

LETTER TO THE EDITOR

Observation of the $3\nu_2 \leftarrow 0$ Overtone Band of H_3^+

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Recent discovery of the 2- μm emission spectrum of the $2\nu_2(2) \rightarrow 0$ overtone band of H_3^+ in Jupiter (1-3) has demonstrated the existence of large amounts of H_3^+ in high vibrational states in the Jovian ionosphere. Subsequent observation of the stronger 4- μm emission spectrum of the $\nu_2 \rightarrow 0$ fundamental band (4-6) indicated that the vibrational states are in equilibrium corresponding to high temperatures.

In this communication we report laboratory observation and theoretical calculations of some spectral lines of the second overtone band ($3\nu_2(1) \leftarrow 0$) of H_3^+ in the 1.4 μm region. It is our hope that this observation may lead to detection of H_3^+ in higher vibrational states in Jupiter and other astronomical objects, and that it may also help in the assignment of the rich laboratory FTIR emission spectrum of hydrogen plasma reported by Majewski *et al.* (7).

The spectroscopy was conducted using a 1.45- μm InGaAsP diode laser operated with a short external cavity (SXC) and mode control techniques developed at McMaster University (8-10). The external cavity forces the normally multilongitudinal mode laser to operate in a single longitudinal mode. Seven such modes could be selected with this laser by changing the SXC length with a piezoelectric positioner. Modes were frequency-tuned by changing the laser temperatures when the laser was biased well above threshold. The tuning range of a particular mode is enhanced by the electrical feedback loop that senses the change in laser voltage when a mode hop is about to occur. This voltage signal is processed and used to alter the SXC length so that the mode hop will be suppressed. Using this technique, the diode laser can be tuned over a 65 cm^{-1} range in steps of a few wavenumbers with no gaps in frequency coverage. The tuning range and sensitivity of SXC-controlled diode lasers are comparable to those of the near-infrared distributed feedback (DFB) diode laser used by Sasada and Amano (11) for the observation of the first overtone of HN_2^+ . Their results along with our present results demonstrate the use of near-infrared diode lasers for molecular ion spectroscopy.

H_3^+ was generated using 1.5 Torr of H_2 with or without 4 ~ 5 Torr of He in a liquid- N_2 cooled multiple-inlet-multiple-outlet discharge cell (12). The current and voltage of 6 kHz AC discharge were kept at ~200 mA and 5 kV peak-to-peak, respectively. These conditions are similar to those of our previous work on the hot bands (13) and to those of the first overtone band (14) of H_3^+ . We used a White cell multiple-path arrangement using two modes of detection: (a) usual multiple path with ion concentration modulation and (b) unidirectional multiple path with velocity modulation (15). With the former method, many H_2 Rydberg transitions (16) were also observed. They were discriminated from the H_3^+ lines by the reduction of their intensities when He is added. The second method of velocity modulation was useful to discriminate H_3^+ lines not only from the H_2 Rydberg line but also from the ubiquitous atmospheric H_2O absorption lines (17) which appeared as a result of spurious modulation of diode frequencies due to electric pickup. Four unidirectional traversals with a bow-tie configuration (18) White cell were used. The good stability and output power of the near-infrared diode laser allowed observation with the sensitivity of $\Delta I/I \sim 10^{-6}$ and the minimum detectable absorption coefficient of $\sim 5 \times 10^{-8}$. After exiting the White cell, the laser radiation

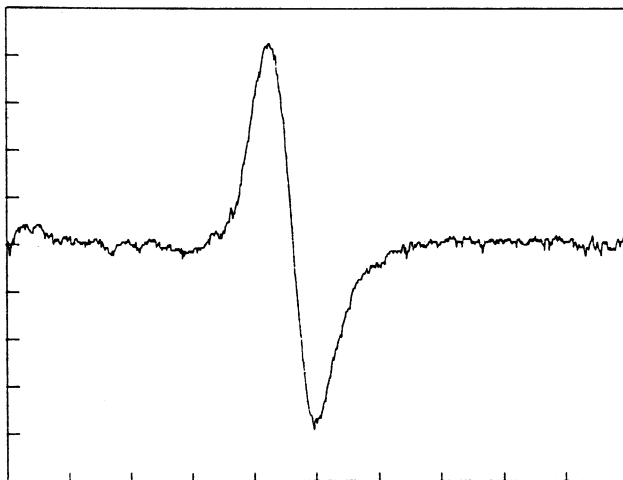


FIG. 1. Observed spectral line of the $3\nu_2$ ($l = 1$) $\leftarrow 0$ overtone band of H_3^+ corresponding to the $J' = 1$, $G' = 2 \leftarrow J = 2$, $K = 2$ transition at 6877.512 cm^{-1} . Wavenumber scan is about 0.95 cm^{-1} for the full trace. The time constant of detection is 3 sec.

was passed through a monochromator, which filtered the emission from the discharge, and was focused onto an InGaAs photodiode. The detected signal was processed by a lock-in amplifier and recorded with a microcomputer.

The strongest observed line corresponding to the $^R P(2, 2)$ transition is shown in Fig. 1. Altogether four lines have been observed in the range of our diode laser, $6860\text{--}6925 \text{ cm}^{-1}$. They are listed in Table I together with the theoretical wavenumbers and intensities. The positions of the spectral lines were determined using a wavemeter (Burleigh) calibrated with H_2O lines (17). We estimate their uncertainty to be 0.05 cm^{-1} . More accurate wavenumber determination of the lines will be carried out in future work by using suitable reference

TABLE I

Theoretical and Observed Wavenumbers of the $3\nu_2$ ($l = 1$) $\leftarrow 0$ Overtone Band of H_3^+

Transitions		Theoretical (cm^{-1})	Observed (cm^{-1})	Intensity ^a $\text{cm/mol} \times 10^{21}$	A_{if} s^{-1}
J',G'	J'',K''				
5,2	5,2	6899.984		1.7	8.9
3,0	3,0	6899.854		3.9	1.8
5,1	5,1	6898.825		2.1	13.1
4,3	4,3	6888.498	6891.792	11.1	6.5
5,3	5,3	6879.669		6.0	10.9
1,2	2,2	6874.953	6877.512	24.0	17.5
3,1	3,1	6872.309		0.3	0.4
5,2	5,2	6863.085		0.7	3.4
1,1	2,1	6863.040	6865.708	9.3	8.4
5,0	5,0	6862.913	6866.338	3.6	11.9

^a Calculated from *ab initio* line strengths assuming a Boltzmann population distribution at 450 K.

lines and an etalon instead of a wavemeter. The present assignment of the transitions is based on first principles calculation and on observed temperature dependence of the relative intensities. The first principles calculation was performed using the TRIATOM program suite (19) and the ab initio potential energy surface of Meyer *et al.* (20). These new calculations extend previous work on hot bands and overtones (21); they are particularly designed to give better converged results for the rotationally excited states of the higher vibrational levels. This work will be reported in detail elsewhere (22). Theoretical wavenumbers relevant to this study are also listed in Table I. The theoretical intensities were computed from the ab initio linestrengths assuming a Boltzmann population of 450 K.

Further measurement will be done when the diodes with appropriate frequencies become available.

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