Near-Infrared Spectroscopy of H$_3^+$

Above the Barrier to Linearity

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ABSTRACT

The first H$_3^+$ transitions above the barrier to linearity have been observed in absorption in the near-infrared using a highly sensitive dual-beam, double-modulation technique with bi-directional optical multi-passing. A total of twenty-two rovibrational transitions of H$_3^+$ have been detected and assigned to the fourth and fifth overtone and combination bands (5ν$_2^1$, 5ν$_2^5$, 2ν$_1$ + 2ν$_2^2$, 3ν$_1$ + ν$_2^1$, ν$_1$ + 4ν$_2^2$, 2ν$_1$ + 3ν$_2^1$, and 6ν$_2^2$). These transitions, which are more than 4600 times weaker than the fundamental band, probe energy levels above 10,000 cm$^{-1}$, the regime in which H$_3^+$ has enough energy to sample linear configurations. Experimentally determined energy levels above the barrier to linearity provide a critical test of ab initio calculations in this challenging regime. The comparison between experimental energy levels and theoretical energy levels from ab initio calculations in which the adiabatic and relativistic corrections are incorporated reveals the extent of higher-order effects such as non-adiabatic and radiative corrections. We compare our results with several recent theoretical calculations.

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I. INTRODUCTION

The molecular ion H$_3^+$, the simplest stable polyatomic molecule, performs an important role in the chemistry of hydrogen-rich plasmas and in the evaluation of theoretical calculations of rovibrational levels in polyatomic molecules. The ground state equilibrium geometry of H$_3^+$ is an equilateral triangle, resulting in unusual spectroscopic properties. An obvious consequence of this high degree of symmetry is that the ion has no permanent dipole moment, and thus no ordinary rotational spectrum. No stable electronic excited states of H$_3^+$ have ever been observed, and in fact theory suggests that a discrete electronic spectrum is unlikely to exist. The only available spectroscopic signature of H$_3^+$, therefore, is its vibrational spectrum.

The initial motivation for the laboratory spectroscopy of H$_3^+$ was to facilitate its astronomical study. As the most abundantly produced molecular ion in interstellar clouds, H$_3^+$, the universal proton donor, plays the most fundamental role in the chemistry of the interstellar medium. The infrared absorption spectrum of H$_3^+$ was first observed in the laboratory by Oka in 1980.$^1$ Trafton et al.$^2$ made the first non-terrestrial observation of H$_3^+$ in the ionosphere of Jupiter in 1987, although it was not positively identified until 1989.$^3$ More recently, H$_3^+$ has been detected in the interstellar medium.$^4,5$ Since then, many additional H$_3^+$ spectra have been recorded, both in the laboratory and in space – and H$_3^+$ has been the focus of many reviews.$^6-15$ With numerous theoretical studies and 17 laboratory spectroscopic studies including over 800 observed transitions, the spectrum of H$_3^+$ below 9000 cm$^{-1}$ is well understood.$^{14}$

Collaborative effort between experimentalists and theorists has been essential in the development of H$_3^+$ spectroscopy: theoretical predictions help the experimentalists’ search for new transitions, and accurate experimental frequencies enable theorists to improve the potential energy surfaces and variational calculations. In this paper, we present the results of a new
laboratory investigation of overtone and combination bands of \( \text{H}_3^+ \), beyond the barrier to linearity and higher in energy than any previously detected transitions. These transitions, which are more than 4600 times weaker than the fundamental band,\(^{16}\) occur in the near-infrared region and were observed in absorption. The detection of these transitions required the development of a high-resolution, high-sensitivity spectrometer.

An experimental setup using the combined techniques of velocity modulation (VM), phase modulation (PM) with heterodyne detection, bi-directional optical multi-passing, and dual-beam subtraction was developed in order to detect these extremely weak \( \text{H}_3^+ \) transitions. The velocity modulation,\(^{17}\) which is commonly used in positive column plasma spectroscopy to modulate and discriminate ion lines from neutral lines, is supplemented by phase modulation and heterodyne detection\(^{18}\) at 500 MHz to minimize the \( 1/f \) noise of the laser. The overall sensitivity is close to shot-noise limited, as detailed in section III.

The primary motivation for continuing the study of vibrational states beyond those spectroscopically probed to date is to assist in the development of theoretical calculations of \( \text{H}_3^+ \). The variational treatment of the kinetics of three protons in the \textit{ab initio} potential surfaces, which has been successful so far, may not be as effective near the barrier to linearity due to a singularity in the Hamiltonian that occurs whenever \( \text{H}_3^+ \) samples a linear configuration. Experimentally determined energy levels are therefore essential as a check for various theoretical techniques for calculating the energy levels to spectroscopic accuracy and studying the higher-order effects such as the adiabatic and non-adiabatic corrections to the Born-Oppenheimer approximation, as well as relativistic and radiative corrections. Although the high energy levels (\( >11,000 \text{ cm}^{-1} \)) in this work are considerably above the highest levels observed thus far in the astronomical plasmas of Jupiter’s ionosphere (6669 cm\(^{-1}\) in the overtone band\(^3\) and 7992 cm\(^{-1}\) in
hot bands,\textsuperscript{19}) they may be observable in Jupiter and other high temperature astronomical objects in the near future.

II. BACKGROUND

A. Quantum Numbers

As a symmetric top molecule with $D_{3h}$ symmetry, $H_3^+$ has three vibrational degrees of freedom resulting in two modes; the totally symmetric ($A'$) mode $\nu_1$ is infrared inactive, and the doubly degenerate ($E'$) bending mode $\nu_2$ is active. Vibrational states are labeled as $v_1\nu_1 + v_2\nu_2^\ell$, where $v_1$ and $v_2$ are the vibrational quantum numbers of the $\nu_1$ and $\nu_2$ modes, and $\ell = v_2, v_2 - 2, \ldots, -v_2$ is the quantum number for vibrational angular momentum.

Because of the small mass of its nuclei and its relatively shallow potential, $H_3^+$ is a highly anharmonic vibrator and the harmonic selection rules ($\Delta v_2 = 1$ and $\Delta \ell = \pm 1$) are not obeyed, especially for the highly excited states reported in this paper. The quantum number $k$ for the projection of the rotational angular momentum $J$ along the symmetry axis identifies the parity of the level,\textsuperscript{20} but is not a convenient quantum number to specify energy and permutation symmetry in excited states of the $\nu_2$ mode, due to the strong Coriolis coupling between the rotational and vibrational angular momentum. Instead, Hougen’s quantum number\textsuperscript{21} $g = k - \ell$ or its absolute value $G = |k - \ell|$ specifies the energy and symmetry of the rovibrational levels. The quantum number $g$ is associated with the spin modification of $H_3^+$; $g = 3n$ ($n$ is an integer) corresponds to \textit{ortho}-$H_3^+$ ($I = 3/2$) and $g = 3n \pm 1$ corresponds to \textit{para}-$H_3^+$ ($I = 1/2$), where $I$ is the quantum number for the total nuclear spin angular momentum $\hat{I} = \hat{I}_1 + \hat{I}_2 + \hat{I}_3$. The electric dipole
selection rules for these quantum numbers are $\Delta g = 3n$ and $\Delta k = \text{odd}$, the latter from the selection rule for parity $(-1)^k$. Although the only rigorously good quantum numbers are the quantum number $F$ for the total angular momentum $\hat{F} = \hat{J} + \hat{I}$ and parity $\pm$ (selection rule: $+ \leftrightarrow -$), $J$ and $I$ can be considered good quantum numbers because of the weakness of the nuclear spin-rotation interaction and the selection rules $\Delta I = 0$ and $\Delta J = 0, \pm 1$ are strongly obeyed. The notation used in this paper for $\text{H}_3^+$ transitions is that detailed in the recent review by Lindsay and McCall\textsuperscript{14} for both the band symbol

$$v_1 v_{1/2}^+ v_{1/2}^- \leftarrow 0$$

and the branch symbol

$$\{p|q|r\} (J', G')^{[p]}$$

where $P$, $Q$, and $R$ represent $\Delta J = -1, 0, +1$; $u$ and $l$ differentiate pairs of levels with the same value of $G$ (and different values of $k$ and $\ell$) for the upper state. When $\Delta G \neq 0$, the value of $\Delta G$ is specified by the leading superscript, where $t$ corresponds to $\Delta G = +3$ and $n$ corresponds to $\Delta G = -3$. For transitions $g' = \pm 2 \leftrightarrow g'' = (\pm 1)$ etc. which formally look like $\Delta G = 1$, $n$ is used. For highly-mixed levels the numerical value of $\Delta G$ is used ($\pm 6, \pm 9, \ldots$). A more thorough discussion of the quantum numbers and selection rules for $\text{H}_3^+$ can be found in the review by Lindsay and McCall.\textsuperscript{14}
B. Theoretical Calculations

Because H$_3^+$ is the simplest polyatomic molecule, a great many \textit{ab initio} theoretical papers have been published on it\textsuperscript{14,22} since the earliest work by Coulson\textsuperscript{23} in 1935. Just as molecular hydrogen has served as the model for the \textit{ab initio} studies of diatomic molecules, H$_3^+$ has been used as a benchmark for theoretical calculation of polyatomic molecules from first principles.

Using an \textit{ab initio} potential energy surface,\textsuperscript{24} Carney and Porter were the first to calculate rovibrational energies of H$_3^+$ in 1976.\textsuperscript{25} This theoretical prediction helped the laboratory detection of the fundamental band of H$_3^+$ and its analysis by Watson.\textsuperscript{1} The accuracy of \textit{ab initio} calculations improved greatly after the laboratory detection. In 1986, Meyer, Botschwina, and Burton\textsuperscript{26} published the MBB potential which, after a small correction by a scaling factor to match the observed $\nu_2$ band origin of H$_3^+$, gave accurate values and predictions for excited vibrational states of H$_3^+$ and its isotopomers. The corrected MBB potential has been used extensively by Miller and Tennyson\textsuperscript{27-29} for a generation of H$_3^+$ calculations based on the variational formalism of Sutcliffe and Tennyson.\textsuperscript{30} Those calculations were essential for the assignment of the laboratory spectrum of hot bands,\textsuperscript{31} overtone bands,\textsuperscript{32} and forbidden transitions\textsuperscript{33} and the astronomical spectrum of Jupiter.\textsuperscript{3} Dinelli, Miller, and Tennyson\textsuperscript{34} also used the \textit{ab initio} potential energy surface published by Lie and Frye\textsuperscript{35} to generate a spectroscopically determined potential surface.

In the last decade, theoretical calculations have been further improved, reaching near spectroscopic accuracy. Watson\textsuperscript{36,37} developed a semi-empirical potential energy surface by adjusting the MBB potential to match the laboratory spectrum and provided accurate predictions,\textsuperscript{38} which we have used over many years.\textsuperscript{14} Röhse, Kutzelnigg, Jaquet, and Klopper
(RKJK)\textsuperscript{39} published a potential energy surface with microhartree accuracy (errors less than 1 cm\textsuperscript{-1}) in 1994. Dinelli, Polyansky and Tennyson\textsuperscript{40} developed a semi-empirical potential based on the RKJK potential which led to the very extensive calculation of Neale, Miller, and Tennyson (NMT),\textsuperscript{41} who gave frequencies and intensities for three million transitions with high accuracy. The adiabatic correction for the breakdown of the Born-Oppenheimer approximation was calculated by Dinelli, La Sueur, Tennyson, and Amos.\textsuperscript{42} The most accurate potential to date is that of Cencek, Rychlewksi, Jaquet, and Kutzelnigg (CRJK),\textsuperscript{43} who took into account adiabatic and relativistic corrections. The most recent calculations based on the CRJK potential have given theoretical values of spectroscopic accuracy.\textsuperscript{44-49} Quite independently, Aguado \textit{et al.}\textsuperscript{50} published a global potential surface which is suitable for dynamical calculations. A recent paper by Lindsay and McCall\textsuperscript{14} summarizes the different theoretical approaches and their agreement with experimental values below the energy of 9000 cm\textsuperscript{-1}.

The energy regime near and above the barrier to linearity is particularly difficult theoretically – until recently, few of the rovibrational calculations performed in this range included the correct boundary conditions for linear geometries. The variational treatment, which is essential in calculating high rovibrational energy levels of H\textsubscript{3}\textsuperscript{+}, encounters a difficulty near the top of the barrier to linearity at the energy of \~10,000 cm\textsuperscript{-1} above the zero-point level. This is because the kinetic Hamiltonian, which is inversely proportional to the moment of inertia, contains a singularity for the linear structure. Fig. 1 shows a one-dimensional cut of the potential energy surface of Röhse \textit{et al.}\textsuperscript{39} in which H\textsubscript{3}\textsuperscript{+} is constrained in an isosceles triangle structure and the two equal H-H bond lengths are varied to minimize the energy for each value of the angle $\theta$, which measures the deviation from linearity. The top of the barrier to linearity is at $\theta = 0$ in this figure.
Watson,\textsuperscript{36} who used the Morse coordinate system with three H-H bond lengths ($r_1$, $r_2$, $r_3$), confined the wavefunctions to vanishingly small amplitudes at linear geometries by introducing an artificial wall of $10^6 \text{ cm}^{-1}$ for linear ($r_1 + r_2 = r_3$) and non-physical ($r_1 + r_2 < r_3$) regions. While this gave accurate results for levels with energy less than 9000 cm\textsuperscript{-1}, Watson did not expect the calculations to be accurate for higher energy levels and advocated the use of hyperspherical coordinates.\textsuperscript{37}

Tennyson and colleagues (NMT)\textsuperscript{41} used the Jacobi coordinates ($r_1$, $r_2$, $\theta$), for which the Hamiltonian has a serious singularity for $r_2 = 0$. Since the analytical solution of the Morse potential ($\propto > r > -\infty$) does not satisfy the boundary condition ($\propto > r_2 \geq 0$), they used a basis set composed of spherical oscillator functions. This has allowed them to handle the singularity problem at linear geometries ($\theta = 0$, $\pi$, or $r_2 = 0$), although a subsequent comparison with experimental energy levels\textsuperscript{14} has shown that this method suffers from poor agreement at high rotational levels ($J > 8$). This shortcoming has been overcome recently by the use of the Radau coordinates ($R_1$, $R_2$, $\theta$), in which the z-axis is perpendicular to the plane of the molecule.\textsuperscript{51}

A more efficient and elegant way to treat the large amplitude motion of H\textsubscript{3}+ is to use hyperspherical coordinates ($\rho$, $\theta$, $\phi$). The basis set of hyperspherical harmonics not only allows rigorous treatment of singularities in the kinetic Hamiltonian, but also retains the D\textsubscript{3h} permutation-inversion symmetry of the system, so that full advantage of the symmetry properties of the molecule may be taken. Although Whitnell and Light\textsuperscript{52} used hyperspherical coordinates in which the z-axis is in the plane of H\textsubscript{3}+ for their calculation of vibrational energy levels ($J = 0$), subsequent rovibrational calculations used Johnson’s Hamiltonian,\textsuperscript{53} which was based on the formulation of Smith and Whitten\textsuperscript{54,55} in which the z-axis is along the axis of the symmetric top.
rotor perpendicular to the molecular plane. The formalism was applied to H$_3^+$ by Bartlett and Howard,\textsuperscript{56} Carter and Meyer,\textsuperscript{57,58} and Wolniewicz and Hinze.\textsuperscript{59} Alijah, Hinze, and Wolniewicz (AHW)\textsuperscript{60} also applied this formalism to H$_3^+$ using both the MBB and RKJK surfaces.

The calculations using hyperspherical coordinates have been extended to above the barrier to linearity by AHW\textsuperscript{60} using the RKJK surface and more recently by Schiffels, Alijah, and Hinze (SAH)\textsuperscript{48,49} using the CRJK surface. SAH published their calculations below 9000 cm$^{-1}$ (Part I)\textsuperscript{48} and from 9000-13,000 cm$^{-1}$ (Part II)\textsuperscript{49} separately. This work is truly \textit{ab initio} since the potential surface is not adjusted to match laboratory data. A comparison by SAH\textsuperscript{48} of these theoretical energy values below 9000 cm$^{-1}$ with experimental ones compiled by Lindsay and McCall\textsuperscript{14} has revealed a systematic deviation on the order of a fraction of a cm$^{-1}$, which can be expressed as

\[
\Delta E = E_{\text{obs}} - E_{\text{calc}} = -b_1 E_{\text{calc}}^0 - \alpha_1 J(J+1) - \alpha_2 G^2
\]  

where $E_{\text{calc}}^0$ is the calculated band origin and $b_1 = 1.0123 \times 10^{-4}$, $\alpha_1 = 2.0436 \times 10^{-3}$ cm$^{-1}$, and $\alpha_2 = -1.3600 \times 10^{-3}$ cm$^{-1}$ are empirical constants. For low rotational levels, the first vibrational term of $\Delta E$ is larger than the second and third rotational terms by two orders of magnitude. Since the adiabatic and relativistic corrections are already included in the CRJK potential, SAH\textsuperscript{48} ascribe $\Delta E$ to the largest of the remaining corrections, that is, the non-adiabatic effect. This leaves the quantum electrodynamic radiative effect as the only remaining sizeable correction.

After applying an empirical correction formula similar in form to Eq. (3) but using coefficients based on a least-squares fit to individual experimental band origins, SAH\textsuperscript{48} found that approximately 500 laboratory-determined energy levels below 9000 cm$^{-1}$ matched with the calculated levels to within 0.1 cm$^{-1}$, except for 6 levels whose deviations range from 0.15 to 0.33 cm$^{-1}$. They also predicted that their data corrected by the extrapolation formula (3) would have
an accuracy of ±0.1 cm⁻¹. SAH⁴⁹ has given predictions for energy levels between 9000-13,000 cm⁻¹ using this formalism. In the calculations of Watson³⁶,³⁸ and NMT,⁴¹ who also give energy levels beyond the barrier to linearity, the non-adiabatic and radiative corrections were incorporated when they adjusted the potential surface to fit experimental data.

C. Laboratory Spectrum

As evaluated and compiled by Lindsay and McCall,¹⁴ 526 energy levels below 9887 cm⁻¹ from vibrational states up to \( v_1 + v_2 = 3 \) have been experimentally determined: \( 0 (62) \), \( v_1 (36) \), \( v_2^1 (132) \), \( 2v_2^0 (43) \), \( 2v_2^1 (116) \), \( v_1 + v_2^1 (63) \), \( 2v_1^0 (1) \), \( 3v_2^0 (21) \), \( 3v_2^2 (14) \), \( v_1 + 2v_2^0 (4) \), \( v_1 + 2v_2^1 (32) \), and \( 2v_1^0 + v_2^1 (2) \), where the numbers in parentheses give the number of determined rovibrational levels. These data are based on 17 experimental papers which report the fundamental, hot bands, overtone bands, combination bands, and forbidden transitions.

Although overtone and combination bands in ordinary molecules are usually much weaker than the fundamental because their transition dipole moments decrease rapidly for higher vibrational excitation, the decrease in the transition dipole moment of \( \text{H}_3^+ \) is less drastic than for heavier molecules. Due to the large vibrational amplitude of the protons, the nuclear motion of \( \text{H}_3^+ \) probes the anharmonic part of the potential surface. We have skipped the third overtone \( (4v_2^2 \leftarrow 0) \) and have searched for the fourth and fifth overtones \( (5v_2^1 \leftarrow 0, 6v_2^2 \leftarrow 0) \) and associated bands. Although these bands are more than five times weaker than the third overtone band,¹⁶ these and other associated bands lie in a region where our Ti:Sapphire laser has high power and good stability. Since the \( 5v_2^1 \) and \( 6v_2^2 \) vibrational energy levels are fully above the linearity barrier (Fig. 1), the observed bands are useful for assessing the accuracy of the various theoretical calculations above the barrier to linearity.
III. EXPERIMENTAL

A liquid-nitrogen cooled, triple-jacketed discharge tube was used to produce $\text{H}_3^+$.\textsuperscript{61} Approximately 500 mTorr of $\text{H}_2$ (and an optional ~10 Torr He) was continuously pumped through multiple gas inlets into the central bore (1 m long, 18 mm diameter). The central bore was evacuated by a mechanical pump through multiple outlets, to keep the gas inside the cell fresh. A second jacket filled with liquid nitrogen cooled the inner bore. The outermost jacket was kept sealed under vacuum to provide thermal insulation for the liquid nitrogen. Two CaF$_2$ windows mounted at the appropriate Brewster angle to minimize reflection losses of the laser beam sealed the plasma tube at each end.

A 20 kHz ac potential of 2-5 kV was applied to the electrodes located at each end of the cell, generating a current of up to 1 A. The applied potential was produced by a sine-wave generator amplified by a Techron 7780 power amplifier (4 kW maximum output) and stepped-up by a transformer. The maximum $\text{H}_3^+$ signal intensity was obtained with a current of ~500 mA rms. These discharge conditions lead to $\text{H}_3^+$ column densities (concentration $\times$ absorption path length) on the order of $10^{14}$ cm$^{-2}$. The resulting plasma is a non-equilibrium system with a rotational temperature of ~300K.

A Coherent 899 Titanium:Sapphire ring laser pumped by a 10 W Verdi laser provided approximately 1 W of continuous power, high spectral purity (500 kHz bandwidth), and a wide tuning range. The mid-wavelength optics set was employed in this work, giving continuous coverage from ~11,000-12,800 cm$^{-1}$. The laser is computer-controlled and can scan over wide regions at lower sensitivity using Coherent’s Autoscan software, or repetitively over smaller regions (~28 GHz) at higher sensitivity using custom software and a National Instruments Data Acquisition (DAQ) Card. Both integration (10 data points per scan step) and co-addition (100
scan segments were averaged for each $\text{H}_3^+$ transition) were used to improve the sensitivity. A time constant of 30 ms was used for each scan segment, which was recorded with the sensitivity setting of the lock-in amplifier at 200 $\mu$V. Each set of 100 scans took approximately 1 hour to record and average.

The combined techniques of velocity modulation$^{17}$ and phase modulation$^{18}$ were used to improve the sensitivity. This method has been used in the visible region by Longsheng Ma and others at East China Normal University in combination with magnetic rotation for paramagnetic ions,$^{62,63}$ and in the mid-infrared by the Oka group.$^{64}$ Fig. 2 shows a schematic of our experimental setup, including the heterodyne detection electronics. We used a New Focus Model 4421 EOM driven by about 2 W of radio frequency power at 500 MHz. High power, high transmission Glan laser polarizers from Coherent permitted us to pass approximately 400 mW of laser power through the EOM (limited by the photorefractive damage threshold of the crystal). A 2 GHz etalon spectrum analyzer enabled us to monitor the amplitude of the sidebands; during scanning we used it to monitor the unmodulated laser beam in order to facilitate calibration of the laser frequency (along with a reference iodine cell heated to $\sim$670 °C and a New Focus Model 2011 InGaAs photodetector). Because single-mode lasers such as the Ti:Sapphire have little noise at 500 MHz, the beat signals can be detected with a high degree of sensitivity. However, the presence of residual amplitude modulation (RAM) can limit the sensitivity of the technique. Various methods exist for limiting the effect of RAM,$^{65-69}$ but the addition of a sample modulation technique such as velocity modulation efficiently eliminates noise and baseline drift caused by RAM.$^{70,71}$ A spectral feature that is both velocity-modulated and phase-modulated will appear (approximately) as a second-derivative lineshape.
In order to increase the path length of absorption, we used bi-directional optical multi-passing. The rf-modulated laser beam was split into two beams with equal intensity by a beam splitter and each beam was passed through the cell cyclically by a set of multiple-reflecting mirrors in a modified White cell arrangement so that the effect of the velocity modulation was not cancelled. We were able to cleanly obtain four passes through the cell in each direction.

The two beams traveling in opposite directions probed velocity-modulated signals with opposite phases and were sent to a set of balanced fast detectors. By balancing the optical power of the two beams with neutral density filters and taking their difference with a New Focus Model 1607-AC fast balanced photoreceiver (650 MHz bandwidth) with two matched silicon photodiodes, the noise was further reduced. The laser noise and noise from the plasma cancelled out, and the double-modulated signal approximately doubled in intensity as the path length effectively doubled.

In order to optimize the heterodyne phase in both channels, we used an rf phase shifter (0-360°, dc-1.0 GHz) from Advanced Technical Materials, Inc. to adjust the overall phase, and optically adjusted the phase of the second channel by varying the displacement of a mirror on a track from the second photodiode to match the phases of the two channels. At 500 MHz, an increase or decrease in the path length of the laser beam by ~30 cm results in a phase shift of 180°. Thus by placing a dogleg mirror on a 30 cm track the phase of the second beam can be optimized (with the maximized peak of the second-derivative signal either positive or negative). Because the detector has three dc outputs (I₁, I₂, and I₁-I₂) in addition to the balanced rf output, we were able to optimize the phase in each detector channel individually so that the subtracted signal (encoded at 500 MHz ± 20 kHz) was maximized for phase modulation. The high frequency output of the detector was sent through a tunable 500 MHz narrow bandpass filter
from K & L Microwave, Inc., amplified, and demodulated in a double-balanced mixer referenced to the radio frequency source.

The partially demodulated signal was then sent through a low-pass filter (<11 MHz) to a phase sensitive detector referenced to the sine-wave generator, where the phase of the velocity modulation was optimized and the signal demodulated at the discharge frequency. The I₁-I₂ dc output of the detector was sent to a second phase sensitive detector, where it was demodulated at the discharge frequency to give a signal processed by the velocity modulation only. This was particularly helpful when searching for weak lines – although the signal-to-noise was much worse for the purely velocity-modulated signal, the presence of an apparent first-derivative lineshape in the velocity-modulated signal at the same frequency as a second-derivative lineshape in the doubly-modulated signal helped confirm the presence of a line. Subsequent co-addition helped improve the signal-to-noise for the transition.

Although the experimental sensitivity is difficult to calculate exactly due to the various components associated with the heterodyne technique, we estimate that our sensitivity limit is close (within an order of magnitude) to the shot-noise limit at our detector, which is ~10⁻⁸ for a bandwidth of 0.33 Hz and a laser power of ~2 mW impinging on each of the photodiodes. Under these conditions, the best S/N obtained was ~20 (with the co-addition τ=3 s), and the weakest transition had a S/N of ~3. This suggests that the fractional absorption of the strongest line of H³⁺ is on the order of 10⁻⁷, and the weakest line has a fractional absorption of ~10⁻⁸.

IV. OBSERVED SPECTRUM

Twenty-two H³⁺ transitions to levels above the barrier to linearity and extending into the visible region have been observed, as shown in Table I. Due to the long time needed to attain the
high sensitivity required to detect these transitions (even the strongest transition could not be
detected with a single scan), we did not scan the entire frequency range of the laser (~1800 cm$^{-1}$).
Instead, we searched for the strongest lines using the intensity information of NMT$^{41}$ and the
predicted frequencies of both NMT and SAH.$^{49}$ Fig. 3 shows two examples of spectral lines –
the strongest line and a more typical line. As observed in Fig. 3, some of the H$_3^+$ lines were
obscured by the presence of molecular hydrogen Rydberg transitions, which appear as either
first- or second-derivative lineshapes because some of the Rydberg transitions are velocity-
modulated along with the H$_3^+$ due to electron impact excitation of H$_2$ into a Rydberg state.$^{61}$
These Rydberg lines were often much stronger than the H$_3^+$ lines, but the addition of 10 Torr of
He to the discharge cell (in addition to ~500 mTorr H$_2$) quenched most of the interfering
Rydberg transitions$^{61}$ (see the lower trace on the right side of Fig. 3). A notable exception is the
very strong Rydberg line at 12246.425 cm$^{-1}$. Even with the addition of 20 Torr of He, the
Rydberg line did not disappear completely. The two nearby H$_3^+$ lines (12246.362 cm$^{-1}$ and
12246.550 cm$^{-1}$) therefore have larger uncertainties than the other H$_3^+$ lines, because the
measurements of their center frequencies (as determined by a second-derivative fitting routine)
are affected by the presence of the Rydberg line.

Also listed in Table I are the rotational and vibrational assignments for the observed
transitions. These assignments were made based on the intensity information of NMT (which
also gives $J$),$^{41}$ the assigned quantum numbers of SAH (which gives vibrational modes, $J$, $G$, and
rovibrational symmetry),$^{49,72}$ and to a lesser extent, the calculated expectation values $\langle v_1 \rangle$, $\langle v_2 \rangle$,
$\langle \ell \rangle$, and $\langle G \rangle$ of Watson.$^{73}$

Using the new transition frequencies and the experimentally observed ground-state
energy levels,$^{14}$ experimental upper-state energy levels were determined. Table II shows the
assigned approximate quantum numbers from SAH$^{49,72}$ and the calculated expectation values of Watson$^{73}$ for each of the observed energy levels (expectation values for five of the energy levels were not available). Watson’s expectation values roughly agree with the assigned approximate quantum numbers of SAH. Because Watson’s expectation values were not available for all of the observed energy levels, the sign of $\ell$ could not be determined for the level at 12505.081 cm$^{-1}$. Also included in Table II are the assigned values of the energy-ordering index $n$ for levels with the same $J$ (starting with $n=1$) and rovibrational permutation inversion symmetry $\Gamma_{(\nu)}$.

Fig. 4 shows the deviations of the calculated upper state energy levels from the experimentally observed energy levels. The new experimental $\text{H}_3^+$ lines are compared to the current published theoretical predictions in Table III. The corrected energies by SAH$^{49}$ using the CRJK potential energy surface have the best accuracy with an average error of -0.26 cm$^{-1}$ and a standard deviation of 0.33 cm$^{-1}$; the uncorrected energies have a larger average error (0.890 cm$^{-1}$) but a slightly smaller standard deviation (0.297 cm$^{-1}$).

Fig. 5 compares the calculated energy levels of SAH$^{49,72}$ corrected with the extrapolation formula (3) to all reported energy levels, including this work. The corrected energy levels of SAH become progressively worse with increasing energy. The source of the offsets in the $\nu_1$, $3\nu_2$, and $\nu_1 + 2\nu_2$ bands can be seen in Figure 4 of SAH$^{49}$ – the band origins for these states are not reproduced well by the correction formula (3). For these bands, a correction formula with coefficients determined from a least-squares fit of the individual experimental band origins is significantly more accurate.$^{49}$ The scatter in the errors for the corrected energy levels above the barrier to linearity suggest that none of these band origins are reproduced very accurately by the
extrapolation correction formula and that more experimental band origins are needed to improve the predictive power of Eq. (3).

V. CONCLUSIONS

This work represents a significant step in the spectroscopy of $\text{H}_3^+$. For the first time, transitions from energy levels above the barrier to linearity have been observed. A comparison among current theoretical predictions for these transitions shows most of the calculations to be within 1 cm$^{-1}$ of the experimental energy levels. The average error for even the most accurate of these calculations, however, is still an order of magnitude worse than the most accurate calculations below 9000 cm$^{-1}$. The availability of experimental data in this region should enable the improvement of theoretical calculations above the barrier.

Although the adiabatic corrections and relativistic corrections for electrons have been theoretically calculated by SAH,$^{48}$ the non-adiabatic corrections have yet to be made on $\text{H}_3^+$ from first principles. The rotation-dependent terms of the non-adiabatic corrections in Eq. (3) can be estimated using the relation between the correction to the moment of inertia $\Delta I_{aa}$ and the rotational $g$-factor $g_{aa}$,

$$\Delta I_{aa} = -\frac{m}{M} g_{aa} I_{aa}$$

where $m$ and $M$ are the electron mass and proton mass, respectively.$^{74}$ The components of the $g$-tensor for $\text{H}_3^+$ theoretically calculated as $g_{aa} = g_{bb} = -0.0686$ and $g_{cc} = -0.0210$ by Oddershede and Sabin$^{75}$ and the $\text{H}_3^+$ rotational constants$^1$ $B = 43.568$ cm$^{-1}$ and $C = 20.708$ cm$^{-1}$ give $\overline{a_1} = 1.63 \times 10^{-3}$ cm$^{-1}$ and $\overline{a_2} = 2.3 \times 10^{-4}$ cm$^{-1}$, compared to SAH’s empirical values $2.04 \times 10^{-3}$ cm$^{-1}$ and $-1.3 \times 10^{-3}$ cm$^{-1}$, respectively. As for non-adiabatic corrections to the vibrational
energy, a scaling of the reduced mass based on the theory of Bunker and Moss\textsuperscript{76,77} fit the experimental results well, as reported by Polyansky and Tennyson\textsuperscript{45,51} although \textit{ab initio} calculations on the non-adiabatic effect of the kind recently published by Schwenke\textsuperscript{78} on H\textsubscript{2}O are highly desirable. Such theoretical values will reveal the extent of the radiative correction. Since all these corrections are larger for higher energies, the experimental values presented in this paper will give a crucial test of the theory.

With continuing improvements in sensitivity (such as more co-addition) this work can be extended to higher overtone bands of H\textsubscript{3}\textsuperscript{+} (6\nu\textsubscript{2} \leftarrow 0, 6\nu\textsubscript{6} \leftarrow 0, 7\nu\textsubscript{2} \leftarrow 0, \text{etc.}), continuing the climb up the energy ladder of H\textsubscript{3}\textsuperscript{+} and further testing the theoretical predictions and potentials. The lack of assigned spectroscopic data in the energy regime from 10,000-35,000 cm\textsuperscript{-1} (until this work) means that the potential is not strongly constrained.\textsuperscript{79} Consequently, none of the potential energy surfaces near the H\textsubscript{3}\textsuperscript{+} dissociation limit (~35,000 cm\textsuperscript{-1}) are considered reliable, and experimental data on higher energy levels is needed to improve them. An improved potential energy surface might finally enable the analysis of the near-dissociation spectrum, which has remained completely unassigned since its initial discovery by Carrington \textit{et al.}\textsuperscript{80} 20 years ago.

\section*{ACKNOWLEDGEMENTS}

The authors wish to thank J. K. G. Watson and A. Alijah for sending us the results of their calculations in advance of publication and for several helpful discussions about their theoretical calculations. We also thank A. Alijah, C. M. Lindsay, R. Jaquet, J. Tennyson, and J. K. G. Watson for their comments on an earlier version of this manuscript. This work was supported by NSF Grant No. PHYS-0099442. B. J. M. has been supported by the Fannie and
John Hertz Foundation and the Miller Institute for Basic Research in Science. J. L. G. is supported by a National Science Foundation Graduate Research Fellowship.

REFERENCES


<table>
<thead>
<tr>
<th>Assignment</th>
<th>Band</th>
<th>Frequency ($\text{cm}^{-1}$)</th>
<th>Rel. Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^u\text{R}(2,2)$</td>
<td>$2v_1+2v_2^2 \leftarrow 0$</td>
<td>11019.358(10)</td>
<td>0.374</td>
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<tr>
<td>R(1,1)</td>
<td>$5v_2^1 \leftarrow 0$</td>
<td>11044.149(10)</td>
<td>0.238</td>
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<td>R(3,3)</td>
<td>$5v_2^1 \leftarrow 0$</td>
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<td>0.683</td>
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<td>P(3,3)</td>
<td>$3v_1+v_2^1 \leftarrow 0$</td>
<td>11111.791(10)</td>
<td>0.164</td>
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<tr>
<td>R(1,0)</td>
<td>$5v_2^1 \leftarrow 0$</td>
<td>11228.613(10)</td>
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<tr>
<td>R(1,1)$^u$</td>
<td>$5v_2^1 \leftarrow 0$</td>
<td>11244.366(10)</td>
<td>0.258</td>
</tr>
<tr>
<td>R(2,1)$^f$</td>
<td>$5v_2^1 \leftarrow 0$</td>
<td>11246.712(10)</td>
<td>0.131</td>
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<td>R(2,2)$^u$</td>
<td>$5v_2^1 \leftarrow 0$</td>
<td>11304.484(10)</td>
<td>0.191</td>
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<td>Q(1,0)</td>
<td>$3v_1+v_2^1 \leftarrow 0$</td>
<td>11318.084(10)</td>
<td>0.181</td>
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<td>R(2,1)$^u$</td>
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<tr>
<td>$^6\text{R}(2,2)$</td>
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<td>0.121</td>
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$^a$The uncertainty in the last decimal place is listed in parentheses.

$^b$The intensities were calculated at 300 K from the Einstein A-coefficients of NMT (Ref. 41).
TABLE II. Experimentally determined energy levels.

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<th>$v_1$</th>
<th>$\langle v_1 \rangle^a$</th>
<th>$v_2$</th>
<th>$\langle v_2 \rangle^a$</th>
<th>$\ell$</th>
<th>$\langle \ell \rangle^a$</th>
<th>$G$</th>
<th>$\langle G \rangle^a$</th>
<th>$J$</th>
<th>$n$</th>
<th>$I_{(v)}$</th>
<th>$u/l$</th>
<th>Energy (cm$^{-1}$)</th>
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<td>$E'$</td>
<td>$l$</td>
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<td>2</td>
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<td>5.790</td>
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<td>-2.274</td>
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<td>3.135</td>
<td>2</td>
<td>14</td>
<td>$A_2''$</td>
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<td>12333.322(20)</td>
</tr>
<tr>
<td>2</td>
<td>---</td>
<td>3</td>
<td>---</td>
<td>1</td>
<td>---</td>
<td>0</td>
<td>---</td>
<td>1</td>
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<td>$A_2''$</td>
<td></td>
<td>12340.630(10)</td>
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<tr>
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<td>---</td>
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<td>---</td>
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<td>$E''$</td>
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<td>---</td>
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<td>$A_2''$</td>
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<td>$A_2'$</td>
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</table>

$^a$Expectation values calculated by Watson (Ref. 73); results for five of the energy levels were unavailable. The sign of $\ell$ could not be determined for the level at 12505.081 cm$^{-1}$ due to the lack of information about this level.
TABLE III. Comparison among theoretical and observed transition frequencies.

<table>
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<tr>
<th>Band</th>
<th>Observed (cm⁻¹)</th>
<th>NMT⁺</th>
<th>AHW⁻ (Röhse)</th>
<th>SAH⁺ (Cencek)</th>
<th>SAH⁻ (Corrected)</th>
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<tr>
<td>2ν₁+2ν₂⁻² → 0</td>
<td>11019.358(10)</td>
<td>0.197</td>
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<td>0.925</td>
<td>-0.17</td>
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<td>5ν₂⁻¹ → 0</td>
<td>11044.149(10)</td>
<td>0.172</td>
<td>-0.563</td>
<td>0.998</td>
<td>-0.12</td>
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<tr>
<td>5ν₂⁻¹ → 0</td>
<td>11053.680(10)</td>
<td>0.203</td>
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<td>0.926</td>
<td>-0.19</td>
</tr>
<tr>
<td>3ν₁+ν₂⁻¹ → 0</td>
<td>11111.791(10)</td>
<td>1.594</td>
<td>3.282</td>
<td>0.704</td>
<td>-0.43</td>
</tr>
<tr>
<td>5ν₂⁻¹ → 0</td>
<td>11228.613(10)</td>
<td>0.230</td>
<td>-0.182</td>
<td>1.062</td>
<td>-0.04</td>
</tr>
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<td>5ν₂⁻¹ → 0</td>
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<td>0.213</td>
<td>-0.001</td>
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<td>-0.01</td>
</tr>
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<td>-0.053</td>
<td>0.996</td>
<td>-0.12</td>
</tr>
<tr>
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<td>11304.484(10)</td>
<td>0.290</td>
<td>---</td>
<td>1.011</td>
<td>-0.09</td>
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<tr>
<td>3ν₁+ν₂⁻¹ → 0</td>
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<td>1.629</td>
<td>3.286</td>
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<td>-0.53</td>
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<td>1.213</td>
<td>0.10</td>
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<tr>
<td>3ν₁+ν₂⁻¹ → 0</td>
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<td>1.604</td>
<td>3.433</td>
<td>0.640</td>
<td>-0.51</td>
</tr>
<tr>
<td>5ν₂⁻¹ → 0</td>
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<td>0.885</td>
<td>0.097</td>
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<td>1.025</td>
<td>-0.14</td>
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<td>0.851</td>
<td>1.008</td>
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</tr>
<tr>
<td>2ν₁+3ν₂⁻¹ → 0</td>
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<td>-1.983</td>
<td>0.499</td>
<td>-0.74</td>
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<td>ν₁+4ν₂⁻² → 0</td>
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<td>0.846</td>
<td>0.946</td>
<td>0.390</td>
<td>-0.82</td>
</tr>
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<td>0.523</td>
<td>-0.69</td>
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<tr>
<td>2ν₁+3ν₂⁻¹ → 0</td>
<td>12253.670(10)</td>
<td>0.399</td>
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<td>0.374</td>
<td>-0.87</td>
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<td>1.191</td>
<td>0.034</td>
<td>1.552</td>
<td>0.37</td>
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</table>

Average error: 0.712 0.606 0.890 -0.26
Standard deviation: 0.523 1.568 0.297 0.33

⁺Neale, Miller, and Tennyson (Ref. 41).
⁻Alijah, Hinze, and Wolniewicz (Ref. 60).
⁶Schiffels, Alijah, and Hinze (Refs. 49, 72).
FIGURE CAPTIONS

FIG. 1. One-dimensional cut of the potential energy surface of Röhse et al. (Ref. 39) along with calculated vibrationless (J = 0) energy levels. This slice of the potential surface was created by varying two equal H-H bond lengths of the H$_3^+$ molecule to minimize the energy for each value of the angle $\theta$, which measures the deviation from linearity (where $\theta = 0$ is the top of the barrier to linearity). The $5\nu_2^1$ and $6\nu_2^2$ levels are completely above the barrier to linearity.

FIG. 2. Experimental setup for the dual-beam, double modulation technique in the near-infrared. The output of the Verdi-pumped Ti:Sapphire ring laser (~400 mW) is split twice and sent into a 2 GHz etalon and through a heated I$_2$ cell before entering the electro-optic modulator (EOM) and accompanying optics. P1 and P2 are high power, high transmission Glan polarizers. A 10 cm lens focuses the laser beam into the center of the EOM, while a second 10 cm lens recollimates the beam. The output of an rf generator is amplified by a high power rf amplifier (PS=power supply) and is sent to the EOM, which modulates the laser beam at 500 MHz. The modulated laser beam is sent through a 1 m focusing lens, and then split into two equal beams with a beamsplitter. The two beams travel through the discharge tube in opposite directions four times each. M1 and M2 are the two modified White cell multiple reflection optics. After exiting the modified White cell, the two beams are phase-matched and optically balanced with neutral density filters.

FIG. 3. Strongest observed line (left) and a more typical H$_3^+$ line buried under two neighboring molecular hydrogen Rydberg lines (right). The addition of 10 Torr of He was usually sufficient to suppress the Rydberg transitions, as shown in the lower right-hand trace. A 2 GHz etalon and
a heated I$_2$ reference cell were used to calibrate the scans after the co-addition. The half-width at half-maximum (HWHM) for the doubly-modulated H$_3^+$ signal was 1.94 GHz.

FIG. 4. Observed minus calculated energy levels (see Table III for references). The calculations of SAH (Ref. 49, 72) most accurately match the experimental data, although their deviation from the observed values seems to increase at higher energies.

FIG. 5. Comparison between the calculated energy levels of SAH (Ref. 49, 72) using the extrapolation correction formula (Eq. 3) and the experimental energy levels reported in Ref. 14 and this work. The scatter in the deviation of the corrected energy levels from the experimental values increases significantly above the barrier to linearity.
FIG. 1
FIG. 2.
FIG. 4
FIG. 5

Old Energy Levels
- 000
- 011
- 020
- 022
- 031
- 033
- 100
- 111
- 120
- 122
- 200
- 211

New Energy Levels
- 051
- 055
- 142
- 062
- 311
- 231
- 222