIF of HgBr molecules are found in Chapter 5. Figure 6.1 is a schematic of the system employed in this study including optics and the flow system.

**Figure 6.1:** Experimental set-up for the PLP-PLIF system to detect HgBr molecules by one photon LIF and Br atoms by two photon LIF.
(6.3) Results

(6.3.1) Temporal profiles of Br with no Hg

Br atom concentrations were influenced by reactions that consumed or produced Br atoms. The base loss rate for Br atoms were determined before Hg was added to the system. Experiments were carried out with [Br] in the range of \((2.5 - 0.23) \times 10^{14}\) molecule cm\(^{-3}\). In this system, the loss of Br atoms was due to the recombination of Br and the CF\(_3\) radical, R6.2, and a first order loss of Br due to diffusion or reaction with impurities, R6.3.

\[
\text{Br + CF}_3 \rightarrow \text{CF}_3\text{Br} \quad \text{(R6.2)}
\]

\[
\text{Br} \rightarrow \text{loss} \quad \text{(R6.3)}
\]

In addition, the Br concentration will be effected by the [CF\(_3\)] available. At high [Br], hence high [CF\(_3\)], observed Br temporal profiles will be buffered by reductions in the [CF\(_3\)] due to the self reaction of CF\(_3\), R6.4.

\[
\text{CF}_3 + \text{CF}_3 \rightarrow \text{C}_2\text{F}_6 \quad \text{(R6.4)}
\]

A series of Br decays were taken at high [Br] to determine the rate coefficients for these reactions. A FACSIMILE fit was used to determine the rate coefficients for R6.2, R6.3, and R6.4 at each temperature and pressure. We found that the observed rate coefficient for Reaction R6.4 demonstrated no pressure or temperature dependence as it was consistently determined to be \((5.0 \pm 1.0) \times 10^{-12}\) cm\(^3\) molecules\(^{-1}\) s\(^{-1}\). The first order loss rates was highly variable, but were consistent throughout a single day. The rate coefficient for reaction R6.3 varied from 200 – 800 s\(^{-1}\). The reaction of CF\(_3\) with Br atoms was independent of pressure and demonstrated a small temperature dependence. The rate coefficient for reaction R6.2 was determined to be \((4.2 \pm 1.0) \times 10^{-11}\) cm\(^3\)
molecules$^{-1}$ s$^{-1}$ at 370 K and $(5.4 \pm 1.0) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 410 K. Figure 6.2 shows typical temporal profiles of Br atoms at high concentration without mercury at 410 K and 600 Torr.

![Figure 6.2: Bromine atom temporal profiles with CF$_3$Br only, measurement conducted in 600 Torr and 410 K.](image)

(6.3.2) **Temporal profiles of Br with Hg$^0$ in Excess**

The rate coefficients for the three relevant mercury reactions: the recombination of Hg$^0$ and Br atoms, (R1.10), the thermal dissociation of HgBr (R6.1) and the reaction of HgBr with Br atoms, R1.29, were determined with Hg$^0$ atom concentrations 25 – 1450 times larger than the Br atom concentration. Under these conditions the [Hg$^0$] should be constant over the time scale of our experiment, as the small loss of the Hg$^0$ due to the reaction with Br atoms was negligible.

For the Br atom decays in the presence of mercury, the resulting decays will be the sum of the Br loss processes minus any Br atom source. The base loss of Br atom due
to reactions R6.2, R6.3 and R6.4 were characterized in the previous section, at high concentrations of Br atoms and CF$_3$ molecules with no mercury in the system. The rate coefficients obtained at high concentrations were then used to fit Br temporal profiles collected at low Br atom and CF$_3$ concentrations with no mercury in the system. We found that the lower concentration data could be fit using the rate coefficients for reactions R6.2 and R6.3 determined in high [Br] and [CF$_3$] experiments. The additional first order loss, R6.3, was not directly transferred; instead it was varied in order to obtain a good fit to the data. All resulting $k_{R6.3}$ were determined to be within the range of values observed in the high concentration experiments. The self reaction of CF$_3$, Reaction R6.4, did not significantly influence the observed fit in low concentration experiments, so it was not included in the mercury reaction system. All Br atom profiles with [Hg$^0$] under $2 \times 10^{14}$ molecule cm$^{-3}$ could be solely characterized by reactions R6.2 and R6.3.

Once [Hg$^0$] were above $2 \times 10^{14}$ molecule cm$^{-3}$ an additional loss of Br atoms was observed due to reaction with Hg$^0$ atoms, R1.10. The Br temporal profiles were also influenced by the reaction of the HgBr molecule with Br atoms. It has been proposed that the HgBr reaction with Br atoms can proceed by two pathways. These pathways are outlined in the following reactions:

$$\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2 \quad (R1.29)$$

$$\text{HgBr} + \text{Br} \rightarrow \text{Hg}^0 + \text{Br}_2 \quad (R1.30)$$

In this system, where mercury atoms are in excess, the regeneration of Hg$^0$ atom from the second channel will not influence the observed rate. Thus for simplicity, in this paper, $k_{R1.29}$ will refer to the total rate of reaction for both channels for the reaction of HgBr
molecules with Br atoms. The final reaction that influenced the Br temporal profiles is the thermal decomposition of HgBr, R6.1.

\[
\text{HgBr} \rightarrow \text{Hg}^0 + \text{Br} \quad (\text{R6.1})
\]

This reaction results in a regeneration of the Br atoms, and the observed temporal profiles will show a Br atom decay until the loss of Br atoms due to reactions R1.10, R6.2, R6.3, and R1.29 is proportional to the regeneration of Br atom from reaction R6.1. The overall Br atom temporal profile can be characterized by equation E6.1.

\[
\frac{d[\text{Br}]}{dt} = -k_{R6.2}[\text{Br}][\text{CF}_3] - k_{R6.3}[\text{Br}]^2 - k_{R1.10}[\text{Br}][\text{Hg}^0] - k_{R1.29}[\text{HgBr}][\text{Br}] + k_{R6.1}[\text{HgBr}] \quad (\text{E6.1})
\]

Figure 6.3 is an example of typical Br temporal profiles, these profiles were obtained at 207 Torr and 420 K, with [Hg\(^0\)] ranging from \((1.5 - 23) \times 10^{14}\) molecules cm\(^3\).
(6.3.3) **Temporal profiles of HgBr with Hg\(^0\) in Excess**

HgBr molecule profiles were obtained under the same experimental conditions as the Br atom profiles. Three of the four reactions in the system influence \([HgBr]\). There is one production term stemming from reaction R1.10, and two loss terms from reactions R1.29 and R6.1. HgBr temporal profiles can be characterized by Equation 6.2.

\[
\frac{d[HgBr]}{dt} = k_{R1.10} [Br][Hg] - k_{R1.29} [HgBr][Br] - k_{R6.1} [HgBr]
\] (E6.2)

A set of typical temporal profiles HgBr molecules is plotted in figure 6.4 for experiments conducted at 207 Torr and 420 K, with \([Hg^0]\) ranging from \((2.0 – 24) \times 10^{14}\) molecules cm\(^{-3}\).

![Graph showing HgBr temporal profiles](image)

**Figure 6.4:** Typical HgBr atom temporal profiles, shown for measurements conducted in 200 Torr N\(_2\) at 420 K.

(6.3.4) **Temporal profile curve fitting procedure**

The Br atom and HgBr molecule temporal profiles were modeled using a combination of visual fitting of a numerical integration model output and a data fitting
program, FACSIMILE (Malleson et al., 1990). A numerical integration model was developed to initially fit the data prior to export into the FACSIMILE program. This numerical integration model was checked by comparing the model output with the output of the ACUCHEM program (Braun et al., 1986) using the same reaction system. As the HgBr reaction system is complex a series of fitting procedure were followed, these steps are outlined below.

The first step in the fitting procedure was to evaluate the Br decays. The first 0.003s of the Br decay will reflect the loss of Br due to reaction R6.2 and R 6.3, which have been characterized with no mercury in the system, and reaction R1.10.

![Figure 6.5](image_url)  

**Figure 6.5:** Fitting procedure for Br atom temporal profiles, shown for measurements conducted in 600 Torr N₂ at 420 K. (black points) Br LIF with [Hg₀] = 0; (black line) fit to Br data with [Hg₀] = 0; (red points) Br LIF with [Hg₀] = 1.3 × 10^{15} molecule cm⁻³; (red line) fit to Br data with [Hg₀] = 1.3 × 10^{15} molecule cm⁻³ where k_{R1.10} = 1.2 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹; (green line) fit to Br data with [Hg₀] = 1.3 × 10^{15} molecule cm⁻³ where k_{R1.10} = 5.0 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹; (blue line) fit to Br data with [Hg₀] = 1.3 × 10^{15} molecule cm⁻³ where k_{R1.10} = 5.0 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹.
Figure 6.5 shows a plot of the Br LIF with $[\text{Hg}^0] = 0$ and with $[\text{Hg}^0] = 1.3 \times 10^{15}$ molecule cm$^{-3}$. The lines on the plot are the model output from the numerical integration using different rate coefficients for $k_{R1.10}'$. These fits shows that although there is significant scatter in the Br LIF a reaction rate coefficient can be clearly defined. Each curve was fit individually to establish error limits and then in FACSIMILE using a simultaneous fit of all Br decays, under the same temperature and pressure conditions that were performed to obtain the best fit for all Br atom temporal profiles. It should be noted that these fits deviate significantly from the observed LIF signal on longer time scales as the influence of the thermal decomposition of HgBr has not been included in the fit. Also, this fitting procedure is highly sensitive to over-estimates of the $k_{R1.10}'$, but is less sensitive to under-estimates. Thus, this fit results in a upper limit for the rate coefficient of reaction R1.10.

Now that the rate coefficient of the reaction of Hg$^0$ and Br atoms has been defined within a range, the HgBr temporal profiles were employed to further define the rate coefficient for reaction R1.10, and establish estimates for the rate coefficients of reactions R6.1 and R1.29. As started earlier, the HgBr temporal profiles will be characterized by an initial production term, which has been characterized by the previous step, and then two primary loss terms; reaction of HgBr with Br atoms, R1.29, and the thermal decomposition of HgBr. An initial fit of the HgBr loss processes, R6.1 and R1.29, were done using the rate determined from the Br decays for the reaction rate coefficient of reaction R1.10, then rate coefficients for reactions R1.29 and R6.1 were varied until a good visual fit was obtain using the numerical integration of E6.2. Figure 6.6 is a plot of a typical HgBr decay; the lines are the numerically integrated model output with varying
rate coefficients for the two loss reactions of HgBr. From figure 6.6 it is evident that the best fits are obtained when both loss processes are included in the reaction system.

![Figure 6.6: Fitting HgBr temporal profiles, shown for measurements conducted in 600 Torr N₂ at 420 K. (points) HgBr LIF with [Hg⁰] = 2.4 × 10¹⁵ molecule cm⁻³ and [Br] = 2.7 × 10¹² molecule cm⁻³; (black line) model output where k_{R1.10}' = 1.2 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, k_{R1.29}' = 3.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, and k_{R6.1}' = 500 s⁻¹; (red line) model output where k_{R1.10}' = 1.2 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ and k_{R1.29}' = 3.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹; (blue line) model output where k_{R1.10}'=1.2×10⁻¹³ cm³ molecule⁻¹ s⁻¹ and k_{R6.1}'=900 s⁻¹.]

In order to perform a simultaneous fit using the FACSIMILE data fitting program all temporal profiles must be in absolute concentration. Therefore, the relative HgBr signals were converted to absolute [HgBr] using the rate coefficients obtained in the numerical integration model. To ensure that no bias was introduced by this procedure, the HgBr decays were initialized with different values for k_{R1.10}', the k_{R1.10}' was varied up to ± 75% of the initial k_{R1.10}', determined by a visual fit of the model output. A FACSIMILE fit was performed for each initialization, simultaneously fitting up to six HgBr and Br decays allowing both k_{R1.10}' and k_{R6.1}' to vary. This was done until the error associated with reaction R1.10 was minimized. This optimized fit was within the error
limits of rate coefficient for reaction R1.10 derived from the Br decays, thus we believe that $k_{R1.10}'$ was fairly well defined.

The rate coefficient for reaction R6.1, the thermal decomposition of HgBr, was determined at each temperature assuming the fastest possible rate coefficient consistent with data at 600 Torr and low [Hg$^0$]. Figure 6.7 is a plot of the HgBr model output with for HgBr temporal profiles obtained at 600 Torr, 420K and [Hg$^0$] = $5.8 \times 10^{13}$ molecule cm$^{-3}$.

Figure 6.7: Fitting HgBr temporal profiles for $k_{R6.1}$, shown for measurements conducted in 600 Torr N$_2$ at 420 K.(points) HgBr LIF with [Hg$^0$] = $5.8 \times 10^{13}$ molecule cm$^{-3}$ and [Br] = $1.6 \times 10^{12}$ molecule cm$^{-3}$; $k_{R1.10}' = 1.2 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; $k_{R1.29}' = 0$ (black line) model output where $k_{R6.1}' = 500$ s$^{-1}$; (red line) model output where $k_{R6.1}' = 300$ s$^{-1}$; (blue line) model output where $k_{R6.1}' = 1000$ s$^{-1}$.

Under these conditions the influence of reaction R1.29 will be minimal. The plot shows the model output from the numerical integration, along with the HgBr LIF signal. The red and blue lines in figure 6.7 are present to show how the model output changes as $k_{R6.1}'$
changes. We found that in general the rate coefficient for reaction R6.1 could be defined within $\pm 100 \, \text{s}^{-1}$, with increasing error as the temperatures were increased.

A FACSIMILE fit was then done for all HgBr decays at 600 Torr at the same pressure, varying only the rate coefficient for reaction R1.29. Figure 6.8 shows the model output of the reaction system for data at 600 Torr 420 K at two [Hg] with and without the loss of HgBr due to reaction with Br atoms.

The data determined at 200 and 400 Torr was fit by assuming that reaction R1.29 is in the high pressure limit. If this assumption is accurate the $k_{R1.29}$ determined at 600 Torr can be used for data collected at 200 and 400 Torr data. We made this assumption and proceeded to fit the HgBr and Br temporal profiles at 200 and 400 Torr using the second order rate coefficients determined for reaction R1.10 and pressure independent rate coefficient determined for reaction R1.29. FACSIMILE fits were preformed, optimizing the $k_{R6.1}$. During the optimization of $k_{R6.1}$ for 200 and 400 Torr, the $k_{R6.1}$ was allowed to vary, however the rate coefficient for reaction R1.10 did not significantly change and was within the reported error limits. The rate coefficients derived from the Br and HgBr profiles at 360 K and 420 K at each pressure are plotted in figures 6.9-6.14. The second order rate coefficients determined for each temperature and pressure are reported in Table 6.1.
Figure 6.8: Fitting HgBr temporal profiles for $k_{R1.29}'$ at 600 Torr N$_2$, shown for measurements conducted at 420 K where $k_{R1.10}' = 1.2 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; $k_{R6.1}' = 500$ s$^{-1}$; [Hg] = 5.8 $\times$ 10$^{13}$ molecules cm$^{-3}$; [Br] = 1.6 $\times$ 10$^{12}$ molecules cm$^{-3}$; (a) HgBr LIF with [Hg$^0$] = 5.8 $\times$ 10$^{13}$ molecule cm$^{-3}$ and [Br] = 1.6 $\times$ 10$^{12}$ molecule cm$^{-3}$; (b) HgBr LIF with [Hg$^0$] = 5.8 $\times$ 10$^{13}$ molecule cm$^{-3}$ and [Br] = 1.6 $\times$ 10$^{12}$ molecule cm$^{-3}$; (solid lines) model output where $k_{R1.29}' = 1.2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; (dashed lines) model output where $k_{R1.29}' = 0$
Figure 6.9: Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 420 K and 600 Torr.

Figure 6.10: Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 420 K and 400 Torr.
**Figure 6.11:** Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 4200 K and 200 Torr.

**Figure 6.12:** Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 360 K and 600 Torr.
Figure 6.13: Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 360 K and 400 Torr.

Figure 6.14: Normalized temporal profiles for Br and HgBr with the numerical integration model fits, for data at 360 K and 200 Torr.
Table 6.1: Second order rate coefficients for the reaction of Hg\(^0\) and Br atoms, \(k_{R1.10'}\), the thermal decomposition of HgBr, \(k_{R6.1'}\), and the subsequent reaction of HgBr and Br atom, \(k_{R1.29'}\).

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>(k_{R1.10'} \pm \text{error (cm}^3\text{molecule}^{-1}\text{s}^{-1}))</th>
<th>(k_{R6.1'} \pm \text{error (s}^{-1}))</th>
<th>(k_{R1.29'} \pm \text{error (cm}^3\text{molecule}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2)</td>
<td>420</td>
<td>200</td>
<td>((4 \pm 3) \times 10^{-14})</td>
<td>250 ± 100</td>
<td>((3.0 \pm 1.0) \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((9.6 \pm 1) \times 10^{-14})</td>
<td>375 ± 125</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((12 \pm 2) \times 10^{-14})</td>
<td>500 ± 120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>200</td>
<td>((4.5 \pm 1.5) \times 10^{-14})</td>
<td>200 ± 40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>((12 \pm 1) \times 10^{-14})</td>
<td>300 ± 40</td>
<td>((3.5 \pm 1.0) \times 10^{-10})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>((15 \pm 2) \times 10^{-14})</td>
<td>375 ± 50</td>
<td></td>
</tr>
</tbody>
</table>

(6.3.5) Deriving temperature and pressure independent rate coefficients

Third order recombination rate coefficients were then determined from linear fits of the plots of the second order rate coefficients, \(k_{R1.10'}\), vs. the concentration of \(N_2\), shown in Figure 6.15. We have included the second order plots from Donohoue et al. (Donohoue et al., 2006) determined for 243 K, 263 K and 293 K for comparison.

![Figure 6.15: Variation of the effective second order rate coefficients for the recombination Hg\(^0\) and Br atoms, \(k_{R1.10'}\), with pressure.](image)

The second order plots show a linear dependence of rate coefficient vs. concentration indicating that the reaction was in the low pressure, third order regime. The effective
second order rate coefficient should be zero at zero pressure in a third order regime. The
data at 360 K demonstrates this behavior, as there is no difference in a slope forced
through zero and an unforced plot. However, as the 420 Torr had a significant error
associated with the \( k_{R1.10} \) determination, the third order plot was forced through zero.
The difference between the forced and unforced slopes was under 20% and within the
precision of the fit. The \( r^2 \) value was actually improved by forcing the plot through the
intercept, from 0.89 for the unforced data to 0.95 for the forced data.

The third order recombination rate coefficients, \( k_{R1.10} \), are listed in Table 6.2. A
third order plot is shown in figure 6.16, this plot includes the third order rate coefficients
determined for reaction R1.10 at lower temperatures with Br atoms in excess reported by
Donohoue et al. The plot also includes four potential fits; the exponential fit from
Donohoue et al. (2006) and an Arrhenius expression for the Donohoue et al. data, as well
as, the Arrhenius and exponential fits using all five third order rates: the two \( k_{R1.10} \)
determined in this work coupled with the Donohoue et al. data.

Table 6.2: Third order rate coefficients for the recombination of Hg\(^0\) and Br atoms,
\( k_{R1.10} \), determined in this work (420 K and 360 K) and data from Donohoue
et al., 2006 (293 K, 263 K, and 293 K).

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>( k_{R1.10} \pm 2\sigma \text{ error} \times 10^{-32} ) (cm(^6) molecule(^{-2}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>243</td>
<td>2.06 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>1.98 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>1.43 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>0.921 ± 0.011</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>0.979 ± 0.013</td>
</tr>
</tbody>
</table>

**Third Order Expression**

\[
(1.49 \pm 0.12) \times 10^{-32} \times \left( \frac{T}{298} \right)^{-0.78 \pm 0.5}
\]
Figure 6.16: Plot of the third order rate coefficients for the recombination of Hg\(^0\) and Br atoms, \(k_{R1.10}\), in N\(_2\). The lines are the fits: (red, solid) Expression from Donohoue et al. (Donohoue et al., 2006); (red dash) Arrhenius fit for the Donohoue et al. data; (black, solid) Exponential expression fit to all data; (black dash) Arrhenius fit to all data.

We find that the best fit for our data is given by equation (E6.3) reported with 2\(\sigma\) errors of precision only.

\[
k_{R1.10,N_2}(243 - 420K) = (1.49 \pm 0.12) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-(1.76 \pm 0.5)}
\]

Due to uncertainty in the calculation of absolute Br atom concentrations, which is discussed below, and other potential errors, we conservatively estimate the error in the rate coefficient to be \(\pm 65\%\). The observed behavior is consistent with a three-body recombination, demonstrating a positive pressure dependence and an inverse temperature dependence. The data is also in agreement with the rate determined with Br atoms in excess detailed in Chapter IV.
The HgBr decomposition was also characterized in this experiment. The observed rates are outlined above in table 6.1 and show positive temperature and pressure dependencies. The pressure dependence observed in the $k_{R6.1}$ is shown in figure 6.17; there is a significant offset at zero for both reactions.

![Figure 6.17: Pressure dependence of the rate coefficient for the thermal decomposition of HgBr, $k_{R6.1}$, at 420 K (closed squares) and 360 K (open squares).](image)

This offset of $\sim 120$ s$^{-1}$ is within the error associated with the precision of the data, but could also be due to an under-estimate of the rate coefficient for the reaction between HgBr and Br atoms, $k_{1.29}$, or due to an additional loss process of HgBr. Additional loss processes and the effect they may have on the derived rate coefficients will be discussed in the following section.

A Van’t Hoff analysis for reaction R6.1 was done to determine the $\Delta H$ for the reaction. Table 6.3 shows the rate coefficients, the equilibrium rate coefficient ($K_C$), the $K_P$, and the resulting $\Delta H$ and $\Delta S$. 
Table 6.3: Van’t Hoff parameters for the recombination of Hg$^0$ and Br atoms.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{R1.10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>$k_{R6.1}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>$K_C$ cm$^3$ molecule$^{-1}$</th>
<th>$K_P$ cm$^3$ molecule$^{-1}$</th>
<th>$\ln(K_P) = \Delta S/R - \Delta H/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>$9.79 \times 10^{33}$</td>
<td>$1.65 \times 10^{17}$</td>
<td>$3.39 \times 10^{16}$</td>
<td>5918</td>
<td>$\Delta S = 8.0$ cal mol$^{-1}$</td>
</tr>
<tr>
<td>420</td>
<td>$9.21 \times 10^{33}$</td>
<td>$2.72 \times 10^{17}$</td>
<td>$5.93 \times 10^{16}$</td>
<td>12098</td>
<td>$\Delta H = 3.6$ kcal mol$^{-1}$</td>
</tr>
</tbody>
</table>

The $\Delta H$ determined by this work was lower than the expected 15.5 kcal mol$^{-1}$ (Tellinghuisen and Ashmore, 1983). This under estimate of the $\Delta H$ could stem from the analysis procedure. It is difficult to distinguish R1.29 from R6.1 in this system; therefore the fit assumed the fastest possible HgBr decomposition that was consistent with the 600 Torr data. This was done because fits at 600 Torr exhibit a stronger dependence on the HgBr thermal decomposition than on reaction R1.29. It is possible that the HgBr thermal decomposition was over-estimated, while reaction R1.29 was under-estimated. In addition it is possible that an additional loss process such as, R6.5,

\[
\text{HgBr} + \text{HgBr} \rightarrow \text{product} \quad (R6.5)
\]

losses due to diffusion, or reaction with impurities may contribute to the HgBr loss resulting in an over-estimate of the thermal decomposition of HgBr.

There are no experimental determined rate coefficients for reaction R1.29 or R6.5, so it is particularly difficult to predict the influence changes in temperature and pressure may have on the observed rate coefficient. In this case we assumed that the reactions were in the high pressure limit and proceed close to the gas kinetic rate, as both reactions are radical radical reactions. However, it is possible that these reactions exhibit more complex pressure and temperature dependencies which have been incorporated into the observed $k_{R6.1}$. Due to these potential errors, the Van’t Hoff analysis was used only as a check for internal consistency, and cannot considered an absolute determination of $\Delta H$. 

(6.3.6) **Potential Sources of Systematic Error**

As the rate coefficient for the reactions are derived from a complex fitting procedure it is important to note the sources of error.

While the observed rate of reaction R1.10 is not directly depending on the [Br] in the system the other reaction in the systems do demonstrate a dependence on [Br] therefore the error in the [Br] must be considered. As discussed in chapter 4 there is some error associated with the determination of the initial bromine atom concentration, the Rodgers et al. equation was employed using the absorption cross-section of CF$_3$Br 213 nm, the [CF$_3$Br], the average laser power, and the laser diameter. The error associated with the first two parameters should be less than 5%. However, there was some uncertainty in homogeneity of the laser beam and thus the fluence. This was assessed by measuring the variation in the fluence across the width of the beam. The error associated with the calibration of the laser power meter, homogeneity within the beam profile and shot to shot variability increase the uncertainty and resulted in an estimated error of ± 50% in the fluence. Therefore, we believe that ± 60% represents a conservative overall estimate of the uncertainty in the Br atom concentrations.

A second source of systematic error could be the influence of secondary chemistry. Any unaccounted loss or production of Br or HgBr impacts the final rate determination for R1.10 and R6.1. Although we believe that we have accounted for the losses of Br atoms in the system. Much less is known about HgBr chemistry so it is difficult to access potential complications. A reaction system was developed that included potential secondary reactions.

\[ \text{HgBr} + \text{Br} \rightarrow \text{products} \quad \text{(R1.30)} \]
\[
\begin{align*}
\text{Hg}^0 + \text{Br}_2 & \rightarrow \text{HgBr} + \text{Br} \quad \text{(R1.39)} \\
\text{Br} + \text{Br} + \text{M} & \rightarrow \text{Br}_2 + \text{M} \quad \text{(R4.1)} \\
\text{HgBr} + \text{HgBr} & \rightarrow \text{products} \quad \text{(R6.5)} \\
\text{HgBr} + \text{Br}_2 & \rightarrow \text{HgBr}_2 + \text{Br} \quad \text{(R6.6)}
\end{align*}
\]

Even after including these reactions with reasonable estimates for the expected kinetic rate coefficients, the resulting fits were within the error limits of the simplified reaction system, so these terms were not included.

However, as mentioned in the previous section, experimentally determined rate coefficients are unavailable for many of these reactions. In addition, reactions R1.29 and R6.5 could proceed by multiple channels, thus it is hard to assess the potential pressure and temperature dependencies. Any additional chemistry which impacts the [HgBr] could be a source of error in our determination of both the rate of thermal decomposition, \( k_{R6.1} \), and the reaction of HgBr and Br atoms, \( k_{R1.29} \).

Considering the errors of precision in the [Br] atoms and errors associated with the data and fitting procedures, we believe that ±65% represents a reasonable estimate of the overall uncertainty in the measured rate coefficient for reaction R1.10. For the reaction R6.1, considering errors associated with the fit, the potential complication of secondary chemistry, particularly of reactions R1.29 and R6.5, and the error in the determination of the initial Br atom concentration, the reported \( k_{R6.1} \) and \( k_{R1.29} \) values should be accurate within a factor of 2.
(6.4) Discussion and Comparison with Previous Work

(6.4.1) Mercury and Bromine Atom Recombination

Previous determinations of the rate coefficient for reaction R1.10 have already been discussed in detail in Chapter IV. Five previous experimental (Ariya et al., 2002; Donohoue et al., 2006; Greig et al., 1970; Sommar et al., 1999; Spicer et al., 2002), an in-situ study (Skov et al., 2004), and two theoretical determinations (Goodsite et al., 2004; Khalizov et al., 2003) have reported values for reaction (R1.10). These results are compared with the current work in Table 6.4 and in Figure 6.18.

Table 6.4: Comparison of literature data for reported rate coefficients for the reaction of Hg atoms with Br atoms, \( k_{R1.10} \)

<table>
<thead>
<tr>
<th>Gas</th>
<th>( T ) (K)</th>
<th>( P ) (Torr)</th>
<th>( k_{R1.10} )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>298</td>
<td>760</td>
<td>((3.2 \pm 0.3) \times 10^{-12})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>(3.0 \times 10^{-13})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>(9.7 \times 10^{-13})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>((2.8 \pm 0.8) \times 10^{-12})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>760</td>
<td>(1.01 \times 10^{-12} \exp\left(\frac{209.03}{T}\right))</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>180-400</td>
<td>760</td>
<td>(1.1 \times 10^{-12} \times \left(\frac{T}{298}\right)^{-2.37})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>243-293</td>
<td>200-600</td>
<td>((1.46 \pm 0.34) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-0.36\pm0.49})</td>
<td>(cm(^6) molecule(^{-2}) s(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>243-420</td>
<td>200-600</td>
<td>((1.49 \pm 0.12) \times 10^{-32} \times \left(\frac{T}{298}\right)^{-0.76\pm0.5})</td>
<td>(cm(^6) molecule(^{-2}) s(^{-1}))</td>
</tr>
<tr>
<td>( He )</td>
<td>243-293</td>
<td>200-600</td>
<td>((4.2 \pm 0.2) \times 10^{-33})</td>
<td>(cm(^6) molecule(^{-2}) s(^{-1}))</td>
</tr>
<tr>
<td>( Air )</td>
<td>233-263</td>
<td>760</td>
<td>(1 \times 10^{-12})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
<tr>
<td>( CF_3Br )</td>
<td>393-448</td>
<td>200</td>
<td>(2.82 \times 10^{-13})</td>
<td>(cm(^3) molecule(^{-1}) s(^{-1}))</td>
</tr>
</tbody>
</table>
Figure 6.18: The second order rate coefficients for the recombination of Hg\(^0\) and Br atoms, \(k_{R1.10}\) at 760 Torr, for this work and previous studies.

The temperature dependent expression results in a rate coefficient of \(3.67 \times 10^{-13}\) \(\text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1}\) for reaction (R1.10) at 298 K and 760 Torr. This work agrees within the error limits of the previous direct determination of the rate coefficient for Hg\(^0\) and Br determined with Br radicals in excess (Donohoue et al., 2006). The strong agreement between these two different direct experimental approaches provides significant evidence for the slower rate coefficient.

In addition, it is evident that the rapid rate coefficient for R1.10 determined in relative rate studies is incompatible with the temporal profiles observed in the LIF system. Figure 6.19 is a plot of the normalized temporal profiles of HgBr and Br radical under the same experimental conditions, 600 Torr, 420 K and \([\text{Hg}^0]\) = \(6 \times 10^{14}\) molecules \(\text{cm}^3\). The two sets of lines are the temporal profiles for Br atom and the HgBr molecule calculated from the numerical integration of the reaction system, E6.1 and E6.2, using the rates from Ariya et al. (red) and Donohoue et al. (black). The observed LIF profiles do not
reproduce the rapid loss of Br or rapid production of HgBr that should be observed if the rate coefficients determined in relative rate experiments were accurate. It is unlikely that the current experimental set-up with Hg atom in excess could be influenced by a secondary reaction that could account for this discrepancy. It is more likely that the relative rate studies were influenced by secondary or heterogeneous chemistry.

![Normalized LIF profiles for HgBr and Br atoms with modeled temporal profiles from numerical integration calculations using the reaction rate coefficient from (red) Ariya et al., 2002 and (black) Donohoue et al., 2006.](image)

**Figure 6.19:** Normalized LIF profiles for HgBr and Br atoms with modeled temporal profiles from numerical integration calculations using the reaction rate coefficient from (red) Ariya et al., 2002 and (black) Donohoue et al., 2006.

Reaction R6.1 has not been directly measured prior to this study. Two theoretical determinations have been reported (Goodsite et al., 2004; Shepler et al., 2007). Goodsite et al reported a rate coefficient of $1.2 \times 10^{10} \exp\left(-\frac{8357}{T}\right) \text{s}^{-1}$. This rate coefficient was estimated by detailed balancing of reaction R6.1 with reaction R1.10. Peterson et al. reported a rate coefficient of $(1.95 \pm 2.3) \times 10^{-20} \exp\left[-7670 \left(\frac{1}{T} \frac{1}{298}\right)\right] \text{cm}^3\text{molecules}^{-1}$.
1 s⁻¹, determined by a quasi-classical trajectories (QCT) calculation. The predict loss of the HgBr molecule at each pressure and temperature is reported along with the observed values in Table 6.5. We assumed a linear pressure dependence for both theoretical estimates. The observed HgBr loss rates are significantly faster than the Goodsite prediction. This is not unexpected, as the Goodsite prediction is a calculated by balancing the decomposition with the forward reaction, R1.10, and the $k_{R1.10}$ reported by Goodsite et al. is significantly faster than our observed rate for reaction R1.10. The direct calculation by Shepler et al. agrees within the error limits with our observed HgBr loss rates at 420 K. However, we observed a temperature dependence that is significantly smaller than predicted by the theoretical estimate. Earlier in this work, we discussed sources of error in our $k_{R6.1}$ determination. Specifically, the coupling of the $k_{R6.1}$ with $k_{R1.29}$ and/or an unidentified HgBr loss process. We attribute the discrepancy in the temperature dependence and in the calculated ΔH to this complication.

**Table 6.5:** Rate coefficients for the thermal decomposition of HgBr, $k_{R6.1}$, at 360 K and 420 K and 200, 400, and 600 Torr; along with the rate predicted by the two theoretical determinations, (Goodsite et al., 2004; Shepler et al., 2007).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (Torr)</th>
<th>$k_{R6.1}$ ± error (s⁻¹)</th>
<th>$k_{R6.1}$ (s⁻¹) (Goodsite et al., 2004)</th>
<th>$k_{R6.1}$ (s⁻¹) (Shepler et al., 2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>200</td>
<td>250 ± 100</td>
<td>7.2</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>375 ± 125</td>
<td>14.4</td>
<td>317</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>500 ± 120</td>
<td>21.6</td>
<td>475</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>---</td>
<td>27.4</td>
<td>602</td>
</tr>
<tr>
<td>360</td>
<td>200</td>
<td>200 ± 40</td>
<td>0.3</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>300 ± 40</td>
<td>0.5</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>375 ± 50</td>
<td>0.8</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>---</td>
<td>1.0</td>
<td>33</td>
</tr>
</tbody>
</table>

We reported a rate coefficient for the reaction of HgBr molecules and Br atoms of $(3.5 ± 0.5) \times 10^{10}$ cm³ molecule⁻¹ s⁻¹ and $(3.0 ± 0.5) \times 10^{10}$ cm³ molecule⁻¹ s⁻¹ for 360 K
and 420 K respectively. There is no experimental determination of a rate coefficient for this reaction; however, Goodsite et al. (Goodsite et al., 2004) reported a theoretical estimate of the rate coefficient of $2.5 \times 10^{10} \times (T/298)^{-0.57}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Assuming that this rate is in the high pressure limit the resulting rate coefficient is $2.47 \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 360 K and $2.45 \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 420 K, these rates agree with our experimentally determined rate coefficients within the error limits.

The rough agreement between the theoretical studies of HgBr decomposition and the reaction of HgBr with Br indicates that, although, some coupling of the rate coefficients of these two reactions maybe occurring, they are within a factor of 2 of the actual rate. This means that any error in the $k_{R6.1}$ and $k_{R1.29}$ should not significantly effect $k_{R1.10}$ fits.

(6.5) Summary

This is the first study that directly monitored the HgBr product of the gas phase reaction of Hg$^0$ with Br atoms, reaction R1.10. The resulting rate coefficient for R1.10 is entirely consistent with the behavior expected for a three body recombination and agrees with the previous direct determination of the rate coefficient for R1.10 (Donohoue et al., 2006) and the two theoretical determinations (Goodsite et al., 2004; Khalizov et al., 2003). As in studies where the Br radical was in excess, we observed a rate coefficient that is an order of magnitude smaller than the rate coefficients reported in relative rate studies. The simultaneous observation of one of the reactants, Br atoms, and the product, HgBr, limits possible complications due to secondary chemistry; thus we believe that the relative rate studies over-estimate the $k_{R1.10}$ by an order of magnitude.
Rate coefficients for reaction R6.1 and R1.29 were also determined in this system. While some error stemming from our inability to completely separate these rate coefficients is present, this work is the first attempt at a direct measurement of these rates and are believed to be accurate within a factor of 2.

This work confirms that the reaction of Hg\(^0\) and Br atom occurs at a rate sufficiently rapid to account for the dynamic mercury chemistry observed in the Arctic (Lindberg et al., 2002; Lu et al., 2001; Schroeder et al., 1998; Steffen et al., 2002) and the Antarctic (Ebinghaus et al., 2002; Sprovieri et al., 2002; Temme et al., 2003). In addition, the Br atom initiated oxidation of Hg\(^0\) could be playing a role in the overall biogeochemical cycling of mercury in the marine boundary layer (MBL) (Laurier and Mason, 2007; Laurier et al., 2003; Malcolm et al., 2003; Mason, 2005; Peleg et al., 2007; Sprovieri et al., 2003; Weiss-Penzias et al., 2003) and in the upper troposphere/lower stratosphere (Landis et al., 2005; Murphy et al., 2006a; Murphy et al., 2006b; Murphy et al., 2003; Swartzendruber et al., 2006; Weiss-Penzias et al., 2007; Weiss-Penzias et al., 2006).

Hg and Br atom reaction system is in fact a complex reaction system defined by reactions R1.10, R1.29 and R6.1. The \([Hg]\) due to reaction with bromine atoms can be expressed by equation, E6.4,

\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Br][Hg] + k_{R6.1} [HgBr]
\]  

(E6.4)

where the \([HgBr]\) can be defined as equation 6.5.

\[
[HgBr] = \frac{k_{R1.10} [Br][Hg]}{k_{R6.1} + k_{R1.29} [Br]}
\]  

(E6.5)

Using these equations we find that the lifetime of Hg\(^0\) due to these reactions is:
employing the rate coefficients determined in this work for reactions R1.10 and R1.29 and the temperature dependent estimate of R6.1 from Shepler et al. (Shepler et al., 2007) a lifetime of Hg\(^0\) due to reaction with solely Br atoms can be obtained. For this calculation we employed the Shepler estimate for reaction R6.1 as the error limits from the rate coefficient determined in this work make extrapolations difficult and speculative. We believe that the Shepler et al. data should provide a good upper limit for \(k_{R6.1}\). The rate lifetime of Hg\(^0\) is calculated for the peak concentrations of Br atom reported by Boudries and Bottenheim (Boudries and Bottenheim, 2000) in equations E6.7 and E6.8.

\[
\tau_{Hg} = \frac{k_{R6.1}}{k_{R1.29} + [Br]} \quad \text{(E6.6)}
\]

As the Br atom concentration is further reduced we find that loss of HgBr due to reaction R1.29 is too slow and the HgBr undergoes thermal decomposition. This means that at [Br] under \(1 \times 10^6\) molecules cm\(^{-3}\) the lifetime of Hg\(^0\) due to reaction with Br atoms is over a year. In this estimate we assume that the only reaction that stabilizes the transient HgBr species is Br atoms. This threshold value for minimum [Br] concentration to drive Br atom driven oxidation has implication for the potential importance of Br atom oxidation of bromine in the MBL and upper troposphere as oxidation due solely to Br atom cannot substantially influence the Hg\(^0\) lifetime. However, in the atmosphere the
reactive HgBr could be stabilized by many secondary species, such as Cl, O₂, ClO, BrO, IO, OH, or I. Thus, the importance of the Hg⁰ oxidation due to the initial reaction with Br atoms cannot be fully understood in lower Br (>10⁶) environments, such as the MBL or upper troposphere/lower stratosphere, without further studies into the reactions of the transient HgBr species.
(7.1) Background

Interest in measuring mercury species in the environment has grown since the 1960’s. The development of Cold Vapor Atomic Absorption Spectroscopy (CVAAS) and Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) techniques were a significant advancement in the detection of mercury in natural environments and enhanced our knowledge of the biogeochemical cycling of mercury. At first, the CVAFS technique had limited applications for atmospheric studies, as low concentrations of mercury in the atmosphere were not directly detectable. However, by coupling the CVAFS technique with the pre-concentration of Hg$^0$ on gold tubes and RGM species on KCl coated annular denuders, reliable, simple, and relatively inexpensive methods to detect mercury species in the atmosphere were developed. Currently, CVAFS instruments are deployed worldwide in both industrial and scientific application.

The CVAFS technique for elemental mercury, typified by the commercially available Tekran Instrument Corporation (Knoxville, TN) Model 2537A, requires a pre-concentration of the Hg$^0$ on gold. The Tekran 2537A performs continuous measurement of TGM in ambient air using dual cartridges with an sample cycle time that can range from 2.5 to 60 minutes, and a detection limit of 0.1 ng m$^{-3}$ for a 7.5 m$^3$ sample or 0.75 ng Hg$^0$ (Tekran, 2007). The Ohio Lumex (Cleveland, OH) Model RA-915+ portable mercury analyzer employs Zeeman corrected CVAAS system. The system has a sampling
time of 1s and a detection limit of 4 – 6 ng m$^{-3}$ in ambient air. This detection limit correlated to an absolute mercury detection limit of [Hg$^0$] = 1.3 – 2.0 pg when sampled at 20 LPM (Lumix, 2007).

Neither of these methods have both a suitable time response and detection sensitivity to perform direct micro-meteorological measurements using the eddy-correlation technique. Aircraft measurements also suffer from the long time response in the CVAFS system, as the 2.5 min integration time can smear rapidly changing air masses together (Radke et al., 2007) making evaluation of aircraft data problematic. The need for a chemical sensor with both a fast time response <1s and a suitable detection limit 0.1 ng m$^{-3}$ is clear and pressing.

Another challenge in measuring the atmospheric concentration of mercury is the identification and characterization of the operationally defined reactive gaseous mercury (RGM) species. Collection of RGM species on KCl coated annular denuders represents a significant advancement in understanding the biogeochemical cycling of mercury; however, recent studies have highlighted the need to understand the true chemical speciation of RGM.

This work will describe work using a novel two-photon laser induced fluorescence (LIF) detection system for Hg$^0$ that results in a significant enhancement of the time resolution without loss of sensitivity. RGM species were also studied in a two-photon LIF system coupled with collection on KCl-coated annular denuders or uncoated surfaces. This coupled technique permits the observation of the RGM decomposition product, Hg$^0$, as it evolves from the KCl coated denuder or uncoated surface. We have
observed the evolved Hg\(^0\) product from a real air sample; as well as, from known RGM species during a programmed thermal cycle.

(7.2) **Laser-based systems for the in-situ detection of Hg\(^0\)**

The initial observation of Hg\(^0\) using a laser based approach was by Rodgers et al. (Rodgers et al., 1982) using the \(6^3P_1–6^1S_0\) and \(7^1S_0–6^3P_1\) transitions with detection at 184.9 nm. They reported a detection limit of \(1 \times 10^9\) atoms cm\(^{-3}\) in N\(_2\) with an integration time of 15 min using a 10 Hz laser system. The observed fluorescence was reduced by a factor of 3 when the bath gas was changed to air and increased by a factor of 50 in He. In 1993, Resto et al. (Resto et al., 1993) monitored chemically bound mercury by electrothermal atomization using the \(6^3P_1–6^1S_0\) and \(7^3S_0–6^3P_1\) transitions with detection at 536.1 nm. They report detection of 100 pg of Hg\(^0\), but they claim with alterations/improvements to the system the detection limit could be reduced to 90 fg.

Significant research has gone into the development of a cavity ring down spectroscopy (CRDS) method for the detection of mercury species. Jongma et al. (Jongma et al., 1995) used the absorption coefficient for Hg\(^0\) from Edner et al. (Edner et al., 1989) of \(3.3 \times 10^{-14}\) cm\(^2\) molecule to obtain a detection of [Hg\(^0\)] = 7 ppt or 60 ng m\(^{-3}\). This work is reported in air and stems from one single measurement of the Hg\(^0\) concentration in their laboratory. This 60 ng m\(^{-3}\) is significantly above the naturally occurring background limit of 1.4 – 1.7 ng m\(^{-3}\). Tao et al. (Tao et al., 2000) performed similar experiments using an 18 cm cavity and reported a detection limit of 25 ng m\(^{-3}\). In their study they do not report the [Hg\(^0\)] actually detected, but it appears to be in excess of 2000 ng m\(^{-3}\). Spuler et al. (Spuler et al., 2000) also used the CRDS technique with a 125
cm cavity and generated Hg\textsuperscript{0} from an uncalibrated permeation tube. Hg\textsuperscript{0} concentrations were determined again from the cross section determined in Edner et al. Spuler detected concentrations as low as 10 ppt (\textasciitilde 85 ng m\textsuperscript{-3}) and report a detection limit of 0.5 ppt. None of the CRDS studies discussed an independently confirmed [Hg\textsuperscript{0}] in their system.

(7.2.1) **Two-photon LIF for the detection of Hg\textsuperscript{0}**

The two-photon LIF experimental approach was explored in two papers from Bauer et al. (Bauer et al., 2002; Bauer et al., 2003). The excitation scheme used in the study included an initial laser excitation at 253.7 nm, the 6\textsuperscript{3}P\textsubscript{1}–6\textsuperscript{1}S\textsubscript{0} transition, followed by excitation with a second laser to the 7\textsuperscript{1}S\textsubscript{0} level at 407.8 nm or to the 7\textsuperscript{3}S\textsubscript{1} level at 435.8 nm. The background signal from the excitation scheme using the 407.8 nm for the secondary excitation was significantly lower than the scheme employing the 435.8 nm transition. This made the preferred excitation scheme 253.7 nm/407.8 nm excitation. They also observed that the 253.7 nm/407.8 nm excitation scheme produced a stronger fluorescence signal at 184.9 nm than at 546.1 nm. The Bauer LIF detection scheme demonstrated linearity over five orders of magnitude, [Hg\textsuperscript{0}] = 1 to 10000 ng m\textsuperscript{-3}. The solar blind PMT detects very little stray light; as no scatter is observed from room light or from the 407.8 nm excitation laser. A small amount of scattered from the 253.7 nm laser was detected; however, it was only detectable at low [Hg\textsuperscript{0}] in He.

The detection limit and sensitivity was evaluated for the system by introducing a steady concentration of Hg\textsuperscript{0} (4 ng m\textsuperscript{-3} in 1 ATM of N\textsubscript{2}) into the cell, this concentration was confirmed by a concurrent concentration determination made with a Tekran 2537A. Figure 7.1 shows a 3 min measurement (1200 laser pulses) for the signal, both lasers
entering the cell, and the background, the 407.8 nm excitation beam blocked. The single shot measurements, a 10 point sliding average and a 100 point sliding average are presented for both the signal and the background in Figure 7.1. From this data a detection limit for the system in N$_2$ was established. A signal to noise ratio of 3.4:1 was calculated for the signal shot measurements, 11:1 for the 10 point averaged data, and the 100 point averaged data had an S/N ratio of 38:1. The resulting detection limits were 1.2 ng m$^{-3}$, 0.4 ng m$^{-3}$ and 0.1 ng m$^{-3}$ respectively. The detection volume for this experiment was 0.60 cm$^3$ (laser diameter = 0.55cm, detection length = 2.54 cm), so the absolute [Hg$^0$] observed at the detection limit was 0.7 fg, 0.2 fg and 0.06 fg, respectively.

![Figure 7.1: Two-photon LIF signal for the detection of Hg$^0$ and background signal from Bauer et al., 2003. Single shot (diamonds); 10 shot average (blue and purple lines); 100 shot averages (light blue and red lines).](image)

The quenching rate for the fluorescence signal varied with bath gas. Quenching of the $6^3P_1$ level has been well studied and O$_2$ is found to be a particularly efficient, about 20 times faster than N$_2$. On the other hand both He and Ar are inefficient quenchers so the fluorescence signal should be stronger. The relative fluorescence efficiencies were determined by monitoring LIF signal with stable mercury flows ([Hg$^0$] = 6 –13 ng m$^{-3}$) in
N$_2$, air, He and Ar. Mercury concentrations in air and N$_2$ were confirmed by concurrent measurement using a Tekran 2537A. All experiments were performed at a total pressure of one atmosphere. The relative fluorescence efficiencies and detection limits for Hg$^0$ are reported in table 7.1 for N$_2$, air, He, and Ar at integration times of 1s and 10s.

**Table 7.1:** Relative Efficiencies and Detection Limits for two-photon LIF of Hg$^0$ in various gases and integration times from Bauer et al., 2003.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Relative Efficiency</th>
<th>Sample Time</th>
<th>S/N ratio</th>
<th>Detection Limit</th>
<th>Absolute [Hg$^0$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1</td>
<td>0.1s</td>
<td>3.4:1</td>
<td>1.2 ng m$^{-3}$</td>
<td>0.7 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1s</td>
<td>11:1</td>
<td>0.4 ng m$^{-3}$</td>
<td>0.2 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10s</td>
<td>38:1</td>
<td>0.1 ng m$^{-3}$</td>
<td>0.06 fg</td>
</tr>
<tr>
<td>Air</td>
<td>0.26</td>
<td>0.1s</td>
<td></td>
<td>4.5 ng m$^{-3}$</td>
<td>2.8 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1s</td>
<td></td>
<td>1.4 ng m$^{-3}$</td>
<td>0.8 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10s</td>
<td></td>
<td>0.4 ng m$^{-3}$</td>
<td>0.2 fg</td>
</tr>
<tr>
<td>He</td>
<td>150</td>
<td>0.1s</td>
<td></td>
<td>0.008 ng m$^{-3}$</td>
<td>0.005 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1s</td>
<td></td>
<td>0.002 ng m$^{-3}$</td>
<td>0.001 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10s</td>
<td></td>
<td>0.0007 ng m$^{-3}$</td>
<td>0.0004 fg</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>0.1s</td>
<td></td>
<td>0.07 ng m$^{-3}$</td>
<td>0.04 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1s</td>
<td></td>
<td>0.02 ng m$^{-3}$</td>
<td>0.01 fg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10s</td>
<td></td>
<td>0.006 ng m$^{-3}$</td>
<td>0.004 fg</td>
</tr>
</tbody>
</table>

As the fluorescence efficiency depends on the quenching of the excitation transition the relative efficiencies will vary slightly with laser power and overlap timing. The variation in power should be limited as long as the $6^3P_1$ transition is saturated.

This excitation scheme, 253.7 nm/407.8 nm excitation with detection at 184.9, was identified as the ideal approach giving the best precision and the best sensitivity of the four tested configurations. However, the Bauer et al. study did consider schemes which would involve the quenching of the $6^3P_1$ level. As this quenching may be significant, this work will further investigate the relative sensitivity of these LIF schemes.
Further Investigations of the two- photon LIF detection scheme for \( \text{Hg}^0 \)

The initial excitation of the \( 6^3\text{P}_1 - 6^1\text{S}_0 \) transition at 253.7 nm is a strong transition from the ground state; thus all two-photon LIF schemes will begin with excitation from this transition. Once the \( 6^3\text{P}_1 \) level is populated by the initial excitation, the excited mercury atom can experience three fates; be directly excited to the \( 7^1\text{S}_0 \) level (LIF scheme #1), be quenched to the \( 6^3\text{P}_0 \) level with subsequent excitation to the \( 7^1\text{S}_0 \) level (LIF scheme #2 & #3), or fluoresce at 253.7 nm returning to the \( 6^1\text{S}_0 \) level (one photon LIF). If the \( 6^3\text{P}_1 \) is rapidly quenched to the \( 6^3\text{P}_0 \) level then a transition from the \( 6^3\text{P}_0 \) will be a more effective and result in a higher sensitivity for mercury atom detection. To test the relative merit of each scheme, a two-photon LIF system was assembled that could easily switch between schemes.

\[
\text{Figure 7.2: Potential LIF schemes for the two-photon LIF of mercury atoms.}
\]

The initial excitation for the two-photon LIF of \( \text{Hg}^0 \) atoms was generated by frequency doubling the 507 nm output of a dye laser. The dye laser was pumped with approximately 100mJ of the third harmonic of an Nd:YAG laser at 355 nm generating a excitation beam at 253.7 nm with an output power between 50 – 100 \( \mu \)J. The secondary excitation at
407.8 nm or 404.6 was produced via a frequency doubled optical parametric oscillator (Spectra Physics, MOPO) pumped by a Nd:YAG laser (Spectra Physics, Pro 270). The maximum output power for the secondary excitation laser was in the range of 0.5 – 1.0 mJ. The laser system is a 10 Hz system so regardless of scheme a data point was collected every 0.1 s.

The beams were overlapped on a dichroic mirror and propagated collinearly through a gas mixture containing mercury. The Pyrex fluorescence cell had four mutually perpendicular side arms. The two laser beams passed co-linearly through two side arms at a 90° angle to the gas flow. Fluorescence was detected through one of the side arms, perpendicular to the excitation beams. The amplified LIF signal was transferred to a digital oscilloscope (Tektronix TDS520C) and the integrated signal area was transferred to a computer for further analysis. The LIF signal was monitored at two different wavelengths corresponding to the $7^3S_1–6^3P_2$ transition at 546.1 nm or the $6^1P_1–6^1S_0$ transition at 184.9 nm. Back to back measurements of the relative LIF signal were obtained for each of the three LIF schemes under the same conditions. The cell was left opened to the laboratory, ~ 760 Torr. No independent measurement was made for [Hg$^0$] during the measurement. However, the mercury in the laboratory air has been measured by a Tekran 2537A prior to and after these measurements and it was found to average around 50 ng m$^{-3}$. Very little fluorescence signal was observed when the laser system was configured in LIF scheme #2. This is due to strong Raleigh and Raman scatter observed on the 546.8 nm detection wavelength. On the other hand good LIF signal was observed when the laser was configured in LIF scheme #1 & #3, where the LIF detection wavelength is 184.9 nm. In the back to back comparison of LIF Scheme #1 and #3, it was
observed that LIF scheme #3 produced significantly less fluorescence; the voltage on the PMT had to be increased from 850 V to 1100V to obtain the same LIF fluorescence signal. The most effective LIF scheme is the original scheme outlined in Bauer et al.

(7.3) **Hg\(^0\) Sampling on a Gold Tube**

A gold tube sampling procedure was developed, which could be coupled with two-photon LIF method to detect \([\text{Hg}^0]\). The sampling on gold tubes provided a method to calibrate the observed Hg\(^0\) LIF signal. In addition, coupling of the two-photon technique with pre-sampling on a gold tube could broaden the applications of the two-photon LIF system.

(7.3.1) **Development and Sampling Procedures**

The experimental design is outlined in Figure 7.3. The system is the LIF detection system, described above, with a small sampling apparatus. For this work the same laser system was employed with one small alteration. The secondary excitation beam was produced by frequency doubling the 815 nm output of a dye laser pumped with the 532 nm 2\(^{nd}\) harmonic of an Nd:YAG laser, rather than the MOPO.
Figure 7.3: Experimental set-up for calibration and pre-concentration experiments using two-photon LIF of Hg$^0$.

A set of gold tubes were constructed using $\frac{1}{4}''$ quartz tubes with a pinched center. These tubes were packed with gold coated glass beads stoppered by quartz wool, the total packed area was 1” in length. To test the efficiency of the gold tubes under our experimental conditions we recorded the LIF signal directly from the oscilloscope under the following conditions:

1) Argon flowing at 0.75 L/min directly into the cell (Blank),

2) Argon flowing at 0.75 L/min through a gold tube and then into the cell (Gold),

3) Argon flowing at 0.75 L/min over a mercury perm tube (1.804pg/s) directly into the cell (Perm), and

4) Argon flowing at 0.75 L/min over a mercury perm tube (1.804pg/s), into a gold tube, and finally into the cell (GoldPerm).
The resulting oscilloscope traces are shown in Figure 7.4 with the [Hg\(^0\)] for each curve.

![Figure 7.4: Gold tube efficiency test. (black line) Hg\(^0\) flow = 40 pg/m\(^3\), Perm; (green line) Ar flow at 0.75 L/min, Blank; (red line) Gold tube before cell with Hg\(^0\) flow = 40 pg/m\(^3\), GoldPerm; and (blue line) Gold tube before cell with Ar flow at 0.75 L/min, Gold.](image)

Under the flow conditions of the experiment the perm tube generates a stable [Hg\(^0\)] of 40 pg m\(^{-3}\). By calculating the added LIF signal we can determine a background [Hg\(^0\)] of 4.6 pg m\(^{-3}\). In both experiments that include the gold tube, Gold and GoldPerm, we see that the observed concentration is reduced to ~ 1 pg m\(^{-3}\). From this experiment it can be concluded that the gold tubes are effectively scavenging mercury from the gas flow under conditions observed in the experiment.

Now that the mercury has been collected on a gold tube, a method to desorb the Hg\(^0\) from the gold must be developed. The gold tube was heated by induction; a 5cm coil of nickel chromium wire was wrapped around the gold tube, this is a method similar to the one employed in the Tekran 2537A. With the application of a small current, the gold coated gold beads were rapidly heated, volatilizing the mercury. The timing of the
heating process was important to the peak shape. If heated too slowly, the signal is broad resulting in decreased sensitivity. If heated too rapidly, the peak exhibits dual peak behavior due to uneven heating. It was determined that the ideal peak shape was obtained when the coil was heated for 45 s with a maximum temperature of 560 °C. The coil would glow red after heating for approximately 15 s. This desorption method produced reproducible peaks; however it was unknown if the mercury was completely released in this time or if residual mercury was left on the gold tube.

An experiment was conducted where a 2 min sample of room air was collected on the gold tube at a sample rate of 1.5 L/min. This sample was then heated as outlined above in two successive cycles, figure 7.5.

![Figure 7.5](image_url)

**Figure 7.5:**  Hg\(^0\) desorption test. (black line) 1\(^{\text{st}}\) heating cycle; (red line) second heating cycle.

It was observed that the second peak was very small, 6.5% of the first peak. We believe that this small signal that can be attributed to the collection of the trace amounts of mercury in the gas flow, 5 pg m\(^{-3}\), during the cooling of the gold tube and between the
cycles. The mercury on the gold trap is completely desorbed and little to no residual mercury signal.

(7.3.2) Calibration of LIF signal

In order to determine the actual concentration of the $\text{Hg}^0$ observed in the system, we ran two types of calibration experiments. The first type of calibration was done using a perm tube as a calibration source. Argon was flowed through the gold tube and cell at a flow rate of 200 sccm. Samples were collected in a four minute cycles. At $t = 0$ the heating coil on the gold tube was turned on. After 45 seconds the heating coil was turned off and the tube was cooled for another 195 second. This cycle was then repeated. For 4 cycles a small flow from a $1.804 \text{ pg s}^{-1} \text{ Hg}^0$ perm tube was introduced into the system in addition to the argon flow. The $\text{Hg}^0$ was passed through the gold tube for 30 -15 s. To ensure the $\text{Hg}^0$ was completely scavenged and not re-volatilize from a hot gold tube the flow was started three minutes after the previous heating cycle began. During these calibration experiments, the perm tube flow had to be switch on and off manually, this introduced some error into the calibration.

The second method of calibration reduced this error by injecting a saturated calibration gas through a septum. The saturated calibration gas was maintained a 6 °C and was allowed to equilibrate for over 24 hours before initial use. The syringe was maintained at 25 °C and the gas was directly injected in the system. This should reduce any loss of mercury in the transfer process due to loss to the walls or diffusion out of the syringe. To ensure that the injection was completely scavenged by the gold tube, the gas was injected about 30 s before the heating cycle, so that the gold tube was cool, and over
10 s. The sampling procedure was similar to the previous calibration procedure; a 200 sccm flow of N\textsubscript{2} was passed over the gold tube. Samples were collected on a 3 min cycles; t = 0 - 45 s heating, t = 45 - 180 s cooling, and injections at t = 150 - 160 s. Cycles were repeated for 100 μL, 50 μL, 20 μL, and 10 μL injections, and blanks. The 10 Hz LIF signal was recorded resulting in a desorption profile with data points every 0.1s. The observed profiles were then corrected for the baseline and a 7 point sliding average was calculated. An integrated area was obtained for each peak. The integrated areas for a series of measurement are listed in Table 7.2 along with the desorption profiles shown in Figure 7.6.

<table>
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<tr>
<th>Type</th>
<th>Total LIF Units</th>
<th>Blank Subtracted LIF Units</th>
<th>Injection of Hg\textsuperscript{0} μL</th>
<th>Blank Subtr. LIF Units per pg Hg\textsuperscript{0}</th>
<th>Obs. [Hg\textsuperscript{0}] (pg)</th>
<th>Calc [Hg\textsuperscript{0}] (pg)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
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<td>1.83 × 10\textsuperscript{-7}</td>
<td>50</td>
<td>19.30</td>
<td>9.49 × 10\textsuperscript{-9}</td>
<td>37.67</td>
<td>39.56</td>
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<td>Inj_50μL_2</td>
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<td>1.81 × 10\textsuperscript{-7}</td>
<td>50</td>
<td>19.30</td>
<td>9.38 × 10\textsuperscript{-9}</td>
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</tr>
<tr>
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<td>1.77 × 10\textsuperscript{-7}</td>
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<td>9.16 × 10\textsuperscript{-9}</td>
<td>37.07</td>
<td>39.56</td>
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<tr>
<td>Average</td>
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<td>1.81 × 10\textsuperscript{-7}</td>
<td>50</td>
<td>19.30</td>
<td>9.37 × 10\textsuperscript{-9}</td>
<td>37.40</td>
<td>39.56</td>
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<td>St. Dev.</td>
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<td>3.86</td>
<td>1.23 × 10\textsuperscript{-8}</td>
<td>24.78</td>
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<td>3.86</td>
<td>1.22 × 10\textsuperscript{-8}</td>
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<td>Average</td>
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<td>4.74 × 10\textsuperscript{-8}</td>
<td>10</td>
<td>3.86</td>
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<td>24.12</td>
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<td>St. Dev.</td>
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<td></td>
<td>0.025</td>
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</table>

| No Hg\textsuperscript{0} injection : All Hg\textsuperscript{0} background from cell and N\textsubscript{2} source |

<table>
<thead>
<tr>
<th>Type</th>
<th>Total LIF Units</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>19.09</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>20.26</td>
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<tr>
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<td></td>
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<td>1.24</td>
</tr>
</tbody>
</table>
Figure 7.6: Hg$^0$ desorption profiles from a gold tube; (black lines) 3 min blank, (red lines) 4 pg Hg$^0$ injection + 3 min blank, and (blue lines) 20 pg Hg$^0$ injection + 3 min blank.

The LIF signal from the Hg$^0$ desorbing from the gold tube will be the sum of the LIF signal from Hg$^0$ injected into the system, H$_{inj}$, and the Hg$^0$ scavenge from the carrier gas, H$_{blank}$.

$$LIF_{total} = LIF_{blank} + LIF_{inj}$$  \hspace{1cm} (E7.1)

where:

$$LIF_{blank} = H_{blank} \times X_{LIF}$$  \hspace{1cm} (E7.2)

$$LIF_{inj} = H_{inj} \times X_{LIF}$$  \hspace{1cm} (E7.3)

Since the observed LIF signal will be directly proportional to the [Hg$^0$], $X_{LIF}$ is the constant which relates LIF signal to absolute Hg$^0$ concentration. To obtain this constant, equations (E7.1) and (E7.3) were rearranged to produce (E7.4)

$$X_{LIF} = \frac{LIF_{total} - LIF_{blank}}{H_{inj}}$$  \hspace{1cm} (E7.4)
Once the $X_{\text{LIF}}$ has been obtained, all LIF signal can be converted into absolute $\text{Hg}^0$ concentrations in pg. The results for a typical calibration series is outlined in table 7.2 along with the standard deviation and % error. We observed that all average $[\text{Hg}^0]$ are within 5% of the expected value with a standard deviation in the measurements of less than 10%. Exact $X_{\text{LIF}}$ values will depend on laser power and PMT voltage; hence the calibration must occur daily.

In order to validate the calibration procedure, LIF desorption profiles from three different days were converted into absolute $[\text{Hg}^0]$ and compared. In figure 7.7, desorption peaks are shown along with the injection volume and observe $[\text{Hg}^0]$. The points are the observed signal, while the line is a 10 point running average.

Figure 7.7: Calibration data for three different days. (points) observed signal; (lines) 10 point running averages.
Figure 7.8: Plot of [Hg\textsuperscript{0}] observed from LIF vs. [Hg\textsuperscript{0}] calculated from injection for three different calibration series.

On each day, a reproducible, ± 5%, injection signal can be observed added to the blank signal. The 3 min blank signals ranged from 24 to 7 pg and demonstrated higher variability than the injections, ± 10%, particularly at when the blank was large, 24 pg. A factor of four decrease was observed in the blank signal. Figure 7.8 shows the linearity of the calibration over an order of magnitude of total mercury concentration, [Hg\textsuperscript{0}] = 7 - 70 pg.

(7.3.3) Potential Complications and Errors

The primary factor which limits the applications of the two-photon approach in its current configuration is the blank signal observed. We calculate a Hg\textsuperscript{0} source of 10 - 35 ng m\textsuperscript{-3}. This concentration is reasonable as the experiments are conducted in a laboratory which has done kinetic measurements where high mercury concentrations were necessary. It should be possible to reduce this background signal, in fact, over the course of the experiments was reduced by a factor of 4.
An additional systematic error could include a loss of mercury from the injection volume. If mercury is lost, it will result in an under estimate of the $X_{\text{LIF}}$ and an over estimate of the total mercury. We believe that these losses are minimal as the observed LIF area from each of the injection volumes were highly reproducible and demonstrated excellent linearity. If there was a systematic loss of mercury we would expect a more pronounced effect at lower injection volumes. As we see no deviation this effect should be limited.

Finally, another underestimate might come from the characterization of the desorption profile. In each profile, the curve was integrated to 12 s, here we see that the signal may not have returned to the baseline value. This would mean that the overall integrated LIF area was slightly underestimated, resulting in a slight under estimate of the overall Hg$^0$ concentration. However, further investigations revealed that the effect of this longer tail was limited and within the error limit of the data.

\[\text{(7.3.4) Applications}\]

The applications of the two-photon LIF system are numerous, first and foremost the direct detection of Hg$^0$ in ambient air. His work confirmed the feasibility of a detection system which can detect in-situ Hg$^0$ on 1 s time scales. This system should be sufficient to perform eddy correlation measurements.

In addition, this technique can be coupled with in-situ sampling on gold tubes which could be deployed independently from the laser instrumentation on an aircraft or balloon platform. The collection on the gold tube is currently limited by the blank signal, ~7 pg. However, even with this blank we can clearly distinguish a 4 pg Hg$^0$ injection. If
samples are collected at a sampling rate of 1.5 L/min in an environment with ambient 
$[\text{Hg}^{0}]$ of 1 ng m$^{-3}$, the sample time needed to observe a desorption peak would be less 
than 150 s, $[\text{Hg}^{0}] = 3.75$ pg, which is similar to that of the Tekran instrument. With 
modest improvements, i.e. reduction of the blank signal which was discussed above, this 
could be reduce to less than 40 s, $[\text{Hg}^{0}] = 1.0$ pg. A reduced sample time would be a 
significant advantage in aircraft and balloon data, as air masses change significantly over 
short periods of time. It is important to recognize that this system is blank, rather than 
signal limited. With improvements in clean handling procedures the blank can be reduced 
and the carrier gas can be switched to Ar or He resulting in an increased sensitivity of 18 
and 150 respectively. Thus the limiting factor for the detection of $\text{Hg}^{0}$ by two-photon LIF 
is the blank signal. Additionally, aircraft studies using the two photon system would 
allow for increased flexibility in sampling time and flow rate as the analysis is not 
dependent on the sampling routine, thus sampling could be optimized for each 
experiment with little to no effect on the analysis procedure. Complications due to 
pressure dependencies would also be mitigated as the pressure at the sampling site could 
only influence the total gas collected not the observed LIF signal.

The final application will be considered in detail in the next section; however, it is 
possible to couple the two-photon LIF detection technique with collection of RGM on a 
KCl coated annular denuder. This new method of detection could be used to validate KCl 
denuder sampling techniques, reduce the sampling time necessary to observe RGM in 
ambient air, and provide information on the speciation of RGM in the atmosphere.
(7.4) Two-photon LIF system for Reactive Gaseous Mercury

(7.4.1) Studies of RGM of Ambient Air Samples

With the advent of CVAFS system, the number of studies evaluating [Hg\(^0\)] in the environment increased significantly. From these studies it became evident that a concurrent determination of the reactive products of Hg\(^0\) oxidation was essential to understanding both the mechanism and impact of atmospheric transformations of Hg\(^0\).

This need brought about the development of three methods to determine RGM concentrations in ambient air. These methods are mist chambers (Lindberg and Stratton, 1998; Stratton and Lindberg, 1995; Stratton et al., 2001), ion-exchange filters (Ebinghaus et al., 1999), and collection on KCl denuders (Landis et al., 2002b, Xiao, 1997 #464). With the introduction of annular KCl annular denuders, the KCl collection technique became the dominant collection method. This method collects RGM, reduces the Hg(II) to Hg\(^0\), and subsequently analyzes the Hg\(^0\) by a CVAAS or CVAFS system with pre-concentration on a gold tube. The procedures employed to properly prepare, sample and analyze KCl coated annular denuders were outlined in Landis et al. (Landis et al., 2002a).

KCl coated annular denuder sampling coupled with CVAFS detection is currently the preferred method of in-situ RGM detection. However, the CVAAS or CVAFS detection methods require high [Hg\(^0\)] or a pre-concentration step. These requirements mean that the CVAFS/KCl denuder technique cannot be used for some applications and technique validation experiments. In this work we have coupled the two-photon LIF detection system with collection of RGM on KCl denuders, uncoated denuders, and an uncoated Pyrex tube in an attempt to perform some of these validation studies and
develop a system, which could be used in situations when the time and/or loading limits are problematic to data acquisition.

(7.4.1a) Development and Sampling Procedures

The two-photon LIF system developed during this work was employed to monitor Hg\textsuperscript{0} atoms evolving from a KCl coated denuder. Figure 7.9 illustrates the experimental set-up.

![Experimental set-up for RGM detection experiments using KCl denuder pre-concentration and two-photon LIF of Hg\textsuperscript{0}.](image)

**Figure 7.9:** Experimental set-up for RGM detection experiments using KCl denuder pre-concentration and two-photon LIF of Hg\textsuperscript{0}.

This set-up is similar to the set-up used for the detection of Hg\textsuperscript{0} evolving from gold tubes, except the gold tube apparatus was replaced with a clamshell tube furnace/KCl denuder assembly.

In-situ air samples were collected on the roof of the administration building at Rosenstiel School of Marine and Atmospheric Science. Samples were collected on a KCl
manual sampling assembly for 30 min to 6 hours at a sample rate of 10 L min$^{-1}$. This sampling rate ensures an aerodynamic aerosol cut-off of <2.5 m. The sampling inlet was not heated; therefore some RGM species may have deposited before the sample region.

After sampling, the KCl denuders were capped and transported down to the lab for immediate analysis. A clamshell tube furnace was heated to 500 °C and maintained at that temperature. The denuder was manually inserted and removed from the oven. O$_2$ is an efficient quencher of the $6^3P_1$ level, thus the denuder had to be pumped down to 200 Torr to remove any ambient air from the annular space. The denuder was returned to 600 Torr filling the annular space with clean N$_2$ gas. The denuder was placed in the clamshell tube furnace for 15 min while the evolving Hg$^0$ signal was directly observed by two-photon LIF. After the heating cycle, the denuders were removed from the oven and allowed to cool. Again during the cooling process the denuders were pumped down to <200 Torr to ensure that air with high [Hg$^0$] was not entrained into the annular space.

The gas lines running from the KCl denuder to the detection cell were kept as short as possible; and not heated. We believe that no mercury was lost on the lines as the peak concentration that evolved from the denuder was less than $1 \times 10^{10}$ molecules cm$^{-3}$, well under the vapor pressure of mercury at room temperature.

Blank samples were obtained by preparing the denuder using the same procedure used as the sampled denuder without the sampling step. Again, as the analysis was carried out in a lab space used for kinetic studies which require high concentrations of Hg$^0$ and RGM, the primary blank signal came from the preparation and analysis procedure done in the lab.
(7.4.1b) Data Analysis

All samples were heated for 15 min; however, we found that the RGM decomposed in the first 5 min. There was a small tail observed after heating, we were unable to determine the source of this shift. The final RGM desorption profile was determined by subtracting the appropriate blank. This curve was then integrated to 5 min and a total LIF signal was obtained. Using the gold tube injection calibration procedure described previously, an $X_{\text{LIF}}$ factor was obtained and the observed signal was converted into absolute [Hg$^0$] or absolute [RGM]. Figure 7.10 is an example of an ambient air sample. The sample was collected for 5 hours and 40 mins. The [RGM] was determined to be 50.54 pg. This is indicative of an average ambient [RGM] of 15.6 pg m$^{-3}$. This is in the range of what is expected for ambient air in Miami.

One concern was the source of the RGM observed on the blank samples. In order to better characterize source of this signal a series of blank measurement were analyzed which differ only in the time which the denuder was flushed with N$_2$. The blanks resulted in [RGM] of 3.6 pg for 10 min N$_2$ flush and 7.3 pg for 20 min N$_2$ flush. If the source of excess RGM was independent of the gas flow, no appreciable increase should be observed; whereas, if the RGM source is within the flow system the excepted blank should double. We observe that the blank concentration does, in fact double; hence the excess RGM source is within the flow system.
(7.4.2) Potential Complications and Errors

Once again the primary limiting factor for the characterization of RGM concentrations by two-photon LIF is the background signal observed. We calculate an additional RGM source of 1.8 ng m\(^{-3}\) this concentration is extremely high and is most likely due to the high background level of Hg\(^0\) and RGM found in the laboratory. It should be possible to reduce this background signal and significantly improve the detection limit for RGM. However, even with the large blank signal the S/N ratio is 14:1. This implies that we can detect absolute [RGM] < 5 pg. Assuming [RGM] in the low pg m\(^{-3}\) the sampling collection time would be < 30 mins. If the blank concentration was reduced the required sampling time could be further reduced. In additional, by switching from an N\(_2\) carrier gas to a He carrier gas a 150 fold improvement in sensitivity would be gained. Therefore, as the blank signal is reduced the system can be switched to He, this
means there is the potential for at least a 1000 fold improvement in the detection limit of
the system and hence a reduction in the sampling time.

Another source of error could be due to outgasing from the annular space upon
heating. As the gas is directly detected in the two-photon LIF system any residual gases
from the annular space may effect the observed desorption profiles. O\textsubscript{2} is an efficient
quencher of the 6\textsuperscript{3}P\textsubscript{1} level. Any outgased O\textsubscript{2} will suppress the LIF signal and lead to an
under estimate of the total LIF area and the total [RGM]. There is also the potential that
the annular space may entrain N\textsubscript{2} gas which contains trace amount of mercury, which
would then be outgases from the annular space during the next heating cycle. This would
lead to an increase in the total LIF and an over estimate of the total [RGM]. To avoid
these problems we pumped the denuder down to 200 Torr to remove any gases the
annular space before analysis and filled the annular space with clean N\textsubscript{2} gas. This should
limit these effects.

(7.4.3) Laboratory Studies to Speciate RGM from a KCl Denuder

One of the most significant uncertainties in our current understanding of the
mercury chemistry is the speciation of RGM. While the ability to sample reactive
mercury species in the environment was an important achievement, the sampled mercury
is chemically uncharacterized. The term RGM has come to define all mercury species
that collect on a KCl denuder and thermally desorb upon heating to 500 °C. As more
studies focus on the transformations and transport of mercury it is important to be able to
characterize the exact chemical speciation of RGM. This work is an initial step in the
development of a method to speciate reactive mercury compounds.
(7.4.3a) Development and Sampling Procedures

The experimental set-up is similar to the set-up used for the direct observation of the Hg\(^{0}\) evolving from the KCl coated denuder, with the addition of a RGM source and a ramped temperature cycle. Three potential RGM species were used in this study, HgCl\(_2\), HgBr\(_2\), and HgO. All species were solid phase and kept in a gas bubbler, in a temperature controlled bath, 5 °C, and under N\(_2\) gas to prevent oxidation. Each bubbler was attached within 6” of the KCl denuder inlet. The inlet was heated to 50°C to prevent deposition of the RGM species before the KCl coating. The denuder was manually inserted and removed from the clamshell tube furnace as required by the heating cycle. A thermal desorption cycle was developed to determine if each reactive mercury species demonstrated a unique desorption profile, i.e. a characteristic profile. The total cycle length was 1 hour; 36 min heating and 24 min sample preparation. The heating cycle consisted of seven 25 °C temperature steps from 100 °C to 250 °C. At each step, the furnace was heated to the desired temperature and held at that temperature for the rest of the 4 min cycle. The 25 °C increase in temperature usually took 1 min, with the furnace temperature remaining constant for three more minutes. After the seventh heating step the oven was rapidly ramped to 500 °C and held. This final cleaning step lasted 8 min and ensured that all the mercury collected on the denuder was removed. This was tested by running successive heating cycles without sampling, in the secondary heating cycle little to no mercury was observed, indicating the denuder was successfully purged in one cycle. The cooling cycle was conducted at reduced pressure and increased flow to ensure that no Hg\(^{0}\) entered the annular space. Once cooled the pressure in the denuder was increased to 600 Torr while clean air flushed the cell. Saturated gases for specific RGM
species were sampled on the denuder for 20s (low load HgX₂) to 10 min (HgO) depending on the species and the desired loading.

(7.4.3b)  Data Analysis

A total of 15 desorption profiles were obtained; 6 HgCl₂, 6 HgBr₂, and 3 HgO. Each profile consisted of 21600 data point (36 min at 10 Hz sampling) and were converted to an absolute [Hg⁰] via the gold tube calibration technique described above. The total RGM load was calculated to be HgCl₂ = 0.54 – 52.4 ng, HgBr₂ = 1.3 – 29.4 ng, and HgO = 0.47 – 0.76 ng. To compare all data, regardless of loading, the temporal profiles were characterized into 8 temperature bins, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, and 500 °C. The 8th bin at 500 °C was the final heating cycle, as any residual mercury evolved in this final cycle, it was not considered in the overall analysis as the variation due to loading was significant. A total [Hg⁰] evolved was calculated by integrating the area under the profile from 0 to 28 min, Hg_total. The [Hg⁰] evolve in each step was determined by integrating the area under the profile during that step, Hg_step. Each step was 4 min long and includes 2400 data points. Figure 7.11 is the raw data collected from all cycles loaded with HgCl₂. The difference is loading is evident.
Figure 7.11: Thermal Desorption profiles for all HgCl$_2$ runs.
To compare all runs regardless of loading two type of analysis were run: a bulk % Hg\textsuperscript{0} evolved at each temperature step and a normalized desorption profile. The percentage of Hg\textsuperscript{0} evolved at the specified temperature was calculated for each bin by dividing the Hg\textsuperscript{0} evolve in each step by the total Hg\textsuperscript{0} evolved from 100 °C to 250 °C, (E7.5).

\[
\% \text{Hg} = \frac{\text{Hg}_{\text{step}}}{\text{Hg}_{\text{total}}} \times 100 \quad \text{(E7.5)}
\]

An average desorption profile was also obtained by normalizing all profiles. This was done by applying equation (E7.6) to each data point in the series.

\[
\text{Hg}_{\text{Norm}} = \frac{\text{Hg}_{\text{measured}}}{\text{Hg}_{\text{total}}} \quad (\text{pg} \ \text{Hg}_{\text{0}}) \quad \text{(E7.6)}
\]

The normalized curves were averaged resulting in a single characteristic desorption profile for each species. These characteristic profiles were then smoothed by applying a 500 point sliding average. The results of these two analyses can be seen in Figures 7.12 - 7.14 for all three of the RGM species. Variation within a temperature step can be observed in Figures 7.15 – 7.21. In each of these graphs the y-axis is the run and the x axis in the % Hg evolved from the KCl denuder at the specified temperature. The bold lines in each section illustrating the average percentage Hg\textsuperscript{0} evolved, with the green line representing the average of the 3 runs with HgO, the blue the average of the 6 HgBr\textsubscript{2} runs, and the red the average of the 6 HgCl\textsubscript{2} runs. The percents and the standard deviation are also included in each graph.
**Figure 7.12:** Thermal Desorption profile for HgCl$_2$. (red) characteristic HgCl$_2$ profile, normalization to 1000 pg; (violet) 500 point sliding characteristic profile (gray bars) Average % of total Hg evolved during the 4 min time step, error bars represent the standard deviation.

**Figure 7.13:** Thermal Desorption profile for HgBr$_2$. (dk. blue) characteristic HgBr$_2$ profile, normalization to 1000 pg; (lt. blue) 500 point sliding characteristic profile (gray bars) Average % of total Hg evolved during the 4 min time step, error bars represent the standard deviation.
Figure 7.14: Thermal Desorption profile for HgO. (dk. green) characteristic HgO profile, normalization to 1000 pg; (lt. green) 500 point sliding characteristic profile (gray bars) Average % of total Hg evolved during the 4 min time step, error bars represent the standard deviation.

Figure 7.15: % Hg$^0$ evolved from a KCl denuder at 100 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg$^0$ evolved for HgO runs; (blue) Average % Hg$^0$ evolved for HgBr$_2$ runs; (red) Average % Hg$^0$ evolved for HgCl$_2$ runs.
Figure 7.16: % Hg$^0$ evolved from a KCl denuder at 125 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg$^0$ evolved for HgO runs; (blue) Average % Hg$^0$ evolved for HgBr$_2$ runs; (red) Average % Hg$^0$ evolved for HgCl$_2$ runs.

Figure 7.17: % Hg$^0$ evolved from a KCl denuder at 150 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg$^0$ evolved for HgO runs; (blue) Average % Hg$^0$ evolved for HgBr$_2$ runs; (red) Average % Hg$^0$ evolved for HgCl$_2$ runs.
Figure 7.18: % Hg\textsuperscript{0} evolved from a KCl denuder at 175 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg\textsuperscript{0} evolved for HgO runs; (blue) Average % Hg\textsuperscript{0} evolved for HgBr\textsubscript{2} runs; (red) Average % Hg\textsuperscript{0} evolved for HgCl\textsubscript{2} runs.

Figure 7.19: % Hg\textsuperscript{0} evolved from a KCl denuder at 200 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg\textsuperscript{0} evolved for HgO runs; (blue) Average % Hg\textsuperscript{0} evolved for HgBr\textsubscript{2} runs; (red) Average % Hg\textsuperscript{0} evolved for HgCl\textsubscript{2} runs.
Figure 7.20: % Hg$^0$ evolved from a KCl denuder at 225 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg$^0$ evolved for HgO runs; (blue) Average % Hg$^0$ evolved for HgBr$_2$ runs; (red) Average % Hg$^0$ evolved for HgCl$_2$ runs.

Figure 7.21: % Hg$^0$ evolved from a KCl denuder at 250 °C during a temperature ramped cycle. (gray bars) % Hg evolved for each individual run; (green) Average % Hg$^0$ evolved for HgO runs; (blue) Average % Hg$^0$ evolved for HgBr$_2$ runs; (red) Average % Hg$^0$ evolved for HgCl$_2$ runs.
No trends were observed in the 28 min cycle, heating to 250 °C, with regard to loading. However, data that includes the final 500 °C step did demonstrate a trend, the percent of total Hg\(^0\) that evolved in the final step was directly proportional to the loading; i.e. high denuder loading resulted in a large % Hg\(^0\) in the final cleaning step.

In order to characterize the difference observed between the RGM species, a two way anova was performed for each temperature step. The resulting p values are listed in Table 7.3, the significant level is assigned to be 0.05. The ANOVA analysis show significants at 6 of the 7 temperature steps. To determine the sources of these differences post-hoc analysis reveal that the desorption profiles for HgCl\(_2\) and HgBr\(_2\) are significantly different at two temperature steps, 175 °C and 250 °C. The HgCl\(_2\) and HgO desorption profiles are significantly different at four temperature steps, 100 °C, 125 °C, 175 °C and 200 °C. The HgBr\(_2\) and HgO desorption profiles are significantly different at five temperature steps, 100 °C, 125 °C, 200 °C, 225 °C and 200 °C.

**Table 7.3:** Calculated p values for a two-way ANOVA at each temperature range with post hoc significance testing between each species, significance level = 0.05, + (significant), - (not significant). The temperatures that are highlighted are ideal temperature for species separation; (blue) HgBr\(_2\), (red) HgCl\(_2\), and (green) HgO

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P value</th>
<th>Post Hoc testing</th>
<th>HgCl(_2) vs HgBr(_2)</th>
<th>HgCl(_2) vs HgO</th>
<th>HgBr(_2) vs HgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.0076</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>0.0090</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.0096</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>0.0261</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.1722</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>0.00007</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.00002</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.22 is a bar graph representing the profile of each species with the addition of a 5 hour ambient air sample made on the roof of the administration building at
the Rosenstiel School of Marine and Atmospheric Science. The trends mentioned above are clearly illustrated in the graph. The ambient air sample has the thermal desorption profile most clearly related to the HgCl$_2$ profile; however, it appears to be slightly exaggerated. This should not be due to loading as our laboratory experiments were conducted under the similar loading conditions. The observed effect might be indicative of a difference species, such as HgClBr, or due to the influence of an environmental variable. Further studies are needed to determine how and if environmental variables influence the RGM profiles.

![Graph showing % Hg evolved from a KCl denuder for each temperature step of a ramped cycle for HgO (green), HgBr$_2$ (blue), HgCl$_2$ (red), and an ambient air (black).](image)

**Figure 7.22:** % Hg$^0$ evolved from a KCl denuder for each temperature step of a ramped cycle for HgO (green), HgBr$_2$ (blue), HgCl$_2$ (red), and an ambient air (black).

This work shows that is possible to broadly characterize RGM species, HgO/HgX$_2$, using a two-photon LIF technique. HgO can be characterized by desorption at temperatures below 125 °C, as the halogenated species do not desorb until heated to 150 °C. Absolute separation of the HgCl$_2$ and HgBr$_2$ species is not possible using this
thermal program. However, HgCl$_2$ and HgBr$_2$ do seem to desorb at a slightly different temperatures, and it maybe possible to separate these species under different conditions.

(7.4.4) Potential Complications and Errors

In this work we attempted to limit the effects of potential complications and eliminate errors; however, this is impossible and the potential error will be discussed below. The annular space in the URG denuder presented a potential problem as upon heating the gas inside the annular space is forced out by thermal expansion and will be entrained in the evolving gas. If there are trace amounts of mercury in this annular gas we will see an increase in the signal as this gas is released. This could slightly shift the characteristic desorption profiles and result in an over estimate of total [RGM]. The gases released by outgasing from the annular space could also result in changes to the thermal profile, as each gas may quench the Hg fluorescence signal differently. A strong quencher, such as O$_2$ released from the annular space will result in a decreased LIF signal and an underestimate of the final [RGM]. Much of the effect of the annular gas can be reduced by conditioning the KCl denuder with N$_2$ prior to use, however, at the high RGM concentrations used in these experiments it was not possible to totally eliminated the effects.

There is also the potential that the denuder experiences uneven heating, i.e. the inner tube is heated at a different rate than the outer tube. If this is the case the characteristic desorption profiles will be deceptively broad as the inner tube releases the Hg$^0$ after the outer tube.
The final complication which has yet to be explored is the introduction of variation within the characteristic profiles due to environmental variables. If the environment in which the sample is collected significantly effects how the RGM and KCl coating interact, than real air samples will vary from the laboratory studies. The effects of these environmental variables should be reduced with simpler temperature ramping cycles, as slight differences the RGM/KCl coating interaction should not result in large shifts as no obvious trend were observed between different denuders.

(7.4.5) Laboratory Studies to Speciate RGM from an uncoated surface

The primary uncertainty in the application of the KCl denuder technique is the fact that little is known about the interaction between the KCl coating and the RGM species. To circumvent these issues we ran a series of experiment using an uncoated denuder and a 20” Pyrex tube. Although neither of these collection apparatus will completely scavenge the RGM in the air, by coupling sampling on an uncoated system with total [RGM] from standardized KCl denuder sampling the concentration for each species could be determined. This work represents the first step in developing this method.

(7.4.5a) Uncoated Denuder

A standard KCl denuder (URG Corporation) was cleaned via the method outlined in Landis et al. (Landis et al., 2002b). Once cleaned the denuder was left uncoated. Known RGM species (HgCl₂ and HgBr₂) were passed over the uncoated denuder for 4 min from gas bubblers held at a constant temperature, 5 °C. Early experiments found that
the first evidence of the thermal decomposition of HgX₂ to Hg⁰ from the uncoated
denuder was observed in the range of 200 – 300 °C. This was significantly higher then
decomposition observed from the uncoated denuder, which was observed at temperature
as low as 125 °C. An eight step thermal decomposition program was developed to
characterize the desorption profiles of HgCl₂ and HgBr₂. The program included: an
initial heating at 100 °C for 6 min, this ensured that any Hg⁰ that may have deposited on
the walls of the denuder was volatilized before any thermal decomposition of HgX₂ was
observed. Then six 10 °C steps from 220 °C to 270 °C were monitored for 3 min. The
final step was a cleaning step where the furnace was heated to 500 °C and held for 13
min. We observed no residual Hg⁰ upon secondary heating; thus this temperature cycle
effectively removed all mercury species collected during the sampling cycle. The thermal
decomposition profiles can be observed for both HgX₂ species in figure 7.23. From this
figure we observe that the peak structure observed in experiments using denuders coated
with KCl disappears indicating the temperature cycle peaks are generated by a chemical
or physical process involved releasing the RGM from the KCl coating. This indicates that
the collected RGM species form a complex with the KCl in the coating.
Figure 7.23: Thermal decomposition profile of RGM species from an uncoated denuder; (red) single shot LIF signal for HgCl$_2$, (violet) 500 point sliding average of LIF signal from HgCl$_2$, (dk blue) single shot LIF signal for HgBr$_2$, (lt blue) 500 point sliding average of LIF signal from HgBr$_2$.

The absolute temperature for decomposition is also higher than the temperature observed in desorption from the KCl coating. This effect could be due to the fact HgX$_2$/KCl complex thermally decomposes at lower temperature. Another explanation could be that at lower temperatures the HgX$_2$ species volatilizes without decomposing to Hg$^0$, as the two-photon LIF system will only detect the Hg$^0$ decomposition product. In this work we did not have a calibrated source of RGM, hence it was not possible to use a mass balance calculation to determine if all RGM evolved as Hg$^0$.

Finally, we observe a broad structure in the thermal desorption profile. This structure could be due to uneven heating within the denuder. If the inner tube is not heated to the expected temperature then the RGM absorbed on the wall of the inner tube will be decompose later than the RGM on the outer wall broadening the observed profile. Another explanation for the broad thermal decomposition profile could be the effect of outgasing from the annular space. Again as the denuder is heated the annular space with
expand releasing the gas inside the inner tube with could contain some Hg\(^0\). As the overall efficiency of RGM collection is limited on a uncoated denuder and small contamination within the annular space could result in a broad thermal decomposition profile.

(7.4.5b) *Uncoated Pyrex Tube*

Experiments with an uncoated denuder revealed that outgasing from the annular space and uneven heating of the denuder could cause significant complication in studying the thermal decomposition of RGM species from an uncoated surface. Hence a 20” Pyrex tube with #25 threaded joints was used in place of an uncoated URG annular mercury denuder. Samples were obtained and analyzed using identical procedure to the uncoated denuder sample described above. Figure 7.24 illustrates the thermal decomposition profiles observed for HgCl\(_2\) and HgBr\(_2\).

![Figure 7.24](image.png)

**Figure 7.24:** Thermal decomposition profile of RGM species from 20” Pyrex tube; (red) single shot LIF signal for HgCl\(_2\), (violet) 500 point sliding average of LIF signal from HgCl\(_2\), (dk blue) single shot LIF signal for HgBr\(_2\), (lt blue) 500 point sliding average of LIF signal from HgBr\(_2\).
Again the absolute temperature of the thermal decomposition was higher than the observed desorption from a KCl coated denuder. However, the profiles did not demonstrate the broad structure observed in uncoated denuder experiments. Instead we observed a narrow peak structure with decomposition peak for HgCl$_2$ at 220 ° and HgBr$_2$ at 230 °. This seems to indicate that on an uncoated surface HgCl$_2$ and HgBr$_2$ do thermal decompose at significantly different temperature.

(7.4.6) Potential Complications and Errors

There are two complications which will influence a system in which RGM is collected on an uncoated surface, The first complication is the fact that the efficiency of RGM collection on the surface will be significantly less than 100% and will vary for each RGM species. As the RGM is not bound on an uncoated denuder the RGM species will be prone to re-volatilization and variations in atmospheric conditions. Hence, the final observed RGM sample will be influence by the total time sampled, if a RGM spike occurred, when it occurred and the atmospheric conditions. However, the purpose of sampling on an uncoated denuder is not to establish total RGM concentration but rather the HgX/HgO ratio. Therefore complications due to re-volatilization and incomplete scavenging maybe overcome; however, further investigations into how these factors influence portioning is needed.

The second potential complication is the loss of RGM species from the denuder as RGM not as Hg$_0$. Any RGM volatilized instead of decomposed will not be detected by the two-photon LIF system. This challenge can be overcome by passing the evolving gas through a coated KCl denuder or KCl coated quartz chips heated to 500 °C before LIF
detection. The heated denuder should act as a surface to decompose the RGM species so that it would be detected by the LIF system. We have not conducted any experiments to determine if RGM is volatilized from the uncoated surface or if the KCl coated denuder effectively decomposes this volatized RGM. This would be the next phase of investigation for this study.

(7.5) Summary

Overall in this work, we have tested the two-photon LIF system for the detection of Hg$^0$ developed by Bauer et al. (Bauer et al., 2002; Bauer et al., 2003) to ensure that the excitation scheme employed there was the most sensitive scheme. We established the feasibility of coupling the two-photon LIF detection of Hg$^0$ with pre-concentration on gold tubes. In this configuration samples could be collected independent of the laser system and analyzed in the laboratory. This approach could be particularly effective in aircraft and balloon studies, but are currently limited by a large blank signal.

We directly analyzed the Hg$^0$ evolving from RGM samples collected on KCl coated annular denuders. This direct observation of the evolving Hg$^0$ species provided insights into the chemical/physical processes which influence RGM collection on the KCl coating. It also can be used to validate and improve current methods used in the analysis RGM species. To this effect we observed the rapid desorption (5 min) of RGM from the KCl coated denuder, that three known RGM species collect on the denuder; HgCl$_2$, HgBr$_2$ and HgO, and the desorption profiles between KCl coated and uncoated denuder indicate the RGM species on the coated denuder undergoes a chemical or physical change.
Initial studies into the possible of speciating RGM from the thermal desorption profiles reveal clear differences between the characteristic desorption profiles of HgO and HgX₂ species and possible difference between the two HgX₂ species. This is the first study with sufficient sensitivity to observe the evolving RGM at low loading levels, which may account for the successful separation. Further investigation into the use of an uncoated surface indicates that 20” uncoated Pyrex tube resulted in a clearly defined peak structure that was significantly different between HgCl₂ and HgBr₂ indicating an uncoated surface may provide a better defined method of qualitatively separating RGM species.
CHAPTER VIII
CONCLUSIONS

The goal of this work was to gain insight into the biogeochemical cycling of mercury. Work was conducted on two parallel threads of research; investigations of the kinetics of potential pathway for the gas phase oxidation of atmospheric mercury and the development of new laser based techniques to be employed for both laboratory and field studies of \( \text{Hg}^0 \) and the products of mercury oxidation. Significant progress was made in attaining both of these goals.

In terms of understanding potential reaction pathways for mercury oxidation, the reaction of mercury atoms with bromine atoms was identified as a viable initiation step for the atmospheric oxidation of mercury. This work did not observe the very fast rates \((k \approx 10^{-11})\) observed in previous relative rate studies. The direct studies performed in this work were performed under several configurations, monitoring both reactant and product species. All experiments agree within the error limits. This suggests that the current atmospheric oxidation of mercury attributed to bromine atoms is at least an order of magnitude too large. As current mercury budgets appear to be incompatible with this slower oxidation of mercury via bromine atoms, this work must also call into question the accuracy of the reduction mechanism, specifically via \( \text{HO}_2 \), as it might be similarly over-estimated.

The lifetime of mercury due to bromine initiated oxidation is strongly dependent on the \([\text{Br}]\) atoms. When only considering the influence of bromine atoms,
\[ \text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \] (R1.10)

\[ \text{HgBr} + \text{M} \rightarrow \text{Hg}^0 + \text{Br} + \text{M} \] (R6.1)

\[ \text{HgBr} + \text{Br} \rightarrow \text{products} \] (R1.29)

Concentrations of bromine atoms must rise above \(1 \times 10^6\) to drive the reaction to the HgBr\(_2\) product. This work demonstrates that while at high bromine atoms concentrations a purely Br atom reaction could account for the observed mercury oxidation, at lower Br atom concentration there must be other stabilizing reactions such as,

\[ \text{HgBr} + \text{O}_2 \rightarrow \text{products} \] (R1.23)

to stabilize the HgBr species. Therefore, in evaluating the importance of halogen oxidation throughout the atmosphere, particularly in lower halogen environments, it is essential to consider these stabilizing reactions, as without them the Br atom initialize oxidation of mercury will be of little importance.

This work also resulted in the validation of a two-photon LIF technique to directly observe Hg\(^0\). This technique was employed in conjunction with Hg\(^0\) pre-concentrated on a gold tube, and pre concentration of known RGM species on a KCl denuder. This work sought to demonstrate the potential advantages of the two photon LIF detection of Hg\(^0\), in that the Hg\(^0\) can be directly observed with the current detection limit using 10 point averaging (10 points at 10 hz = 1s) of 0.002 ng m\(^{-3}\) in He, 0.4 ng m\(^{-3}\) in N\(_2\), and 1.4 ng m\(^{-3}\) in Air. This means that the two photon LIF system could provide ambient [Hg] on the scale of 1-2s in its current configuration and by replacing the 10 hz laser system with a high repetition laser these time could be reduced to less than a second making the technique useful in performing eddy-correlation experiments.
In addition, the direct detection of the Hg$^0$ evolving from a KCl-denuder provides a solid foundation to evaluate current RGM sampling practices and the development of techniques to potential speciate RGM. A more complete summary of this work is provided in the following sections.

(8.1) Kinetic Studies

In the course of this work, the following kinetic rate coefficients were determined.

\[ \text{Hg}^0 + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M} \quad (\text{R1.11}) \]
\[ \text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \quad (\text{R1.10}) \]
\[ \text{HgBr} + \text{M} \rightarrow \text{Hg}^0 + \text{Br} + \text{M} \quad (\text{R6.1}) \]
\[ \text{HgBr} + \text{Br} \rightarrow \text{products} \quad (\text{R1.29}) \]
\[ \text{HgCl} + \text{O}_2 \rightarrow \text{products} \quad (\text{R1.24}) \]
\[ \text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M} \quad (\text{R3.1}) \]
\[ \text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} \quad (\text{R4.1}) \]

Each rate coefficient is listed in table 8.1 along with the bath gas and temperature and pressure ranges. For reactions R1.10, R1.11, R1.24, R6.1 and R1.29, this work was the first direct measurement of the kinetic rate coefficient for the reaction.
Table 8.1: Rate coefficient measurements from this work.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Gas</th>
<th>T (K)</th>
<th>P (Torr)</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl + Hg + M → HgCl + M</td>
<td>N₂</td>
<td>243-298</td>
<td>200-600</td>
<td>(2.2 ± 0.5) × 10⁻³² exp (680 ± 400) ( \frac{1}{T} - \frac{1}{298} ) (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>293</td>
<td>200-600</td>
<td>(9.37 ± 0.95) × 10⁻³³ (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td>Br + Hg + M → HgBr + M</td>
<td>N₂</td>
<td>243-298</td>
<td>200-600</td>
<td>(1.46 ± 0.34) × 10⁻³² ( \frac{T}{298} )⁻¹ (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>293</td>
<td>200-600</td>
<td>(1.49 ± 0.12) × 10⁻³² ( \frac{T}{298} )⁻¹ (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td>HgBr + M → Br + Hg + M</td>
<td>N₂</td>
<td>360</td>
<td>200-600</td>
<td>1.65 × 10⁻¹⁷ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>420</td>
<td>200-600</td>
<td>2.72 × 10⁻¹⁷ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>HgBr + Br → products</td>
<td>N₂</td>
<td>360</td>
<td>200-600</td>
<td>(3.5 ± 1.0) × 10⁻¹⁰ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>420</td>
<td>200-600</td>
<td>(3.0 ± 1.0) × 10⁻¹⁰ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>HgCl + O₂ → products</td>
<td>N₂</td>
<td>298</td>
<td>300</td>
<td>(2.7 ± 0.6) × 10⁻¹⁷ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>298</td>
<td>300</td>
<td>(3.2 ± 0.2) × 10⁻¹⁷ (cm³ molecule⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>Cl + Cl + M → Cl₂ + M</td>
<td>N₂</td>
<td>243-298</td>
<td>200-600</td>
<td>(8.4 ± 2.3) × 10⁻³³ exp (850 ± 470) ( \frac{1}{T} - \frac{1}{298} ) (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>293</td>
<td>200-600</td>
<td>(5.17 ± 0.49) × 10⁻³³ (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td>Br + Br + M → Br₂ + M</td>
<td>N₂</td>
<td>243-298</td>
<td>200-600</td>
<td>(4.31 ± 0.21) × 10⁻³³ ( \frac{T}{298} )⁻² (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>293</td>
<td>200-600</td>
<td>(1.43 ± 0.17) × 10⁻³³ (cm⁶ molecule⁻² s⁻¹)</td>
</tr>
</tbody>
</table>

(8.1.1) Reaction of Hg⁰ with Halogen Atom

One of the primary goals of this work was to evaluate the potential gas phase oxidation of elemental mercury by halogen atoms. The direct determination of the rate coefficient for the reaction of mercury with halogen atoms is essential to furthering our understanding of the biogeochemical cycling of mercury.

We have reported recombination rate coefficients for the reaction of mercury and chlorine atoms, \( k_{R1.11} \), and the reaction of mercury and bromine atoms, \( k_{R1.10} \). In both
cases the observed rate coefficients show pressure, temperature and third body deactivation efficiencies, which are consistent with three-body recombination.

Prior to and concurrent to this work a series of relative rate studies and theoretical studies were conducted for reaction R1.10 and R1.11. A relative rate study by Ariya et al. reported rate coefficients for both reactions R1.10 and R1.11 at 1 ATM and 298 K. The rates observed in the Ariya et al. system were significantly faster that the rate coefficients observed in the this work, \((1.0 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}\) for reaction R1.11 and \((3.2 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}\) for reaction R1.10. This study was conducted in a static 2 L or 3 L Pyrex flask. For both reactions the observed rate coefficient depended on the reference molecules, the concentration of the reference molecule, the concentration of an OH scavenger, and the identity of the buffer gas.

Spicer et al. also reported rate coefficients for both the halogen atom reactions. In his work, Spicer et al. used a 17.3 m³ environmental chamber and multiple reference molecules. As in the Ariya et al. study, Spicer found that the observed rate coefficients depended on the reference molecule. Ultimately, Spicer et al. reported a value of \(6.4 \times 10^{-11} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}\) for reaction R1.11 and \(9.7 \times 10^{-13} \text{ cm}^3 \text{molecules}^{-1} \text{s}^{-1}\) for reaction R1.10.

In addition to the experimental work described above, there has been one theoretical determination for the Cl atom reaction with \(\text{Hg}^0\) (Khalizov et al., 2003) and three theoretical determinations of the rate coefficient for the reaction of Br and \(\text{Hg}^0\) atoms (Goodsite et al., 2004; Khalizov et al., 2003; Shepler et al., 2007). Khalizov et al. (Khalizov et al., 2003) determined the recombination rate coefficient for reactions for R1.10 and R1.11 using electronic structure calculations to obtain molecular parameters
and the capture rate or high-pressure limit. Once this high pressure limit was obtained, Khalilov et al. determined a pressure dependent rate coefficient by assuming a strong collisional deactivation. The calculation makes the physically unrealistic assumption that every collision of the buffer gas with the initially formed energized HgBr* complex deactivated the complex to produce a stable HgBr molecule that cannot dissociate to products. Thus, the rates obtained by this method should be considered an upper limit for the reaction. They obtained rate coefficients at 298 K, 760 Torr of $2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction R1.11 and $2.07 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction R1.10, both of which are slower than the rate coefficient observed in the Ariya et al. study.

The second theoretical study of reaction (R1.10) was carried out by Goodsite et al. (Goodsite et al., 2004). This study employed the RRKM theory using a master equation formulation to predict the rate coefficient the reaction of Hg with Br atoms. In this work, they take into account that not all collision will transfer enough energy to stabilize HgBr*. The rate coefficient obtained using this approach was $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.

The final theoretical study for the Hg + Br reaction system was carried out by Shepler et al. (Shepler et al., 2007). Shepler first calculated potential energy surfaces using coupled cluster theory with single and double excitations and a perturbative treatment of triple excitations [CCSD(T)], after calculating these potentials a quasiclassical trajectories analysis was used to calculate the collisional induced dissociation of HgBr. The recombination reaction was calculated by balance with the dissociation rate. Shepler et al. report a rate for the recombination of Hg and Br atom of $9.8 \times 10^{-13}$ at 289 K 760 Torr.
Overall the relative rate studies resulted in rate coefficients for reaction R1.11 that were 18.5 and 118 times faster than the rate coefficient determined in our direct study. For reaction R1.10 the rate coefficients from the relative rate studies were 9 and 3 times faster than the rates determined in this work. Both relative rate studies demonstrated a large dependence of the measured relative rate coefficient with respect to the reference compound. This is a clear indication that these studies are influenced by secondary chemistry. The large discrepancy observed between measurements conducted in air and nitrogen and the non-linearity observed in the relative rate plots in both bath gases are further evidence of the presence of secondary chemistry. In addition, the relative rate studies tend to be faster than the theoretical determinations.

The slower rate coefficients observed in this work were determined under two experimental conditions. One method in which the halogen radical was in excess and Hg$^0$ atom were monitored by one photon LIF. The other method was performed with Hg$^0$ atoms in excess concentration while the halogen atoms were monitored by two photon LIF. In the case of the reaction of Hg with Br atoms, the resulting HgBr product was also monitored while Hg atoms were in excess. We found that all the data collected in these two configurations were consistent and the expected behavior for a three body recombination. The large discrepancy between the direct determinations of the rate coefficients for reaction R1.11 and R1.10 and the rate coefficients determined in relative rate studies, as well as, the fact that the theoretical estimates, which can be considered an upper limit, report rate coefficients slower than the rates reported in the relative rate studies; must call into question the viability of using the relative rate method to determine kinetic rate coefficients for mercury halogen reactions.
To evaluate the importance of the recombination of Hg\(^0\) and halogen atoms, we must first calculate a second order rate coefficient for each reaction appropriate for the environmental conditions. An estimate of the average concentrations of each reactant is also needed, as the lifetime will depend on both the reaction rate coefficient and the concentration of the species. One of the regions of interest to many scientists is the Arctic at polar sunrise, as during this time dramatic atmospheric mercury depletions episodes (AMDEs) have been observed. In the Arctic, we would expect an average temperature of 260 K and a pressure of 1 ATM resulting in an effective second order rate coefficient of \(8.7 \times 10^{-13} \text{ cm}^2 \text{ molecules}^{-1} \text{ s}^{-1}\) for reaction of Hg with Cl atom and \(5.3 \times 10^{-13} \text{ cm}^2 \text{ molecules}^{-1} \text{ s}^{-1}\) for the reaction of Hg with Br atoms. The rate coefficient reported for the recombination of bromine and mercury atoms is calculated from the temperature independent rate reported in Chapter 6 (E6.3), thus the lifetimes reported here vary slightly from those in Chapter 4. Boudries and Bottenheim (Boudries and Bottenheim, 2000) estimated peak concentrations of halogen during polar sunrise, Cl atoms = \(10^4\)-\(10^5\) molecules cm\(^{-3}\) and Br atoms = \(10^7\)-\(10^8\) molecules cm\(^{-3}\). Using these concentrations and the rate coefficient determined in this work at 260K the lifetime of mercury during polar sunrise in the Arctic due to reaction with Cl atoms can be estimated at 3.7 years – 134 days. This suggests that the recombination reaction of mercury with chlorine atoms does not contribute significantly to the chemistry of mercury depletion events. The lifetime of mercury due to bromine in the Arctic at polar sunrise was determined to be between 2.2 days and 5.2 hours. This means reaction R1.10 could play a significant role in AMDEs. However, the importance of the recombination of mercury and bromine atoms, reaction R1.10, will depend on the stability and reactivity of the HgBr species.
The halogen initiated reaction of mercury could also be playing a role in environments other than the Arctic. In 2004, Hedgecock et al. (Hedgecock and Pirrone, 2004) reported a lifetime of mercury in the MBL of 10.5 days due to reaction with Br atom, OH radical and O$_3$. This lifetime was calculated using the very rapid kinetic rate coefficient determined by Ariya et al. (Ariya et al., 2002) and a steady state Br concentration of [Br] = 3.1 × 10$^5$ molecules cm$^{-3}$. Using these parameters the lifetime of Hg$^0$ due to reaction with bromine atoms is 11.5 days. If we perform the same calculation using the rate coefficient for reaction R1.10 determined in Chapter 6 of this work at 760 Torr and 298 K, we find that lifetime of Hg$^0$ due to the reaction with bromine increases to 102 days. Using the Hedgecock et al. lifetimes of 133 days for reaction with OH and 578 days for reaction with O$_3$ we obtain an overall lifetime of 52.5 days for Hg$^0$ in the MBL. The factor of 5 increase in the lifetime of Hg$^0$ using our rate coefficient for reaction R1.10 highlights the need for direct determination of rate coefficients for Hg$^0$ reactions in order to elucidate the overall biogeochemical cycling of mercury.

Accessing the overall importance of the halogen initiated reaction is difficult as the concentration of Br and Cl atom in many environments is still unclear. It has been proposed that halogen chemistry could be playing a role in the oxidation of atmosphere mercury in the MBL (Laurier et al., 2003; Mason, 2005; Sprovieri et al., 2003; Weiss-Penzias et al., 2003), coastal environments (Laurier and Mason, 2007; Malcolm et al., 2003), saline lakes (Peleg et al., 2007), and the upper atmosphere/lower troposphere (Landis et al., 2005; Murphy et al., 2006a; Murphy et al., 2006b; Murphy et al., 2003; Swartzendruber et al., 2006; Weiss-Penzias et al., 2007; Weiss-Penzias et al., 2006). As mentioned above these lifetimes only consider the initial reaction of mercury and
bromine atoms, in order to calculate a true lifetime of mercury due to reaction with Br atoms the loss processes of the unstable HgBr species must be considered.

(8.1.2) Loss processes of the HgBr molecule

In this work two potential loss processes of HgBr were determined from the temporal profiles of HgBr with Hg\textsuperscript{0} atoms in excess and at elevated temperatures, 360-420 K. Rate coefficients for reaction R6.1 and R1.29 are reported in table 8.1. There was some error in the determination of these rate coefficients as it was not possible to unambiguously separate these two reactions. Hence we believe that the results reported in this work are good initial estimates and are accurate within a factor of 2.

Considering Hg and Br atom reaction system studied in this work, the [Hg\textsuperscript{0}] in the environment due to reaction R1.10, R1.29 and R6.1 can be expressed by equation, E6.4,

\[
\frac{d[Hg]}{dt} = -k_{R1.10} [Br][Hg] + k_{R6.1} [HgBr]
\]  

(E6.4)

where the [HgBr] can be defined as equation 6.5.

\[
[HgBr] = \frac{k_{R1.10} [Br][Hg]}{k_{R6.1} + k_{R1.29} [Br]}
\]  

(E6.5)

Using these equations we find that the lifetime of Hg\textsuperscript{0} due to these reactions is:

\[
\tau_{Hg} = \frac{k_{R6.1}}{k_{R1.10}} \frac{[Br]}{[Br]^2}
\]  

(E6.6)

Using the \( k_{R1.10} \) at 260 K from this work, a \( k_{R1.29} \) extrapolated to 260 K from the high temperature determination in this work, and the temperature dependent estimate of \( k_{R6.1} \) from Shepler et al. (Shepler et al., 2007) a lifetime of Hg\textsuperscript{0} due to reaction with Br atom
can be obtained. For this calculation we employed the Shepler estimate for reaction R6.1 as the error limits from the rate coefficient determined at high temperatures make extrapolations difficult and speculative. We believe that the Shepler et al. data should provide a good upper limit for $k_{R6.1}$. The rate lifetime of Hg$^0$ is calculated for the peak concentrations of Br atom reported by Boudries and Bottenheim (Boudries and Bottenheim, 2000) in equations E6.7 and E6.8.

$$\tau_{Hg@260K} = \frac{0.0128}{4.85 \times 10^{-10} + 1 \times 10^8} \frac{1}{5.35 \times 10^{-13} \times (1 \times 10^8)^2} = 6.6 \text{ hours}$$ \hspace{1cm} (E6.7)

$$\tau_{Hg@260K} = \frac{0.0128}{4.85 \times 10^{-10} + 1 \times 10^7} \frac{1}{5.35 \times 10^{-13} \times (1 \times 10^7)^2} = 7.9 \text{ days}$$ \hspace{1cm} (E6.8)

As the Br atom concentration is further reduced we find that loss of HgBr due to reaction R1.29 is too slow and the HgBr undergoes thermal decomposition. This means that at $[Br]$ under $1 \times 10^6$ molecules cm$^{-3}$ the lifetime of Hg$^0$ due to reaction with Br atoms is over a year. In this estimate we assume that the only reaction that stabilizes the transient HgBr species is Br atoms. However, in the atmosphere the reactive HgBr could be stabilized by many secondary species, such as Cl, O$_2$, ClO, BrO, IO, OH, or I. Therefore, in order to understand the overall lifetime of Hg$^0$ due to the Br atoms further studies into the reactions of the HgBr product are necessary. This work is the first study that determined a rate coefficient for an HgBr reaction and can provide the base for future work.
(8.1.3) Reaction of HgCl with O₂

A second order rate loss for R1.24 was determined in a LIF system configured to detect fluorescence from HgCl molecules. We found that the HgCl temporal profile could be described by a pseudo first order loss of HgCl with O₂ in excess. The pseudo first order loss increased with increasing O₂ partial pressure. The observed rates did not demonstrate a strong dependence on the bath gas, indicating that quenching from the third body may not be necessary for reaction R1.24. This is the first time this rate coefficient had been directly measured.

(8.1.4) Halogen Atom Self Reaction

The rate coefficient for self reaction of Cl atoms was measured as second order rate coefficients in a two photon LIF system. The measurements adhered to the expected temperature, pressure, and bath gas dependences expected for a third order reaction in the low pressure limit. We found that the rate we measured for the Cl atom self reaction agreed with previous measurements conducted in helium and are between the most recently reported measurements in nitrogen. The difference between our rate coefficient and the most recent rate coefficient reported by Hippler et al. (Hippler and Troe, 1976) is less than 10%, while our results are about 20% lower than the value reported by Widman et al. (Widman and DeGraff, 1973). Our rate coefficient lies within the error limits of both of the reported rates. The good agreement between the measurements suggests that our calculation of the initial Cl atom concentration is accurate and the uncertainty estimate is conservative.
The Br atom self reaction was also measured in an LIF system as a second order rate coefficient. The observed rate demonstrated an inverse temperature dependence, positive pressure dependence, and a decrease in the rate coefficient as the bath gas was switched from N$_2$ to He.

However, our observed rate is significantly slower than many of the observed rate coefficients reported in other studies. Upon further analysis it was determined that, although many all of these studies report strong agreement between the observed rate a previous literature values, there was in fact a factor of two discrepancy in much of the data due to the differences in the relationship used to derived a kinetic rate coefficient. The kinetic rate coefficient observed in this work for reaction R4.1 agreed well with two early studies (Clarke and Burns, 1972; Ip and Burns, 1969), but was a factor of 2 – 3 slower than the rates reported by Strong et al. (Strong et al., 1957), DeGraff et al. (DeGraff and Lang, 1970), Clyne et al. (Clyne and Woon-Fat, 1973), and Hippler et al. (Baer et al., 1991; Hippler et al., 1978).

(8.2) **Method development**

In order to advance our understanding of the biogeochemical cycling of mercury it is essential to develop new methods to monitor ambient mercury species. The second portion of this work was the development of new lased based methods to monitor ambient mercury species.
(8.2.1)  \textit{HgX LIF}

In this work, we developed a one photon LIF technique to detect both HgCl and HgBr radicals. The HgCl species was excited at the (1,0) transition of the \( \text{D}^3\Pi_{3/2} \rightarrow \text{X}^2\Sigma \) band at 249.5 nm, while the subsequent fluorescence was detected by a filter pack/PMT assembly centered at 262 nm. The HgBr molecule was initially excited by a probe laser pulse tuned to the (2,0) transition of the \( \text{D}^3\Pi_{3/2} \rightarrow \text{X}^2\Sigma \) band at 256.08 nm and monitored by observation of the resulting fluorescence from the \( \text{B}^2\Sigma \rightarrow \text{X}^2\Sigma \) fluorescence band at 500 nm by a filter pack/PMT assembly. These new LIF techniques provide new pathways to evaluate the kinetics and mechanisms of mercury halogen chemistry.

(8.2.2)  \textit{Observations of Hg}^0: \textit{Direct LIF detection and collection on gold tubes}

In this work we tested and verified the two-photon LIF system for the detection of Hg\(^0\) developed by Bauer et al. (Bauer et al., 2002; Bauer et al., 2003) to ensure maximum sensitively for Hg\(^0\) detection.

In addition, we demonstrated the feasibility of coupling the two-photon LIF detection of Hg\(^0\) with pre-concentration on gold tubes. This coupling of gold tube pre-concentration is particularly important in studies where the integration time and sampling artifacts associated with Hg\(^0\) make the use of current sampling technologies problematic. Specifically, this work could be used to in aircraft and balloon studies where [Hg\(^0\)] are low.

The detection limit for the two photon LIF technique coupled with collection on the gold tubes is currently limited by a large blank signal, \( \sim 7 \text{ pg} \). The sample time needed to observe a desorption peak above this blank signal was still short, less that 30 s.
sampling at a rate of 10 L/min in an environment with ambient $[\text{Hg}^0]$ of 1 ng m$^{-3}$. With modest reductions in the blank signal the sample time can be reduced to 10 s under the same conditions, $[\text{Hg}^0] = 1.7$ pg. A 10 s sample time would be a significant advantage in aircraft and balloon data, as air masses change significantly over short periods of time. It is important to recognize that this system is limited by the blank signal, this blank is due to the fact that the laboratory used to develop this technique was also used to perform kinetic studies of mercury reactions; hence the background level are high. We believe that by employing clean techniques the blank could be significantly reduced thus increasing the detection limit of the system.

(8.2.3) *Observations of RGM: Using LIF detection of Hg$^0$ and the development of potential method to chemical speciate RGM samples*

In this work two types of experimental procedures were developed to monitor Hg$^0$ evolving from RGM samples collected on KCl coated annular denuders. First we directly monitored the Hg$^0$ evolving from the KCl denuder heated to 500°C. This direct observation of the evolving Hg$^0$ species provided insights into the chemical/physical processes which influence RGM collection on the KCl coating. In this work we observed the rapid desorption (5 min) of RGM from the KCl coated denuder. In addition, it was determined that three known RGM species collect on the denuder; HgCl$_2$, HgBr$_2$ and HgO, although at this time we cannot say that HgO is thoroughly scavenged by the KCl denuder.

The second type of experiments performed with the two photon LIF system were initial studies into the possibility of speciating RGM. The thermal desorption profiles of
HgO and HgX\textsubscript{2} species from a KCl coated denuder reveal clear differences between the characteristic profiles of these species. However, complications due to the uneven heating of the inner and outer tub of the denuder, the thermal expansion of gas from annular space of the inner tube in the denuder, and potential complications due to the release of Hg from the HgX-KCl complex resulted in only small differences in the thermal desorption profiles for the two HgX\textsubscript{2} species. Further investigation into the use of an uncoated surface to overcome the complications discussed above indicates that an uncoated Pyrex tube may provide a better defined method of separating RGM species.
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