High-Resolution Sub-Doppler Lamb Dips of the ν_2 Fundamental Band of H_3^+

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The high-resolution sub-Doppler Lamb dips of the ν_2 fundamental band transitions of H_3^+ have been observed using an extended negative glow discharge tube as an ion source and a periodically poled lithium niobate optical parametric oscillator as a radiation source. The absolute frequency of the $R(1,0)$ transition was measured to be 81720371.550 MHz with an accuracy of 250 kHz using an optical frequency comb. In addition, we have investigated the linewidth of the Lamb-dip signal of the $R(3,0)$ transition systematically and obtained its pressure-broadening parameter, which may shed some light on the reaction of H_3^+ with H_2. This is the first observation of the infrared saturated spectrum and the first determination of the pressure-broadening parameter of the ro-vibrational transitions of a molecular ion.

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The triatomic hydrogen molecular ion, H_3^+, is the simplest polyatomic molecule. The discovery of H_3^+ was presented by J. J. Thomson in 1911 [1]. It is the dominant ionic species in hydrogen plasmas and the universe, and it plays a key role in the chemical evolution of interstellar matter and also in planetary atmospheres [2–4]. High-resolution spectroscopy provides crucial information for determining the molecular structure [5], refining the potential energy surface [6], and providing accurate energy levels up to the dissociation limit [7] of this fundamental molecular ion. In addition, the high-precision spectroscopy of H_3^+ is a benchmark for highly accurate quantum calculations of polyatomic molecules [7,8].

Since the first laboratory identification of the ν_2 fundamental band of H_3^+ by Oka [5], extensive spectroscopic investigations have been carried out. A comprehensive summary of the high-resolution spectroscopic works up to 2001 was given by Lindsay and McCall [9]. More recent results are covered in The Royal Society Discussion Meetings on "Astronomy, physics and chemistry of H_3^+" and on "Physics, chemistry and astronomy of H_3^+," held in 2000 and 2006, respectively. Details of the discussions are presented in Refs. [10,11]. The majority of the experiments performed in the past on the ν_2 fundamental band employed cooled gas discharges as ion sources, combined with difference frequency sources, color center lasers, or diode lasers as radiation sources. In those experiments, the frequency measurements relied on the frequencies of reference gases. Later, Fourier transform spectrometers were more often used to record the H_3^+ spectra, where the frequency measurements were referenced against the He-Ne laser frequency. In any case, the observed lines were Doppler broadened, and the frequency accuracy was limited to about 0.002 cm^{-1}.

Furthermore, Fukushima *et al.* [12] and Xu *et al.* [13] used supersonic jet expansion sources to observe infrared transitions of H_3^+ along with other ions and attained sharper linewidths. Davis *et al.* applied a slit nozzle source to observe the $R(1,0)$ transition of the ν_2 fundamental band of this ion [14]. The linewidth could potentially be much narrower than the Doppler width. However, as they relied on Doppler-broadened reference lines for the frequency calibration, the accuracy of the frequency measurements was also limited to uncertainties similar to those expected from the Doppler broadening.

A major difficulty of molecular ion spectroscopy has been how to produce a high-enough number density of the ions of interest. One of the common reaction conditions employed in direct absorption and Fourier transform spectroscopy was that the total gas pressure was on the order of one to several Torr of H_2 with or without buffer gases. In order to observe line features narrow enough to warrant precise frequency measurements, relatively low gas pressure discharge ion sources or supersonic jet expansion sources are needed. Simply reducing the sample gas pressures does not succeed in producing high concentrations of ionic species without employing unrealistically large discharge cells to overcome ambipolar diffusion loss. Besides, although the transition dipole moment for the ν_2 fundamental band of H_3^+ is relatively large for an infrared transition, suitable light sources of sufficient power are still needed to observe saturation dips and derive precise transition frequencies. Recently, the McCall group has observed the Lamb dips of electronic transitions of N_2^+

using cavity enhanced velocity modulation spectroscopy [15,16]. The transition frequencies were determined to an accuracy of 300 kHz using an optical frequency comb (OFC) [17]. The pressure broadening of the Lamb dips was also measured, and the large extrapolated linewidth at zero pressure was not understood.

In this work, we employed a periodically poled lithium niobate (PPLN) mid-IR optical parametric oscillator (OPO) with enough power to saturate molecular ro-vibrational transitions as a radiation source and an extended negative glow discharge that has been used for rotational spectroscopy in microwave to THz regions as an ion source [18,19]. The frequency measurement of the line center was performed by an OFC and the accuracy can be better than 1×10^{-5} cm^{-1} (300 kHz). This is, to our best knowledge, the first observation of the saturated spectrum of ro-vibrational lines of a molecular ion. In addition, we present the first determination of the pressure-broadening parameter of the $R(3,0)$ transition. The lower state of this transition is of an ortho spin state, which is located at 516.873 cm^{-1} above the forbidden $J = K = 0$ level. Collisional processes with H_2 should involve reactive chemical processes of the proton hop and the hydrogen exchanges and nonreactive elastic and inelastic scatterings which preserve the spin state. Therefore systematic measurements of the pressure-broadening parameters of various transitions of both ortho and para modifications should shed light on the reaction of H_3^+ with H_2 [20].

The details of our PPLN OPO are presented in Ref. [21]. Briefly, its pump radiation was generated by an α-DFB diode laser or an external cavity diode laser. The pump beam was then amplified by an ytterbium-doped fiber amplifier. Precise frequency tuning of the idler wave was made by scanning the pump frequency while the signal frequency was fixed. In our setup, the idler frequency can be continuously tuned over 50 GHz, and the idler power reached 200 mW at 6 W pump.

An extended negative glow discharge tube was used in our experiment. The benefit of the extended negative glow discharge was maintaining a high concentration of H_3^+ at a discharge pressure lower than 100 mTorr. Our tube was made of a double-jacketed Pyrex tube of 2.5 m in length and 40 mm in diameter. Chilled ethanol at $-70\,^{\circ}$C can be flowed through the outer jacket for cooling the discharge plasma. A solenoid coil was wrapped around the outer vacuum housing for generating an axial magnetic field up to 300 Gauss. The discharge tube was sealed with CaF_2 Brewster windows. Hydrogen was flowed through the discharge tube and the pressure used was 30–80 mTorr. The discharge was excited by a 5-kV dc high voltage power supply. The typical discharge current was 17 mA at 2.7 kV. The negative glow region was extended from the cathode to the anode by the applied axial magnetic field. The negative glow region is a nearly field-free region, and ions observed in this region would have little or no drift velocity [22], which has been verified experimentally [23–25]. This is advantageous for the observation of a Lamb dip. The Lamb-dip signal comes from the ions with zero velocity component along the laser beam which lies on the axis of the discharge tube in our experiment. Therefore, the center frequency of Lamb dip is not affected by the drift velocity of ions [26].

The Lamb-dip observations were performed by the conventional pump-probe scheme, shown in Fig. 1, where the idler wave was sent through the discharge tube and about 8% of the incident power was retroreflected by a thick glass. To reduce interference effects the thick glass was dithered by a range of 50 μm at 32 Hz using an electromagnetic transducer (EMT). First, the absorption profile of the $R(1,0)$ transition was recorded by scanning the idler

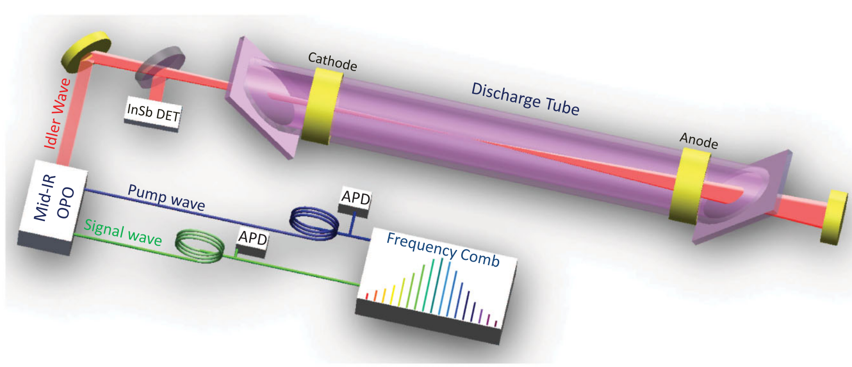

FIG. 1 (color online). Experimental scheme for the saturation spectroscopy of H_3^+. A detailed description with experimental conditions for the $R(1,0)$ transition is as follows. A 168-mW, 3668-nm idler wave was focused to a waist of 1.63 mm at the center of a discharge tube by a gold-coated spherical mirror and 8% of the incident power was retroreflected by a thick glass. The discharge tube was filled with flowing hydrogen of 30–80 mTorr, and an axial magnetic field of 300 Gauss was applied for extending the negative glow region. The outer jacket of the discharge tube was cooled by flowing ethanol to increase the populations of the low rotational levels of H_3^+. The discharge current was about 17 mA. A small fraction of the probe beam was split off by a CaF_2 plate and collected by an InSb detector (InSb DET). A 1062-nm pump wave and a 1495-nm signal wave, leaked through one of the OPO cavity mirrors, were mixed with the supercontinuum of a fiber-based OFC through 3-dB directional couplers. The beat notes of the pump and signal waves were monitored by avalanche photodiodes (APDs) to determine the absolute frequency of the $R(1,0)$ transition.

frequency across its center while the ion concentration was modulated by applying a 95 Hz zero-offset AC magnetic field. The absorption signal was detected by a liquid nitrogen cooled InSb detector and processed by a lock-in amplifier. Figure 2(a) shows the Doppler broadened absorption profiles of the $R(1,0)$ transition at six different pressures. Each profile was fitted to a Gaussian lineshape, and the fitted Doppler width (HWHM) was 315 MHz, corresponding to a translational temperature of 300 K. When the pressure was decreased to 33 mTorr, a saturation dip appeared with $\sim 8\%$ depth and ~ 5 MHz width (HWHM). The Lamb dip shows a small shift from the peak of the Doppler background. This shift is due to the small drift velocity of the H_3^+. In our experiment, the ion drift velocity was anti-parallel to the strong pump beam and parallel to the weak probe beam. Therefore, the Doppler background signal due to the pump beam was down-shifted from the transition center and up-shifted for the Doppler background signal due to the probe beam. Since the absorption coefficient of the pump beam was smaller due to stronger saturation, the peak of the combined Doppler background was shifted slightly to higher frequency. The estimated drift velocity (~ 30 m/s) is comparable to the experimental result in Ref. [23].

We employed a fiber-based OFC [27] to measure the absolute transition frequency. The repetition rate (~ 250 MHz) and the carrier-envelope offset frequency of the OFC were stabilized against a 10 MHz quartz oscillator which was phase-locked to a GPS-referenced Rb-atomic clock. The overall accuracy was better than 10^{-12} at a 1000-second integration time. For frequency measurements, we first locked the signal frequency to a nearby comb line and then locked the pump frequency to the Lamb dip. In order to obtain a suitable error signal for pump frequency locking, we performed wavelength modulation spectroscopy by modulating the idler frequency at a few tens of kHz. Figure 2(b) shows an example of the third-derivative signal of the Lamb dip obtained at a modulation width of 28 MHz for a hydrogen pressure of 45 mTorr. The signal-to-noise ratio was 85 at 1 Hz bandwidth. The pump frequency was locked to the zero point of this third-derivative signal. In determination of the absolute frequency, the beat frequencies of the pump wave ($f_{p,\mathrm{beat}}$) and the signal wave ($f_{p,\mathrm{signal}}$) were measured against the OFC simultaneously. Finally, we can determine the transition frequency by $nf_{\mathrm{rep}} \pm f_{p,\mathrm{beat}} \pm f_{s,\mathrm{beat}}$, here n is an integer. To determine the correct transition frequency, we need to make measurements for 2 to 3 different repetition frequencies.

Figure 3 plots the measured frequencies obtained for the $R(1,0)$ line. The average frequency is 81720371.550 MHz with a 1σ standard deviation of 109 kHz. Since H_3^+ is a closed-shell equilateral triangular molecule, it has very small magnetic moment and zero permanent dipole moment. Therefore, the Stark and Zeeman shifts are all very small in an extended negative glow discharge, and can

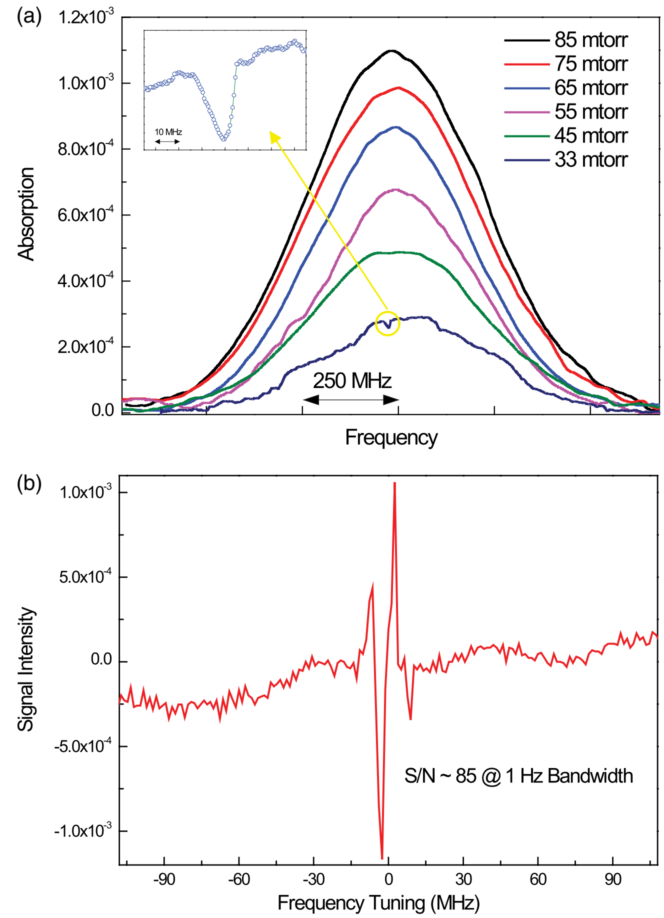

FIG. 2 (color online). (a) The Doppler-broadened line profiles of the $R(1,0)$ transition at six different pressures observed using concentration modulation. Here, all line profiles are put together to show the signal size and the appearance of Lamb dip at low pressure. Their transition centers are not exactly at the same position. The inset shows the Lamb dip in a larger scale, providing a linewidth of 4.7 MHz (HWHM). (b) The third derivative signal of the Lamb dip obtained using the wavelength modulation method. The pump wave is modulated at a frequency of 32 kHz with a modulation width of 28 MHz.

be neglected. The estimated uncertainty including the offset of pump frequency locking is 250 kHz. The frequency determined agrees very well with the value given by McKellar and Watson [28], but the accuracy was improved by three orders of magnitude. At present, the most accurate theoretical calculation is reported in Ref. [7] and the result for this transition is ~ 3 GHz (or 0.1 cm^{-1}) lower than our measurement. Precise non-adiabatic calculation with relativistic corrections, QED corrections and corrections due to the finite size of the proton are needed for further theoretical improvements [29].

The observation of a Lamb dip enables us to measure the true transition linewidth and the pressure broadening parameter as well. The pressure broadening parameter enables one to understand the molecular processes in the discharge plasma. Therefore, measurements of the pressure

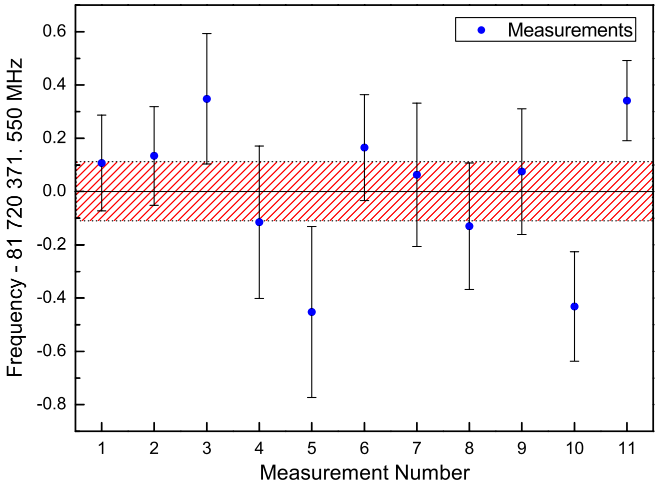

FIG. 3 (color online). Transition frequency measurements of the $R(1,0)$ transition. For each measurement, the beat frequencies of pump and signal waves were counted 200 times and the standard deviation of the obtained transition frequencies is indicated as the error bar. The average of 11 measurements is 81720371.550 MHz with 1σ standard deviation of 109 kHz (marked by the red band).

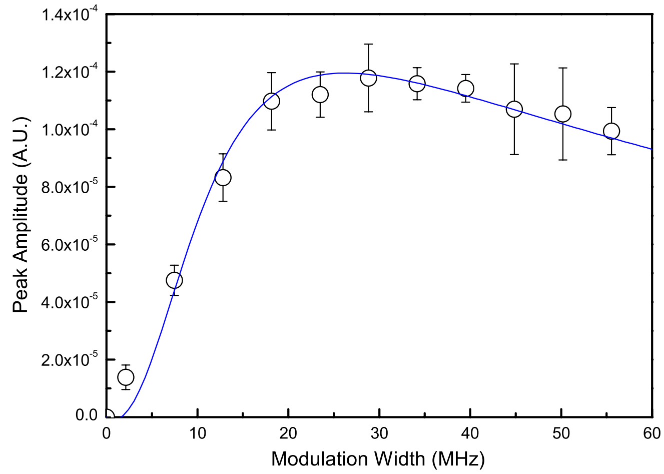

FIG. 4 (color online). Linewidth investigation of the H_3^+ $R(3,0)$ transition. The data points were acquired for 42 mTorr hydrogen pressure and 80 mW idler power and fitted to an approximate formula in Ref. [34]. The fitted HWHM linewidth is 3.65 MHz with an uncertainty of 0.17 MHz.

broadening parameter can provide useful information for the studies of the state-to-state collisions, the molecular formation process and the mechanism of ion production. The pressure broadening parameters of pure rotational transitions of HCO^+ in Ar, He and H_2 have been reported [30–33]. However, to the best of our knowledge, no one has measured the pressure broadening parameter of ro-vibrational transitions of a molecular ion.

To investigate the Lamb-dip linewidth of the $R(3,0)$ transition at 2930.163 cm^{-1}, we measured the dependence of the peak amplitude of the third-derivative signal on the modulation width. The linewidth was determined by fitting the experimental data using an approximate formula given in Ref. [34]. Figure 4 shows an example of linewidth determination. In order to obtain the pressure broadening parameter, we carefully measured the linewidth $\delta\nu$ at five different idler powers P (80, 100, 120, 140, 150 mW) and at six different discharge gas pressures p (33, 45, 52, 60, 70, 80 mTorr). The power broadened linewidth can be written as:

$$\delta\nu = \delta\nu_0\sqrt{1 + \frac{I}{I_s}} \tag{1}$$

where I is the idler intensity, I_s is the saturation intensity, $\delta\nu_0$ is the homogeneous linewidth at zero power, which includes transit time broadening (0.68 MHz), pressure broadening (γp) and lifetime broadening (19 Hz, calculated using the A-coefficient from the H_3^+ resource center [35] and can be neglected). Since the saturation intensity I_s is propotional to $\delta\nu_0^2$ [36], therefore, all measured linewidths (in MHz) were fitted to the following equation:

$$\delta\nu = (0.68 + \gamma\cdot p)\sqrt{1 + \frac{P}{A(0.68 + \gamma\cdot p)^2}} \tag{2}$$

where γ was the pressure broadening parameter and A was a fitting parameter related to the saturation intensity.

The pressure broadening parameter for the half width at half maximum (HWHM) was determined to be 28.0 ± 2.8 MHz/Torr. Since the neutral hydrogen molecule was the dominant species in the discharge tube, the evident broadening mechanism is due to H_3^+-H_2 collisions and the only reaction channels are proton hop and hydrogen exchange. In the low energy limit case, the reactive collision rate can be estimated by the Langevin model. For H_3^+-H_2 interaction, the Langevin rate was calculated to be 1.9156×10^{-9} $cm^3\,s^{-1}$, corresponding to a pressure broadening parameter of 9.8 MHz/Torr at 300 K translational temperature [37]. Our result shows the non-reactive, elastic and inelastic, collisions without proton hop or hydrogen exchange between H_3^+ and H_2 contribute substantially to the pressure broadening. In the low energy limit, the statistical model indicates that reactive collisions are 9 times more frequent than non-reactive collisions [20]. The pressure broadening parameter is expected to be slightly larger than value derived from the Langevin rate if the reactive collision can be accounted by the Langevin rate. One possible reason for the disagreement between our measurement and the statistical model is that the translational temperature in our experiment (300 K) is higher than the low energy limit. Further investigations on this problem will be performed in the future.

In summary, this work demonstrated the first observation of the saturation spectrum of H_3^+. The frequency measurement results showed substantial improvement in the measurement accuracy, namely by three orders of magnitude compared with previous measurements. This opens up the way to test theoretical calculations including QED effects in this fundamental molecule. Besides, we were able to perform the first measurement on the pressure broadening parameter of one ro-vibrational H_3^+ transition. Systematic measurements of the pressure-broadening parameters of various ortho and para transitions may shed light on $H_3^+ + H_2$ reaction. Recent investigations indicate that further studies for $H_3^+ + H_2$ reaction are needed for better determination of the ortho-para ratio of H_3^+ in plasmas [38], which has been used to estimate the interstellar cloud temperatures [39].

We believe that our experimental approach will find wide applications in studies of molecular ion spectroscopy and reactive molecular collisions [40]. In the future, we would like to improve the signal-to-noise ratio by cooling the discharge plasma with liquid nitrogen and using a multipass cell or a resonant cavity to perform systematic measurements on transition frequencies and pressure-broadening parameters of the transitions of the H_3^+ ν_2 fundamental band. We will also extend similar high-resolution spectroscopy studies to other protonated molecular ions, e.g., HeH^+ and H_3O^+ in the midinfrared region.

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