Photodissociation of Peroxynitric Acid in the Near-IR

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Received: September 14, 2001; In Final Form: January 14, 2002

Temperature-dependent near-IR photodissociation spectra were obtained for several vibrational overtone transitions of peroxynitric acid (HNO₄) with a tunable OPO photolysis/OH laser-induced-fluorescence system. Band-integrated photodissociation cross-sections (⟨σ,ω⟩), determined relative to that for the 3ν₁ OH stretching overtone, were measured for three dissociative bands. Assuming unit quantum efficiency for photodissociation of 3ν₁ we find 2ν₁ + ν₃ (8242 cm⁻¹) = (1.21 × 10⁻²⁰) (independent of temperature), 2ν₁ (6900 cm⁻¹) = 4.09 × 10⁻¹⁸ * e⁻¹⁸⁶(5/7) (295 K > T > 224 K), and ν₁ + 2ν₃ (6252 cm⁻¹) = 1.87 × 10⁻¹⁸ * e⁻¹⁴¹⁰(7/7) (278 K > T > 240 K) cm² molecule⁻¹ cm⁻¹. The photodissociation cross-sections are independent of pressure over the range 2 to 40 Torr. Temperature-dependent quantum yields (φ) for these transitions were obtained using integrated absorption cross-sections (⟨σ,ω⟩) of HNO₄ overtone vibrations measured with a FTIR spectrometer. In the atmosphere, photodissociation in the infrared is dominated by excitation of the first overtone of the OH stretching vibration (2ν₁). Inclusion of all dissociative HNO₄ overtone and combination transitions yields a daytime IR photolysis rate of approximately 1 × 10⁻³ s⁻¹. This process significantly shortens the estimated lifetime of HNO₄ in the upper troposphere and lower stratosphere.

I. Introduction

Chemistry in Earth’s atmosphere is typically initiated by photolysis of photolabile compounds via excitation to dissociative electronic states, usually in the ultraviolet. Donaldson et al.¹ have suggested, however, that photodissociation by excitation of vibrational overtone transitions may be important for a number of atmospherically relevant compounds. In particular, they calculated that excitation of overtones of the OH stretching vibrations could significantly reduce the atmospheric lifetimes of hydrogen peroxide, nitric acid, and peroxynitric acid (HNO₄). The idea here is that the significantly higher actinic flux in the visible/near-infrared can more than compensate for the very weak band strengths of these transitions. Because the OH overtone band intensities decrease by approximately 1 order of magnitude for each additional quantum of excitation,² this process most strongly influences the chemistry of HNO₄ as it contains the weakest bond (D₀(HO₂−NO₂) = 95.3 ± 3.4 kJ/mol).³ It was suggested by Donaldson et al.¹ that excitation of the 2nd and 3rd overtone of the OH stretch in HNO₄ would be fully dissociative. In this work, we have investigated the photodissociation cross sections for HNO₄ between 900 and 2000 nm.

HNO₄ has been observed in the atmosphere⁴ and is calculated to play a significant role in the chemistry of the nitrogen and hydrogen free radical families.⁷ It is thought to be formed exclusively in the gas phase via the reaction

\[
\text{HO}_2 + \text{NO}_2 + M \rightarrow \text{HNO}_4 + M \quad (1)
\]

Thermal decomposition (reaction 1) is fast in the lower atmosphere. Above 7 km, however, the lifetime with respect to this process becomes long (>1 day) compared with the other known loss processes:

\[
\begin{align*}
\text{HNO}_4 + h\nu & \rightarrow \text{HO}_2 + \text{NO}_2 \\
& \quad \rightarrow \text{OH} + \text{NO}_3 \quad (2a)
\end{align*}
\]

and

\[
\text{OH} + \text{HNO}_4 \rightarrow \text{products} \quad (3)
\]

Assuming the products of reaction 3 are H₂O, O₂, and NO₂, the combination of reactions 1 and 3 represents a NO₂-catalyzed loss of odd hydrogen radicals (HO = OH + HO₂):

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (1 + 3)
\]

Calculations suggest that in the stratosphere⁵ and at higher NO₂ concentrations in the upper troposphere⁶ this process represents a significant sink of odd-hydrogen radicals. Photolysis (reaction 2) on the other hand is a null cycle with respect to HO₂ loss.
An underestimate of the photolysis rate therefore leads to an underestimate of the concentration of OH.

Evidence for significant photodissociation of HNO₄ in the red or near-infrared region of the spectrum was presented by Wennberg et al.¹⁰ Measurements of the concentration of OH and HO₂ obtained in the lower stratosphere with the sun at the horizon (that is when the atmosphere is screened from light, λ < 700 nm, by absorption and scattering) suggested a large, but unknown, near-IR source of these free radicals. Wennberg et al. were able to significantly improve the simulations of the HO₂ measurements assuming that absorption, arbitrarily placed at 800 nm, produced a photolysis rate of 1 × 10⁻⁵ s⁻¹ for HNO₄.¹⁰ This rate exceeds by nearly an order of magnitude, however, the photolysis rate of HNO₄ calculated from the absorption in the 2nd and 3rd OH overtones even if a 100% dissociation efficiency is assumed for these transitions.¹¹

In this work, we have combined near-IR tunable laser photodissociation spectroscopy with absorption cross-section measurements to estimate the absolute photodissociation quantum yield for a number of vibrational bands of HNO₄. We have discovered that photoexcitation of the first OH stretching overtone (near 6900 cm⁻¹) provides the dominant contribution to the near-infrared photolysis of HNO₄. The energy supplied by this excitation is, however, significantly less than the 0 K dissociation threshold (Dₒ); it appears that a combination of internal rotational and vibrational energy as well as collisional energy transfer to the photoexcited HNO₄ closes the energy deficit. We find that, under typical conditions of the upper troposphere/lower stratosphere, the combined effect of the infrared transitions yields a clear-sky photolysis rate for HNO₄ of approximately 1 × 10⁻⁵ s⁻¹. In the lower stratosphere and upper troposphere, the 24-hour average photolysis rate due to overtone excitation often exceeds that due to electronic excitation in the UV.

II. Experiment

A. Synthesis of HNO₄. Preparation of HNO₄ was as described by Kenley et al.¹² Briefly, ~1 g of NO₃BF₄ (Aldrich, 95%) was slowly added to ~5 mL of 95+%, chilled H₂O₂ (distilled from 70 wt %) in a N₂-purged glovebox. Once synthesized, the HNO₄ solution was transferred to a sealed glass bubbler, which was immersed in an ice/water bath. HNO₄ was introduced into the gas phase by passing pre-cooled N₂ flow through the bubbler. An alternative preparation of aqueous HNO₄ solutions based on the method described by Appelman¹³ was also used for some photodissociation studies.

B. HNO₄ Absorption Cross-Sections. The HNO₄ absorption spectrum was determined over the spectral region of 1200–10500 cm⁻¹ using a commercial Fourier Transform infrared (FTIR) spectrometer, equipped with a MCT-A detector, a CaF₂ beam splitter, a white light source, and a jacketed, multipass glass sample cell with CaF₂ windows. Measurements were conducted with a flowing source of HNO₄; a carrier flow of N₂ was introduced via a flow controller (at 40 sccm) upstream of the bubbler. Pressure inside the absorption cell and bubbler was monitored with a 1000 Torr (full scale) capacitance pressure sensor. Pressure inside the absorption cell and bubbler was maintained at 1000 Torr (full scale) capacitance pressure sensor. Measurement of the concentration of OH and HO₂ obtained in the lower stratosphere with the sun at the horizon (that is when the atmosphere is screened from light, λ < 700 nm, by absorption and scattering) suggested a large, but unknown, near-IR source of these free radicals. Wennberg et al. were able to significantly improve the simulations of the HO₂ measurements assuming that absorption, arbitrarily placed at 800 nm, produced a photolysis rate of 1 × 10⁻⁵ s⁻¹ for HNO₄.¹⁰ This rate exceeds by nearly an order of magnitude, however, the photolysis rate of HNO₄ calculated from the absorption in the 2nd and 3rd OH overtones even if a 100% dissociation efficiency is assumed for these transitions.¹¹

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C. Photodissociation Spectra. The photodissociation spectrum of HNO₄ was obtained using a tunable optical parametric oscillator (OPO) laser system¹⁴ coupled with a sensitive hydroxyl radical detection system.¹⁵ The photolysis laser is a type II BBO OPO (developed at Caltech) pumped by the 3rd harmonic (355 nm) of a pulsed Nd:YAG laser. At a Nd:YAG pulse repetition rate of 100 Hz, some 2–4 mJ/pulse of radiation is produced in the idler beam of the OPO at wavelengths between 800 and 2200 nm with a frequency width of a few wavenumbers. Radiation (idler, signal, and residual 355 nm) exiting from the OPO passes through a 700 nm long-pass filter placed at an angle to remove the 355 nm and the OPO signal and to guide a small fraction of the OPO signal into a pulsed wave meter for accurate frequency determination. The idler beam is collimated to a size of ~4 mm² and directed through the photolysis chamber containing HNO₄ before being intercepted by a thermal power meter. A schematic of the laser-induced-fluorescence (LIF) chamber is shown in Figure 1. A mechanical shutter is utilized to modulate the photolysis beam, allowing for differentiation between the photolysis signal and background signal produced by the UV probe laser scatter, photolysis of HNO₄ by the UV probe laser, and HNO₄ thermal decomposition. The latter represents the major contribution to the background above 273 K and disappears almost completely below 253 K.

Co-aligned with the photolysis laser is a second laser beam used to excite OH fluorescence. Tunable ultraviolet (UV) light is produced by frequency doubling the output of a dye laser which is pumped by a frequency-doubled, diode-pumped Nd: YAG laser operated at 5–8 kHz pulse repetition frequency. This radiation (~1.0 µJ pulse⁻¹), near 282 nm, is used to pump the OH molecules into the first vibrationally excited level of the A-state. Subsequent collisions with nitrogen bath gas rapidly relax OH into the A(v = 0) state. OH fluorescence near 309 nm is detected in a single-photon counting mode by a photo-
multiplier tube perpendicular to the gas flow and laser axes as described elsewhere.\(^{15}\)

As in the absorption experiments, HNO\(_4\) is introduced into the flow with N\(_2\) carrier gas. The gases then pass through a jacketed, glass inlet line and eventually into a cooled flow system. The pressure in the HNO\(_4\) bubbler (30–100 Torr) is monitored with a 1000 Torr (full scale) capacitance pressure transducer and is adjusted using a Teflon needle valve located between the bubbler and the photolysis chamber. Pressure in the flow (2–40 Torr) is measured with 10 and 100 Torr capacitance pressure transducers. Typical HNO\(_4\) concentrations in the flow are \((5–30) \times 10^{13}\) molecule cm\(^{-3}\) estimated from the parallel FTIR measurements. The circulation of chilled methanol maintains temperature control between 300 and 223 K as measured by a calibrated thermistor.

At photolysis wavelengths greater than 950 nm, H\(_2\)O is expected to be the major photoprodut of HNO\(_4\) photolysis (Reaction 2a); the formation of OH is energetically precluded. Conversion of HO\(_2\) to OH is achieved by addition of NO to the gas flow via

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]  

(4)

The NO density of approximately \(2 \times 10^{14}\) molecule cm\(^{-3}\) is chosen to ensure complete conversion to OH in less than half a millisecond, as directly verified in separate variable pump–probe delay measurements. Subsequent removal of OH occurs on a time scale of a few milliseconds consistent with reaction 3 being the primary OH loss mechanism in the flow tube. At higher NO relative densities and total pressures the three body recombination process

\[
\text{HO} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}
\]  

(5)

contributes to the OH loss as well. At the experimental pressures and NO concentrations employed, recombination via H\(_2\)O + NO\(_2\) is unimportant.

### III. Results

Near- and mid-infrared HNO\(_4\) absorption spectra were measured using a FTIR spectrometer. Fundamental vibrational modes \((\nu_1 - \nu_3)\) of HNO\(_4\) were identified in the mid-IR region between 1200 and 3700 cm\(^{-1}\) and their relative strengths were determined. The relative band intensities of the fundamentals \((f_{\text{abs}})\) were found to be within 7\% of those measured by May and Friedl.\(^{16}\) Two combination bands, located at 6252 and 8242 cm\(^{-1}\), and \(2\nu_1\) and \(3\nu_1\), the overtone bands, were also observed in the near-IR. Absolute integrated absorption cross-sections for these near-IR bands were calculated using the known band intensities of \(3\nu_1\)\(^{11}\) and \(\nu_1\).\(^{16}\) A comparison of the near-IR integrated absorption cross-sections is given in Table 1 and the near-IR features are shown in Figure 2 along with the \(\nu_1\) fundamental. The strengths of the stronger fundamentals \((\nu_2 - \nu_3)\) could not be reliably measured simultaneously with \(\nu_1\) and the overtones because of the high number density of HNO\(_4\) used.

Uncertainties in the HNO\(_4\) band strengths arise from several factors including baseline drifts, the signal-to-noise ratio in the FTIR spectra, and uncertainty in the absolute band intensities of \(3\nu_1\) and \(\nu_1\). Impurities also affect the precision of the band intensity measurements because all of the HNO\(_4\) bands overlap somewhat with HNO\(_3\), H\(_2\)O, and H\(_2\)O bands. HNO\(_3\) in particular is difficult to account for because of the strong overlap of the bands. Great care was taken to subtract the impurities from the FTIR spectra of HNO\(_4\). Nevertheless, the literature values for the absolute band intensities of \(3\nu_1\) and \(\nu_1\), \((3.8 \times 10^{-20}\) and \(6.10 \times 10^{-20}\) cm\(^2\) molecule\(^{-1}\) cm\(^{-1}\)), respectively\(^{11,16}\), are not consistent within the measurements uncertainties with the relative strengths determined here and we have chosen to split the difference. A value of \(3\nu_1\) = \(3.3 \times 10^{-20}\) cm\(^2\) molecule\(^{-1}\) cm\(^{-1}\) was used in the normalization to obtain the band strengths reported in Table 1: the quoted errors reflect the uncertainty in \(3\nu_1\). Errors in the integrated band strengths propagate directly into the integrated photodissociation cross-sections reported below.

Near-IR induced dissociation of HNO\(_4\) is evidenced here by the LIF detection of OH following HNO\(_4\) IR excitation and conversion of HO\(_2\) to OH in reaction with NO. The OH LIF signal requires both IR and UV probe radiation and appears only in the presence of NO. Figure 3 shows a sample photodissociation spectrum obtained by scanning the excitation frequency of the near-IR laser in the region of the OH stretch overtone. Several distinct dissociative bands attributable to various HNO\(_4\) overtone and combination bands are observed in the photolysis frequency range 5000 to 11000 cm\(^{-1}\). No known impurities present in the HNO\(_4\) solution (e.g., HNO\(_3\)) produce IR-induced OH LIF signals under such conditions.

### TABLE 1: Absolute Integrated Band Strengths of HNO\(_4\) Fundamental and Overtone Vibrational Transitions (in cm\(^2\) molecule cm\(^{-1}\)) Used in This Work

<table>
<thead>
<tr>
<th>band and center (cm(^{-1}))</th>
<th>(4\nu_1)</th>
<th>(3\nu_1)</th>
<th>(2\nu_1 + \nu_3)</th>
<th>(2\nu_1)</th>
<th>(\nu_1 + \nu_2)</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f_{\text{abs}}) previous measurements</td>
<td>(3.0 \pm 1.8) (\times 10^{-21})</td>
<td>(3.8 \pm 1.1) (\times 10^{-20})</td>
<td>(6.10 \pm 0.73) (\times 10^{-18})</td>
<td>(4.90 \pm 0.59) (\times 10^{-17})</td>
<td>(1.25 \pm 0.18) (\times 10^{-17})</td>
<td>(3.08 \pm 0.46) (\times 10^{-17})</td>
<td>(3.80 \pm 0.67) (\times 10^{-17})</td>
<td>(3.90 \pm 0.59) (\times 10^{-17})</td>
<td>(3.90 \pm 0.59) (\times 10^{-17})</td>
</tr>
<tr>
<td>this work</td>
<td>(3.3 \pm 0.7) (\times 10^{-20})</td>
<td>(1.6 \pm 0.3) (\times 10^{-20})</td>
<td>(9.5 \pm 1.9) (\times 10^{-19})</td>
<td>(2.7 \pm 0.5) (\times 10^{-19})</td>
<td>(7.2 \pm 1.4) (\times 10^{-19})</td>
<td>(9.5 \pm 1.9) (\times 10^{-19})</td>
<td>(2.7 \pm 0.5) (\times 10^{-19})</td>
<td>(7.2 \pm 1.4) (\times 10^{-19})</td>
<td>(9.5 \pm 1.9) (\times 10^{-19})</td>
</tr>
</tbody>
</table>

\(^{a}\) The relative integrated band absorbances obtained from the FTIR measurements (second row) were normalized to the integrated band strength of the \(3\nu_1\) overtone reported in Zhang et al.\(^{11}\) and the band strength of \(\nu_1\), reported in May and Friedl.\(^{16}\) \(^{b}\) Ref 11. \(^{c}\) Ref 16.
Photodissociation of Peroxynitric Acid

Figure 3. A sample photodissociation spectrum of HNO₄ recorded at 243 K. In addition to the OH stretching overtones 2ν₁ and 3ν₁, several weaker features are visible between 6000 and 8000 cm⁻¹. They are assigned to combinations of ν₁ and 2ν₁ with other HNO₄ vibrations. The position of the dissociation energy of HNO₄ is marked with an arrow. The magnified spectrum (offset for clarity) shows no evidence of dissociation between bands. The relative intensities are not accurate in this spectrum as it was taken under slightly saturated conditions.

Figure 4. The effect of temperature on the photodissociation band intensities. The intensity of the 2ν₁ band relative to that of the 3ν₁ band increases markedly with temperature. The spectra are scaled to have the same area of the 3ν₁ band and offset for clarity.

giving strong additional evidence that it comes from HNO₄. The photodissociation signal was found to vary linearly with laser power of both the UV-LIF and IR radiation. The relative band intensities did not depend on the fraction of NO present in the cell (50–1300 ppmv) or the total gas pressure (2–40 Torr).

Photodissociation spectra of four selected bands, namely the 3ν₁ OH-stretch overtone, a combination band assigned to 2ν₁ + ν₃, the 2ν₁ OH-stretch overtone, and a second combination transition tentatively assigned to ν₁ + 2ν₃, were examined as a function of temperature. All these bands are also observable in the FTIR spectrum of HNO₄ (Figure 2). After accounting for variations in the IR laser power and removing the background signal due to the UV probe laser scatter, UV photolysis of HNO₄, and HNO₄ thermal decomposition, integrated band dissociation cross-sections at each temperature were calculated relative to 3ν₁. To minimize the effect of small drifts in the probe laser power and/or changes in the HNO₄ concentration on the relative intensity measurements, all photodissociation scans were immediately followed and/or preceded by scans over the 3ν₁ reference band. While the normalized intensity of the 2ν₁ + ν₃ combination band is independent of temperature, both 2ν₁ and ν₁ + 2ν₃ combination band exhibited strong temperature dependence. This dependence is demonstrated for 2ν₁ in Figure 4, which shows photodissociation spectra normalized for constant 3ν₁ taken at 283, 244, and 224 K.

TABLE 2: Vibrational Frequencies of HNO₄ (in cm⁻¹) Observed in Combination with the 2ν₁ Vibrations (centered at 6900 cm⁻¹) Compared to the Known Experimental and Theoretical Frequencies of PNA Fundamentals

<table>
<thead>
<tr>
<th>band center (±10 cm⁻¹)</th>
<th>band center</th>
<th>tentative assignment</th>
<th>ab initio frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>7020</td>
<td>120</td>
<td>O–NO₂ torsion (ν₁)</td>
<td>134</td>
</tr>
<tr>
<td>7150</td>
<td>250</td>
<td>asym. NOO/ONO bend</td>
<td>298</td>
</tr>
<tr>
<td>7260</td>
<td>360</td>
<td>HOON torsion (ν₁)</td>
<td>377</td>
</tr>
<tr>
<td>7580</td>
<td>680</td>
<td>sym. NOO/ONO bend</td>
<td>682</td>
</tr>
<tr>
<td>7840</td>
<td>940</td>
<td>OO stretch (ν₁)</td>
<td>988</td>
</tr>
<tr>
<td>8240</td>
<td>1340</td>
<td>OOH bend (ν₁)</td>
<td>1452</td>
</tr>
</tbody>
</table>

* The vibrational labels are from Friedl et al.¹⁸ The correctness of the assignment of the NOO/ONO bend fundamentals is still debated.

* Observed only in combination with the NO stretch of Friedl et al.¹⁸

IV. Discussion

A. Vibrational Assignment. The exceptional sensitivity offered by the method of photodissociation spectroscopy enables observation of very weak vibrational bands, some of which are either well below the detection limit of the absorption measurements or obscured by the impurities. Three reproducible features appear in the photodissociation spectrum on the blue side of the 2ν₁ band separated by some 120, 250, and 350 cm⁻¹ from the 2ν₁ band center (Figure 3). Two additional extremely weak features are visible 680 and 940 cm⁻¹ above 2ν₁. Finally, a stronger feature is observed 1350 cm⁻¹ above 2ν₁, which is also easily discernible in the FTIR spectrum (Figure 2). The bands presumably correspond to combinations of 2ν₁ with various lower frequency modes of HNO₄. The tentative assignment of these bands is based on the comparison with known fundamental vibrations of HNO₄¹³,¹⁷–¹⁹ as given in Table 2 and discussed further below.

The agreement between the observed vibrational frequencies of HNO₄ in the 2ν₁ state and the experimental frequencies of HNO₄ fundamentals (Table 2) is quite reasonable and is also consistent with the anticipated direction of frequency shifts due to the cross anharmonicities. For example, an excitation of the OH stretch is expected to lower the OOH bending frequency somewhat prompting the assignment of the 8250 cm⁻¹ band to a combination of the first OH stretching overtone (2ν₁) with the OOH bending vibration (ν₁). An alternative assignment of this band to a combination of 2ν₁ with the NO₂ symmetric stretch (ν₂), which is a very bright vibration at 1304 cm⁻¹ in the fundamental range of the spectrum, would require an unphysically large coupling between the OH stretch and vibrations localized on the NO₂ end of the molecule. Similarly, excitation of 2ν₁ should have little influence on the OO stretch (ν₁), in agreement with our observations (Table 2). The reason for the relatively large difference in the frequency of the symmetric NOO/ONO bend (680 cm⁻¹ vs 648 cm⁻¹) is not clear at present, however the correctness of this assignment is still being debated.¹⁹

A possible alternative assignment for the lowest frequency feature at 7020 cm⁻¹ in the blue wing of 2ν₁ would be that of a sequence band of type 2ν₁ + ν₃ − ν₁. A shift of 120 cm⁻¹ between 2ν₁ and its sequence band would then imply a fairly large interaction between ν₁ and ν₃ modes induced, perhaps, by a strong hydrogen bonding between the H atom and an oxygen atom of the NO₂ group. However, the existence of such an interaction is not consistent with the predicted non-hydrogen bonded equilibrium structure of HNO₄,¹⁹ and also with the small observed effect on the frequency of the HOON torsion (ν₁) induced by the 2ν₁ excitation. One way to definitively disqualify the sequence band assignment is to carefully compare the
relative intensities of the 2ν₁ and 7020 cm⁻¹ bands in the photodissociation and FTIR spectra. If the 7020 cm⁻¹ band were a sequence, it would access a significantly higher energy level in the upper state compared to 2ν₁ and, therefore, dissociate with an increased quantum yield. Our measurements suggest that this is not the case, although a large interference from HNO₃ and H₂O₂ impurities makes qualitative measurements of FTIR intensities between 7000 and 7300 cm⁻¹ quite difficult. In conclusion, the weak bands between 2ν₁ and 3ν₁ can all be confidently assigned to different 2ν₁ + νᵢ combinations as shown in Table 2.

B. Photodissociation Quantum Yields. Two separate pieces of spectroscopic information are required to estimate the photodissociation quantum yields. The FTIR absorption spectrum of HNO₄ provides relative integrated band strengths for different fundamental and overtone vibrations of HNO₄ (Table 1). All infrared active vibrations appear in the absorption spectrum irrespective of the subsequent fate of the photoexcited peroxynitric acid molecules. In the photodissociation spectrum (Figure 3), only excitations resulting in the fragmentation of peroxynitric acid are observed. The latter can be thought of as a convolution between the absorption spectrum and photodissociation quantum yield, which is expected to vary for different excited states. To put the relative photodissociation cross-sections on an absolute scale additional information about the photodissociation quantum yields is required.

The most straightforward way of tying the photodissociation cross-sections to an absolute frame of reference is to postulate that the excitation into the 3ν₁ state of HNO₄—the highest energy feature in the spectrum—results in 100% dissociation. The 3ν₁ state of HNO₄ lies some 2000 cm⁻¹ above the known dissociation limit of the molecule. Because no barrier to dissociation is expected for a simple bond fission of this kind, a HNO₄ molecule excited in this transition should fragment within a few vibrational periods. With the assumption of unit photodissociation quantum yield for the 3ν₁ state, the absolute photodissociation band strength f∫[abs,3ν₁]dν = f∫[abs,3ν₁]dν (φᵢ is the quantum yield) for the other overtone vibrations of HNO₄ can be determined relative to 3ν₁ as follows:

\[
f\int \sigma_{abs,\nu_i} d\nu = \left( \frac{\int \sigma_{diss,2\nu_1} d\nu}{\int \sigma_{diss,3\nu_1} d\nu} \right) \times \int \sigma_{abs,3\nu_1} d\nu \tag{6}\]

where \(\int \sigma_{abs,3\nu_1} d\nu = 3.3 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}\) (Table 1). Effective temperature-dependent quantum yields for each vibrational band are similarly determined by combining the integrated absorption cross-sections with the temperature-dependent photodissociation band strengths.

Photodissociation band strengths and quantum yields are shown in Figure 5. For the purposes of atmospheric modeling, the integrated photodissociation cross-sections and quantum yields were fitted to purely empirical functions of temperature in a manner common for kinetics measurements (summarized in Table 3). Significant extrapolation beyond the temperature and pressure range used in this study should be done with caution. It is likely, for example, that the quantum yield for 2ν₁ may be lower at one atmosphere total pressure.

Unfortunately, we have no convenient way of experimentally verifying the assumption of the unit photodissociation efficiency for the 3ν₁ state (i.e., φ₃ν₁ = 1). One obvious approach would involve a comparison of the relative photodissociation intensities from two separate bands above the dissociation limit, say of 3ν₁ and 4ν₁, with their corresponding relative intensities in the absorption spectrum. As the 4ν₁ band falls outside our OPO scanning range and the band strengths for higher overtones are not known with sufficient accuracy, the only band available for such a comparison is the 2ν₁ + ν₁ combination band at 8250 cm⁻¹. The position of this state with respect to the HNO₄ dissociation limit (7970 ± 280 cm⁻¹) is, however, somewhat uncertain rendering the intensity comparison less conclusive. Nevertheless, the photolysis quantum yield of 0.76 ± 0.25 with no significant temperature dependence inferred for this state is consistent with the assumption of the unity dissociation quantum yield for states above the dissociation threshold.

As the photodissociation experiments are conducted at nontrivial pressures of the buffer gas (2–40 Torr), competition between various collision-induced processes and the intramolecular energy transfer leading to dissociation of the excited HNO₄ molecule has to be considered. A photodissociation quantum yield of unity, as assumed here for the 3ν₁ state, would require dissociation to occur on a sufficiently faster time scale than the rate of vibrational quenching of the excited molecules. Rotational energy transfer normally occurs on the time scale of hard sphere collisions (≈10⁷ s⁻¹ at 1 Torr), whereas vibrational energy quenching usually proceeds at a much slower rate. We have conducted simple RRKM calculations that show for the internal energy of the 3ν₁ state, the unimolecular dissociation of HNO₄ occurs at a microcanonical rate of ≈10¹¹ s⁻¹. Details of the RRKM calculations are not reported here, except for the fact that input parameters were chosen to provide the best fit for the pressure-dependent HNO₄ unimolecular decomposition rate data.⁵,⁰ The several orders of magnitude difference between the decomposition rate and the collision rate strengthens the validity of the φ₃ν₁ = 1 assumption under the conditions of our experiment.

One of the most intriguing findings of this study is the finite dissociation probabilities for excitations below the HNO₄ dissociation threshold. Bands lying below \(D_0 = 7970 ± 280\) cm⁻¹ by as much 1720 cm⁻¹ (ν₁ + 2ν₃) and 1070 cm⁻¹ (2ν₁) reproducibly appear in the photodissociation spectrum. Simple
back-of-the-envelope calculations, as well as direct power dependence measurements, indicate that multiphoton photodissociation processes (IR + probe or IR + IR) are not responsible. There are two mechanisms of supplying enough energy for dissociation: collision-induced activation of pre-excited molecules and coupling of internal rotational and vibrational energy into the dissociation coordinate. Although both mechanisms are likely to be important under the present experimental conditions, the lack of a pressure dependence on the integrated photodissociation band strengths suggests that a rapid intramolecular energy redistribution may be the dominant source of the near-threshold photodissociation.

In the case of the near-threshold photodissociation of NO₂, an excellent fit to the wavelength-dependent photodissociation quantum yield was obtained with a simple model that assumed that all molecules with total (i.e., \( hν + \) internal) energy above \( D₀ \) fall apart.\(^{21}\) Even better agreement with experimental data was obtained if a simple collision excitation treatment was included.\(^{22}\) We have modeled the observed HNO₄ quantum yields in a similar way treating the molecule as a near-prolate symmetric top with \((B + C)/2 = 0.1345 \text{ cm}^{-1}\) and \(\Delta = 0.4001 \text{ cm}^{-1}\). The twelve fundamental vibrations of HNO₄ were treated as harmonic oscillators and the internal energy probability distribution was calculated according to

\[
P(E) = \frac{(2J + 1)}{Q} e^{-\left(E_{\text{rot}}(n_1,n_2,...,n_{12}) + E_{\text{vib}}(J,K)\right)/RT}
\]  

using explicit counting over all possible combinations of vibrational and rotational quantum numbers with energies below 4000 cm\(^{-1}\). In eq 7, \(Q\) is the vibration–rotation partition function, \(J\) is the overall angular momentum (\(J = 0, 1, 2, \ldots\)), and \(K\), which runs from \(-J\) to \(J\), is the projection of \(J\) on the \(A\)-axis of the molecule.

The results are shown in Figure 6 for two temperatures, 273 and 223 K. The top panel shows the total vibration–rotation energy distribution. The distribution is substantially broader than one would calculate from the rotational energy levels alone because of the large number of low-frequency vibrations in HNO₄. In fact, the mean rotational energy of HNO₄, \(\langle E_{\text{rot}}(273 \text{ K}) \rangle > \approx 285 \text{ cm}^{-1}\), is lower than the mean vibrational energy, \(\langle E_{\text{vib}}(273 \text{ K}) \rangle > \approx 380 \text{ cm}^{-1}\), for the entire range of temperatures employed in the present work. The influence of the lowest frequency modes can be seen in Figure 6 as partially resolved humps on top of the internal energy distribution profile. At higher total energies, the distribution approaches a classical exponentially decaying limit.

In the lower panel of Figure 6, the probability that the internal energy will exceed a given energy threshold and the experimentally determined quantum yields for the \(v₁ + 2v₃\) and \(2v₁\) bands are shown. Satisfactory agreement between these two values is observed using this simplistic Boltzmann model treatment. Better agreement is obtained if the dissociation energy of HNO₄ is reduced by just 200 cm\(^{-1}\), well within the error bars of the presently accepted value (\(D₀ = 7970 \pm 280 \text{ cm}^{-1}\)).\(^{5}\) The neglect of collision effects and the relatively large uncertainty associated with the reported quantum yields do not, however, justify the adjustment to \(D₀\) based on the results presented here; a spectroscopically accurate determination of HNO₄ dissociation energy would greatly aid in the interpretation of the photodissociation yields.

C. Atmospheric Implications. Observation of large near-IR photodissociation probabilities of HNO₄, especially for the \(2v₁\) band, confirms the importance of overtone driven photochemistry in the atmosphere and supports the suggestion that HNO₄ is the missing source for HO₂ production in the lower stratosphere at high solar zenith angles. The clear sky near-IR photolysis rate for HNO₄, \(J(\text{HNO}_4)\), can be estimated for each vibrational band using the relationship:

\[
\text{Table 3: Temperature-Dependent Photodissociation Cross-Sections, Dissociation Quantum Yields, and Clear Sky Atmospheric Photodissociation Rates for Several Overtone and Combination Bands of HNO}_4^a
\]

<table>
<thead>
<tr>
<th>band</th>
<th>band center (cm(^{-1}))</th>
<th>(f_{\text{tot},\text{phot}}(\phi) \text{ d}ν) (cm(^{-2}) molecule(^{-1}) cm(^{-1}))</th>
<th>quantum yield ((\times 10^{15} \text{ photons cm}^{-2} \text{s}^{-1} \text{cm}^{-1}))</th>
<th>solar flux(^{24}) ((\times 10^{-6} \text{ s}^{-1}))</th>
<th>photolysis rate ((\times 10^{-6} \text{ s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4v₁</td>
<td>13105</td>
<td>1</td>
<td>2.51</td>
<td>0.075</td>
<td></td>
</tr>
<tr>
<td>3v₁</td>
<td>10900</td>
<td>2.12 \times 10^{-20}</td>
<td>0.76</td>
<td>4.36</td>
<td>0.53</td>
</tr>
<tr>
<td>2v₁ + 3v₃</td>
<td>8240</td>
<td>4.09 \times 10^{-18} \text{e}^{-1265/T}</td>
<td>0.14 (at 240 K)</td>
<td>4.90</td>
<td>6.41 (at 240 K)</td>
</tr>
<tr>
<td>2v₁</td>
<td>6900</td>
<td>1.87 \times 10^{-10} \text{e}^{-1010/7T}</td>
<td>0.02 (at 240 K)</td>
<td>5.10</td>
<td>0.027 (at 240 K)</td>
</tr>
<tr>
<td>v₁ + 2v₃</td>
<td>6250</td>
<td>(278 K &gt; T &gt; 240 K)</td>
<td>3.72</td>
<td>1.23</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)The uncertainty in the pre-exponential factor is dominated by the uncertainty in the 3v₁ band strength (20%) while the uncertainty in the exponential factor is statistical error associated with the empirical fit of the data (10% for 2v₁ and 29% for v₁ + 2v₃). The combined clear sky photolysis rate is on the order of \(1 \times 10^{-5} \text{ s}^{-1}\) at 240 K, largely invariant with changes in the solar zenith angle.

Figure 6. Calculated HNO₄ vibration–rotation energy distribution. (a). Internal energy distribution of HNO₄ at 273 K (solid line) and 223 K (dashed line). (b). Probability that the internal energy of HNO₄ exceeds a given energy threshold (lines). Experimentally measured quantum yields for 2v₁ and v₁ + 2v₃ bands, which lie 1070 and 1720 cm\(^{-1}\) below \(D₀\), respectively, are shown as open (273 K) and closed (223 K) circles. Adjusting the dissociation energy of HNO₄ by a mere 200 cm\(^{-1}\) would greatly improve the agreement between the model and experiment.
\[ J(\text{HNO}_4) = \int \sigma_{\text{dis}}(v,T) I(v) \, dv \approx \langle I(v) \rangle \int \sigma_{\text{dis}}(v,T) \, dv \]  

where \( \sigma_{\text{dis}}(v,T) \) is the temperature- and frequency-dependent photodissociation cross-section of \( \text{HNO}_4 \) as measured in the action spectra and \( I(v) \) is the frequency-dependent top of the atmosphere solar radiance. Negligible scattering or absorption is expected at these wavelengths (the \( \text{H}_2 \text{O} \) overtones are sufficiently shifted to the blue and do not provide significant attenuation in the stratosphere and upper troposphere). For these calculations, the reflectivity of the surface (albedo) is assumed to be 0. Results for the individual bands and for the sum of all known bands at a temperature of 240 K are given in Table 3. The total photolysis rate of 8.3 \( \times \) 10^{-6} s^{-1} obtained here is in good agreement with that required to match the missing HO\(_2\) source (\( J\)-value = 1 \( \times \) 10^{-5} s^{-1}) as depicted in Figure 1 of Wennberg et al.\(^{10}\) Incorporation of these near-IR photolysis rates into a photochemical model was also found to significantly improve the simulations of solar occultation Fourier Transform spectroscopy (FTS) measurements of \( \text{HNO}_4 \) obtained in the stratosphere.\(^{23}\) Particularly at high latitudes, where the sun never reaches high into the sky, the near-IR photolysis of \( \text{HNO}_4 \) contributes significantly to the total loss rate of this important reservoir. Calculations that neglect this process overestimate the rate of reaction 3 and therefore underestimate the average OH density.

Acknowledgment. This work was funded in part by NASA’s Atmospheric Effects of Aviation Program (NAG5-9307;11157) and by The National Science Foundation (ATM-9724500; -0094670). S.A.N. thanks the Camille and Henry Dreyfus Foundation for financial support.

Supporting Information Available: Table of the peroxy-nitric acid photodissociation band strengths and photodissociation rate versus inverse temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes