GAS-PHASE FORMATION RATES OF NITRIC ACID AND ITS ISOMERS UNDER URBAN CONDITIONS

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Abstract

Ozone formation in urban smog is controlled by a complex set of reactions which includes radical production from photochemical processes, catalytic cycles which convert NO to NO₂, and termination steps that tie up reactive intermediates in long-lived reservoirs. The reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \) (1a) is a key termination step because it transforms two short-lived reactive intermediates, \( \text{OH} \) and \( \text{NO}_2 \), into relatively long-lived nitric acid. Under certain conditions (low VOC/NOx), ozone production in polluted urban airsheds can be highly sensitive to this reaction, but the rate parameters are not well constrained. This report summarizes the results of new laboratory studies of the \( \text{OH} + \text{NO}_2 + \text{M} \) reaction including direct determination of the overall rate constant and branching ratio for the two reaction channels under atmospherically relevant conditions:

\[
\begin{align*}
\text{OH} + \text{NO}_2 + \text{M} & \rightarrow \text{HONO}_2 + \text{M} & \text{(1a)} \\
& \rightarrow \text{HOONO} + \text{M} & \text{(1b)}
\end{align*}
\]

where the overall rate constant is \( k_1 = k_{1a} + k_{1b} \) and the branching ratio is \( k_{1b}/k_{1a} \).

Measurements of the pressure dependence of the \( \text{OH} + \text{NO}_2 \) bimolecular rate coefficient \( k_1 \) have been performed in \( \text{N}_2, \text{O}_2, \text{Air} \) and \( \text{He} \) (50-900 Torr) at 298 K and in \( \text{Air} \) at 315 K. Measurements of the \( \text{HOONO}/\text{HONO}_2 \) branching ratio have been made over the range 50-750 Torr at 298 K. Theoretical calculations of the integrated intensities and correction factors for the HOONO integrated absorbance have been completed. The results of these three studies have been combined to provide fitted fall-off parameters for \( k_{1a} \) and \( k_{1b} \) over the range of pressures studied at 298 K and 315 K, and recommendations have been made for incorporations in atmospheric chemistry models.
**Executive Summary**

This project reports a comprehensive experimental examination of the kinetics and mechanism of the reaction of hydroxyl radicals with nitrogen dioxide, i.e.

\[
\text{OH} + \text{NO}_2 + \text{Air} \rightarrow \text{HONO}_2 + \text{Air} \quad (\text{1a})
\]

\[
\rightarrow \text{HOONO} + \text{Air} \quad (\text{1b})
\]

This reaction converts two reactive free radical species (OH and NO2) into a relatively long-lived species (nitric acid, HONO2) by the predominant product channel 1a. As a result, reaction (1) exerts a large effect on the efficiency of the chain reactions which produce ozone in photochemical smog, and destroy ozone in the lower stratosphere. In the urban atmosphere, reaction 1a is also an important source of nitric acid, which in turn plays a key role in secondary aerosol formation.

The predictions of ozone production in urban airshed models are highly sensitive to the rate coefficients for reactions 1a and 1b, especially under conditions of low VOC/NOx ratios; however, there is very little available laboratory data in air under relevant conditions of pressure and temperature, leading to significant uncertainty. The principal objective of this project was to reduce these uncertainties by carrying out two separate, but related, laboratory investigations:

**Investigation 1:** Measurements of the rate coefficient for the overall reaction \(k_1 = k_{1a} + k_{1b}\) under conditions relevant to the urban atmosphere. This work is described under Task 1 in the narrative summary.

**Investigation 2:** Measurements of the branching ratio for reaction 1 \(k_{1b}/k_{1a}\) as a function of total pressure. This work is described under Task 2 and Task 3 in the narrative summary.

Taken together, these two investigations provide a new quantitative recommendation for the rate constant for the loss of OH and NO2 by reaction (1) at ambient atmospheric conditions, and lower the statistical uncertainty. The principal results of the two investigations are summarized below:

**Investigation 1:** The Pulsed Laser Photolysis-Pulsed Laser-Induced Fluorescence (LP/LIF) technique was used to measure overall rate coefficients \(k_1\) over the pressure range 50-900 Torr of helium, oxygen, nitrogen and air buffer gases at 298 K and 315 K. This task used the laboratory resources of the NASA/Jet Propulsion Laboratory’s Chemical Kinetics and Photochemistry Group. In order to obtain the highest possible accuracy for the rate coefficient determinations, (1) the experiment was designed to operate at high repetition rates, to provide superior sensitivity especially at high air pressures, and (2) the concentration of NO2 in the LP/LIF reactor was measured directly in the reaction zone, using broad-band UV-visible spectroscopy. The reaction was found to be in the fall-off region between third-order and second-order kinetics. The low pressure- and high pressure-limiting rate coefficients for air buffer gas were found to be:

\[k_{o,1}(298 \text{ K}) = (1.6 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}\]

\[k_{e,1}(298 \text{ K}) = (3.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\]
315 K  \( k_{0,1}(315 \text{ K}) = (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \)
\( k_{\alpha,1}(315 \text{ K}) = (2.3 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

These values may be converted into bimolecular rate coefficients using the fall-off equation given in the narrative summary, which based on the expression used by the NASA Data Evaluation. For the temperature dependence, we recommend a linear interpolation between these two sets of parameters (holding the conventional parameters \( m \) and \( n \) set to zero). The resulting rate coefficients are 7-15% smaller than the values currently recommended by the NASA and IUPAC data evaluation panels.

**Investigation 2:** Task 2 involved an experimental determination of the branching ratio between channel (1a) and channel (1b). This is the first study to measure this ratio directly at atmospheric pressures. Experiments were performed with the California Institute of Technology (Caltech) Infrared Cavity Ringdown Spectroscopy (IR-CRDS) apparatus. The products of reactions 1a and 1b (HONO2 and HOONO, respectively) could be detected directly in absorption with this approach. Product yields were measured promptly following pulsed photolysis of gas mixtures over the pressure range 50-700 Torr of nitrogen buffer gas. The infrared absorbances of the products were converted into branching ratios using ratios of infrared band strengths for HONO2 and HOONO derived from the results of high-level quantum chemical calculations. The goal of Task 3 (a collaboration with theoretical chemists at the Ohio State University, Purdue University, and the University of Texas, Austin) was the theoretical determination of these band strength ratios, with ancillary experiments at Caltech performed to test the theoretical model. The branching ratio was found to depend weakly on the total nitrogen pressure. The results were fit to a second-order expression given by:

\[
k_{1b}/k_{1a} = (0.0630 \pm 0.0020) + (1.80 \pm 0.18) \times 10^{-4} P - (1.05 \pm 0.26) \times 10^{-7} P^2
\]

where \( P \) is the total pressure in Torr. No temperature measurements were performed, but previous work at low pressure suggests that there is at most a small variation in ratios over the temperature range 298 K to 315 K.

**Recommendation for Models**

The rate coefficients for the individual channels, \( k_{1b} \) and \( k_{1a} \), can be obtained by multiplying the total rate constant \( k_1(T) \) from Task 1 by the yield determined from the branching ratio. Due to the rapid decomposition of HOONO back to reactants OH and NO2 under lower atmospheric (1 atm, room T or higher) conditions, reaction (1b) is effectively a null reaction. Thus, only channel (1a) is relevant, and our reported value of \( k_{1a} \) can be used as the effective loss rate of OH and NO2 to form the sink HONO2. We therefore recommend that only the rate coefficient for formation of nitric acid be used in models:

**Reaction 1**

\[
k_{0,1a} (298 \text{ K}) = (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\alpha,1a} (298 \text{ K}) = (2.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
k_{0,1a} (315 \text{ K}) = (1.4 \pm 0.3) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\alpha,1a} (315 \text{ K}) = (1.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}
\]
Overall, the rates recommended in this study are somewhat lower than previous estimates and recommendations. It should be noted that this study covers a fairly narrow range of temperatures and pressures which are relevant to the lower atmosphere and cannot be generally extrapolated to all conditions. For the temperature-dependence, we recommend a linear interpolation between the two temperatures studied. Any future revisions of the total rate coefficient $k_1$, if based on measurements solely of the total reaction, must be multiplied by the branching ratio given above from Task 2. This correction will account for the HOONO channel.
**Narrative**

**Introduction**

Ozone formation in urban smog is controlled by a complex set of reactions which includes radical production from photochemical processes, catalytic cycles which convert NO to NO₂, and termination steps that tie up reactive intermediates in long-lived reservoirs. The reaction $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \ (1)$ is a key termination step because it transforms two short-lived reactive intermediates, OH and NO₂, into relatively long-lived nitric acid. For this reason, the spatial and temporal distributions of ozone from urban airshed models are highly sensitive to the rate constants assumed for reaction $(k_j)$. In addition, $\text{O}_3$ isopleths are very sensitive to $k_j$, particularly at low VOC/NOₓ ratios. This has important implications for $\text{O}_3$ control strategies. Russell and co-workers have shown that when the uncertainty in the $\text{OH} + \text{NO}_2$ rate constant is propagated through an urban airshed model, there is a corresponding uncertainty of 35 ppbv in the calculated $\text{O}_3$ concentration at a downwind site (a 25-50% uncertainty in total $\text{O}_3$).[1] Recent studies have shown that the $\text{OH} + \text{NO}_2$ reaction can also produce peroxynitrous acid, $\text{HOONO}$, in addition to nitric acid, $\text{HONO}_2$.\[2-5\] Complications arising from this channel introduce an additional 10-30% rate constant uncertainty.

This report elucidates key features of the $\text{OH} + \text{NO}_2 + \text{M}$ reaction including the overall rate constant $k_1$ and branching ratio for the two reaction channels $k_{1a}/k_{1b}$:

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \ (1a)
\]
\[
\rightarrow \text{HOONO} + \text{M} \ (1b)
\]

This information is essential to improve the predictive capabilities of urban airshed models with respect to oxidant formation, especially at downwind locations.

**Background**

**Kinetic Rate Parameters**

There have been numerous previous studies of reaction 1 using direct techniques. Most of these studies have been carried out in discharge-flow systems at total pressures under 10 Torr.[6-9] A number of studies have employed the flash photolysis, laser photolysis or high-pressure discharge-flow methods which permit higher pressures to be used.[10-21] Many of the high pressure studies encompass the pressure range around 1 atm and two studies focused on the high-pressure limit at pressures exceeding 100 atm.[17, 18]. However, there are only three studies that obtained data at 500 Torr and above using N₂ bath gas[10, 14, 15] and only the recent study of D'Ottone et al. [15] reached 700 Torr of N₂. The majority of the previous studies cover the range of conditions appropriate for the upper troposphere and stratosphere but not the urban atmosphere. The reason for the lack of data at pressures directly relevant to the urban atmosphere is because N₂ quenches electronically excited OH very efficiently. Previous studies using laser-induced fluorescence to measure the relative OH concentration suffer a drastic loss of sensitivity at N₂ pressures near 1 atm, introducing uncertainties into the derived rate constants which are too large to permit a meaningful value to be reported. Table 1 lists the studies which reported rate constants for reaction 1 near 1 atm pressure.
of N₂. The bimolecular rate constants at 298 K from the three studies listed in Table 1 are compared in Figure 1.

Table 1 - Previous studies of the OH + NO₂ + M reaction at N₂ pressures of 500 Torr and above.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Technique</th>
<th>Temp. Range K</th>
<th>N₂ Pressure Range Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anastasi and Smith (1976)</td>
<td>LP/RA</td>
<td>298</td>
<td>5-500</td>
</tr>
<tr>
<td>Donahue et al. (1997)</td>
<td>DF/LIF</td>
<td>298</td>
<td>2-600</td>
</tr>
<tr>
<td>D’ Ottone et al. (2001)</td>
<td>LP/LIF</td>
<td>273</td>
<td>100-700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>30-700</td>
</tr>
</tbody>
</table>


Figure 1 - Comparison of the effective bimolecular rate constant of Reaction 1 in pure Nitrogen at 298 K obtained in the studies listed in Table 1. The rate constant recommendations from the NASA[22] and IUPAC[23] evaluations are also indicated. Rate constants are in cm³ molecule⁻¹ s⁻¹.

The ordinate of these plots is the log of the effective bimolecular rate coefficient k₁, in units of cm³ s⁻¹. Equation (1) is a termolecular rate law, and the rate coefficient should have units of cm⁶ s⁻¹. However, the convention is to subsume the dependence on buffer gas concentration [M] in the termolecular rate expression into the effective coefficient k₁(T,[M]).
Figure 1 shows that the rate constant data from the three studies range over about a factor of 2 when extrapolated to 760 Torr total pressure. In particular, the data of the Harvard group, Donahue et al., disagrees substantially from that of D’Ottone et al, the only two studies that provide data above 200 Torr.

Rate constants obtained at specific values of air pressure and temperature are fitted to a semi-empirical expression derived by Troe and co-workers which describes the fall-off behavior for termolecular and unimolecular reactions in the regime in between the low pressure and high pressure limits.[24-26]

$$k([M], T) = \frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}} F_c^\left(1 + \frac{1}{N} \log\left(\frac{k_0[M]}{k_\infty}\right)^2\right)^{-1}$$  

Eq. 1

where:

- $k_0(T) = k_0^{300} (T/300)^{-n}$, the low-pressure limiting rate constant with units of cm$^6$ molecule$^{-2}$ s$^{-1}$
- $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$, the high-pressure limiting rate constant with units of cm$^3$ molecule$^{-1}$ s$^{-1}$
- $N = 0.75 - 1.27 F_c$, where the “broadening factor”, $F_c$, can be calculated from expressions derived by Troe and is different, in principle, for every reaction.

The NASA Panel on Data Evaluation recommends a value of $F_c = 0.6$ for every reaction in its tables,[22] while the IUPAC Data Evaluation Panel recommends a value of 0.41.[23] The NASA approach gives satisfactory fits to the experimental fall-off curves for all reactions of atmospheric interest, and the use of a uniform value of $F_c$ simplifies the entry of kinetic parameters in atmospheric models.

In this study we have fit the experimental data to the termolecular fall-off parameters for $k_1$, assuming the NASA value of $F_c=0.6$. Additionally, because the current study only determines the rate coefficient curve at two temperatures, we set $n = m = 0$.

Instead values of $k_0$ and $k_\infty$ are reported specifically for 298 K and 315 K. We recommend that a linear interpolation be made between the two temperatures.

The recommendations of the NASA/JPL[22] and IUPAC[23] data evaluation panels (upon which most atmospheric model calculations are based) for the pressure-dependent rate constant in Nitrogen differ by values greater than 25% in the range of pressures of tropospheric interest. This discrepancy is due to the fact that the IUPAC expression emphasizes a fit to the higher pressure limit obtained in the very high pressure measurements in He obtained by Hippler et al.[4], and is a sign of the uncertainty in the data.

There is only one data set available in Air at atmospheric pressures, that of D’Ottone et al.[15]

All studies were done in the pseudo-first-order kinetics regime, with excess NO$_2$, and uncertainties in the NO$_2$ concentration measurements typically led to significant systematic uncertainties in the reported rates. In addition, most rate measurements measure loss of OH, and do not explicitly take into account the existence of HOONO formation (with the exception of recent high pressure measurements by Hippler et al.).
Product Branching Ratio $k_{1b}/k_{1a}$

The existence of HOONO as a minor product of reaction (1) has also played a role in the disagreement between past experiments as it is sometimes ambiguous whether $k_1$ or $k_{1a}$ was measured. Robertshaw and Smith[20] first proposed the existence of the HOONO channel to resolve a discrepancy in the pressure dependence of reaction (1). The effective bimolecular rate constant $k_1$ has an anomalous fall-off curve; the observed high pressure rate constant $k_1^\infty$ is significantly larger than the high pressure limit extrapolated from low pressure data. The discrepancy can be removed if the HOONO channel is insignificant at low pressures, but becomes comparable to the HONO$_2$ channel at high pressures.

The pressure and temperature dependence of $k_{1a}$ and $k_{1b}$ has been modeled by Golden and Smith,[27] Matheu and Green,[28] and Troe.[29] While all three sets of calculations suggest that HOONO formation should compete with the HONO$_2$ channel in the reaction OH + NO$_2$, the resulting branching ratios at 1 atm and 298 K vary from >1% (Matheu and Green) to 2.5% (Troe) to 30% (Golden and Smith). However, rate constants, fall-off curves, and product yields cannot be calculated quantitatively from first principles, because our knowledge of the transition states, relaxation processes, and potential surfaces (especially for HOONO formation) is too limited. These models rely to some extent on experimental data, and thus cannot accurately predict branching ratios without direct measurements of HOONO.

Direct evidence for formation of HOONO in the gas phase by reaction (1b) has been reported only recently. In 2001, Donahue et al.[3] described a series of $^{18}$OH isotopic scrambling experiments that support the existence of reaction (1b) and led to an estimate of the low pressure branching ratio of $k_{1b}/k_{1a} = 0.17$ at room temperature. Nizkorodov and Wennberg[5] then reported the first spectroscopic observation of gas phase HOONO from the reaction of OH and NO$_2$. They reported observation of the 2$\nu_1$ overtone spectrum of HOONO formed in a low pressure discharge flow cell using action spectroscopy, detecting OH by LIF after predissociation of the overtone-excited molecules. They observed several bands which they tentatively assigned to the conformers of HOONO and combination bands. They estimated that the HOONO yield was 5±3% at 253 K and 20 Torr. In 2002, Hippler et al.[4] reported kinetic evidence for channel 1b. They observed a bi-exponential decay in the OH LIF signal in the reaction OH + NO$_2$ at 5-100 bar and 430-475 K, which they modeled as rapid loss of OH by reactions (1a) and (1b), followed by slower decomposition of HOONO by the reverse rate $k_{-1b}$. They found the enthalpy of reaction 1b at this temperature range to be $\Delta H_2(0)= 19.8$ kcal/mol, in good agreement with the theoretical predictions of the cis-cis HOONO dissociation energy $D_0$.

In 2002 at the Okumura laboratory at Caltech, Bean et al.[2] made the first spectroscopic measurement of the HOONO/HONO$_2$ branching ratio produced from reaction (1) based on direct infrared absorption detection of the OH stretch fundamental vibrational bands of HOONO and HONO$_2$. They accomplished this by exploiting the exceptionally high sensitivity of infrared cavity ringdown spectroscopy. In those experiments, the HOONO yield formed in a low pressure discharge flow cell was measured to be 8.2±2.0/-2.7% at room temperature and a pressure of $P = 20$ Torr in a mixture of He, N$_2$ and other gases. The results are consistent with the recent Golden-
Barker-Lohr calculations. However, they only pin down the low pressure limit, and do not provide information on the rate at atmospheric pressure, which lies in the critical fall-off region. Furthermore, the branching ratios were determined using theoretically computed absorption-cross sections derived in the harmonic limit.

**Scope of the Present Work**

New experimental measurements have been performed under this Contract, to address directly the deficiencies in the laboratory database for reaction (1) under conditions relevant to the troposphere boundary layer. Specifically:

- Highly accurate measurements of $k_1$ over a range of conditions relevant to the urban atmosphere ($M = \text{air}, 273 < T < 310 \text{ K}, 50 < P < 900 \text{ Torr}$) have been carried out with an improved Pulsed Laser Photolysis - Pulsed Laser Induced Fluorescence technique.
- The pressure-dependent branching ratio, $k_{1b}/k_{1a}$ has been measured over a range of conditions relevant to the urban atmosphere ($T=298 \text{ K}, 25 < P < 760 \text{ Torr}$).
- High level calculations were performed, including mechanical and electrical anharmonicity, to better estimate the relative HOONO and HONO$_2$ absorption band strengths.

The measured total rates of reaction (1) have been combined with the measured pressure-dependent branching ratio to calculate separate falloff parameters for the individual pathways, $k_{1a}$ and $k_{1b}$. The work reported here reduces uncertainties in the rate constant for reaction (1).
Introduction

The radical termination reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \) (1) is an important sink for \( \text{HO}_x \) and \( \text{NO}_x \) radicals in the troposphere and stratosphere. Model predictions of tropospheric ozone production and stratospheric ozone loss are highly sensitive to the rate constants of this radical termination reaction. The uncertainty in rate constant for reaction (1) has important consequences for the prediction of tropospheric ozone production and photochemical smog.

There have been numerous previous studies of reaction (1) using different techniques covering the range of conditions appropriate for the upper troposphere and lower stratosphere. There are limited kinetics studies of reaction (1) relevant to urban tropospheric conditions (~760 Torr pressure with \( \text{M} = \text{air}, \text{N}_2 \) and \( \text{O}_2 \)). The available rate constants from the previous studies vary by a factor of two. Hence an accurate re-determination of the temperature and pressure dependences of rate constants for reaction (1) is a high priority for atmospheric photochemical model studies.

The main objective of this work is to measure highly accurate rate constants for reaction (1) over a range of conditions relevant to the urban atmosphere (\( \text{M} = \text{air}, T = 298 \) and 315 K). In the present work, the measurement of rate constants have been carried out under tropospheric conditions with an improved Pulsed Laser Photolysis - Pulsed laser Induced Fluorescence technique augmented by in situ optical absorption measurements of \( \text{NO}_2 \) concentration.

Experimental

The experimental investigation of the title reaction was carried out using the Pulsed Laser Photolysis, Laser Induced Fluorescence (PLP-LIF) technique in which \( \text{OH} \) radicals are generated by pulsed photolysis of suitable precursors on time scales that are short compared to the subsequent decay, and are detected by laser induced fluorescence.

Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence

A schematic diagram of the PLP-LIF system is shown in Figure 2. The experiments were carried out using an octagonal stainless steel reaction cell. Gas mixtures entered the mixing column \( \approx 30 \) cm upstream of the photolysis region to ensure proper mixing of the gas. The gas flows were controlled by a gas handling system with calibrated flowmeters. Flowmeters were calibrated volumetrically, by measuring the time rate of displacement of soap bubbles in calibrated volumetric glassware. The accuracy following calibration was \( \pm 0.5\% (1\sigma) \). The temperature inside the reaction cell was measured by using a J-Type thermocouple that could be inserted into the reaction volume where the focus of the telescopic lens system and the laser beams intersect. The pressure in the cell was monitored with 10 and 1000 Torr capacitance manometers over the range of 50 to 900 Torr of buffer gases (Air, \( \text{N}_2 \), \( \text{O}_2 \) and \( \text{He} \)). The capacitance manometers were recently purchased and the factory calibration was used. Pressure readings should be accurate to \( \pm 1\% (1\sigma) \). Typical flow rates, regulated using calibrated mass flow controllers, were between 500 and 1400 sccm, resulting in linear gas velocities.
in the reaction cell of > 50 cm s\(^{-1}\). These conditions ensured that a fresh gas sample was photolyzed at each laser pulse, and prevented build up of products.

The laser pump, laser probe and the fluorescence detection axes were mutually perpendicular to each other as shown in Figure 2.

Figure 2 - Schematic diagram of the PLP-LIF system used to study the kinetics of OH + NO\(_2\) + M at high pressures (~800 Torr) of Air, N\(_2\), O\(_2\) and He at room temperature.

**Generation of OH radicals**: The photolysis of HONO\(_2\) at 248 nm (KrF excimer laser) was used as the source of OH radicals. The repetition rate of the photolysis laser was 20-30 Hz. Typically, about 10\(^{15}\) HONO\(_2\) cm\(^{-3}\) were photolyzed at a laser fluence of (0.6-1.1) mJ cm\(^{-2}\) to generate \(\approx (5-10) \times 10^{10}\) cm\(^{-3}\) of OH in each photolysis pulse. HONO\(_2\) was transported to the photolysis cell by bubbling a 15-20 sccm flow of Air, N\(_2\), O\(_2\) or He through neat anhydrous HONO\(_2\) prepared in the laboratory.

\[
\text{HONO}_2 + \nu (248 \text{ nm}) \rightarrow \text{OH} (X^2\Pi, \nu = 0) + \text{NO}_2
\]  

(2)

**Detection of OH radicals**: The time-resolved OH signal, which was required to determine rate constants for reaction 1, was obtained by laser-induced fluorescence. Excitation of the \(A^2\Sigma (\nu = 1) \leftarrow X^2\Pi (\nu = 0), Q_{11} (1)\) transition at 281.997 nm was achieved using the frequency doubled emission from a diode-pumped solid state (DPSS)-pumped dye laser.
(Rhodamine 6G) operating at a pulse repetition rate of 10 kHz. Fluorescence from OH was collected by a lens and baffle system through a 308 nm interference filter and detected by a photomultiplier tube (PMT) operating in photon counting mode. The photon count rate vs. time was recorded by a multi-channel scalar board in a personal computer. In this way, the OH kinetic decay is recorded from each photolysis pulse. This differs from the approach used in most other LP/LIF systems in which the OH signal is measured at a fixed delay time with respect to the photolysis pulse using analog detection. The OH kinetic decay is built up from a series of photolysis pulses with successively longer OH probe pulse delays.

The OH fluorescence is quenched efficiently by N2, O2 and air, hence the fluorescence yield and the signal-to-noise ratio degrade as the pressure increases. In the present experimental system, due to the high repetition rate (10 kHz) of the OH probe laser and the use of photon counting detection with enhanced collection efficiency, the OH detection sensitivity is enhanced. These features of the JPL LP-LIF apparatus make it possible to measure rate constants at total pressures of 1 atm and above with high measurement precision.

Optical Absorption measurements of NO2

The concentration of the excess reactant (NO2) was determined by in situ optical absorption in the reaction cell. The NO2 absorption spectrum between 410 - 450 nm was recorded by a spectrograph/diode array system with a resolution of ~ 0.2 nm. The concentrations were determined by least-squares fitting of the measured data to a reference UV absorption spectrum[30] degraded to a spectral resolution of 0.2 nm.

Figure 3 shows the measured spectrum, scaled reference spectrum and fit residuals for a typical NO2 concentration determination using the in-situ spectrometer. The estimated uncertainty of the [NO2] measurement method was ≤ 5% (2σ), with the principal contribution to the uncertainty arising from uncertainties in the absorption cross sections of the reference spectrum.

Nitrogen (99.9993%), Oxygen (99.9993%), Air (99.9993%) and Helium (99.9993%) buffer gases were supplied by Air Products and used without further purification. NO (99%) was supplied by Matheson. NO2 was synthesized from the reaction of NO with excess O2 and stored in 20L darkened glass storage bulbs. Anhydrous HNO3 was prepared in the laboratory from the reaction of NaN03 with H2SO4.
Results and Discussion

The PLP-LIF studies were carried out under pseudo-first order conditions with
\([\text{NO}_2] \gg [\text{OH}]_0\). The decay of OH is described by:

\[
[\text{OH}]_t = [\text{OH}]_0 \exp\left[-(k_1[\text{NO}_2] + d)t\right]
\]

where \([\text{OH}]_t\) is the OH concentration at time \(t\) after the laser pulse, \(k_1\) is the bimolecular rate coefficient for the reaction with \(\text{NO}_2\) and \(d\) is a parameter which accounts for diffusion of \(\text{OH}\) out of the reaction zone, and reaction of \(\text{OH}\) with \(\text{HONO}_2\). The use of low OH concentrations ensures that secondary loss of OH is very low. This was confirmed by showing that the variation of the photolysis laser fluence, and thus radical concentrations, by a factor of three had no measurable influence on the measured first-order OH decay constant.

Overview of Results  Figure 4 shows a plot of \(k_1\) versus pressure in \(M = \text{air, N}_2, \text{O}_2\) at 298 K. The data show pressure dependences that are typical of reactions that are in the fall-off regime between second and third order behavior. The reaction collision

\[\]
Efficiencies vary in the expected manner for these buffer gases ($M = \text{air, } N_2, O_2$) with $N_2$ being the most effective collisional partner.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Fall-off curve for the OH $+ \text{NO}_2 + M$ (air) reaction, along with $M = N_2$ and $O_2$ at 398 K.}
\end{figure}

The total error in $k_1$ at any particular pressure covered in the present work is $\approx 7\%$ and derives mainly from estimated errors in the measurement of the $\text{NO}_2$ concentration, absorptions path length and the fitting error. The 7% error is represented by the vertical error bars at each pressure in Figure 4. The rate constants obtained as a function of buffer gas concentration [$M$] have been fitted to a semi-empirical expression derived by Troe and co-workers which describes the falloff behavior for termolecular and unimolecular reactions in the regime in between the low pressure and high pressure limits[10, 13, 15] in Eq. (1), as described above in the Introduction. In the present study, the NASA value of $\tilde{r}_c=0.6$ has been assumed.
Nitrogen at 298 K

Our measurements carried out in N$_2$ buffer gas are compared with prior studies [10, 13-15, 21] and the NASA/JPL 2002[22], IUPAC 1997[23] recommendations in Figure 5 over the pressure range 50-900 Torr. At pressures below 100 Torr, the data sets agree within the respective error bars. Above 200 Torr, there are two distinct set of data. Our measurements lie approximately 10% lower than the data of D'Ottone et al[15] and 20% above the data of Brown et al, Wine et al, and Donahue et al. [13, 14, 21]

![Figure 5 - Plot of our second order rate constants ($k_1$) for OH + NO$_2$ in N$_2$ at 298 K compared with literature data.](image)

Most of the previous measurements in N$_2$ buffer gas have been limited to 250 Torr, excluding the measurements of D'Ottone et al[15] and Donahue et al[14, 31] whose data extended to 700 Torr of N$_2$. In the present experiments, we have extended the fall-off curve to 900 Torr of N$_2$ and air. Table 2 presents a comparison of the various kinetic methods and NO$_2$ measurement techniques employed in previous studies. The measurements of D'Ottone et al [15] used the PLP-LIF technique which is similar to the present work while Donahue et al[14] used the high pressure flow tube technique. Comparing our data with that of D'Ottone et al [15] over the pressure range of 50 – 900 Torr in N$_2$ bath gas, a discrepancy of 10% is observed. This is possibly related to the differing methods for the measurement of [NO$_2$], the principal source of uncertainty in the rate constant determination. As shown in Table 1, D'Ottone et al [15] used external absorption cells located upstream and downstream of the reaction cell to measure [NO$_2$].
The absorption measurements were carried out with a Hg lamp monitoring the absorption at a single wavelength (365 nm). In the present experiment, we measure the NO\textsubscript{2} concentration inside the reaction cell rather than outside the cell. Also we record the absorption spectrum between 410 to 450 nm using spectrograph and photodiode array which enables the entire spectrum to be fitted instead of a single wavelength. With this technique, we avoid errors due to intensity drift in the light source. Also, the signal-to-noise of the measurement is significantly enhanced due to the multiplex advantage.

Above 200 Torr pressure, the NASA/JPL 2002[22] and IUPAC 1997[23] recommendations overestimate our data by 10%-25%. The recent IUPAC (2005) recommendations for M = N\textsubscript{2} are in excellent agreement with the present data. A fit of our data in M = N\textsubscript{2} to the JPL formulation of the three-body fall-off expression gives

\[ \begin{align*}
  k_{0,1}(298 \text{ K}, \text{N}_2) &= (1.7\pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\
  k_{\infty,1}(298 \text{ K}, \text{N}_2) &= (3.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\end{align*} \]

compared with values \( k_0 = 2.0 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \) and \( k_\infty = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) recommended in NASA/JPL 2002.

Table 2- Summary of literature measurements of \( \text{OH} + \text{NO}_2 + \text{M} \)

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Method</th>
<th>Location of absorption measurement</th>
<th>NO\textsubscript{2} calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wine et al (1979)</td>
<td>FP/RF</td>
<td>External absorption cell</td>
<td>Hg lamp(365nm)</td>
</tr>
<tr>
<td>Anastasi &amp; Smith (1976)</td>
<td>FP/RA</td>
<td>------</td>
<td>From measured mole fraction</td>
</tr>
<tr>
<td>Brown et al (1999)</td>
<td>PLP/LIF</td>
<td>External absorption cell</td>
<td>Hg lamp(365nm)</td>
</tr>
<tr>
<td>Donahue et al (1997)</td>
<td>HP-DF/LIF</td>
<td>External absorption cell</td>
<td>Indirect (using tracer)</td>
</tr>
<tr>
<td>D'Ottone et al (2001)</td>
<td>PLP/LIF</td>
<td>External absorption cell</td>
<td>Hg lamp(365nm)</td>
</tr>
<tr>
<td>This work</td>
<td>PLP/LIF</td>
<td>Inside the reaction cell</td>
<td>Spectral fitting between 410 - 440nm</td>
</tr>
</tbody>
</table>
Oxygen at 298 K

Figure 6 shows our measurements in M = O₂ (298 K) over the pressure range 50-600 Torr compared with the data from previous studies. Our data agree with the results of D'Ottone et al.\[15\] at pressures below 200 Torr. Above 200 Torr, our data are about 5% lower than the data of D'Ottone et al. The room temperature data in M = O₂ compared with N₂ is shown in Figure 4. As is consistent with previous work, we find that molecular oxygen is a less efficient stabilizer, leading to lower (5-20%) bimolecular rate constants.

Figure 6 - Plot of our second order rate constants (k₁) for OH + NO₂ in O₂ at 298 K compared with literature data
**Air at 298 K**

Our measurement in \( M = \text{air at 298 K} \) compared with D’Ottone et al. is shown in Figure 7. Again, our results are lower than the data of D’Ottone et al [15] by 10-15\%. A fit of our data \( M = \text{air} \) to the JPL formulation of the three-body fail-off expression would give \( k_0 = (1.6 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{molecule}^{-2} \text{s}^{-1} \) and \( k_x = (3.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \).

![Graph](image)

**Figure 7** - Plot of our second order rate constants \((k_i)\) for \( \text{OH} + \text{NO}_2 \) in Air at 298 K compared with literature data.
Air at 315 K
Measurement of rate constants in M= air were carried out above room temperature (315 K). A comparison of the 298 K and 315 K data is shown in Figure 8. These data are fit to the fall-off expression, yielding: $k_0 = (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $k_\infty = (2.3 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Figure 8 - Plot of our second order rate constants ($k_1$) for OH + NO$_2$ in Air at 315 K compared with the room temperature data.
Helium at 298 K

We performed additional measurement in $M = \text{He}$ at room temperature, because the most extensive studies of the pressure dependence of reaction 1 have been done in helium. Quenching of LIF signal from He is substantially lower, so far more data is available over a wider pressure range. Figure 9 shows a comparison of the pressure dependence obtained in the work together with prior studies in helium. Over the range of pressures studied here, 50 – 900 Torr, the agreement between our data and prior studies is quite good including the data point at 300 Torr reported by Forster et al.[17]. Extrapolation of our data above 1000 Torr, $M = \text{He}$ appears to be somewhat less consistent with the data obtained in the high pressure experiments (1 -150 atm) of Forster et al. [17] (scaled down by the later correction factor of Hippler et al.) and of Hippler et al.[4]. The good agreement with experiments at similar pressures provides additional confidence that our approach is sound.

![Figure 9 - Plot comparing our measurements of $k_1(298)$ in He with literature data.](image_url)
Summary and Implications

In the present experiment, OH + NO₂ +M rate constants in N₂, O₂, air and He at 298 K and 315 K have been measured under urban tropospheric conditions. The overall uncertainty in the measured rate constant is estimated to be ~ 7%. Our results are significantly lower than the NASA/JPL 2003[22] and IUPAC 1997[23] recommendations at pressures above 200 Torr, but are in excellent agreement with the IUPAC 2005 recommendations. Our results in N₂, O₂ and Air show measurably different third-body efficiencies in the range of pressure between 50 and 800 Torr, O₂ being less efficient than N₂. Our results in He are in good agreement with the data of Anastasi & Smith[32], D’Ottone et al[15] and Wine et al[21] but are considerably different from the very high pressure measurements of Hippler et al[4] and Forster et al[17]. Future experiments will extend these measurements to low temperature.

The three body recombination rate in air in the present study is consistently lower than prior literature data. At pressures relevant to the lower troposphere (~700 Torr) in air, the recombination rate differs by 15 - 20%. This lowering of the rate constants for this reaction 1 as seen in the present study would increase the efficiency of the HOₓ-driven catalytic ozone destruction cycle in the stratosphere. In the troposphere, the observed decrease in the rate constant at pressures near 1 atm will result in increased ozone formation. Since our experiments in Task II indicate that HOONO decomposes slowly compared to the measurement time in this experiment (see below), the measurements here are determinations of the total loss of OH from reaction 1, \( k_i = k_{1a} + k_{1b} \).
Task II - HOONO/HONO$_2$ Branching Ratio (Caltech)

Introduction

The importance of the reaction OH + NO$_2$ + M in the troposphere, and especially polluted urban environments, stems from its production of nitric acid (HONO$_2$). Nitric acid is a stable molecule which acts as a sink for HO$_x$ and NO$_x$ radicals, both of which are critical to the formation of photochemical smog. It has been well documented in the past few years that, in addition to nitric acid, reaction 1 also produces the less stable peroxynitrous acid (HOONO) [2, 4, 5, 14]. HOONO is weakly bound (19.6 kcal/mol), and re-dissociates rapidly under atmospheric conditions. HOONO thus does not act as a sink for HO$_x$ and NO$_x$, and the effective loss rate is determined solely by the rate coefficient $k_{1a}$. As a result, the interpretation of the measured total rates of reaction 1 for the purposes of airshed modeling should explicitly take into account the branching ratio of HOONO to HONO$_2$.

This branching ratio has been measured previously at 20 Torr of a He/H$_2$/N$_2$ mixture by using infrared cavity ringdown spectroscopy (IR-CRDS) to measure the integrated absorbance of both HONO$_2$ and HOONO[2]. The most stable conformer HOONO is the cis-cis isomer. Studies show that this isomer is the only one present at room temperature.[33] The OH stretch frequency of cis-cis HOONO is shifted 250 cm$^{-1}$ to the red of HONO$_2$ by an internal hydrogen bond, thus providing a unique spectroscopic signal for the two molecules. The high sensitivity of cavity ringdown is ideal for this measurement due to the low concentrations of HOONO. By coupling a pulsed ringdown apparatus to a photolysis cell for the generation of OH radicals, the HOONO branching ratio can be measured over a wide range of atmospherically-relevant pressures.

Basic Approach

In this work, we initiate the radical chemistry by laser photolysis of a gas mixture containing OH precursors in the presence of NO$_2$. This approach is in contrast to the previous branching ratio determination by our group, in which we used a low pressure discharge flow method to generate OH. The photolysis method allows us to produce sufficient OH at high pressures in a clean manner. All kinetics were modeled to take into account secondary chemistry.

We again use IR-CRDS for product detection, because it provides superior sensitivity, approximately two to four orders of magnitude better than conventional absorption methods with time resolution of 10-100 µs. The high temporal resolution allows us to look at products promptly, after reaction has been completed but well before secondary reactions, diffusion, or wall losses, can change the apparent product concentrations.

Product abundances are determined by obtaining the complete $v_1$ (OH stretch) band in the infrared for both HOONO and HONO$_2$ at each pressure, and integrating to obtain the band absorbance. The spectral resolution is sufficient to identify unambiguously the contribution of each species, even in the presence of interference from background, either baseline effects or absorption by other molecules. The actual concentrations are derived using our best theoretical estimates of the relative HOONO and HONO$_2$ $v_1$ band strengths (see Task 3).
The primary complications are the following:

- The radical concentrations are fairly high (and atypical of the natural atmosphere), but all relevant reaction rates are well known and the secondary chemistry can be modeled. Experimental conditions were designed to ensure the least bias due to secondary reactions. Furthermore, unlike solution phase chemistry, the collisions are predominantly still in the bimolecular regime. Even at 1 atm, the duration of a collision (picoseconds or less) is 100 to 1000 times shorter than the mean time between collisions (order of 1 nanosecond), which will be dominated in any case by collisions with the buffer gas.

- The OH is initially produced with an excess of vibrational energy. Under the conditions of the current experiment, the OH should be relaxed to thermal temperatures. As a check, we have performed additional experiments adding SF6 (a good vibrational quencher) and used alternate chemistry (reactions involving CH4).

- Since we elected to form OH by chemistry that also initially involved H atoms, we were unable to perform the experiments in the presence of O2. Some H atoms could recombine to form H2O2.

- In order to convert from our measured integrated absorbances for the two species to relative concentrations, we rely on calculations of the ratio of their integrated absorption cross sections. These calculations are discussed in detail in Section III below.

- The use of IR-CRDS to measure the branching ratio introduces a further complication: Integrated intensities measured by cavity ringdown methods when the linewidth of the laser is larger than that of the absorber (such as ours) have been shown to be quantitative only for very small absorbances[34-36] and are nonlinear at high absorbances. The HOONO measurements fall in the small absorbance limit, but the large HONO2 absorbances generated in these experiments fall outside the linear regime of our CRDS apparatus. We carried out calibration experiments for the nitric acid band as a function of pressure and concentration so that our observed integrated absorbances could be corrected to represent the true integrated absorbance of HONO2.

### Methods and Materials

**Photolysis and Chemistry**

We initiated the reaction OH + NO2 + M via the following reaction scheme.

\[
\begin{align*}
O_3 + \text{hv}(248\text{nm}) & \rightarrow O(^1D) + O_2 \quad (3) \\
O(^1D) + H_2 & \rightarrow OH + H \quad (4a) \\
H + NO_2 & \rightarrow OH + NO \quad (5) \\
OH + NO_2 + M & \rightarrow HONO_2 + M \quad (1a) \\
& \rightarrow HOONO + M \quad (1b)
\end{align*}
\]

Both reaction 4a and reaction 5 are known to produce OH with a high degree of vibrational excitation.[37] As a result, some experiments were carried out with the OH production from the reaction

\[
O(^1D) + CH_4 \rightarrow OH + CH_3 \quad (4b)
\]
While this chemistry was an efficient and clean way to make OH with few unwanted byproducts, it required a system free of O\textsubscript{2} to prevent the rapid formation of HO\textsubscript{2}. As a result, the branching ratio measurements were all done in a gas mixture which was mostly N\textsubscript{2} (>90%) with the remainder essentially all H\textsubscript{2}. While these measurements could not be carried out in air, the branching ratio is not expected to have a significant dependence upon the nature of the bath gas.

Ozone was produced from an ozonizer (Osmonics V10-0) and then trapped on silica gel (6-12 mesh) at -78\degree C. The ozone was then delivered to the cell by flowing nitrogen across the silica gel. The concentration of ozone in the nitrogen flow was measured by 248nm absorption through a 1cm quartz cell upstream of the reaction cell and was stable over the course of a day. Hydrogen and methane were introduced as pure gas flows. NO\textsubscript{2} was introduced as a 4% mixture in nitrogen (Matheson). All reactant gases and a nitrogen dilution flow were mixed in a glass cross about 5 cm from the photolysis region. All gas flows were through calibrated mass flow transducers (Edwards Model 831 and Omega Model 1700) so that final concentrations in the photolysis cell could be calculated. Calibration was performed as described above in Task I and did not influence our branching ratio measurements. Concentrations of the reactant gases were varied systematically to check for any unexpected correlations. Typical concentrations used for the pressure-dependent measurements are listed in Table 3.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration range / molecules cm\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{3}</td>
<td>1-10×10\textsuperscript{15}</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>1-10×10\textsuperscript{16}</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>1-10×10\textsuperscript{17}</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>balance to pressure</td>
</tr>
</tbody>
</table>

The apparatus used for these measurements was a gas flow cell which combines pulsed laser photolysis for the initiation of chemistry and pulsed infrared cavity ringdown spectroscopy for the detection of products (see Figure 10). The general design uses a rectangular photolysis cell which is coupled on both ends to Teflon blocks. These blocks provide feedthroughs for gas inputs, a pumpout port and pressure gauges, and serve to link the photolysis cell to the ringdown mirrors. Pressures were measured with capacitance manometers which had recently been calibrated relative to calibration standards at JPL and were therefore accurate to ±1\% (1\sigma).
Three photolysis cells with different lengths were employed for the experiments. Progressively longer cells were fabricated to study the impact of lower initial radical concentrations while maintaining reasonable signal to noise. The shortest cell was made entirely of quartz and was 3 cm long with interior dimensions of 1 cm x 1 cm. The other two cells were made from square stainless steel tubing (1 cm x 1 cm inside) with Suprasil windows glued onto cut-out sections on the sides. One cell was 7.5 cm long with a 6 cm photolysis window. The other was 13.5 cm long with a 10 cm photolysis window. In both cases the photolysis windows were epoxied to the cells with Torr Seal. Both stainless steel cells were coated with FluoroPel polymer to minimize interactions between the reagents and the cell walls.

Photolysis was initiated with the 248 nm pulse from a KrF excimer laser. The output beam was a slightly diverging 1 cm x 2.5 cm rectangle but was subsequently reshaped using a +50 cm focal length cylindrical lens and -30 cm focal length circular lens to match the width of our photolysis window on the long axis of the beam and create a gently focusing 2-5 mm beam along the short axis. The laser flux was varied over the range 1-50x10^15 photons cm^-2 to test for any possible dependence of the measured branching ratio on the photolysis energy.

**Detection of Reaction Products**

Absorption spectra of the reaction products were recorded by pulsed cavity ringdown spectroscopy.[38-40] A mid-infrared laser pulse was injected into an optical cavity made by two high-reflectivity infrared mirrors (R = 99.98%, centered at \( \lambda = 2.8 \) \( \mu m \), 6 m radius of curvature) sealed to the ends of the detection cell. Each mirror was separated from the main flow of gas by a purge volume approximately 15 cm long.
Nitrogen flowed over the mirrors and through the purge volumes to protect the mirrors and to minimize losses in reflectivity due to deposition.

We produced tunable (2.7-3.3 µm) mid-IR in a two-stage optical parametric amplifier (OPA) by mixing the second harmonic of an Nd:YAG laser and the output of a tunable dye laser (DCM laser dye) in a pair of KTP crystals.[41] The OPA produced an IR beam with energy $E \approx 1$ mJ/pulse and diameter $d \approx 2$ mm after transmission through three filters to remove the residual 532 and 630 nm light. The IR linewidth was $\Gamma \approx 1$ cm$^{-1}$. The IR wavelength was typically calibrated using the frequencies of known HONO and HONO$_2$ peaks in the spectrum. The IR beam was sent through a series of two iris and a +1 m focal length lens to improve the beam quality and then aligned into the cavity. The residual beam exiting the cell was focused tightly onto a 1-mm diameter InSb detector (Infrared Associates). Each ringdown trace was amplified and then accumulated with a 50 MHz bandwidth digital oscilloscope card with 14-bit digitizer (GageScope 1450). For each point in a spectrum, typically 16 ringdown traces were averaged and then fit to a single exponential function and constant baseline by the Levenberg-Marquardt algorithm.[42]

The ringdown lifetime of radiation trapped in an evacuated optical cavity of length $L$ with mirrors of reflectivity $R$ is $\tau_0 = L/c(1 - R)$, where $c$ is the speed of light.[43-45] Typical empty-cell ring-down times were $\tau_0 \approx 10$ µs, in good agreement with the stated mirror reflectivities (99.98% at the peak wavelength). In the presence of an absorber, the lifetime is given by $\tau = L/c(1 - R + \alpha L_s)$, where $\alpha = [X]*\sigma_X$ is the extinction coefficient of the absorber X and $L_s$ is the absorption path length through the sample. The measured extinction coefficient is then

$$\alpha = \frac{L}{cL_s} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

Spectra of reaction products were typically recorded by scanning the spectral region of interest alternating 16 shots with the excimer on and then 16 shots with the excimer off and then subtracting the two. This subtraction eliminated background due to species present in the absence of reaction, as well as to the wavelength-dependent ringdown loss of the mirrors. The movement of the dye laser and OPA as well as the collection, averaging, and fitting of ringdown traces are controlled by a program written in Labview. Excimer on-excimer off spectra were then fit with reference spectra of all known bands in the region of interest and the integrated absorbance of the $\nu_1$ bands of HONO$_2$ and HOONO measured.

**HONO$_2$ Calibration Experiments: The correction factor ($1+f$)**

The $\nu_1$ band of nitric acid has a highly congested spectrum containing many very sharp features. The apparent cross section of our ringdown apparatus for such a species at large concentrations is likely not constant due to a systematic under-emphasis of the narrowest and strongest features when the ringdowns are fit to a single exponential function. In order to correct our measured integrated absorbances so they reflect the true concentration of nitric acid, correction factors have been derived both theoretically and experimentally.

A program has been written which convolves an assumed high resolution spectrum and laser profile into an effective multi-exponential CRDS decay at each
spectral point. These multi-exponential decays are then fit to a single exponential by the same algorithm used in our CRDS experiments. For our assumed spectrum we used the Doppler-limited FTIR spectrum of nitric acid obtained from Goldman and Pine, as shown in Figure 11, pressure broadened with Lorentzian lineshapes to various pressures. The results shown here assume a Gaussian laser profile with FWHM = 1.0 cm⁻¹, shown in the top portion of Figure 11, although the results were insensitive to the precise shape and width of the assumed laser profile. To make quantitative comparisons to our experimental results it was also necessary to assume $\sigma_{\text{obs}} = 1.23 \times 10^{-17}$ cm molecule⁻¹ for the $v_1$ integrated intensity and a typical background $1/\tau_0 = 144000$ s⁻¹.

![Figure 11 - Spectrum used for CRDS simulations of the HONO $v_1$ integrated absorbance. Inset shows an expanded portion of the spectrum with the Gaussian laser profile used shown in grey.](image)

A schematic of the apparatus used to verify the results of these calculations is shown in Figure 12. Nitric acid was introduced by flowing N₂ through a temperature-controlled bubbler containing pure nitric acid. The nitric acid flow was diluted with N₂ before entering the first flow cell (Cell A) where the concentration was measured by direct UV absorption. The nitric acid concentration was then further diluted with N₂ before entering the second flow cell (Cell B) where the absorption to be calibrated is measured with IR-CRDS. The ringdown mirrors, data collection, and fitting of ringdown
Traces for these experiments were identical to those described above.

Cell A was 30.2 cm long with an inside diameter of 1.0 cm and UV-grade quartz windows glued to the ends. The nitric acid concentration was measured in Cell A by UV absorbance at 184.9 nm. 184.9 nm radiation is produced by an Hg pen-ray lamp (UVP), collimated through a series of lenses and irises, passes through cell A, and is detected with a PMT using a 184.9 nm interference filter to eliminate detection of 254 nm radiation. The second flow cell, cell B, was the same as for the ringdown apparatus described above, but with the photolysis cell in the center replaced by a glass flow cell. The center of cell B, which contained the nitric acid, was 18.0 cm long with an inside diameter of 2.0 cm. The total mirror-mirror length of Cell B was 47 cm, but had purge flows of N₂ over the ends to prevent the high reflectivity ringdown mirrors from interacting with nitric acid.

The effective pathlength of sample, $L_s$, was measured independently under the flow and pressure conditions used in these experiments in order to quantify diffusion from the sample region into the purge volumes. The apparatus used for measuring $L_s$ was identical to Cell B described above, but with the CRDS mirrors replaced with UV-grade quartz windows.

All flows are measured with Edwards mass flow transducers. The transducers were calibrated volumetrically by measuring the displacement of soap bubbles at various flow rates. The estimated accuracy following calibration was ±0.5% (1σ). The pressure is measured from ports in the center of both cells using MKS Baratron capacitance manometers. The manometers were calibrated relative to standardized calibration heads at JPL. The estimated accuracy following calibration was ±1.0% (1σ).
The nitric acid used was synthesized by adding concentrated H$_2$SO$_4$ to NaNO$_3$ under vacuum and collecting the nitric acid vapor in a liquid N$_2$ cold trap. When not being used the sample was stored in a liquid N$_2$ dewar. After storage, the sample would contain small quantities of the decomposition product NO$_2$. After bubbling for about 5 minutes, the NO$_2$ would completely degas leaving pure nitric acid. This process was confirmed by connecting our flow system to a Nicolet FTIR spectrometer and monitoring the NO$_2$ absorption in time. All tubing, valves, and joints between and including Cell A and Cell B were either glass or Teflon to minimize surface decomposition. All nitrogen used was flowed through a sieve trap to ensure the complete removal of trace water.

Results

A sampling of the results of our HONO$_2$ calibrations is shown in Figure 13. The calculations and experiments were in good agreement. Both showed the expected lowering of apparent integrated intensity for the $v_1$ band as the concentration increased. As expected, the amount of absorbance “lost” at a given concentration decreased as the pressure increased, due to pressure broadening of the spectrum. As a result of these calibrations, the observed nitric acid $v_1$ integrated absorbances were scaled by correction factors $(1 + j)$ derived as a function of both pressure and observed integrated absorbance.

![Figure 13 - Calculated and measured calibration data for the HONO$_2$ $v_1$ integrated absorbance.](image)

A typical product spectrum of Reaction 1 with H$_2$ as the source of OH is shown in Figure 14. Features due to HONO$_2$, HOONO and HONO are all clearly present. This same spectrum with the scaled reference spectra used for fitting the observed spectral features is shown in Figure 15. The raw data is shown in black, while the sum of the component spectra is shown in red. A typical product spectrum of Reaction 1 with CH$_4$ as the OH source is shown in Figure 16. In addition to the features seen in Figure 14, a
Formaldehyde band is also present at 3495 cm\(^{-1}\), although its location between the HOONO and HONO\(_2\) \(v_1\) bands does not further complicate the analysis of the spectrum.

Figure 14 - IR-CRDS spectrum of the products of the reaction OH + NO\(_2\) using O\(^{(1)}\)D + H\(_2\) as the OH source.
Figure 15 - spectrum shown in previous figure, fit with spectral components due to HONO₂ (green), HONO (blue), and HOONO (purple).

Figure 16 - IR-CRDS spectrum of the products of the reaction OH + NO₂ + M using O\(^{1}\)D + CH₄ as the OH source.
All of the HOONO/HONO$_2$ branching ratio measurement data is given in Table 4. This data is plotted in the top portion of Figure 17. The bottom portion of Figure 17 shows the data averaged at each pressure with the 1 $\sigma$ standard deviation of the data shown for each pressure. The conversion from the raw integrated absorbance data shown in Table 4 to the branching ratios shown in Table 4 was done as follows. Nitric acid $v_1$ integrated absorbances were multiplied by the scaling factors described above. A HONO$_2$ ringdown correction term $f$ accounts for the underestimation of the HONO$_2$ absorbance due to the above-mentioned ringdown effect. The apparent HONO$_2$ integrated absorbance listed in col. 4 was subsequently multiplied by $(1+f)$. HOONO integrated absorbances were multiplied by 1.35 to account for absorption which is shifted from the main peak through OH-stretch/torsion coupling and therefore not observable in our spectra (discussed in Task III). The ratio of calculated HONO$_2$/HOONO band intensities of 2.71 was used (discussed in Task III).

**Table 4 – Branching ratio data.**

OH source indicates reactant with O(1D). A HONO$_2$ ringdown correction term $f$ indicates that the HONO$_2$ integrated absorbance listed in column 4 was subsequently multiplied by $(1+f)$ when calculating the branching ratio.

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<td>750</td>
<td>H2</td>
<td>3118</td>
<td>76579</td>
<td>0.100</td>
<td>0.135</td>
</tr>
</tbody>
</table>
Discussion

The error bars shown in the lower panel of Figure 17 represent the scatter in our data points from one data set to the next. There are three main sources of this scatter. The signal to noise ratio at the peak of the HOONO band was generally low, especially at the highest pressures, where the background noise increased. This led to uncertainty in the fit of the HOONO band. We also observed at times a constant offset between the excimer on and excimer off data, presumably due to slight changes in the alignment of the ringdown cavity due to local heating or photoacoustic effects. This baseline appeared to be constant within a scan, but varied randomly from scan to scan and could be negative or positive. The subtraction of this baseline led to some uncertainty in the derived integrated absorbances, especially for weak bands such as HOONO. There is also some
random uncertainty in the subtraction of the other absorbing species surrounding H\textsubscript{2}HOONO, especially the 2\textnu\textsubscript{2} band of trans-HONO which overlaps with the R-branch of HOONO. This uncertainty is fairly small, however, as the P and Q-branches of the HOONO band are free from interference.

Many experiments were performed to investigate potential sources of systematic errors in our branching ratio measurements. The delay time between initiation of the chemistry by photolysis and probing of the products at constant reactant concentrations was varied to investigate the possible influence of HOONO dissociation. The ratio of the concentrations of OH and NO\textsubscript{2} were varied to look for evidence of the potential influence of the reaction OH + HOONO. Evidence of N\textsubscript{2}O\textsubscript{4} was observed in our high pressure data, so an experiment was conducted at high pressure which varied the amount of N\textsubscript{2}O\textsubscript{4} and look for the potential influence of OH + N\textsubscript{2}O\textsubscript{4} on the branching ratio. Lastly, we were concerned about potential influence of vibrationally excited OH produced from O(\textdelta\textsuperscript{1}D) + H\textsubscript{2} and H + NO\textsubscript{2} on the product branching ratio. As a result, a series of experiments were carried out with O(\textdelta\textsuperscript{1}D) + CH\textsubscript{4} as the source of OH. While the OH produced in this manner is not without vibrational excitation, it is much colder than that produced when using H\textsubscript{2}. None of the experiments described above showed any variation in the HOONO/HONO\textsubscript{2} branching ratio outside the normal scatter in our measurements. As a result, we conclude that while some of these processes may have a small impact on the branching ratio, the uncertainty they introduce is encompassed in the error bars shown on the lower graph of Figure 17.

In addition to the experimental uncertainties discussed above, there are some significant potential systematic errors in our conversion of experimentally measured HOONO and HONO\textsubscript{2} integrated absorbances to a product branching ratio. The uncertainty in our correction factors to the HONO\textsubscript{2} integrated absorbance, which increase the HONO\textsubscript{2} integrated absorbance, is estimated to be 15%. Since the correction factors lead to an increase in the nitric acid integrated absorbance from 10-30%, the uncertainty in the correction factor leads to a 2-5% uncertainty in the calculated branching ratios. The uncertainty in the calculated ratio of cross sections for the two \textnu\textsubscript{1} bands is estimated to be on the order of 10%. The HOONO integrated absorbance not included in the main peak is 25±5% (see Task 3 for further discussion) leading to a 5% uncertainty in the calculated branching ratio. As a result, when these uncertainties are added in quadrature the overall systematic uncertainty (1\sigma) is 12%, about the same as the random experimental uncertainty. The branching ratio data has been fit to a second order polynomial in five ways, as shown in Table 5. The only fit which gives significantly different fit parameters comes from fitting the raw data with no systematic uncertainty included in the least squares fitting routine, as is shown in the top portion of Figure 17. All fits which contain either systematic or experimental uncertainty or both give very similar fit parameters, with the only variation in the uncertainty in those fit parameters. The fit of the raw data with each point given the systematic uncertainty (row 2) has been used for calculations of \(k_{1b}\) and \(k_{1a}\) discussed previously in Task I.
Table 5 – Fit parameters to the branching ratio \((k_{10}/k_{12})\) data as a function of pressure.

Data was fit to the functional form \(BR = K_0 + P*K_1 + K_2*P^2\). \(1\sigma\) uncertainties in the fit parameters are given. Pressures are in Torr.

<table>
<thead>
<tr>
<th></th>
<th>(K_0)</th>
<th>(K_1)</th>
<th>(K_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw data (no uncertainty)</td>
<td>0.0652±0.027</td>
<td>1.66±0.20\times10^{-4}</td>
<td>-9.0±2.7 \times10^{-8}</td>
</tr>
<tr>
<td>raw data (systematic uncertainty)</td>
<td>0.0608±0.020</td>
<td>1.79±0.18 \times10^{-4}</td>
<td>-10.8±2.6 \times10^{-8}</td>
</tr>
<tr>
<td>averaged data (no uncertainty)</td>
<td>0.0604±0.029</td>
<td>1.86±0.19 \times10^{-4}</td>
<td>-10.8±2.5 \times10^{-8}</td>
</tr>
<tr>
<td>averaged data (experimental uncertainty)</td>
<td>0.0606±0.065</td>
<td>1.87±0.55 \times10^{-4}</td>
<td>-10.9±7.3 \times10^{-8}</td>
</tr>
<tr>
<td>averaged data (exp+systematic uncertainty)</td>
<td>0.0604±0.088</td>
<td>1.87±0.75 \times10^{-4}</td>
<td>-11±10 \times10^{-8}</td>
</tr>
</tbody>
</table>
Task III - Calculation of HOONO and HONO$_2$ Absorption Band Intensities

Objectives
To determine the integrated absorption intensity ratios used in the branching ratio measurements by high level theory, with experimental checks performed to validate the calculations.

Background

The HOONO/HONO$_2$ branching ratios reported in the cavity ringdown experiment (Task 2) are derived from measurements of the absorbance of the observed $v_1$ (OH stretch) bands of the relevant species, integrated over the observed band profile. The concentration ratios thus depend upon the ratio of the respective band intensities (integrated cross sections):

$$\frac{n_{\text{HOONO}}}{n_{\text{HONO}_2}} = \frac{I_{\text{HONO}}}{I_{\text{HONO}_2}} \times \frac{\int A_{\text{HOONO}}(\nu)d\nu}{\int A_{\text{HONO}_2}(\nu)d\nu}$$

While the absolute integrated absorption intensity of the nitric acid $v_1$ band has been measured (to within 10%), the HOONO intensity is not known and is not readily measured. The reactions and photodissociation of HOONO have not yet been studied, so titration or photometric methods cannot be used.

In order to derive the branching ratio, we therefore need to rely on theoretical calculations of integrated vibrational intensities. Fortunately, since we are measuring branching ratios, only the relative intensities are needed. It is well known that such calculated ratios are more robust, as significant cancellations occur when comparing similar vibrations.

Modern quantum chemical calculations of closed-shell, semi-rigid molecules such as nitric acid can be performed with a high degree of accuracy for electronic energies. The accuracy of the method used here, Coupled Clusters with Singles and Double Excitations with perturbative treatment of Triple Excitations, or CCSD(T), has been well established for electronic structure calculations.

To predict infrared spectroscopic properties, one must use the electronic structure results to compute vibrational frequencies and transition dipole matrix elements. Two approximations are commonly made. The first is the so-called double harmonic approximation. For a normal mode $i$, the energy levels $\varepsilon_i$ and the intensity of the fundamental ($v_i = 0$ to 1) transition are:

$$\varepsilon_i = (n + \frac{1}{2})\hbar v_i$$

$$I_i = \left| \frac{1}{2} \left( \frac{\partial \mu}{\partial q_i} \right)_0 \right|^2$$
This approximation assumes that the vibration behaves as a simple harmonic oscillator, and that the dipole transition moment depends solely on the first derivative of the dipole moment $\mu$ with respect to the normal mode coordinate $q_i$ (mechanical and electrical harmonicity). While errors in absolute intensities can be 30-40%, the errors in the ratio are expected to be much less.

A second common assumption is that all molecules absorb within the observed band envelope. At thermal energies, a significant population of molecules are vibrationally excited. If those excited molecules have OH stretch vibrations that absorb infrared radiation at significantly different frequencies (sequence bands), then integration of the observed fundamental band will not include the population of such molecules. Such shifts of the position of sequence bands occurs when there is strong coupling of the observed mode (OH stretch, in this case) with other vibrations.

One must go beyond the simple harmonic oscillator to describe correctly vibrational frequencies and intensities. Normally, one can use perturbation theory to compute corrections to vibrational energies and intensities. Typically, inclusion of cubic and quartic anharmonic force constants allow one to approach near spectroscopic accuracy. Typically, the accuracies are <1% on vibrational frequencies, and 10-20% for absolute intensities, which are generally more difficult to measure. These are complex calculations requiring on the order of 2000 high order force constants coupling the nine degrees of freedom in a pentatomic molecule like HOONO.

Even perturbation theory can lead to significant errors if the amplitude of the vibrations is large and the harmonic oscillator approximation breaks down. *Cis-cis* HOONO has two such modes, the low frequency torsional rotation of the heavy atoms about an ON bond, and that of the OH group about the OO bond (the HOON dihedral angle). The latter HOON dihedral motion may in particular critically affect the OH vibration, because it breaks the weak internal hydrogen bond; this can cause the OH frequency to shift by $+250$ cm$^{-1}$, and the intensity to increase by a factor of $>2$. In this case, one must explicitly map out the potential energy surface and numerically solve the vibrational Hamiltonian. Since a full nine dimensional calculation is not feasible at the highest levels, one must select a subset of the space or degrees of freedom.

Our earlier low pressure branching ratio determination was based on very high level quantum chemistry calculations, the CCSD(T)/AUG-ccpVTZ level, but made the double harmonic approximation. The previous double-harmonic estimate of the intensity ratio was

$$\frac{I_{1,\text{NO}}}{I_{1,\text{HOONO}}} = 2.71$$

In this approximation, there is no coupling among modes, and hence effectively one assumes that all molecules are detected. The goal of Task III is to improve on our theoretical estimates of the absorption intensity ratio using vibrational perturbation theory, and to compute population corrections for *cis-cis* HOONO by explicitly calculating the effects of OH-stretch/OH-torsion coupling.
Approach

For nitric acid, second order vibrational perturbation theory to compute cubic and quartic anharmonicities is sufficient to obtain frequencies and intensities. However, for \textit{cis-cis} HOONO, one must both perform second order perturbation calculations and treat the torsional motion of the HO group \((q_9)\), and its coupling to the OH stretch mode \((q_1)\).

We have been collaborating with Professor John F. Stanton on calculations of HOONO and related species. He has completed a high level (CCSD(T)/ANO) calculation of the full quartic force field of HONO\(_2\) and of all isomers of HOONO within the second order vibrational perturbation theory (VPT2). He has provided results on the intensities of the fundamental IR frequencies and intensities of the \(v_1\) (OH stretch) vibration. We report his results here.

In a collaboration with Professors Joseph Francisco (Purdue) and Anne McCoy (Ohio State), we have developed a full two-dimensional calculation of the HOONO OH stretching-OH torsion potential energy and dipole moment surfaces.

1) We have computed the relevant portion of the HOONO potential energy and dipole moment surfaces using highly accurate \textit{ab initio} methods (CCSD(T)/cc-pVTZ), coupled with rigorous vibrational calculations to determine vibrational band positions and intensities. We have employed a 2D model, which explicitly treats coupling of the OH stretch and the OH internal rotation (HOON torsion).

2) Using these calculations, we have succeeded in assigning the structure of the OH first overtone spectrum, previously observed by action spectroscopy by Nizkorodov and Wennberg\[5\]. These results demonstrate that we have quantitatively described the coupling of the OH stretch and torsion modes involved. At least one other mode, which we have neglected, is important.

3) As a further test, we performed cavity ringdown spectroscopy of the overtone spectrum of \textit{cis-cis} HOONO, in the laboratory of Paul Wennberg.

Results and Discussion.

\textit{High level quantum chemistry calculations with VPT2}

Prof. John F. Stanton, U Texas, with researcher Mychel Varmer have computed properties of HOONO, HONO\(_2\), and related species using state-of-the-art methods. At our request, they have computed accurate values of the HOONO and HONO\(_2\) \(v_1\) intensities, taking into account anharmonicities using analytic gradients and second order vibrational perturbation theory (VPT2). These calculations are full nine dimensional expansions of the potential energy and dipole surface about the geometry at the potential minimum, with anharmonic force constants derived to 2\textsuperscript{nd} order PT. They are derived from analytic derivatives at the CCSD(T)/triple-zeta with double polarization.

The results are given in Table 6.
Table 6 – comparison of HOONO frequency and intensity calculations.

<table>
<thead>
<tr>
<th></th>
<th>Harmonic</th>
<th>Harmonic</th>
<th>Anharmonic</th>
<th>Experiment</th>
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</thead>
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<tr>
<td></td>
<td>CCSD(T)/AUG-cc-pVTZ Francisco</td>
<td>CCSD(T)/ANO Stanton</td>
<td>CCSD(T)/ANO Stanton</td>
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<tr>
<td>HOONO</td>
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<td></td>
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<tr>
<td>$\omega_1$, cm(^{-1})</td>
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<td>3320</td>
<td>3306(^a)</td>
<td></td>
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<tr>
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<td>6415</td>
<td>6350(^c)</td>
<td></td>
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<tr>
<td>$I_1$, km/mol</td>
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<td>33.4</td>
<td>27.0</td>
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<tr>
<td>HONO(_2)</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>3560</td>
<td>3550</td>
<td></td>
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<tr>
<td>$I_1$, km/mol</td>
<td>95.4</td>
<td>88.6</td>
<td>73.2</td>
<td>75(^b)</td>
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<td>$I_{1,HONO_2}/I_{1,HONO}$</td>
<td>2.87</td>
<td>2.65</td>
<td>2.71</td>
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</tbody>
</table>

\(^a\) Bean et al.[2]  
\(^b\) Chackerian et al.[46]  
\(^c\) Fry et al.[33]  

There is excellent agreement between Stanton’s CCSD(T)/ANO prediction for the $\nu_1$ frequency of cis-cis HOONO (3320 cm\(^{-1}\)) using the quartic force-field, and the experimental value (3306 cm\(^{-1}\)). Theory similarly predicts the vibrational frequencies of the OH stretch and 2$\nu_2$ overtone of HONO\(_2\) to a similar degree of accuracy.

The anharmonicity-corrected CCSD(T)/ANO prediction of the infrared intensity of the $\nu_1$ stretch $I_{1,HONO_2}$ is 73.2 km/mol, also in good agreement with the most recent experimental value, 75 km/mol, obtained by Chackerian et al.

Based on the CCSD(T)/ANO calculations and VPT2, we have obtained a ratio of the nitric acid to cis-cis HOONO infrared intensities of

$$\frac{I_{1,HONO_2}}{I_{1,HONO}} = 2.71$$

This is very close to the ratio of the intensities computed in the harmonic approximation, 2.86, despite the large discrepancies in the absolute intensities (approximately 30%). This suggests that taking the intensity ratio for like bonds (OH stretch) leads to large cancellations of error.

**Calculation of Stretch-Torsion Coupling**

Based on our full two-dimensional calculation with Francisco and McCoy, we have predicted the fundamental $\nu_1$ band of cis-cis HOONO, taking into account coupling
of the OH stretch with the HOON torsion, \( \nu_9 \). The details are reported in the attached publication.

As can be seen in the calculated spectrum shown in Figure 18, the origin line near 3300 cm\(^{-1} \) dominates the spectrum. This line corresponds to the pure OH stretch transition with no initial torsional excitation. The absolute position (3270 cm\(^{-1} \)) is off by about 30 cm\(^{-1} \) (1%), but since this calculation neglects 7 of 9 modes, we do not expect it to reproduce the absolute position exactly. Relative shifts of combination bands with the torsional mode should be fairly accurate. The second dominant band seen in the simulated spectrum, at approximately 3375 cm\(^{-1} \), is the sequence OH stretch band \( \nu_9=1\rightarrow1 \), where \( \nu_9 \) is the torsional vibration quantum number. In other words, this is the OH stretch excitation for excited molecules with one quantum of torsional excitation. The \( \nu_9=2\rightarrow2 \) sequence band is also visible, red-shifted to approximately 3430 cm\(^{-1} \). The broad, multiple-band feature around 3600 cm\(^{-1} \) comprises a series of \( \Delta \nu_9=1 \) bands that sample the broad shelf of the torsional potential surfaces, shown in Figure 19. For ease of visualization, we show in this figure the vibrationally adiabatic torsional potential, obtained by averaging the two-dimensional surface over a specific \( \nu \) state in the OH stretch. This adiabatic surface is obtained using the torsional angle dependence of the equilibrium frequency and anharmonicity, and adding to the electronic torsional potential energy surface \( U_e(\tau) \):

\[
U_v (\tau) = \omega_x (\tau) \left( \nu + \frac{1}{2} \right) - \omega_x x_x (\tau) \left( \nu + \frac{1}{2} \right) + U_e (\tau)
\]

The transitions mentioned above are shown in Figure 19. This sampling of initially torsionally excited population results in the broad, complex spectrum shown in Figure 18.

The validation of this 2-D model was achieved by comparison of the first OH overtone cavity ringdown absorption spectrum and action spectrum with model predictions. The difference between these two spectra is due to the dissociation threshold for HOONO falling in the first OH overtone region. The resulting quantum yield variation was also modeled. The details of this validation are described in the attached publication. In both cases, this simple 2-D model was shown to reproduce the major features in the spectra. Only one experimentally observed band, suspected to be a combination band with a mode not treated in this model, was not reproduced in the model of the first OH overtone spectrum. This gives us confidence in the same model's predictions for the fundamental band (shown in Figure 18).

The fundamental band at 3306 cm\(^{-1} \) detected in the cavity ringdown experiment probes only the \( \nu_9=0 \) level. Elementary statistical mechanical calculations, as well as inspection of the simulated spectrum (Figure 19), indicate that about 28 ± 5% (1\( \sigma \)) of the population (all molecules with \( \nu_9>0 \)) have OH stretch bands that are displaced to the blue and hence not included in the CRDS integration of the intensity of the band at 3306 cm\(^{-1} \). The error bars of 5% in this case reflect our estimate of the agreement between model and experiment from the OH first overtone (shown in attached publication). As a result of these calculations, the measured HOONO integrated absorbances listed in Table 4 have been multiplied by 1.4 when the branching ratio is calculated.
Figure 18. The calculated OH-stretch absorption spectrum of cis-cis HOONO predicted using a two-dimensional model incorporating torsion-stretch coupling.
Figure 19 Vibrationally adiabatic potential energy surfaces $U_{\nu_{OH}}$ for $\nu_{OH}=0$ and 1, plotted as a function of $\tau$. The thin lines on each of the adiabatic potential curves represent the energies $E(\nu_{OH}, n)$ of the torsional states that are associated with the specific $\nu_{OH}$ quantum level. Sequence band transitions mentioned in the text are shown as vertical arrows (three center transitions).
Discussion and Recommendations

**Task I**

The rate of reaction 1 has been measured over the range 50-900 Torr. A fit of our \( k_1 \) data with \( M = \text{air} \) to the JPL formulation of the three-body fall-off expression gives

\[
298 \text{ K} \quad k_0 = (1.6 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\
\kappa_c = (3.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

\[
315 \text{ K} \quad k_0 = (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \\
\kappa_c = (2.3 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

The overall uncertainty in these rate measurements is estimated to be \( \approx 7\% \).

At 760 Torr and 298 K, we find an effective bimolecular rate of

\[
k_{1} = (1.0 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

This value is 14% and 7% lower than the rates derived from the NASA/JPL and IUPAC(2005) recommendations respectively.

**Task II**

With the aid of the calculations presented in Task III, the HOONO/HONO\(_2\) branching ratio has been measured over the range 25-770 Torr at 300 K. A fit of the branching ratio data to a second order polynomial leads to the expression

\[
\text{BR} = 0.0608 \pm 0.0020 + (1.79 \pm 0.18) \times 10^{-4} P - (1.08 \pm 0.26) \times 10^{-7} P^2
\]

where the 1σ uncertainties of the fit parameters are included in parenthesis and \( P \) is in Torr. At 750 Torr and 298 K, the measured branching ratio is \( k_{1b}/k_{1a} = 0.14 \pm 0.02 \).

These branching ratios were measured in a gas mixture consisting of 90% \( \text{N}_2 \), 9% \( \text{H}_2 \), and 1% \( \text{NO}_2 \). Our assumption is that the branching ratio is relatively insensitive to the composition of the gas. There was insufficient time to complete the temperature dependence, but results from previous experiments at low pressure indicate that there is little variation in the branching ratio at an effective pressure of \( P_{\text{eff}} = 13 \text{ Torr} \).

**Task III**

The HONO\(_2\)/HOONO relative intensity has been calculated with high level quantum chemistry calculations and second order vibrational perturbation theory. We find the ratio to be 2.71. Additionally, calculations show that 27% of the total HOONO \( v_1 \) band intensity lies outside the main peak due to stretch-torsion coupling and is therefore not observed in the experiments described by Task II. These correction factors were incorporated into the analysis of the HOONO and HONO\(_2\) spectra to determine the branching ratio given above.

**Rate Parameters**

From the branching ratio and our experimental data \( k_1 \) in \( M = \text{Air} \), we derived the fall-off parameter for the separate HOONO and HONO\(_2\) channels from
\[
k_{la} = k_1 \frac{1}{1 + BR}
\]
\[
k_{lb} = k_1 \frac{BR}{1 + BR}
\]

Parameters for fits of our data to the NASA/JPL formulation of the three body fall-off expression for 298 K and 315 K are shown in Table 7. Table 8 gives our falloff fit parameters compared with the NASA/JPL recommendation and the master equation results of Golden et al fitted to the NASA/JPL formulation reported in NASA/JPL 2002.

**Table 7 – Fitted falloff parameters (NASA/JPL formulation, M = air)**

<table>
<thead>
<tr>
<th></th>
<th>HOONO</th>
<th>HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_0 ) ( \text{cm}^6 \text{molecules}^{-2} \text{s}^{-1} )</td>
<td>( k_0 ) ( \text{cm}^6 \text{molecules}^{-2} \text{s}^{-1} )</td>
</tr>
<tr>
<td>298 K</td>
<td>( (8.6\pm0.4)\times10^{-32} )</td>
<td>( (9.2\pm0.8)\times10^{-12} )</td>
</tr>
<tr>
<td>315 K</td>
<td>( (7.7\pm0.8)\times10^{-32} )</td>
<td>( (8.7\pm0.3)\times10^{-12} )</td>
</tr>
</tbody>
</table>

**Table 8 - Comparison of the fitted falloff parameters (NASA/JPL formulation, M = air ).**

<table>
<thead>
<tr>
<th></th>
<th>HOONO</th>
<th>HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_0 (298) )</td>
<td>( k_0 (298) )</td>
</tr>
<tr>
<td>NASA/JPL 2002</td>
<td>1.0\times10^{31}</td>
<td>2.0\times10^{10}</td>
</tr>
<tr>
<td>Golden et al</td>
<td>9.1\times10^{32}</td>
<td>4.2\times10^{11}</td>
</tr>
<tr>
<td>Present work</td>
<td>(8.6\pm0.4)\times10^{-32}</td>
<td>(9.2\pm0.8)\times10^{-12}</td>
</tr>
</tbody>
</table>

**Lifetime of HOONO at Atmospheric Pressure**

In Task II, there was no observed variation in the HOONO/HONO₂ branching ratio at 750 Torr over the range of delay times used (1-100 ms). This implies that the lifetime of HOONO with respect to unimolecular decomposition at 750 Torr is longer than 100 ms. Additionally, the unimolecular decay rate \( k_{-lb} \) of HOONO at 760 Torr can be calculated from our value of \( k_{lb} \) in conjunction with an estimate of equilibrium constant for HOONO formation and decomposition,

\[
k_{-lb} = k_{lb} / K_{eqlb}.
\]

Assuming a value of \( K_{eqlb} = 1.92\times10^{12} \text{ cm}^3 \text{ molecule}^{-1} \),[22] the estimated lifetime of HOONO with respect to decomposition back to OH and NO₂ is on the order of 1 second, consistent with our experimental lower limit. This lifetime has two implications:

- The lifetime of HOONO is significantly longer than the timescale of the reactions observed in the experiments described in Task 1. There, OH pseudo-first order decay times were on the order of 10 ms or less, and any HOONO formed by channel lb would not have redissociated back to OH. Thus, the rate constants
reported are indeed a measure of $k_1$, the total loss through both channels 1a and 1b.

- In the atmosphere, HOONO decay back to OH and NO$_2$ by collisional dissociation, $k_{-1b}[M]$, will dominate over other loss processes. The lifetime to photolysis should be on the order of minutes to hours, and the lifetime with respect to reaction with OH should be on the order of $10^6$ seconds, even assuming upper limit values of $k = 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $[OH] = 10^7$ molecules cm$^{-3}$. As a result, HOONO is a very short-lived transient, and channel 1b is not a net sink for OH and NO$_2$.

**Modeling Recommendations**

We recommend that our results can be incorporated into urban airshed models in one of two ways.

(1) **COMPLETE MECHANISM**

The full reaction scheme, including both reaction 1a and 1b can be used:

\[
\begin{align*}
OH + NO_2 + M & \rightarrow HONO_2 \quad k_{1a} \\
& \rightarrow HOONO \quad k_{1b} \\
HOONO + M & \rightarrow OH + NO_2 \quad k_{-1b}
\end{align*}
\]

In this case, the rate of collisional dissociation of HOONO back to OH and NO$_2$, reaction $(-1b)$ must also be incorporated into the models. The parameters to be used in Eq. 1 are

\[
\begin{align*}
\text{Reaction 1a - } k_{0,1a} (298 \text{ K}) &= (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\infty,1a} (298 \text{ K}) &= (2.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
k_{0,1a} (315 \text{ K}) &= (1.4 \pm 0.3) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\infty,1a} (315 \text{ K}) &= (1.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{Reaction 1b - } k_{0,1b} (298 \text{ K}) &= (8.6 \pm 0.4) \times 10^{-32} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\infty,1b} (298 \text{ K}) &= (9.2 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
k_{0,1b} (298 \text{ K}) &= (7.7 \pm 0.8) \times 10^{-32} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \\
k_{\infty,1b} (298 \text{ K}) &= (8.7 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}
\end{align*}
\]

These rates must be used together with the rate for collisional dissociation of HOONO, $k_{-1b} (298 \text{ K, 1atm}) = 6.6 \times 10^{-1} \text{ s}^{-1}$

(2) Due to the rapid decomposition of HOONO back to OH and NO$_2$ under typical urban conditions, our reported value of $k_{1a}$ can be used as an effective loss rate of OH and NO$_2$ to form the sink HONO$_2$. We therefore recommend that the values to be used in models be
Reaction 1 -

\[ k_{0,1a}(298 \text{ K}) = (1.5 \pm 0.1) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \]
\[ k_{\infty,1a}(298 \text{ K}) = (2.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \]

\[ k_{0,1a}(315 \text{ K}) = (1.4 \pm 0.3) \times 10^{-30} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \]
\[ k_{\infty,1a}(315 \text{ K}) = (1.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \]

For temperatures between 298 K and 315 K a linear interpolation between these values should be used. It should be noted that this study covers a fairly narrow range of temperatures and pressures which are relevant to the lower atmosphere can not be generally extrapolated to all conditions.
Publications

Glossary
branching ratio  ratio of the rates of two product channels of a reaction. In this case \( \frac{k_{1b}}{k_{1a}} \)

CRDS  cavity ringdown spectroscopy

HNO₃  nitric acid

HONO₂  nitric acid

HOONO  peroxynitrous acid

IR  infrared

\( k_i \)  the effective bimolecular rate constant for the reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{products} \)

\( k_{1a} \)  the effective bimolecular rate constant for the reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M} \)

\( k_{1b} \)  the effective bimolecular rate constant for the reaction \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HOONO} + \text{M} \)

NO₂  nitrogen dioxide

NO  nitric oxide

NOₓ  oxides of nitrogen

O₂  molecular oxygen

O₃  ozone

OH  hydroxyl radical

PLP-LIF  Pulsed Laser Photolysis, Laser Induced fluorescence

\( 1+f \)  Correction factor for absorbance measurements by CRDS
References


