THE ASTROPHYSICAL JOURNAL, 347:L51–L54, 1989 December 1

LABORATORY OBSERVATION OF THE $2\nu_2$ BAND OF THE H_3^+ MOLECULAR ION

W. A. MAJEWSKI, P. A. FELDMAN, AND J. K. G. WATSON
Herzberg Institute of Astrophysics, Ottawa

AND

S. MILLER AND J. TENNYSON
Department of Physics and Astronomy, University College London
Received 1989 August 9; accepted 1989 September 7

ABSTRACT

Wavenumbers and assignments are reported for lines of the $2\nu_2$ vibrational band of the H_3^+ molecular ion, observed in the range 4500–5100 cm^{-1} as pressure-enhanced emission lines from a hollow-cathode electrical discharge through molecular hydrogen. The assignments are based on ab initio calculations, previously tested for the ν_2 fundamental and for difference bands, and here extended up to angular momentum states with $J = 12$. Calculated Einstein A_{if} coefficients of the lines are presented and imply a rotational temperature of about 1800 ± 200 K in the laboratory spectrum, which is probably due to emission by excited H_3^+ formed in the exothermic reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. The H_3^+ $2\nu_2$ band has recently been identified in emission from the auroral "hot spots" of Jupiter, and the present more extensive data will assist in further astronomical searches for this ion.

Subject headings: infrared: spectra — laboratory spectra — line identifications — planets: Jupiter — planets: spectra

I. INTRODUCTION

The H_3^+ molecular ion is of great importance in the physics and chemistry of plasmas consisting predominantly of hydrogen (Oka 1983), and therefore plays an important rôle in interstellar ion-molecule reaction schemes (Herbst and Klemperer 1973; Watson 1976). The first spectroscopic observation of the H_3^+ ion was the detection by Oka (1980) of the ν_2 infrared fundamental in the absorption spectrum of hydrogen gas in an electrical discharge. This identification was greatly assisted by the ab initio calculations of Carney and Porter (1974, 1976, 1980). Subsequently, extensive infrared absorption spectra of the deuterium isotopomers of H_3^+ have also been observed, as well as microwave transitions of H_2D^+; detailed references through 1986 are given by Majewski *et al.* (1987).

The infrared *emission* spectrum of H_3^+ was first observed using a specially constructed hollow-cathode electrical discharge cell (Majewski *et al.* 1987), which allowed stable operation with a high current density and a wide range of pressures in a small volume of gas. The emission lines of H_3^+ were discriminated from the many infrared transitions between excited states of the parent H_2 molecule (Crosswhite 1972) by means of the pressure dependence of the intensities, with higher pressures favoring the production of H_3^+ through the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H\,. \qquad (1)$$

The lines of neutral H_3, previously identified in the difference between the cathode and anode glows of a hollow-cathode discharge cell (Dabrowski and Herzberg 1980; Herzberg and Watson 1980; Herzberg *et al.* 1981; Herzberg *et al.* 1982) are also observed to be enhanced at higher pressures in this cell (Majewski and Watson 1987). They are thought to be formed in hollow-cathode discharges mainly by the dissociative recombination of H_5^+ with electrons (Miderski and Gellene 1988), $H_5^+ + e^- \rightarrow H_3 + H_2$.

Here we report the laboratory observation of the $2\nu_2$ band of the H_3^+ ion in emission in the 2 μm region from the same cell. This laboratory spectrum was of great assistance in the recent assignment of this band in the auroral emission spectrum of Jupiter (Drossart *et al.* 1989). In the present communication we report a more extensive set of line wavenumbers and assignments than those observed from Jupiter. These measurements should assist in other astronomical searches for the H_3^+ ion.

II. OBSERVED SPECTRA AND ASSIGNMENTS

At the time (early 1985) of the original observations of the ν_2 band (Majewski *et al.* 1987) with this cell, spectra were also recorded in the wavenumber region of the $2\nu_2$ band, because the Einstein A_{if} coefficient of this band was predicted to be about 1.4 times that of the fundamental (Carney and Porter 1976). The experimental conditions were similar to those employed for the fundamental (Majewski *et al.* 1987), and emission spectra were recorded at pressures of about 10 and 50 torr. The lines were calibrated against known lines of H_2 and have an absolute accuracy of about 0.01 cm^{-1} when they are free from overlapping by H_2 lines. A number of pressure-enhanced lines were observed in the predicted region, 4500–5200 cm^{-1}. For example, Figure 1 shows one strong and two weaker pressure-enhanced lines near 4640 cm^{-1}, together with the more numerous lines ascribed to neutral H_2. At that time no progress was made in assigning the lines, and the possibility existed that they might be due to neutral H_3. However, the experimental determination of the ionization potential of H_3 by Helm (1986, 1988) made it possible to improve the predictions of the higher Rydberg states of H_3, and this showed that it is unlikely that the band centers of any Rydberg-Rydberg transitions of neutral H_3 lie in this wavenumber region. This suggested that the observed lines must indeed belong to H_3^+. The major difficulty in making assignments was found to be the very high rotational temperature of the H_3^+ in this cell, which meant that the strongest lines were difficult to predict by extrapolation from existing data.

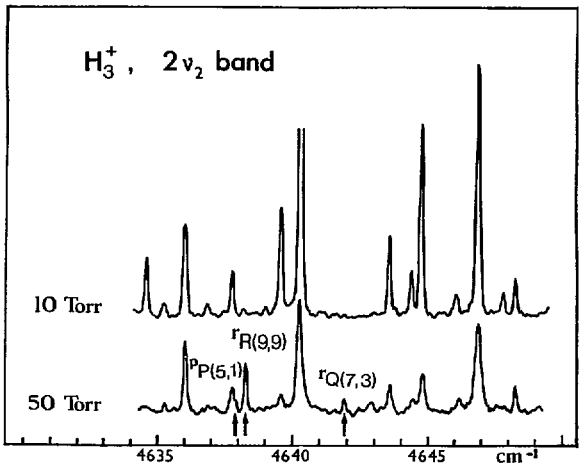

FIG. 1.—Emission spectra recorded with pressures of 10 and 50 torr of H_2 in the discharge cell. The three clear pressure-enhanced lines can be assigned to the indicated transitions of H_3^+. The line at 4638.338 cm^{-1} was observed in the Jupiter spectrum. The failure to observe the other two lines on Jupiter may be partly due to interference by CH_4 absorption.

Two advances in 1988 have now led to the assignment of these lines. The first was the advent of high-quality predictions of the rotational levels of the $2\nu_2$ state (Miller and Tennyson 1988*a*). These employ the ab initio potential energy surface of Meyer, Botschwina, and Burton (1986). Similar calculations for the ν_2 band have been found to give excellent agreement with experiment (Miller and Tennyson 1988b).[1] Calculations of the transition wavenumbers and line strengths for the difference bands have been presented elsewhere (Miller and Tennyson 1989). The second advance was the observation of the difference band $2\nu_2-\nu_2$ in the same wavenumber region as the ν_2 fundamental (Bawendi *et al.* 1988; Xu *et al.* 1989). A combination of information from these two sources made it possible to assign many of the lower J transitions of the $2\nu_2$ band. These lines turned out to be relatively weak. For the present work ab initio calculations to higher values of $J \leq 12$ have been carried out and make it possible to assign many more lines in the observed spectrum. The observed and ab initio wavenumbers of the lines of the $2\nu_2$ band, together with their estimated relative intensities and ab initio Einstein A_{if} coefficients, are presented in Table 1. The laboratory spectrum is to some extent incomplete because of interference by the many lines of H_2 in this region, which can easily mask some of the lines of H_3^+. This problem becomes worse at the higher wavenumber end of the spectrum where the density of H_2 lines is greater. Because of the background of H_2 lines, it is also difficult to measure the relative intensities of the H_3^+ lines quantitatively, but the qualitative estimates in Table 1 could be fitted using the ab initio Einstein A_{if} coefficients to give an approximate rotational temperature of $T_{rot} = 1800 \pm 200$ K for the $2\nu_2$ band in this cell. (In this fit, the anomalously strong line at 4861.849 cm^{-1} was omitted.) The possible deviation from the equilibrium ortho/para ratio was found to be insignificant.

The comparison between the observed and ab initio wavenumbers in Table 1 again shows excellent agreement. Fitting the differences on the assumption of a constant shift gives the offset $\nu_{obs} - \nu_{calc} = (0.403 \pm 0.045)$ cm^{-1} with a standard deviation of 0.315 cm^{-1} in the fit. For the ν_2 fundamental (Miller and Tennyson 1988*b*), the offset is (0.187 ± 0.020) cm^{-1} with a standard deviation of 0.154 cm^{-1} in the fit, showing a consistent trend. These results testify to the excellence of the potential of Meyer, Botchwina, and Burton (1986) and to the accuracy of the vibration-rotation calculations.

The assignments were monitored by fits to an effective Hamiltonian (Watson 1984) using either polynomial or Padé-function (Watson *et al.* 1984; Majewski *et al.* 1987) representations of the centrifugal corrections. The $2\nu_2$ state has two vibrational substates with $|l_2| = 0$ (A_1') and 2 (E'). These are well separated, with predicted term values of 4777.31 and 4997.68 cm^{-1}, respectively (Miller and Tennyson 1988*a*), but they are coupled by rotational l-type doubling matrix elements, which are quite large for the higher J levels of this molecule. Thus the energy levels must be calculated as eigenvalues of an effective Hamiltonian matrix containing both substates. In the $2\nu_2$ band, transitions from the $|l_2| = 2$ component only are allowed as a perpendicular band $E'-A_1'$ at low J, but the character of the states becomes increasingly mixed at higher J.

Effective Hamiltonian fits of either the observed or the ab initio wavenumbers were generally rather unsatisfactory. In order to obtain even a moderately reasonable fit (to better than, say, 0.2 cm^{-1}), it was necessary either to include a large number of centrifugal terms or to omit several of the lines. In either case, these effective Hamiltonians have little predictive power. It was therefore decided not to include the results of such fits until a more effective model can be devised.

III. DISCUSSION

Reaction (1) is exothermic by 1.70 eV $\approx$ 13,700 cm^{-1} (Oka 1983), and the present spectrum is probably the chemiluminescence of the H_3^+ produced in this reaction. This would explain the high vibrational temperature, indicated by the intensity of the observed vibrational emission, and the high rotational temperature of about 1800 K. Previous evidence of internal excitation of H_3^+ from reaction (1) has been obtained in beam experiments such as those of Blackley, Vestal, and Futrell (1977).

The immediate interest of the present spectrum is the recent identification of 23 lines of this H_3^+ band in the emission spectrum observed from an infrared "hot spot" in the southern auroral region of Jupiter (Drossart *et al.* 1989). There are two such hot spots, one in each hemisphere. They are localized regions from which strong infrared emission of CH_4, C_2H_2, C_2H_6, and other molecules has been observed. A number of the unidentified lines reported by Trafton, Lester, and Thompson (1989) from both hemispheres of Jupiter agree with lines observed by Drossart *et al.* (1989) and in the present work, and can be assigned to H_3^+. Other lines of Trafton, Lester, and Thompson (1989) remains unassigned. While the H_3^+ ion was previously detected in the mass spectrum of the magnetosphere of Jupiter (Hamilton *et al.* 1979), and its rôle in Jovian chemistry has been discussed by a number of authors (e.g., McConnell and Majeed 1987), this was the first spectroscopic evidence for its presence.

In the Jupiter spectrum the ortho/para ratio for H_3^+ departs significantly from its equilibrium ratio (Drossart *et al.* 1989). This observation was interpreted in terms of the production of H_3^+ from H_2 molecules with a lower rotational temperature, so that the lower temperature of the H_2 nuclear spins is frozen into the H_3^+ produced. In the present experiment the tem-

[1] Note that, in the paper of Miller and Tennyson (1988*b*), the first member of eq. (2) for the A_{if} coefficients should be divided by $(2J_i + 1) = (2J' + 1)$. The numerical values of A_{if} quoted in their Tables 1 and 2 should also be divided by $(2J' + 1)$.

TABLE 1

OBSERVED AND CALCULATED LINES OF THE $2\nu_2$ BAND OF H_3^+

OBSERVED WAVENUMBER (cm^{-1})	OBSERVED INTENSITY (arbitrary units)	ASSIGNMENT						CALCULATED WAVENUMBER (cm^{-1})	CALCULATED E' (cm^{-1})	CALCULATED A_{if} (s^{-1})	FITTED INTENSITY (arbitrary units)
		J'	G'	U'	J''	K''	o/p				
4539.759	8	4	3	+2	5	0	o	4539.484	5810.346	72	7.5
4557.057[a].....	3	4	6	+2	4	3	o	4556.883	5215.387	35	5.9
4578.742	5	5	6	+2	5	3	o	4578.502	5658.641	52	7.6
4587.373	7	5	2	+2	6	1	p	4586.619	6326.970	45	1.9
4607.205	4	6	6	+2	6	3	o	4606.887	6183.721	58	6.6
4637.992[b].....	2	4	2	+2	5	1	p	4637.488	5887.398	55	2.8
4638.338	17	10	12	+2	9	9	o	4638.688	6668.656	171	21.7
4641.987	5	7	6	+2	7	3	o	4641.550	6782.988	64	5.3
4664.303	5	2	3	+2	3	0	o	4663.949	5180.662	65	6.4
4677.285	3	3	5	+2	3	2	p	4677.032	5104.913	43	3.1
4685.558	9	9	11	+2	8	8	p	4685.694	6332.426	164	12.4
4691.962	7	4	5	+2	4	2	p	4691.684	5459.909	60	4.3
4700.139	2	3	2	+2	4	1	p	4699.645	5532.956	56	2.9
4712.309	5	5	5	+2	5	2	p	4711.921	5898.647	68	4.2
4732.053	14	8	10	+2	7	7	p	4732.158	6033.880	158	13.7
4735.941	8	6	5	+2	6	2	p	4735.264	6414.529	72	3.5
4744.797	4	4	1	+2	5	2	p	4744.124	5930.849	63	3.1
4756.345	3	12	13	+2	11	10	p	4756.442	8108.318	133	3.3
4771.641	5	2	2	+2	3	1	p	4771.097	5265.703	64	3.0
4777.228	34	7	9	+2	6	6	o	4777.123	5772.677	151	28.6
4788.544[c].....	...	11	12	+2	10	9	o	4788.666	7644.484	132	8.8
4795.018[a].....	3	2	4	+2	2	1	p	4794.697	5031.976	56	3.2
4804.406[c].....	...	3	4	+2	3	1	p	4804.080	5298.686	70	4.5
4805.287	4	3	1	+2	4	2	p	4804.609	5572.834	78	4.1
4814.521	8	5	0	−2	6	3	o	4813.846	6390.680	60	5.2
4816.361	9	4	0	−2	5	3	o	4815.465	5895.604	89	9.2
4818.901	4	4	4	+2	4	1	p	4818.456	5651.768	75	4.7
4820.616	15	6	8	+2	5	5	p	4820.503	5549.281	144	14.2
4823.348	5	10	11	+2	9	8	p	4823.076	7218.733	131	5.6
4839.508	5	5	4	+2	5	1	p	4839.030	6088.940	75	4.1
4859.209	13	9	10	+2	8	7	p	4858.897	6831.068	128	6.8
4861.849	42	5	7	+2	4	4	p	4861.606	5363.481	136	13.3
4876.985[b].....	7	2	1	−2	3	2	p	4876.231	5304.112	98	4.6
4895.520	12	8	9	+2	7	6	o	4895.237	6481.318	123	15.5
4900.393	22	4	6	+2	3	3	o	4900.138	5215.387	127	22.9
4907.869[c].....	...	1	3	+2	1	0	o	4907.381	4994.314	155	11.1
		3	0	−2	4	3	o	4907.827	5566.330	100	10.7
4914.214[b].....	...	3	3	+2	3	0	o	4913.634	5430.347	148	17.6
4930.981	6	5	2	−2	6	5	p	4929.693	6167.744	80	4.2
4931.604	7	7	8	+2	6	5	p	4931.277	6169.328	118	8.4
4935.969[b].....	10	3	5	+2	2	2	p	4935.667	5104.913	114	8.8
4942.862	23	5	3	+2	5	0	o	4941.722	6212.584	125	12.7
4955.988	3	1	1	−2	2	2	p	4955.262	5124.508	147	4.8
4966.862	10	6	7	+2	5	4	p	4966.504	5895.176	111	8.6
4968.162[c].....	...	2	4	+2	1	1	p	4967.871	5031.976	93	5.5
4971.559	13	2	0	−2	3	3	o	4970.645	5285.893	141	13.6
5000.506	13	5	6	+2	4	3	o	5000.138	5658.641	101	16.1
5054.742	5	4	2	+2	4	1	p	5054.087	5887.398	58	3.2
5061.864	4	3	4	+2	2	1	p	5061.407	5298.686	70	4.8
5094.212	6	2	3	+2	1	0	o	5093.729	5180.662	91	9.8

[a] Jupiter measurement.
[b] Shoulder on an H_2 line.
[c] Apparently coincident with an H_2 line.

perature of the H_2 is above room temperature, and so the ortho/para ratio of the H_2 should differ by less than 1% from its high-temperature limiting value of 3/1. For the H_3^+ produced, the departure from the high-temperature limiting ortho/para ratio of 1/1 should then not be significant to the present accuracy, and this agrees with the observations.

The Jupiter results are the first observation of extraterrestrial H_3^+. Attempts to observe the ν_2 fundamental band in absorption in the interstellar medium have so far been unsuccesful (Oka 1981; Geballe and Oka 1989). The Jupiter work suggests that the emission spectrum of the $2\nu_2$ band should also be considered as a possible means of detecting interstellar H_3^+, and the laboratory wavenumbers reported here should assist in astronomical searches.

The emission lines of neutral H_3 in the present cell are generally stronger than those of H_3^+, presumably because the very much larger A_{if} coefficients (King and Morokuma 1979) more than compensate for the much smaller populations. With the presence of H_3^+ established on Jupiter, it would be of great interest to search for the Rydberg-Rydberg spectrum of neutral

H_3 produced by the electronic recombination of H_3^+ or H_5^+. Among the well-established bands of H_3 (Dabrowski and Herzberg 1980; Herzberg and Watson 1980; Herzberg *et al.* 1981; Herzberg *et al.* 1982), the best suited for such observations is probably the $3d$–$3p$ $^2E'$ band (Herzberg *et al.* 1982) with lines in the range 3900–4500 cm^{-1}. This band has strong lines at 4002.48 cm^{-1} and 4017.71 cm^{-1}, which could be used for an initial search.

We are grateful to J. W. C. Johns for use of his Bomem Fourier-transform spectrometer; to M. Vervloet for help with measurements and calibration; to M. G. Bawendi, B. D. Rehfuss, and T. Oka for communicating data in advance of publication; and to J.-P. Maillard and P. Drossart for discussions of the Jupiter spectrum. S. M. would like to acknowledge financial support from the Science and Engineering Research Council (U.K.).

REFERENCES

Bawendi, M. G., Rehfuss, B. D., and Oka, T. 1988, 43rd Symposium on Molecular Spectroscopy, Columbus, Ohio, Paper RA10.
Blackley, C. R., Vestal, M. L., and Futrell, J. H. 1977, *J. Chem. Phys.*, **66**, 2392.
Carney, G. D., and Porter, R. N. 1974, *J. Chem. Phys.*, **60**, 4251.
———. 1976, *J. Chem. Phys.*, **65**, 3547.
———. 1980, *Phys. Rev. Letters*, **45**, 537.
Crosswhite, H. M. 1972, *The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke* (New York: Interscience).
Dabrowski, I., and Herzberg, G. 1980, *Canadian J. Phys.*, **58**, 1238.
Drossart, P., *et al.* 1989, *Nature*, **340**, 539.
Geballe, T. R., and Oka, T. 1989, *Ap. J.*, **342**, 855.
Hamilton, D. C., *et al.* 1980, *Geophys. Res. Letters*, **7**, 813.
Helm, H. 1986, *Phys. Rev. Letters*, **56**, 42.
———. 1988, *Phys. Rev. A*, **38**, 3425.
Herbst, E., and Klemperer, W. 1973, *Ap. J.*, **185**, 505.
Herzberg, G., Hougen, J. T., and Watson, J. K. G. 1982, *Canadian J. Phys.*, **60**, 1261.
Herzberg, G., Lew, H., Sloan, J. J., and Watson, J. K. G. 1981, *Canadian J. Phys.*, **59**, 428.
Herzberg, G., and Watson, J. K. G. 1980, *Canadian J. Phys.*, **58**, 1250.
King, H. F., and Morokuma, K. 1979, *J. Chem. Phys.*, **71**, 3213.
Majewski, W. A., Marshall, M. D., McKellar, A. R. W., Johns, J. W. C., and Watson, J. K. G. 1987, *J. Molec. Spectrosc.*, **122**, 341.
Majewski, W. A., and Watson, J. K. G. 1987, 42nd Symposium on Molecular Spectroscopy, Columbus, Ohio, Paper WF3.
McConnell, J. C., and Majeed, T. 1987, *J. Geophys. Res.*, **92**, 8570.
Meyer, W., Botschwina, P., and Burton, P. 1986, *J. Chem. Phys.*, **84**, 891.
Miderski, C. A., and Gellene, G. I. 1988, *J. Chem. Phys.*, **88**, 5331.
Miller, S., and Tennyson, J. 1988*a*, *J. Molec. Spectrosc.*, **128**, 530.
———. 1988*b*, *Ap. J.*, **335**, 486.
———. 1989, *J. Molec. Spectrosc.*, **136**, 223.
Oka, T. 1980, *Phys. Rev. Letters*, **45**, 531.
———. 1981, *Phil. Trans. Roy. Soc. London*, **A303**, 543.
———. 1983, in *Molecular Ions: Spectroscopy, Structure and Chemistry*, ed. T. A. Miller and V. E. Bondybey (Amsterdam: North-Holland), p. 73.
Trafton, L., Lester, D. F., and Thompson, K. L. 1989, *Ap. J. (Letters)*, **343**, L73.
Watson, J. K. G. 1984, *J. Molec. Spectrosc.*, **103**, 350.
Watson, J. K. G., *et al.* 1984, *Canadian J. Phys.*, **62**, 1875.
Watson, W. D. 1976, *Rev. Mod. Phys.*, **48**, 513.
Xu, L. W., Bawendi, M., Rehfuss, B. D., Gabrys, C., and Oka, T. 1989, 44th Symposium on Molecular Spectroscopy, Columbus, Ohio, Paper RA3.

P. A. FELDMAN, W. A. MAJEWSKI, and J. K. G. WATSON: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

S. MILLER and J. TENNYSON: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK