Absolute infrared vibrational band intensities of molecular ions determined by direct laser absorption spectroscopy in fast ion beams

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The technique of direct laser absorption spectroscopy in fast ion beams has been employed for the determination of absolute integrated band intensities $S(n)$ for the $v_1$ fundamental bands of $\text{H}_2\text{O}^+$ and $\text{NH}_2^+$. In addition, the absolute band intensities for the $v_1$ fundamental bands of $\text{HN}_3^+$ and $\text{HCO}^+$ have been remeasured. The values obtained in units of cm$^{-2}$ atm$^{-1}$ at STP are 1880(290) and 580(90) for the $v_1$ fundamentals of $\text{HN}_3^+$ and $\text{HCO}^+$, respectively; and 4000(800) and 1220(190) for the $v_1$ fundamentals of $\text{H}_2\text{O}^+$ and $\text{NH}_2^+$, respectively. Comparisons with ab initio results are presented.

INTRODUCTION

As a result of the rapid evolution of infrared laser spectroscopy of molecular ions throughout the last decade, over 60 ions (including isotopomers) have now been investigated in detail with this approach. While the knowledge deduced from this substantial body of work has had considerable impact in several areas of science, it has thus far been restricted principally to that derived from frequency measurements (structures, band origins, etc.). Consequently, several important properties of molecular ions remain poorly characterized. In particular, our knowledge of molecular ion electric dipole moments and their derivatives, as well as ionic collision cross sections, is very limited, as compared with that available for neutral molecules.

Recent "third-generation" molecular ion spectroscopy experiments have begun to address these shortcomings. For example, Laughlin et al. have reported a general method for determining the permanent dipole moments of molecular ions; Pursell et al. recently published the first observation of microwave-IR double resonance in a molecular ion and have used it to determine collision cross sections for $\text{HN}_3^+$. There is considerable practical motivation for measuring these properties of molecular ions. For example, the existence of reliable dipole moments and infrared band intensities would facilitate the in situ determination of ion densities in plasmas, planetary atmospheres, or in the interstellar medium. Moreover, they provide a more rigorous test of the quality of ab initio molecular wave functions than do structures and vibrational frequencies.

In a previous article, we reported the first direct determination of molecular ion vibrational band intensities using the newly developed technique of direct laser absorption spectroscopy in fast ion beams (DLASFIB). This approach exploits the capability of an ion beam method to conveniently determine absolute ion densities, whereas such information is difficult to extract from measurements carried out in discharge plasmas. The only other experimental determinations of molecular ion vibrational band intensities were made with the use of indirect monitoring of vibrational populations through secondary processes, such as chemical reactions or photodetachment. In the ICR experiments of Heninger and Mauclaire et al., radiative lifetimes of the $v = 1$ and $v = 2$ states of NO$^+$ and $v = 1$ of HCl$^+$ were measured by monitoring the effect of vibrational excitation on charge exchange or ion molecular reactions. The principal difficulty with such experiments is that of finding suitable reactions that not only bracket the vibrational populations, but which are also free from competing side reactions. Okumura et al. were able to determine the vibrational lifetimes of $\text{CH}^-$ ($v = 1$) and $\text{CH}_2^-$ ($\upsilon_1 = 1$ to 4) in an ion trap experiment. In that work, the ion of interest is confined in the trap for a specific time under collisionless conditions. The vibrational population is then probed by photodetaching the ions at a frequency below that required to detach the ground state, and then monitoring the relative amount of signal as a function of trapping time.

In Ref. 6 we reported results for the $v_1$ bands of $\text{HN}_3^+$ and $\text{HCO}^+$. Subsequent to the publication of that work, several minor errors have been discovered. In particular, measurements of the total ion current and the overlap of the laser radiation with the ion beam were found to be slightly in error, and the conversion to standard intensity units was carried out with an incorrect temperature. These errors have been corrected in the present work, and their effects on the results is discussed. Subsequent improvements in the DLASFIB experiment have enabled us to extend the absolute intensity measurements to the $v_1$ vibrations of $\text{NH}_2^+$ and $\text{H}_2\text{O}^+$. The results for these molecular ions are presented below.

EXPERIMENTAL

A general description of the DLASFIB spectrometer has been given in Refs. 6 and 11, and only those details specific to the present experiments are given here. A schematic of the experiment is given in Fig. 1. The apparatus consists of an ion beam overlapped coaxially with a tunable infrared
laser beam. The ion optical configuration is the straight-line design described in Ref. 6, and shown in Fig. 2. In this configuration, the ion source is placed directly in front of the interaction region; the laser is then propagated through the source into the interaction region.

The source used to generate the ions is an uncooled cold cathode source, as diagrammed in Fig. 2. Unlike sources used earlier with this spectrometer, it was constructed such that the laser beam could be transmitted through it. It consists of two hexagonally shaped iron plates 3.8 cm across that are separated by a 4 cm long Pyrex tube with a 9 mm inner diameter. Viton o-rings are used to make vacuum seals between the Pyrex piece and the iron plates. One of the plates is 1 cm thick with a 3 mm hole drilled through the center, and has a 6 mm hole drilled into the side which opens up at one face near the center of the plate. The 3 mm hole is used to transmit the laser through the source, and the 6 mm hole serves as the gas inlet. The opposite end plate has a corresponding 3 mm hole in the center of it from which the ions are extracted. In addition, it has a 22° taper cut into the side facing the ion optics. Small magnets can be placed around that end of the source, which serves to stabilize the discharge and to increase the total number of ions extracted from the source by about 30%. However, in the present experiments the magnets were not used, since they cause the ion loss to be nonlinear as a function of the distance from the source, as discussed later.

Gas mixtures consisted of 3:1 H₂ to N₂/CO/NH₃ and 6:1 H₂ to H₂O for the production of the corresponding protonated neutrals. Gas pressures were approximately 2 × 10⁻⁴ Torr in the chamber and 200 mTorr inside the source. The chamber pressure was measured with a calibrated VEECO ion gauge and the source pressure was calculated using the pumping speed of the system and the conductance of the source. A capacitance manometer connected to the gas line into the source was used to monitor the relative gas pressures.

The source was operated with the electrode adjacent to the ion optics floating at the beam voltage. It was found that operating this electrode with a positive polarity (i.e., the ions are extracted from the anode) resulted in higher ion currents; moreover, the ions extracted were representative of those found in a negative glow plasma, viz. predominantly protonated neutral species. Operating with the opposite polarity resulted in lower ion currents, and the ions extracted were characteristic of an electron impact source, viz. ionized neutrals. For the absolute intensity measurements the discharge voltage was maintained at 3 kV. With 600 kΩ of ballast resistors in series, the discharge current was 3 mA or less. Higher ion current could be obtained by operating the source at higher discharge voltages, but the corresponding higher discharge current resulted in a shorter source lifetime due to sputtering of metal onto the Pyrex tube. This would eventually lead to the source becoming unstable, and ultimately short circuiting. Under the given experimental conditions, we were able to optimize the production of the desired ions (from 70% HN⁺ to over 90% H₂O⁺) in the corresponding discharges. Total currents extracted from the source were ~20 to 30 pA, with about 10–15 pA actually being transmitted through the field-free interaction (drift) region. Using Eq. (1) from Ref. 12 (after correcting an error in the exponent of the charge to mass ratio), the space-charge limited current transmitted through the drift region can be calculated as

\[ I_{\text{max}} \left( \mu A \right) = 0.9 \left( \frac{Z}{m} \right)^{1/2} V^{3/2} \left( \frac{2d}{L} \right)^{3/2}. \]  

For a drift region of length \( L = 7.9 \) cm and an aperture diameter \( d = 0.2 \) cm, the space–charge limited current realized for mass 29 ions at 3 kV is 70 μA, which is about 7 times higher than the current actually observed.

The design of the ion optical system used to transport the ions from the source to the interaction (drift) region has been described in Ref. 6 and is shown in Fig. 2. To maximize the current, ions are extracted directly out of the anode of the source, and are immediately focused by an asymmetric three element electrostatic lens into the center of a segmented drift region. The first segment is 2.54 cm long, the second is 5.08 cm, and the combined effective path length is 7.9 cm. The
drift region was segmented for two reasons: (1) this configuration allowed for a better determination of ion loss as a function of transmission through the region (axial loss), and (2) because the two regions are electrically independent, they could either be scanned together or separately, thus facilitating a convenient test of the dependence of measured line strengths on the geometry of the ion optical system. Apertures with \( d = 2 \text{ mm} \) were used at the entrance and exit of each segment, and a guard plate with a 2 mm diameter aperture was placed before the entrance to the first segment such that the current measured in either region actually represented ions transmitted through that segment. These features were critical for determining the axially averaged ion current and density. The 2 mm apertures then determine the radially averaged density, which can be calculated from 12:

\[
\frac{n(\text{ions})}{\text{cm}^2} = \frac{1.432 \times 10^{12} I_{\text{av}} / A (\text{m/amu})^{1/2}}{(r/cm)^3 V^{1/2}}. \tag{2}
\]

For the typical currents obtained, the corresponding density is \( \sim 1 \times 10^7 \text{ cm}^{-3} \).

Frequency scanning of the spectrometer was achieved by setting the color center laser at a fixed frequency, floating the ion source at the desired beam voltage, and then "Doppler shifting" the ions into resonance by applying a slow (80 s) 100 V ramp to the drift regions. The tuning rate can be determined by taking the first derivative of the first-order Doppler shift relation:

\[
\nu_{\text{eff}} \approx \nu_r \left(1 \pm \frac{\nu_c}{c}\right) = \nu_r \left[1 \pm \left(\frac{2\nu_{\text{acc}}}{mc^2}\right)^{1/2}\right]. \tag{3}
\]

\[
\frac{\partial \nu}{\partial V} (\text{MHz/V}) = \frac{0.6946\nu_{\text{acc}}}{m^{1/2}V^{1/2}}. \tag{4}
\]

Equation (4) indicates that the resolution of the experiment increases with beam voltage, since for a fixed spread in the ion velocities (given in volts), the linewidth (in frequency units) decreases as the inverse square root of the ion voltage. Modulation of the ion absorption signal is accomplished by combining a 10 V peak-to-peak 400 kHz square wave with the ramp voltage, and detecting at 1/2 using a fast lock-in amplifier (EGG model 5202).

After exiting the second interaction region, ions are bent by a 90° quadrupole deflector, either to a Faraday cup (F2) for measurement of the total ion current, or with the polarity reversed on the quadrupole, to a Wien velocity filter (Coultron 300) for mass analysis. The Wien filter enables one to qualitatively optimize the production of a given ion before scanning and to quantitatively determine the actual composition of the ion current.

The Faraday cup (F2) used to measure the total ion current was modified relative to that used in our previous work. Originally F2 was a metal plate, but it was determined, by monitoring the current hitting the guard plate in front of F2, that secondary electrons were being sputtered from the plate. In fact, depending on the alignment, up to 2 \( \mu \text{A} \) of negative current could be measured on the guard plate. To eliminate this effect, a true Faraday cup was built by drilling a 6 mm hole through the center of F2 and attaching a 9.5 mm diameter, 4 cm long tube with a 45° angled bottom. The current subsequently measured on the guard plate was then found to be always positive, and could be aligned to be less than 0.2 \( \mu \text{A} \). At the same time the amount of current on F2 was found to be 30% lower than previously measured. The systematic error that this change induces in the line strength is about 25%, because to calculate the line strengths, the axially averaged current is used. To determine this axially averaged current, the ion loss was modeled in several different ways. Since these all gave approximately the same answer, the linear loss model was used because it was the simplest. In this model, the average ion current in a given drift segment is taken to be the mean of the entrance and exit currents. For the combination of two drift regions, the axially averaged current is given by

\[
I_{\text{av}} = F2 + \frac{1}{2}D1 + \frac{1}{2}D2. \tag{5}
\]

If the axial ion loss was truly linear, the current hitting the first drift region (D1) would be exactly one half of the current measured on the second drift region (D2). While the exact result was rarely realized, the conditions could be adjusted such that the ratio was reasonably close to 1/2; consequently the linear model was deemed adequate to describe the ion loss.

The laser employed in this study was the same as in the previous DLAS/FIB experiments.\(^{5,11}\) A color center laser (Burleigh FCL20E) pumped by a Kr\(^+\) laser (Spectra Physics 171) provides continuously tunable single mode radiation from 2900 and 4100 cm\(^{-1}\). While the FCL has a 1 MHz single mode linewidth, the effective linewidth due to jitter when the laser is not actively stabilized is closer to 4 MHz. Even without locking, the frequency stability was better than a few MHz per minute. Because the FCL is capable of producing several milliwatts of radiation, we were able to expand the laser beam with a telescope to a beam waist of \( \omega = 5 \text{ mm} \) (1/e\(^2\) intensity) at the chamber and still have sufficient power for laser noise limited sensitivity (40 \( \mu \text{W} \)). The laser beam profile across the ion optics aperture was then very nearly homogeneous. For example, given a 2 mm diameter aperture, a laser beam with a 5 mm waist results in an intensity at the edge of the aperture which is 92% of the intensity at the center. This homogeneity of the laser beam is critical for the measurement of line strengths, because the radial distribution of the ion beam is not easily quantified. By expanding the laser as described, the measured line strength becomes independent of the radial ion distribution. This was verified experimentally by expanding the laser to a larger beam waist and determining the same line strength. In our previous work, the laser beam was expanded to a diameter of 5 mm, corresponding to a beam waist \( \omega = 2.4 \text{ mm} \), which gives an intensity at the edge of the aperture that is 71% of the intensity at the center. At the time this was thought to be satisfactory, but a more careful determination has subsequently indicated that overlap variation was still problematic for that beam diameter. It is impossible to quantitatively determine the associated error, however, since it depends on the particular alignment of the laser and ion beams used at that time.

Absorption signals were detected using dual beam subtraction with a pair of small (0.5 mm diameter elements), fast (3 dB at 400 kHz), and quiet (detector noise of 90 nV/Hz\(^{1/2}\)) InSb detectors obtained from Cincinnati Elec-
tronics (model SDD-1963-S1). The use of background subtraction and the ability to modulate at high frequency (400 kHz) resulted in a sensitivity (minimum detectable fractional absorption) of $2 \times 10^{-7}$ for a 1 s time constant, which is about a factor of 4 lower than the shot noise limited sensitivity calculated for the power levels used (40 $\mu$W). At a modulation frequency of 400 kHz, the sensitivity is limited by a combination of laser and electronic noise. Modulating at higher frequencies (600–800 kHz) results in the system becoming detector noise limited, but the sensitivity decreases due to detector roll-off and loss of modulation efficiency.

The latter factor is due to the modulation period becoming comparable to the ion transit time through the drift region, i.e., as the modulation frequency increases, the drift region is not filled with ions of the same velocity before the modulation voltage changes, so that not all of the ions can simultaneously contribute to the absorption signal. Modulating 3 kV ions at 400 kHz with a 7.9 cm drift region corresponds to a 10% loss in the signal for HN$_2^+$, and 5% for NH$_2^+$ (which is taken into account in the following calculations).

Spectra were recorded and stored on the PDP-11/23 computer used to control the experiment. This facilitated convenient manipulation of the data when determining fractional absorptions and linewidths.

**RESULTS**

Table I lists typical experimental parameters for the ionic transitions studied in this work. Equation (6) gives the relation between these experimental parameters and the corresponding line strength for an inhomogeneously (Doppler) broadened vibration–rotation transition from an initial state $i$ to a final state $f$. Here $n$ is the ion density, $l$ is the path length, and $\Gamma_D$ is the Gaussian full-width at half-maximum (FWHM):

$$S_f = \left( \frac{\pi}{4 \ln 2} \right)^{1/2} \frac{\Delta P}{P} \frac{1}{nl} \Gamma_D.$$  

(6)

There was a typographical error in a similar equation given in our previous Letter. In the text, the linewidth was given as the FWHM, whereas the equation given was for the half-width at half-maximum (HWHM). This error did not affect any of the results reported.

The fractional absorptions listed in Table I were corrected for detector frequency response and the modulation efficiency of the ions. The detector frequency response was measured by frequency modulating a diode laser while scanning over an OCS rovibrational transition. The modulation efficiency was calculated by using the ratio of the first Fourier component of the signal to that of the corresponding square wave, which is a function of the mass of the ion, the length of the drift region, the beam voltage, and the modulation frequency. These corrections were confirmed experimentally by measuring the line strength as a function of the modulation frequency.

The ion density is calculated using Eq. (2) with the average ion current calculated from Eq. (5). Densities obtained ranged from $1.11 \times 10^4$ cm$^{-3}$ for HN$_2^+$ to $1.60 \times 10^6$ cm$^{-3}$ for H$_2$O$^+$. Mass spectra taken before and after each set of measurements are used to determine the fraction of the total ion current constituted by the ion being studied. Because the intensity units used here are cm$^{-2}$ atm$^{-1}$ STP, the ion density is converted to pressure at STP. The validity of using Eq. (5) to calculate the axially averaged ion current was confirmed by scanning the two drift regions either separately or simultaneously. In particular, scanning only the second segment produced the same line strength as obtained when scanning both drift regions. The results obtained when scanning only the first segment were somewhat less consistent. This was attributed to ion current striking the front of the first drift region because of imperfect alignment of the guard plate in front of it.

Linewidths were determined by least-squares fitting of the spectra to Gaussian line shapes. To insure meaningful fits, transitions were signal averaged until a reasonable signal-to-noise ratio was obtained ($>5:1$). For HN$_2^+$ this required only one to two scans, while for NH$_2^+$, at least 5 to 10 scans had to be averaged. Typical data for the NH$_2^+$ Q$^0$ A(2)→A(1) (4) transition are shown in Fig. 3. The linewidths observed were between 2 to 2.5 V FWHM for all four ions studied. This represents a slight improvement over the linewidths observed in the multilaser ion beam configuration described in Ref. 11, where the linewidths were closer to 3 V. The linewidths are converted to frequency units using Eq. (4). Because the tuning rate is inversely proportional to

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>$\Delta P / P$ (10$^{-7}$)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$n$ (10$^{-12}$ atm)</th>
<th>$\Gamma_D$ (cm$^{-1}$)</th>
<th>$S_f$ (Gaussian cm$^{-2}$ atm$^{-1}$ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN$_2^+$</td>
<td>R(9)</td>
<td>18.4</td>
<td>7.9</td>
<td>4.13</td>
<td>0.000 584</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.11)</td>
<td>(17.5)</td>
<td></td>
<td></td>
<td>(39.2)</td>
</tr>
<tr>
<td>HCO$^+$</td>
<td>R(9)</td>
<td>6.1</td>
<td>8.9</td>
<td>4.65</td>
<td>0.000 617</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.25)</td>
<td>(18.5)</td>
<td></td>
<td></td>
<td>(12.3)</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>P$_2$ (3)</td>
<td>9.4</td>
<td>13.8</td>
<td>5.86</td>
<td>0.000 751</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.58)</td>
<td>(22.5)</td>
<td></td>
<td></td>
<td>(18.1)</td>
</tr>
<tr>
<td>NH$_2^+$</td>
<td>Q$^0$ (4)</td>
<td>6.0</td>
<td>11.7</td>
<td>4.83</td>
<td>0.000 818</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.30)</td>
<td>(24.5)</td>
<td></td>
<td></td>
<td>(15.2)</td>
</tr>
</tbody>
</table>

*Corrected for electronic and detector response and modulation efficiency.
Pathlength $l = 7.9$ cm.
the square root of the mass, the lighter ions (NH$_4^+$, H$_2$O$^+$) have slightly larger linewidths than the heavier ions (HN$_2^+$, HCO$^+$). The highest signal-to-noise ratio (SNR) data for HN$_2^+$ were also fit to a Voigt profile in order to determine the relative contributions of homogeneous and inhomogeneous broadening, and to insure a correct accounting for the signal contributed from the wings of the transition. Because the SNR was only 30–50:1, this ratio could not be determined very precisely, but the lines were clearly predominantly (> 65%) inhomogeneously broadened. The average value obtained for the Voigt parameter $a = (\ln 2)^{1/2}(\Delta \nu_{L}/\Delta \nu_{G})$ was 0.4 ± 0.2. A comparison of the integrated absorptions obtained with both Voigt and Gaussian line shape analyses revealed that for $a = 0.4$ the Gaussian values were lower than the Voigt values by 12%. Because Voigt fits require a higher SNR, all of the data were treated as having Gaussian line shapes, and the resulting line strengths were increased by 12% on the basis of the above analysis.

The integrated line strengths obtained for the four transitions studied in this work are given in Table II. These particular transitions were used because they were among the strongest in their respective vibrational bands. While the units for integrated line strengths are cm$^{-2}$ atm$^{-1}$ (STP), the temperature in STP relates only to the conversion from number density to atmospheres. Because the ions are created in a discharge, their internal temperatures are not equilibrated, and must be determined explicitly in order to calculate vibrational band strengths. Rotational temperatures were easily determined by making appropriate Boltzmann plots for each ion. For HN$_2^+$, lines with $J = 3$–25 in the $R$ branch were used, resulting in $T_R = 600(20)$ K. This is considerably hotter than the temperature measured in our previous work [420 (20) K], but the conditions are somewhat different; in particular the pressure used inside the source was higher in the present work. For HCO$^+$, lines with $J = 6$–20 in the $R$ branch were used, yielding $T_R = 560(25)$ K. For H$_2$O$^+$, lines with $J = 3$–6 in the $K = 3$ component of the $a-a$ band were used, resulting in $T_R = 525(25)$ K. For NH$_4^+$, lines with $J = 4$–9 in the $A-A Q$ branch were used, yielding $T_R = 400(20)$ K.

The only ion for which a vibrational temperature could actually be measured was HN$_2^+$. The $v_3$ hot band ($v_3 + v_5 - v_1$) for this ion was observed by Owtrutsky et al., and the $v_3$ and $v_5$ hot bands have been measured by Rehfuss et al. Only the bending hot band could be observed in the present experiment; the temperature of the $v_2$ mode was found to be $T_v = 500(50)$ K. The fact that the other hot bands were not observed establishes an upper limit on the population in these excited vibrational states, and supports the use of the $v_2$ population to characterize the overall vibrational temperature. Because no hot bands have been observed (or at least assigned) for the three other ions, their vibrational temperatures were assumed to be the same as the respective rotational temperatures determined above.

### Table II. Integrated line strengths.$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>$S_{IF}$ (cm$^{-2}$ atm$^{-1}$ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN$_2^+$</td>
<td>$R(9)$</td>
<td>39.2(5.5)</td>
</tr>
<tr>
<td>HCO$^+$</td>
<td>$R(9)$</td>
<td>12.4(1.9)</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>$P_{2}(3)$</td>
<td>18.0(3.4)</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>$Q(0):A2(1)$–$A1(1)$</td>
<td>15.4(2.3)</td>
</tr>
</tbody>
</table>

$^a$Uncertainties are 1.$

### Calculations

The relationship between the integrated line strength $S_{IF}$ for a single vibration–rotation transition and the integrated infrared band intensity $S_0$ is

$$S_{IF} = S_0 R_{IF}. \quad (7)$$

In this expression, $F$ represents the Herman–Wallis vibration–rotation interaction correction.$^{13,16}$ Given the level of precision of the present experiment, this factor was taken to be unity. One crude check of this approximation is to ascertain how well a Boltzmann plot can reproduce the relative intensities for a given branch of a vibrational band. For HN$_2^+$ the rotational temperature was determined using the $R$ branch with $J = 3$ to 25. All of the transitions fit to within the 10% reproducibility level of the experiment, with no systematic error observed. Similar results were obtained for the other ions as well. A second test of this approximation is to compare the transitions in the $R$ branch to transitions in the $P$ branch (and $Q$ branch if applicable). No anomalous intensities were observed for any of the four ions. Tetrahedral molecules have an extra "eigenvector factor" for taking
into account the depletion of an allowed line intensity by vibration–rotation mixing, which results in the observation of so-called "forbidden" transitions.¹⁷ This depletion is usually less than 10%, and for the above reasons it was taken to be insignificant for NH₄⁺.

In Eq. (7), Rᵣ is the rotational term that represents the fraction of the total band strength that is accounted for in the line strength of a single rovibrational transition. The general expression for Rᵣ is

\[ Rᵣ = gᵣ Aᵣ e^{-Eᵣ/(kTᵣ)} qᵣ \frac{Vᵣ}{v₀} (1 - e^{-(hv₀)/(kTᵣ)}) \]  

(8)

In this expression, gᵣ is the total degeneracy of the lower state, Aᵣ is the Hönfl-London factor which depends on the type of rovibrational transition, Eᵣ is the energy of the initial state above the ground state, qᵣ is the rotational partition function, νᵣ is the frequency of the rovibrational transition, v₀ is the band center frequency, and the last term accounts for stimulated emission. The form used for Eq. (8) emphasizes the fact that the ions do not necessarily have their various internal degrees of freedom equilibrated.

It is clear that Rᵣ has a strong dependence on the rotational temperature, and only a weak dependence on the vibrational temperature. What is not so obvious is the dependence of the band intensity Sₒ₀ on the vibrational temperature. Sₒ₀ for fundamental vibrations decreases with increasing temperature because a higher population exists in the upper vibrational states. To account for this in our previous Letter, we included the vibrational partition function qᵥ in the Rᵣ term. This is not a conventional treatment, and it is not rigorously correct. The correct relationship for a band intensity measured at two different vibrational temperatures is, neglecting corrections associated with the intensity units used,

\[ Sₒ₀(T) = Sₒ₀(T') \frac{qᵥ(T')}{qᵥ(T)} \]  

(9)

In relation to our previous treatment, the “extra” term of qᵥ(T) is in almost all cases very nearly equal to one, since the standard intensity unit cm⁻² atm⁻¹ (STP) corresponds to a temperature of 273 K; unless the molecule has a very low frequency vibration or has inversion doubling of its vibrational levels, qᵥ ≈ 1. In fact, it should be noted for comparison that qᵥ is usually taken to be unity in ab initio calculations. The singular exception in the group of molecules studied here is H₂O⁺, which possesses an inversion-doubled ground state with a 55 cm⁻¹ splitting, and consequently qᵥ(273) = 1.80.

The explicit expression for Rᵣ for the linear molecules HN⁺ and HCO⁺ is given by¹⁸

\[ Rᵣ = |m| e^{-Eᵣ/(kTᵣ)} qᵣ \frac{Vᵣ}{v₀} (1 - e^{-(hv₀)/(kTᵣ)}) \]  

m = J + 1 R branch,

m = −J P branch.  

(10)

Both the rotational and vibrational partition functions were calculated with the standard high temperature formulas, and are given in Tables III and IV, respectively. Table III also lists the corresponding values for Rᵣ. The resultant band intensities are listed in Table V. The vibrational transition moment is calculated from Sₒ₀ using Eq. (11), and corresponding values are listed in Table VII:

\[ | \langle \mu_v \rangle |^2 = Sₒ₀ qᵥ/(11.183v₀) \]  

(11)

Here μᵥ is in Debye, Sₒ₀ is in cm⁻² atm⁻¹ (STP), and v₀ is in cm⁻¹.

The ν₁ vibration of NH₄⁺ is a triply degenerate perpendicular vibration of a spherical rotor, and the appropriate expression for Rᵣ is given by¹⁷

\[ Rᵣ = \frac{1}{3} e_ᵣ (2J + 1) qᵣ \frac{Vᵣ}{v₀} (1 - e^{-(hv₀)/(kTᵣ)}) \]  

(12)

Here eᵣ is the spin statistical weight of the initial state, which equals 5 for states with A symmetry. The partition function qᵣ was calculated by using a direct summation, while qᵥ was calculated using the standard high temperature formula. The vibrational transition moment is calculated from the band intensity using¹⁷

\[ | \langle \mu_v \rangle |^2 = \frac{Sₒ₀ qᵥ}{33.549v₀} \]  

(13)

The ν₁ vibration of H₂O⁺ is a doubly degenerate perpendicular vibration of a symmetric top that possesses a large inversion doubling. This doubling results in the existence of two distinct ν₁ subbands, labeled as s-s and a-a bands. To within experimental precision, these two subbands have equivalent integrated band strengths; the band strength listed in Table V is that obtained for one band using the P₃(3) a-a transition. In using Eq. (8) to calculate Rᵣ, the appropriate degeneracy is gᵣ = (2)(2J + 1)(1 + δ₆₃ₙ), and the correct Hönfl-London factor for a perpendicular transition with ΔJ = ΔK = −1 is given by

### Table III. Rotational factors

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Tᵣ (K)</th>
<th>qᵣ</th>
<th>Rᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN⁺</td>
<td>R(9)</td>
<td>600(20)</td>
<td>269</td>
<td>0.02684</td>
</tr>
<tr>
<td>HCO⁺</td>
<td>R(9)</td>
<td>560(25)</td>
<td>266</td>
<td>0.02706</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>P₃(3)</td>
<td>525(25)</td>
<td>609</td>
<td>0.01097</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Q₀(4)A₁ A₂ (1)-A₁(1)</td>
<td>400(20)</td>
<td>763</td>
<td>0.01283</td>
</tr>
</tbody>
</table>

*Vibration–rotation interactions explicitly neglected.

### Table IV. Vibrational partition functions

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Tᵣ</th>
<th>qᵥ(Tᵣ)</th>
<th>qᵥ(273)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN⁺</td>
<td>500(50)</td>
<td>1.365</td>
<td>1.060</td>
</tr>
<tr>
<td>HCO⁺</td>
<td>560</td>
<td>1.292</td>
<td>1.026</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>525</td>
<td>2.201*</td>
<td>1.802</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>400</td>
<td>1.022</td>
<td>1.002</td>
</tr>
</tbody>
</table>

*Calculated by direct summation.
**TABLE V. Integrated band intensities \( S^0 \) (cm\(^{-2}\) atm\(^{-1}\) at STP).**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vibration</th>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN(_2^+)</td>
<td>(v_1)</td>
<td>1880(290)</td>
<td>2760 CEPA-ED(^{25})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2610 CEPA-EV(^{25})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3490 SCF(^{25})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3235 SCF(^{26})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>950 CEPA-ED(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1120 CEPA-EV(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>850 SCF(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>805 SCF(^{28})</td>
</tr>
<tr>
<td>HCO(^+)</td>
<td>(v_1)</td>
<td>580(90)</td>
<td>2545 SCF(^{29})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2470 SCF(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2115 SCF-Cl(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2225 SCF(^{31})</td>
</tr>
<tr>
<td>H(_2)O(^+)</td>
<td>(v_j)</td>
<td>2000(400)</td>
<td>2545 SCF(^{29})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2470 SCF(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2115 SCF-Cl(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2225 SCF(^{31})</td>
</tr>
<tr>
<td>NH(_3^+)</td>
<td>(v_1)</td>
<td>1220(190)</td>
<td>860 SCF(^{32})</td>
</tr>
</tbody>
</table>

\(a\) Extrapolated to \(T_e = 273\).

\(b\) Superscript numbers are references.

\(c\) Value is for one inversion component only.

\(d\) See text for explanation of scaling factor used in converting units.

**TABLE VI. Integrand band intensities \( S^0 \) (cm\(^{-2}\) atm\(^{-1}\) at STP) of associated neutral molecules.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vibration</th>
<th>Experimental values(^a)</th>
<th>Theoretical values(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>(v_1)</td>
<td>259.41(^{15})</td>
<td>251 CEPA-1 ED(^{36})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>278.04(^{16})</td>
<td>258 CEPA-1 EV(^{36})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>239.65(^{15})</td>
<td>323 SCF(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>321 MP2(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>283 CISD(^{37})</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>(v_1)</td>
<td>13(^{38})</td>
<td>20.97 CPA(^{+})(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.18(^{39})</td>
<td>26.8 CI(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35.2 SCF(^{30})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.17 CISD(^{37})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>67.11 MP2(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>49.77 6-31G(^{\ast})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.48 SCF(^{40})</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>(v_3)</td>
<td>287.1(^{17})</td>
<td>355.2 CISD(^{37})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>266.6 MP2(^{27})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>484.1 SCF(^{41})</td>
</tr>
</tbody>
</table>

\(a\) Superscript numbers are references.

\(b\) Value is for the sum of the two unresolved inversion components.

\(c\) See text for explanation of scaling factor used in converting units.

\(d\) Superscript numbers are references.

The theoretical transition moment for the \(v_3\) band of H\(_2\)O\(^+\) was calculated by using Eq. (11), and is listed in Table VII.

**DISCUSSION**

The experimentally determined integrated vibrational band intensities are given in Table V, along with theoretical values. The theoretical values given for HN\(_2^+\) and HCO\(^+\) are different from those given in Ref. 6 because they have now been converted to \(T_e = 273\) K. The new values of 1880(290) and 580(90) cm\(^{-1}\) atm\(^{-1}\) (STP) obtained for HN\(_2^+\) and HCO\(^+\) represent an increase in the measured integrated band intensities of 60% and 38%, respectively, relative to our previous results. Twenty-five percent of this increase can be attributed to the decrease in the ion current measured with the new Faraday cup. This correction was quantitatively determined in the present experiments because results for both the old F2 plate and the new Faraday cup were compared directly. The remaining increase is attributed to the use of an insufficiently expanded laser beam in the previous set of experiments. The quantitative effect of this systematic error cannot be determined reliably, because it depends on the overlap of the laser with the ion beam, which is not necessarily reproducible.

When comparing the new experimental results to the old values, one notes that the integrated line strength for the \(R(9)\) transition of HN\(_2^+\) is increased by 25%, from 31.0(8) to 39.2(5.5) cm\(^{-1}\) atm\(^{-1}\) (STP). This increase in signal fortuitously agrees with the systematic error caused by incorrectly measuring the ion current with the old Faraday cup. It then appears (incorrectly) that the remaining increase in band intensity is due to the higher rotational temperature measured in this set of experiments \((T_R = 600\) K vs \(T_R = 420\) K). It is important to realize that this temperature was measured in both cases using the exact experimental conditions under which the line strengths were measured. Specifically, in both cases the straight-line ion optical system (SLS) was used to measure both the absolute intensity and the rotational temperature. The higher temperature ob-
served in the current set of experiments results in an effective decrease in the observed line strength, which offsets the increase that results from better ion-laser overlap and correct measurement of the ion current. The fact that both band intensities did not increase by the same amount is a result of previous (nonquantifiable) differences in the overlap and/or the relatively low signal-to-noise obtained for HCO⁺ signals.

Although the experimental values for the integrated band intensities for the ν₁ fundamental vibrations of HN₅⁺ and HCO⁺ have now been increased by approximately 50%, there is still substantial disagreement with ab initio results. Of the values listed in Table V, the CEPA-1 ED values calculated by Botschwina et al. are expected to be the most accurate, as this high level of theory gives the best agreement with experiment for similar neutral molecules (Table VI). This same method has been used to calculate the vibrational band intensities of the isoelectronic species HCN₃⁺ producing an agreement with experiment to within 10% for the ν₁ vibration. For HN₅⁺, the experimental value is 32% lower than the ab initio result of 2760 cm⁻² atm⁻¹ (STP), 25 while for HCO⁺ the experimental value is 39% lower than the theoretical value of 950 cm⁻² atm⁻¹. This corresponds to 3.0 σ and 4.1 σ, respectively, with respect to the experimental uncertainty. While the absolute values of the experimental band intensities are 35% lower than the theoretical results, our value for the ratio of the band intensities (HN₅⁺ /HCO⁺) is 3.2(5), which agrees quite well with the theoretical value of 2.9.

The experimental value for the band intensity of the ν₃ fundamental vibration of NH₅⁺ is in better agreement with theory. However, the only intensity results are the unpublished SCF calculations of Dixon and Komornicki, who report a value of 860 cm⁻² atm⁻¹ (STP). 32 This is within 1.9 σ of our value of 1220(190) cm⁻² atm⁻¹ (STP). It is surprising that our value is the higher one, since normally SCF calculations tend to overestimate intensities. For comparison, in Table VI experimental and theoretical values are listed for the ν₃ fundamental of the isoelectronic molecule CH₄. The SCF value of 484 cm⁻² atm⁻¹ (STP) 34 is over 1.5 times greater than the experimental value 27 of 287.

The best agreement between theory and experiment is found for the ν₃ band of H₂O⁺. SCF calculations have been performed by Colvin et al. 50 and SCF-CI calculations have been carried out by Swanton et al., employing the double-harmonic approximation. The Swanton et al. value of 2115 cm⁻² atm⁻¹ (STP) is in close agreement with our experimental value of 2000(400), and the Colvin et al. value of 2545 agrees to within 1 σ. Similar calculations have been carried out for the ν₁ fundamental of the corresponding neutral molecule NH₃, with comparable agreement (Table VI). Pracna et al. have also calculated transition moments for H₂O⁺ 证据 (Ref. 31) and NH₃, 34 but their value of 0.16 D for the transition moment for the ν₁ of H₂O⁺ does not agree with our value of 0.30 D, given in Table VII. However, this seems to be a conversion error, as their value for the transition moment for the ν₁ of NH₃ of 0.0112 D is correspondingly lower by a factor of 4 than the value they give in km mol⁻¹. Accordingly, we have scaled their values for the transition moments by the same factor of 4 when converting to cm⁻² atm⁻¹ (STP).

While we are confident that we have corrected minor errors in the determination of the ion intensity in and the measurement of the ion current transmitted through the interaction regions, there are other possible sources of systematic error that should be discussed. There are two possible sources of error in the determination of the axially averaged ion current. The first possible error results if ion current strikes the front of the first drift region. This would result in our band strengths being too low. Evidence against this consists of obtaining the same line strength when scanning just the second drift region (so that the first drift region acts as a filter, thus insuring that any ion current measured on the second drift region results from ions striking the far end of it) as when the two drift regions were scanned together. If there was significant current impinging on the front of the first drift region, the line strength obtained from scanning both drift regions would be consistently lower than the value obtained when only the second segment was scanned. This was found not to be the case. The second potential source of error results if the ion loss is not linear as a function of distance traveled. Fitting the ion loss to an exponential function changed the calculated line strength by less than 5%. In addition, it was determined that the line strength would scale with ion current as long as the ion beam was not too badly misaligned. Severe misalignment would result in a low value for the line strength.

Another possible source of error is the treatment employed for the line shapes. As discussed earlier, the signal-to-noise ratio was high enough to allow fitting of the transitions to Voigt line shapes only for the case of HN₅⁺. Careful inspection of the highest signal-to-noise data, along with the corresponding fits to the three types of profiles tested—Gaussian, Lorentzian, and Voigt—supported the use of the Voigt profile to describe the line shape, and the contention that the lines were predominantly inhomogeneously broadened. If the line shapes were entirely Lorentzian, the band intensities reported are 16% too low. If they are entirely Gaussian, the values are 12% too high. If the true line shapes are actually some other profile, the error cannot be quantitatively determined. Since the area under the fitted Voigt line shapes very closely matches the area under the observed line shapes, it is clear that such error would be less than 20%.

The other two obvious experimental perturbations, saturation and space charge effects, are not likely to be significant. The average ion current obtained in this experiment is a factor of 7 lower than the space charge limited current calculated using Eq. (1), hence such effects are not expected to be significant. Similarly, saturation is not likely to be a problem. The homogeneous contribution to the linewidth was determined to be approximately 3 MHz, which is on the order of the transit time broadening of ions through the drift region, as well as of the effective laser linewidth. The Rabi frequency can be calculated using 22

\[
R = \frac{\langle \mu \rangle \left( \frac{P}{a} \right)^{1/2}}{\sqrt{3}} \frac{13.8 \text{ MHz}}{\text{D}} \left( \frac{\text{cm}^2}{\text{W}} \right)^{1/2}.
\]

Using a transition moment of 0.23 D and a typical laser pow.
er of 23 μW, the calculated Rabi frequency is only 50 kHz.

The potentially most serious source of error results from a possible unaccounted population in excited vibrational states. As mentioned earlier, HN$_2^+$ is the only ion for which hot bands have been assigned, and we did not observe transitions from any of the vibrationally excited states except for the first excited state of the ν1 bend. This establishes an upper limit for the unaccounted population for HN$_2^+$ of \( \sim 30\% \). The ion most likely to have significant excited state population is H$_2$O$^+$ because of its low frequency bending vibration. The consequence of a significant excited state population would be that the reported experimental values for the band intensities would be systematically low.

In our treatment of line strength, all vibration–rotation interaction perturbations have been explicitly neglected. Coriolis mixing could conceivably induce a J-dependent intensity variation, but these effects are probably small for strongly allowed bands, such as those studied in this work.

The possible systematic errors discussed above could possibly cause our values to be in error by as much as a factor of 2. The uncertainties given in Table V are determined from the reproducibility of the measurements, and therefore only reflect the precision of the experiment. In any case, we have demonstrated a new technique that for the first time permits the direct measurement of molecular ion vibrational intensities at a level of accuracy such that meaningful comparisons with theory can be made. It is hoped that this work will inspire calculations of the same high level of theory for all four molecules studied, as well as calculations for other ions that potentially could be studied using our experimental technique, as this would make for the most meaningful comparisons. It would facilitate quantitative comparisons if future theoretical studies were to explicitly state what values were used for partition functions, and if conventional units were used.

We anticipate that the results obtained from this experiment will facilitate the in situ monitoring of ion densities in plasmas and the determination of column densities in the atmosphere and the ISM. The recent infrared detection of H$_2$ in the Jovian atmosphere is an example of a situation in which an experimental determination of the absolute infrared band strength would clearly be useful. Such applications make this technique a valuable one for extending the type of information available for molecular ions.

ACKNOWLEDGMENTS

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31D. A. Dixon and A. Komornicki (private communication).


