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A search for interstellar H_3^+

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Based on the results of recent laboratory observation of the infrared ν_2 fundamental band of the H_3^+ molecular ion, the possibility of observing this important ion in interstellar space is discussed. An observation of this spectrum has been attempted with the aid of the high-resolution Fourier transform spectrometer on the 4 m Mayall telescope of the Kitt Peak National Observatory.

1. Introduction

The triatomic hydrogen molecular ion H_3^+ is the simplest well-bound polyatomic system. According to the most recent *ab initio* calculation (Dykstra *et al.* 1978), the formation energy of H_3^+ from three protons and two electrons is 36.533 eV. Subtracting from this value the Rydberg energy of hydrogen atom formation and the dissociation energy of H_2 we obtain the formation energy of H_3^+ from a proton and H_2 of -4.579 eV. This proton affinity to H_2 is even greater than the dissociation energy of H_2 of 4.478 eV.

Because of this high stability of H_3^+, the ion molecule reaction

$$H_2 + H_2^+ \longrightarrow H_3^+ + H + \Delta E \tag{1}$$

is exothermic with $\Delta E = 1.844\,\text{eV} = 178.0\,\text{kJ/mol}$, even though it starts from the well-bound species. The cross section for this reaction can be calculated from Langevin's formula (1905)

$$\sigma(v) = 2\pi e(\alpha/\mu)^{\frac{1}{2}}/v \tag{2}$$

where α is the polarizability of H_2, μ is the reduced mass; $\sigma \approx 1.5\,\text{nm}^2$ for the thermal velocity v of 1 km/s for laboratory conditions and *ca.* 5 nm² for $v = 300$ m/s for interstellar Space. Thus reaction (1) is extremely efficient and H_3^+ rather than H_2^+ is the dominant hydrogenic molecular ion both in a hydrogen discharge in the laboratory and in molecular clouds in space.

In the scheme of ion–molecule reactions that is now believed to be the most efficient mechanism for producing interstellar molecules (Herbst & Klemperer 1973), the H_3^+ ion plays a crucial role. It acts as an efficient protonator through the reaction

$$H_3^+ + X \longrightarrow HX^+ + H_2. \tag{3}$$

Thus, for example, the important and abundant molecular ions HCO^+ and HNN^+ are mainly produced through this chemical reaction with X = CO and N_2, respectively. Since the proton affinities of CO and N_2 are even higher than that of H_2, these reactions are exothermic. The cross sections of these reactions are similar to that for (1). In fact, (3) with X = CO is believed to be the chief destruction mechanism of H_3^+ in interstellar space because of the large abundance

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of CO. The role of H_3^+ as a protonator is so universal that as many as 70 reactions of the type of equation (3) were considered in Suzuki's (1979) treatment of chemical reactions in molecular clouds.

This ubiquitous molecular ion has been well known to mass spectroscopists since its accidental discovery by J. J. Thomson (1912). However, its astronomical observation has been hampered because of the lack of a laboratory spectrum of it in any wavelength region. The recent discovery (Oka 1980) of the infrared ν_2 band of this ion makes such an observation possible. In this paper I describe the results of the first such attempt.

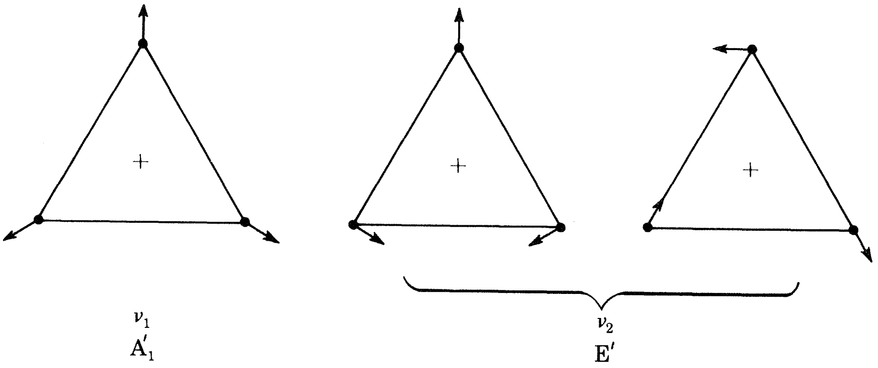

FIGURE 1. Normal coordinates of H_3^+.

2. LABORATORY SPECTRUM

Among the three types of spectrum of H_3^+, i.e. the electronic, the vibrational and the rotational, only the vibrational spectrum is suitable for observation. The optical spectrum of H_3^+ has never been observed, probably because it dissociates when an electron is excited (Herzberg 1967). This ion possesses no dipole moment and hence no strongly allowed rotational transitions. The $\Delta K = 3$ rotational spectrum induced by centrifugal distortion of the molecular ion (Watson 1971) is very weak and difficult to observe, although spontaneous emission processes caused by such a mechanism may be significant in discussing thermal equilibrium of interstellar H_3^+ (Oka *et al.* 1971).

Because of its equilateral triangular structure, H_3^+ has the totally symmetric ν_1 vibrational mode and the doubly degnerate ν_2 mode (figure 1); the former mode is infrared inactive. The vibrational transition dipole moment for the ν_2 fundamental band is calculated to be 0.156 D† from the Einstein coefficient for spontaneous emission given in the extensive *ab initio* calculation by Carney & Porter (1976). This is a large dipole moment considering the fact that the transition dipole moment of the intense ν_2 band of NH_3 is 0.24 D (Shimizu *et al.* 1971).

The intensity of spectral lines in terms of the absorption coefficient is given (Townes & Schawlow 1955) by

$$\gamma = \frac{8\pi^3\nu}{3hc}\, n(H_3^+) f(T_{\text{rot}}, T_{\text{vib}}) \left[1 - \exp\left(\frac{-h\nu}{kT_{\text{vib}}}\right)\right] |\mu_{ij}|^2 \phi(\nu, T_{\text{trans}}), \tag{4}$$

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† $1\,\text{D} = 3.336 \times 10^{-3}$ C m.

TABLE 1. OBSERVED FREQUENCIES OF THE ν_2 BAND OF H_3^+

transition $\nu_2(J, \lvert K-l \rvert)_{\mathrm{I,II}}(J, k)$	frequency / $\mathrm{cm^{-1}}$	intensity† / $10^{-6}\ \mathrm{cm^{-1}}$
$(5,1)_{\mathrm{I}} \leftarrow (4,1)$	3029.823	0.1*
$(5,2)_{\mathrm{I}} \leftarrow (4,2)$	3024.547	0.2*
$(7,6)_{\mathrm{II}} \leftarrow (6,6)$	3015.240	0.2*
$(5,3)_{\mathrm{I}} \leftarrow (4,3)$	3014.358	0.7*
$(5,4)_{\mathrm{I}} \leftarrow (4,4)$	3008.115	0.5*
$(6,5)_{\mathrm{II}} \leftarrow (5,5)$	2956.072	0.4*
$(4,0) \leftarrow (3,0)$	2930.163	2.3*
$(4,1)_{\mathrm{I}} \leftarrow (3,1)$	2928.351	1.3*
$(4,2)_{\mathrm{I}} \leftarrow (3,2)$	2923.361	1.6*
$(4,3)_{\mathrm{I}} \leftarrow (3,3)$	2918.026	3.8
$(5,3)_{\mathrm{II}} \leftarrow (4,3)$	2894.610	0.7*
$(5,4)_{\mathrm{II}} \leftarrow (4,4)$	2894.488	0.5*
$(4,3)_{\mathrm{II}} \leftarrow (3,3)$	2829.923	10
$(3,1)_{\mathrm{I}} \leftarrow (2,1)$	2826.113	5.9
$(3,2)_{\mathrm{I}} \leftarrow (2,2)$	2823.136	5.0
$(3,2)_{\mathrm{II}} \leftarrow (2,2)$	2762.068	10
$(2,1)_{\mathrm{I}} \leftarrow (1,1)$	2726.219	11
$(2,0) \leftarrow (1,0)$	2725.898	30
$(2,1)_{\mathrm{II}} \leftarrow (1,1)$	2691.444	11
$(3,3) \leftarrow (3,3)$	2561.493	3.4
$(2,2) \leftarrow (2,2)$	2554.664	4.6
$(2,1)_{\mathrm{I}} \leftarrow (2,1)$	2552.987	1.4*
$(1,1) \leftarrow (1,1)$	2545.418	8.9
$(1,0) \leftarrow (1,0)$	2529.724	30
$(2,1)_{\mathrm{II}} \leftarrow (2,1)$	2518.207	5.6
$(3,0) \leftarrow (3,0)$	2509.075	3.2
$(3,1)_{\mathrm{II}} \leftarrow (3,1)$	2508.131	1.6*
$(3,2)_{\mathrm{II}} \leftarrow (3,2)$	2503.347	1.5*
$(4,2)_{\mathrm{II}} \leftarrow (4,2)$	2492.534	0.2*
$(0,1) \leftarrow (1,1)$	2457.90	5.9

† Calculated intensities at 200 K. Lines marked with asterisks were observed at a temperature of 450 K.

where $n(H_3^+)$ is the density of H_3^+ per cubic centimetre, T_{rot}, T_{trans} and T_{vib} are the rotational, translational and vibrational temperatures, respectively, $\phi(\nu, T_{\mathrm{trans}})$ is the Doppler broadened normalized line shape function and μ_{ij} is the transition dipole matrix element. The absorption $\alpha = -\ln(I/I_0)$ is given by multiplying γ by the optical path l. For an astronomical observation we use the column density $n(H_3^+)\,l$.

The laboratory experiment gave the values $n(H_3^+) \approx 3 \times 10^{10}\ \mathrm{cm^{-3}}$ and $T_{\mathrm{rot}} \approx T_{\mathrm{trans}} \approx 200\ \mathrm{K}$ for a liquid N_2 cooled hydrogen discharge with a pressure of *ca.* 100 Pa and a current density of *ca.* 60 mA cm^{-2}. For this condition the strongest absorption after the optical path of 32 m, that is for the column density of $10^{14}\ \mathrm{cm^{-2}}$, was about 10 %. This value agreed approximately with the value predicted from (4) on the assumption that $T_{\mathrm{vib}} \ll h\nu/k \approx 4000\ \mathrm{K}$. A linewidth (h.w.h.m.) of about 0.01 cm^{-1} was observed and was due to the Doppler shift for the thermal velocity of H_3^+ of *ca.* 1 km s^{-1}.

Observed frequencies are summarized in table 1. The small discrepancies between the observed frequencies given in table 1 and those given in Oka (1980) are due to more accurate calibration of frequencies in this work. Readers are referred to Oka (1980) for more details of the laboratory observation, analysis of the spectrum and molecular constants. A more detailed paper will be published soon. Here we consider only the rotational level structure of the ground state of H_3^+, which is needed for discussing the feasibility of detecting this molecular ion in interstellar Space.

The rotational level structure of H_3^+ in the ground vibrational state is shown in figure 2 in terms of three quantum numbers: J for the total angular momentum, K for the rotational angular momentum around the threefold symmetry axis and ± for the parities of wavefunctions with respect to inversion. The level structure is similar to that of NH_3 except that there is no inversion doubling. In fact if one takes the lower components of the inversion doublets of NH_3 one obtains qualitatively the same structure as shown in figure 2. This is natural because a planar molecule can be considered as the limiting case of non-planar molecules with the barrier of inversion set equal to 0. As in NH_3, H_3^+ molecules are composed of two spin modifications: *ortho*-H_3^+ with the total nuclear spin quantum number $I = \frac{3}{2}$ and associated with levels $K = 3n$ (shown in figure 2 with bold lines), and *para*-H_3^+ with $I = \frac{1}{2}$ with levels $K = 3n \pm 1$. The former has a spin degeneracy $(2I+1)$ of 4 and the latter 2.

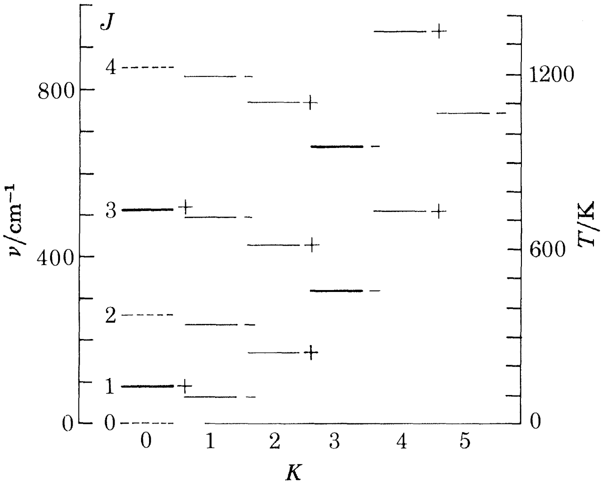

FIGURE 2. Rotational levels of H_3^+ in the ground vibrational state with quantum numbers J, K, parity ±, and *ortho* (bold line) and *para* (thin line) specified.

Because of the large rotational constants of H_3^+, $B_0 = 43.620\ \text{cm}^{-1}$ and $C_0 = 20.331\ \text{cm}^{-1}$ (J. K. G. Watson, unpublished), only several lowest rotational levels are populated even for the laboratory plasma temperature of 200 K. The most populated is the $J = 1$, $K = 0$ level of *ortho*-H_3^+, which is occupied by about 30 % of the total molecular ions at this temperature (note that the lowest $J = 0$, $K = 0$ level is not allowed owing to the Pauli principle). The two strongest lines listed in table 1, which are most suitable for astronomical observation, start from this most populated level. The $J = 1$, $K = 1$ level is lower than the $J = 1$, $K = 0$ level by 23.167 cm^{-1}, but is less populated because of the lower spin weight. However, this is not necessarily so in interstellar Space. If the rotational excitation temperature is below 48 K, the lowest *para*-level is more populated than the lowest *ortho*-level. It has been shown in the laboratory (Oka, unpublished) that *ortho*-H_3^+ and *para*-H_3^+ equilibrate quickly through the exchange reaction

$$H_3^+ + \tilde{H}_2 \longrightarrow H_2\tilde{H}^+ + H\tilde{H}. \tag{5}$$

3. Interstellar conditions

The results of the laboratory spectrum summarized in the previous section are translated into the language of observational astrophysics as follows: if the H_3^+ molecular ions exist in a molecular cloud with a column density of $10^{14}\,cm^{-2}$, an average velocity of $1\,km\,s^{-1}$, and a rotational excitation temperature of 200 K, we expect absorption of *ca.* 10 % at $2725.898\,cm^{-1}$ and $2529.724\,cm^{-1}$ provided there is an infrared source behind the molecular cloud. This value of absorption may increase by a factor of about 2 if the excitation temperature is lower, but decrease by a factor of 5 through the limited instrumental resolution of $0.041\,cm^{-1}$ used in our observation.

We have a dilemma here. Theory predicts that H_3^+ is abundant in carbon-depleted clouds with large magnitudes of optical extinction (de Jong *et al.* 1980), the type of clouds in which deuterium fractionation is efficient. Thus H_3^+ must be relatively abundant in clouds such as TMC-1 and L 134; these clouds are also of low kinetic and excitation temperature. But there is no infrared source.

The most promising area of observation seems to be the Orion Molecular Cloud, in which dense molecular clouds and intense infrared sources coexist. In this source HCO^+ column densities of $2 \times 10^{15}\,cm^{-2}$ with linewidth (h.w.h.m.) of *ca.* $14\,km\,s^{-1}$ (plateau), $3 \times 10^{14}\,cm^{-2}$ with *ca.* $1.1\,km\,s^{-1}$ (ridge I), and $2 \times 10^{14}\,cm^{-2}$ with *ca.* $1.3\,km\,s^{-1}$ (ridge II) have been reported (Rydbeck *et al.* 1981). From these results and those from the laboratory it is estimated that if the ratio of column densities $n(HCO^+)/nH(_3^+)$ is 10 in all regions, an absorption of 5 % is expected. The ratio in question has been predicted by Herbst & Klemperer (1973) to be from 0.07 to about 0.01. For a more depleted cloud de Jong *et al.* (1980) predict this ratio to be on the order of 1. We should also keep in mind that since the spatial resolution of an infrared telescope is much higher than that of a millimetre telescope, these estimates are subject to a large change if the millimetre observation is the result of averaging over many features.

Let us now consider the possibility of observing the H_3^+ spectrum in emission. Here a comparison with the H_2 quadrupole emission spectrum is useful. The rate-determining process of the production of H_3^+ is the ionization of H_2 into H_2^+ which is converted quickly to H_3^+ (equation (1)). Equating the production rate with the destruction rate through (3) we obtain (Dalgarno *et al.* 1973)

$$\zeta n(H_2) = kn(X)\,n(H_3^+), \tag{6}$$

where ζ is the cosmic ray ionizing flux (*ca.* $10^{-17}\,s^{-1}$) and k is the rate constant for (3) *ca.* $10^{-9}\,cm^2\,s^{-1}$). For the typical CO concentration $n(CO) \approx 10/cm^3$, we thus obtain

$$n(H_3^+)/n(H_2) \approx 10^{-8}/n(X) \approx 10^{-9}. \tag{7}$$

This factor of 10^{-9} is approximately cancelled by the intensity ratio of the dipole spectrum and the quadrupole spectrum, i.e.

$$I_\mu/I_Q \approx (\lambda/a)^2 \approx 10^9, \tag{8}$$

where λ is the wavelength of radiation and a is the molecular dimension (Heitler 1953). Equation (8) is confirmed by the laboratory spectrum of H_2 (D. R. Rao and T. Oka, unpublished) and H_3^+ (Oka 1980) as shown in figure 3.

These considerations indicate that the *absorption* of H_3^+ in a molecular cloud would be similar to that of H_2. However, the *emission* of H_3^+ is expected to be much less than that of H_2 because of the slow pumping by collision. The factor of 10^9 in (8) applies also to the spontaneous emission rate if we neglect the wavelength dependence. Thus the spontaneous emission lifetime t_e of the ν_2 state of H_3^+ is on the order of 10 ms, while that of the excited state of H_2 is on the order of a year. Therefore while the collisional excitation rate t_c is sufficiently fast for H_2 excitation in a dense region it is far too slow for H_3^+ excitation. This reduces the emission from H_3^+ with respect to that from H_2 by a factor of $t_e/t_c = 10^{-2}n\sigma v$. For this ratio to be appreciable we need an enormously high density of H_2 of *ca.* $10^{12}/\text{cm}^3$ or more.

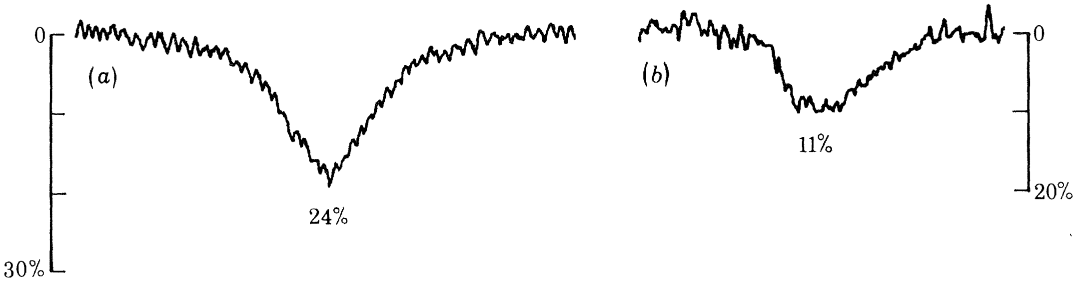

FIGURE 3. Comparison of (*a*) H_2 and (*b*) H_3^+ absorption lines in the laboratory. The H_2 $v = 1 \leftarrow 0$ $Q(1)$ transition at 4155.2540 cm^{-1} with 1 atmosphere pressure and 64 m path length (column density *ca.* $2 \times 10^{23}\ \text{cm}^{-2}$) gives about twice as much absorption as that of H_3^+ ν_2 $R_0(1)$ transition at 2725.898 cm^{-1} with the column density of $10^{14}\ \text{cm}^{-2}$, demonstrating the relation in equation (8).

The infrared emission from H_3^+ inside the dark cloud at the time of formation is very low owing to the small ζ, $10^{-17}\ \text{s}^{-1}$. It seems that the only possibility of observing this type of emission is that from the area where the ionization of H_2 is very rapid either by intense short wavelength radiation or by shock wave.

4. OBSERVATION

Observation was made for 2 days on 1981 March 23–25, with the coudé Fourier transform spectrometer with high resolution (*ca.* $0.041\ \text{cm}^{-1}$) on the 4 m Mayall telescope of the Kitt Peak National Observatory. A liquid He cooled narrow band filter with the centre wavenumber of $2725.898\ \text{cm}^{-1}$ and the full width at half maximum of *ca.* $65\ \text{cm}^{-1}$ combined with a broad band filter was used with the infrared detectors to reduce noise. This wavenumber region was chosen aiming at one of the strongest transitions $[\nu_2, J = 2, |K-l| = 0] \leftarrow [J = 1, K = 0]$ and its satellite $[\nu_2, J = 2, |K-l| = 1]_{\text{I}} \leftarrow [J = 1, K = 1]$ which are only $0.322\ \text{cm}^{-1}$ apart. The former corresponds to *ortho*-H_3^+ and the latter *para*-H_3^+. Two other transitions $[\nu_2, J = 3, |K-l| = 2]_{\text{II}} \leftarrow [J = 2, K = 2]$ and $[\nu_2, J = 2, |K-l| = 1]_{\text{II}} \leftarrow (J = 1, K = 1]$ are expected within the pass band of the filter used.

The search for absorption was made in seven infrared sources, the Becklin–Neugebauer source of Orion ($10^{-14}\ \text{W cm}^{-2}$), carbon stars IRC +10216 ($7 \times 10^{-13}\ \text{W cm}^{-2}$) and CIT ($10^{-13}\ \text{W cm}^{-2}$), cool and hot stars α Tau ($3 \times 10^{-13}\ \text{W cm}^{-2}$), α Lur ($2 \times 10^{-14}\ \text{W cm}^{-2}$) and R Leo where the numbers in brackets show the infrared flux of each source at 3.7 μm. Telluric absorption lines were removed by taking the ratio of the observed spectrum to that of α CMa, which is known to have no discrete spectrum of its own. Unfortunately the spectrum of the most important source, the BN source of Orion, turned out to be not of excellent quality because of noise from the observation conditions, and the minimum detectable absorption was on the order of 20 %. This sets an upper limit on the H_3^+ column density of $5 \times 10^{14}\,\mathrm{cm^{-2}}$. The sensitivity of the spectrometer for the other sources ranged between 5 and about 30%.

The search for emission was made in the peak 1 position of Orion where very strong H_2 quadrupole emission has been observed (Beckwith *et al.* 1978) and the compact H I region NGC 7027. The negative results set an upper limit for the emission infrared flux of $10^{-16}\,\mathrm{W\,cm^{-2}\,\mu m^{-1}}$ at 3.6″ aperture.

More observations will be attempted for this important and fundamental molecular ion.

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