Near infrared $3\nu_2$ overtone band of H_3^+

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Near infrared spectrum of the $3\nu_2$ overtone band ($\nu_2=3\leftarrow 0$) of H_3^+ has been observed at 1.4 μm. The spectrum is weaker than the ν_2 fundamental band by a factor of ~250. High sensitivity plasma spectroscopy using velocity modulation and unidirectional multiple passing has enabled us to observe 15 rovibrational transitions. Short-external-cavity InGaAsP diodes were used as tunable near infrared radiation sources. The narrow tuning range and the availability of diodes limited the observation to a fraction of observable transitions. Nevertheless, the observed results provide information on the rovibrational energy of the $3\nu_2(l=1)$ state which may be used to further improve the variational calculations by Miller and Tennyson.

I. INTRODUCTION

The infrared spectrum of the H_3^+ molecular ion provides the most powerful experimental means of studying the intramolecular dynamics of the molecule and the means by which this astrophysically important molecule[1] can be detected in space. Since the initial observation of the fundamental ν_2 absorption band,[2] improvements in both laser technology and detection methods have made it possible to observe in the laboratory much weaker hot bands $2\nu_2(l=2)-\nu_2$, $2\nu_2(l=0)-\nu_2$, and $\nu_1+\nu_2-\nu_1$ (Ref. 3), and overtone bands $2\nu_2(l=2)$ (Refs. 4 and 5) and $3\nu_2(l=1)$ (Ref. 6). Forbidden transitions ν_1 and $\nu_1+\nu_2-\nu_2$ were also reported.[7] These observations have provided accurate information on excited vibrational states of this most fundamental polyatomic system. The laboratory measurements, in conjunction with the recent variational calculations[8] based on *ab initio* potential,[9] have also made possible the recent identification of the fundamental and overtone H_3^+ emission in the polar regions of Jupiter,[10–13] and the fundamental emission in Uranus,[14] Saturn,[15] and supernova 1987A.[16] Analysis of these spectra provides a useful means to determine the physical conditions in these astronomical objects.[17] Since this molecular ion is undoubtedly formed hot in both laboratory and astrophysical plasmas, it is important to measure and understand the spectrum of vibrational excited states.

This paper updates the list of observed near-infrared transitions of the $3\nu_2$ overtone absorption band of H_3^+, which is the highest overtone of this ion that has yet been reported measured. Fifteen transitions have been observed to date, including four that were previously published.[6] The ions were produced in an a.c. glow discharge cell and the spectrum was detected with unidirectional multipass optics[18] and velocity modulation.[19] Three near infrared short-external-cavity InGaAsP diode lasers were used as tunable radiation sources. The transitions were assigned with the help of the remarkably accurate variational calculations of Miller and Tennyson[20] which have been indispensable in the assignments of all hot and overtone bands that have been observed so far. We find that the observed values are consistently higher than the calculated values by ~3 cm^{-1} indicating a softness of the *ab initio* potential surface.

II. EXPERIMENT

A. Laser source

The spectrum of the band for $J<6$ covers the frequency region of ~6600–7600 cm^{-1}, and the transitions are quite weak with an estimated maximum fractional absorbance of $\sim 2\times 10^{-5}$ over a 4 m path length. A widely tunable, high-power and low-noise radiation source is therefore required. At present, the most suitable source of tunable radiation at this frequency is the semiconductor diode laser based on InGaAsP, which has wide use in optical communication systems. These lasers and similar lasers based on GaAs have recently been used in many spectroscopic investigations.[21] We used InGaAsP lasers in a short-external-cavity (SXC) configuration[22] to achieve laser operation in a single longitudinal mode. The laser frequency was tuned by altering the laser temperature with thermoelectric coolers, and mode control techniques[22,23] were employed to prevent a change in longitudinal mode (a mode hop) during tuning. The SXC with mode control allowed laser frequency tuning of up to 10 cm^{-1} in a single scan with no mode hop, and complete frequency coverage over a 250 cm^{-1} range was attained with each laser using a module that allowed extended temperature tuning.[24] The laser injection current was set such that ~5 mW of power was emitted. The intensity noise of these lasers at the discharge modulation frequency is $3-4\times 10^{-6}/\sqrt{Hz}$ of the total laser power, and the laser linewidths were ≤20 MHz. The frequency of the laser was calibrated with a wavelength meter which has an accuracy of ~0.07 cm^{-1}.

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B. Ion production and multipass optics

The laser radiation was collimated with two plano-convex lenses and focused to the entrance of a multiple-pass system which contained an a.c. discharge cell in which H_3^+ was produced. The cell is liquid-N_2 cooled and is equipped with multiple inlets and outlets for even gas flow.[3] The optimum absorption signal was obtained with 1.5 torr of H_2 and a discharge current of 180 mA (rms) and 5 kV (rms), and a discharge modulation frequency of 6 kHz. The addition of 4–5 torr of He resulted in less electrical noise and a more stable discharge, but reduced the magnitude of the H_3^+ absorption, resulting in no net increase in signal-to-noise ratio (SNR). The reduction of intensity of the H_3^+ absorption for the $3\nu_2$ band may be attributed to the increase in population of the higher vibrational and rotational states caused by the addition of He to the discharge.[3]

A unidirectional multipass optical configuration was employed to increase the sensitivity, and velocity modulation was used to detect the absorption signals from the ions. Although up to eight passes through the discharge cell could be obtained, we found the optimum SNR was with four passes, giving a total path length of 4 m. The light exiting the multipass optical cell was sent to a monochromator with a grating blazed at 1.0 μm to filter out the extraneous emission from the discharge, which degraded the SNR. The output of the monochromator was focused onto an InGaAs detector, and this signal was demodulated by a lock-in amplifier referenced to the modulation frequency of the discharge.

To detect very weak transitions, we attempted noise subtraction to reduce the detection of laser intensity noise and background drift caused by electrical pickup on the laser current. Noise subtraction has been tried unsuccessfully with Pb-salt diode lasers, but it was thought that the superior beam quality and stability of the InGaAsP diode lasers might allow this technique to work. Noise subtraction was implemented by splitting the IR beam into two beams of equal intensity, passing each beam through the multipass cell in opposite directions. The output from each direction was focused onto matched InGaAs detectors, and these signals were subtracted and demodulated by the lock-in amplifier. The SNR increased by 3–5 when noise subtraction was implemented, although in principle, this technique should allow the shot-noise limit to be reached. The present noise level of the system for a 0.1 Hz detection bandwidth is $\approx 3\times10^{-7}$ of power incident on the detector, limited by the intensity noise of the diode laser.

III. OBSERVED RESULTS

In ordinary molecules the second overtone band is weaker than the fundamental by several orders of magnitude. In H_3^+, however, the band is not as weak because of the small mass of the proton and the relatively shallow potential. Recent variational calculations by Dinelli, Miller, and Tennyson[25] predict that the overtone transition is weaker than the fundamental by a factor of ~250. This is considerably weaker than the hot bands[3] (~1/40) and the first overtone bands[5] (~1/5), but the high sensitivity afforded by InGaAsP diode lasers has allowed us to observe these transitions with good signal-to-noise ratio.

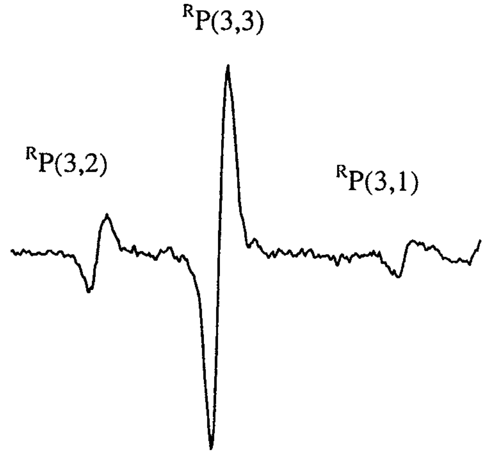

FIG. 1. A trace with three $^RP(3,k)$ transitions (k=3,2,1) in 6808–6806 cm^{-1}. Unidirectional multiple pass of 4 m, velocity modulation at 6 kHz, and laser intensity noise subtraction were used to record the signal. The total scan is ~1.3 cm^{-1}. The time constant was 3 s.

Since H_3^+ was produced in a pure hydrogen plasma, the absorption signals of H_3^+ were easily identified. The signals were confirmed to be from an ionic species by reversing the polarity of the discharge and observing the corresponding change in polarity of the absorption signal. Rydberg transitions of H_2 were also observed. These transitions behave like ionic transitions (of negative charge since the Rydberg states are formed as a result of electron bombardment), but they may be distinguished from those of H_3^+ on the basis of the signal phase, linewidth, and also their disappearance when a few torr of He are added to the discharge. A trace of the $^RP(3,1)$, $^RP(3,3)$, and $^RP(3,2)$, transitions is shown in Fig. 1.

Assignment of the transitions was accomplished using the variational calculations of Miller and Tennyson,[8,20] which have been invaluable in assigning all the hot and overtone bands that have yet been observed. Assignment was based on comparison of the frequency and intensity of the measured transitions with the theoretical results. The $^RQ(5,0)$ and $^RP(2,1)$ transitions could not be assigned strictly from theoretical calculations because of their similar intensity and nearly coincidental frequency. These lines were distinguished on the basis of their temperature dependence which was determined by comparing the relative intensities of the transitions in water-cooled and liquid-N_2 cooled discharge cells. The observed spectral lines are listed in Table I. The accuracy of the listed wave numbers was limited by that of our wave meter which was ~0.07 cm^{-1}. When absorption lines of H_2O were available in the scan, the wave number was calibrated to the lines reducing the uncertainties to 0.04–0.020 cm^{-1} depending on the proximity of the reference lines.

The $3\nu_2$ overtone band (band origin at 1400 nm) appears in the gap of the two infrared regions at 1320 nm and at 1550

TABLE I. Observed transitions of the $3\nu_2$ overtone band of H_3^+.

Transition $(J,G,U \leftarrow J',k')$	Observed[a] (cm^{-1})	Theoretical[b] (cm^{-1})	Obs.-calc.[b] (cm^{-1})	Intensity (Theor.)[c] cm^{-1}/molecule (10^{-19})
5,4,1 4,4	7265.882 (50)	7262.594	3.288	0.186
2,0,1 1,0	7241.245 (50)	7238.493	2.752	1.220
2,1,1 1,1	7237.285 (50)	7234.512	2.773	0.315
4,3,1 3,3	7234.957 (50)	7231.753	3.204	0.686
3,2,−1 2,2	7192.908 (20)	7189.700	3.208	0.452
2,1,−1 1,1	7144.212 (40)	7141.177	3.035	0.370
4,3,1 4,3	6891.619 (20)	6888.499	3.120	0.092
5,3,1 5,3	6883.091 (50)	6879.669	3.422	0.025
1,2,1 2,2	6877.546 (40)	6874.953	2.593	0.433
5,0,1 5,0	6866.340 (40)	6862.913	3.427	0.151
1,1,1 2,1	6865.731 (40)	6863.040	2.691	0.011
2,0,1 3,0	6811.164 (40)	6808.713	2.451	0.110
2,2,1 3,2	6807.724 (20)	6805.114	2.610	0.141
2,3,1 3,3	6807.297 (20)	6804.796	2.501	0.758
2,1,1 3,1	6806.665 (20)	6804.010	2.655	0.069

[a]The numbers in the parentheses are uncertainties of the observed wave numbers.
[b]Recent calculations (Refs. 26 and 27) in which the potential was adapted to the observational results and reduce the discrepancy by 1 order of magnitude.
[c]The calculated intensities are at 300 K.

nm where standard communication diode lasers are available. We therefore had to rely on off-standard diode lasers whose wavelengths happened to be in the region of the $3\nu_2$ overtone band. Availability of such diodes and the wide span of the H_3^+ spectrum seriously limited the complete coverage of the band. A log scale stick diagram of the whole band is shown in Fig. 2 in which observed lines are marked. The complete spectrum will be obtained when appropriate diode lasers become available. In spite of the limited coverage, these spectral lines provide first information of the $3\nu_2$ state. Recently, Watson[26] and Dinelli *et al.*[27] developed computer programs to use observed spectral lines to improve the H_3^+ potential surface.

While the absorption of the $3\nu_2$ overtone band is weaker than that of the ν_2 fundamental band by a factor of 250, the spontaneous emission of the overtone band ($15.7\ s^{-1}$) is lower than that of the fundamental band ($128.8\ s^{-1}$) by a factor of only 8.[25] It is our hope that this overtone transition will someday be detected in hot astronomical objects.

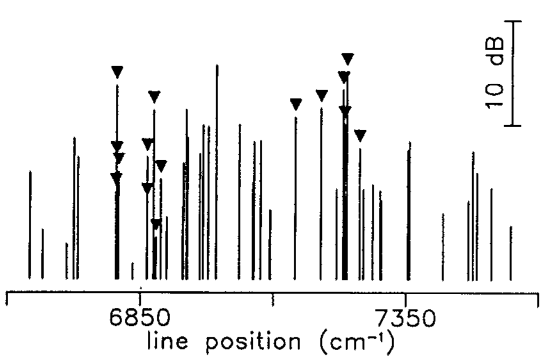

FIG. 2. Computer generated log scale stick diagram of the $3\nu_2$ overtone band from Miller and Tennyson's calculation (Ref. 20) assuming a temperature of 300 K. The strongest line is 1.18×10^{-19} cm/molecule. The lines marked with an inverted triangle have been observed and are reported in this paper.

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