First-principles Calculations on the Astrochemistry and Spectroscopy of H_3^+

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The H_3^+ molecular ion features prominently in interstellar medium (ISM) reaction schemes. It is the main protonating agent and provides a major channel for deuterium fractionation. Yet all attempts to detect H_3^+ in the ISM by using infrared absorption techniques have so far failed.

We have performed a series of ro-vibrational calculations of spectroscopic accuracy using a high-quality potential-energy surface due to Meyer, Botschwina and Burton. With these we have built up an extensive data set of ro-vibrational energy levels and transition intensities. From the energy levels we have generated partition functions and hence temperature-dependent equilibrium constants for the fractionation reactions $H_3^+ + D \rightarrow H_2D^+ + H$ and $H_3^+ + HD \rightarrow H_2D^+ + H_2$, as well as the H_3^+ forming reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$. At the low temperatures typical of the ISM, the fraction of H_2D^+ rises rapidly and our theoretical estimates are at their most reliable.

Emission spectra of H_3^+ from both the ν_2 and $2\nu_2$ bands have been observed by several groups in the polar regions of Jupiter. These are now being used to both monitor and map the complicated auroral activity of Jupiter. Recently, we have also assigned ν_2 emissions in the spectrum of supernova SN1987a and observed these emissions in Uranus. These successes suggest that searching for H_3^+ in emission may well provide a better observational handle on this chemically active and important species. The role of proton in hopping in the thermalisation of the H_3^+ *ortho/para* ratio will be discussed.

The fundamental molecular ion H_3^+ is thought to play a pivotal role in interstellar chemistry.[1] It is rapidly formed from ionised molecular hydrogen by the strongly exothermic reaction:

$$H_2 + H_2^+ \rightarrow H_3^+ + H; \quad \Delta H = -16\,300 \text{ K} \tag{1}$$

In models of the interstellar medium (ISM), H_3^+ is responsible for starting the chain of ion–molecule reactions by protonation:

$$H_3^+ + X \rightarrow H_2 + HX^+ \tag{2}$$

where X = CO, N_2, O_2, O, C, N, HCN *etc.* H_3^+ is also thought to be the main progenitor in deuterium fraction *via* the exothermic reactions

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2; \quad \Delta H = -232 \text{ K} \tag{3}$$

$$H_3^+ + D \rightleftharpoons H_2D^+ + H; \quad \Delta H = -509 \text{ K} \tag{4}$$

Despite its perceived importance, H_3^+ has yet to be observed in the ISM. A number of attempts have been made to observe H_3^+ from absorption features in the infrared continuum of suitable stars. These are difficult observations to make and thus far have led only to upper limits on the abundance of H_3^+ in a number of cold clouds.[2–4] These studies have also cast doubt[4] on the tentative assignment of H_2D^+ transition in NGC2264.[5]

Infrared spectra of H_3^+ have been observed in emission from Jupiter[6] and recently Uranus[7] (see below). Emission features have also been assigned to H_3^+ in the spectrum of supernova SN1987a.[8] The lowest value of the H_3^+ rotational temperature derived from these observations is 650 K.[9] These observations suggest an alternative approach to searching for H_3^+ in the ISM *via* emissions in hot, possibly shocked, regions of the ISM.

Besides our involvement in the above astrophysical detections, we have for a number of years performed first-principles calculations of the ro-vibrational spectrum of H_3^+ and its isotopomers.[10–12] These calculations have not only been instrumental in assigning much of the laboratory spectra of the ion,[13] they also provide the oscillator strengths needed to turn detections (non-detections) of H_3^+ into column densities (upper limits).

In this paper, we summarise the results of recent calculations which are now yielding data suitable for modelling, address the problem of *ortho/para* ratios in H_3^+ and the role of proton hopping in thermalising this ratio, finally we end with a report on recent attempts to observe H_3^+.

Ro-vibrational Calculations

The variational techniques used to calculate the ro-vibrational spectra of H_3^+ and other triatomic systems have recently been reviewed by Tennyson *et al.*[14] The reader is referred to this and the original articles[10–12] for further information on these nuclear motion calculations. The electronic simplicity of the H_3^+ molecule has meant that highly accurate *ab initio* electronic potential-energy surfaces are available for these systems.[15,16] With these we have been able to predict H_3^+ transition frequencies with an accuracy of one part in 10000 in the best case.[17]

In the course of our calculation on H_3^+ we have built up large data sets of both energy levels, and transition frequencies and intensities. Some of the transition data have been published[18] and a new version[19] is currently in preparation using our latest results[12] and the most recent laboratory data.[17]

From such data compilations one can generate parameters which form the input for astrophysical models. Fig. 1 and Tables 1 and 2 show examples of the data these calculations can yield as input to models.

The deuterium fractionation reactions (3) and (4) are highly temperature dependent in the temperature range of the ISM. It is possible to compute equilibrium constants, as a function of temperature, using known energy differences and the partition functions obtained by explicitly summing over the ro-vibrational energy levels of H_3^+ and H_2D^+. This has been done by Sidhu *et al.*[20] for these reactions and the H_3^+ formation reaction (1).

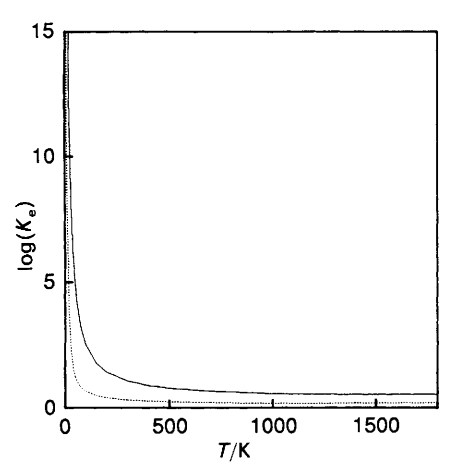

Fig. 1 Calculated equilibrium constants, K, as a function of temperature[20] for reactions $H_3^+ + D \rightarrow H_2D^+ + H$ (solid curve) and $H_3^+ + HD \rightarrow H_2D^+ + H_2$ (dashed curve)

Table 1 Calculated band origins (in cm^{-1}) and Einstein A coefficients (in s^{-1}) for the low-lying bands of H_3^+ from Dinelli *et al.* where states up to $(0,4^4)$ at 9650 cm^{-1} are considered[a]

			A_{if}			
symmetry	(ν_1, ν_2^l)	band origin	A_1 $(0,0^0)$	E $(0,1^1)$	A_1 $(1,0^0)$	A_1 $(0,2^0)$
E	$(0,1^1)$	2521.28[b]	128.8			
A_1	$(1,0^0)$	3178.35[c]	0	0.846		
A_1	$(0,2^0)$	4777.02	0	139.2	0	
E	$(0,2^2)$	4997.42	144.6	256.0	0.211	0.024

[a] A_{if} for $E \rightarrow A_1/A_2$ transitions in Dinelli *et al.* should be divided by 2. [b] Observed 2521.31.[39] [c] Observed 3178.3.[40]

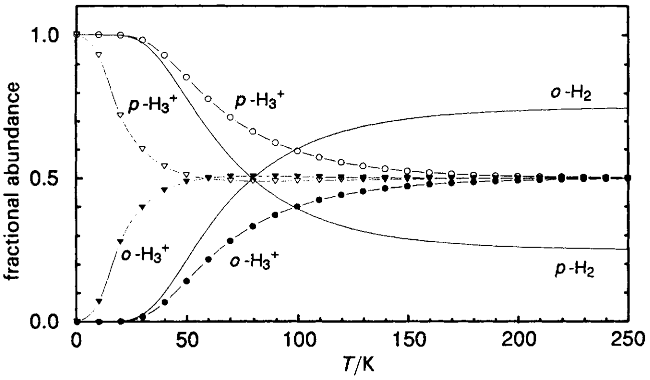

Fig. 2 Equilibrium fractional abundances of *ortho*- and *para*-H_2 and resulting *ortho* and *para* fractions of H_3^+. See text for details

For modelling, rate constants are generally used rather than equilibrium constants. However, as the forward deuterium fractionation reactions are generally assumed to proceed at the Langevin rate, the equilibrium constants can be used to determine the much more temperature-sensitive reverse rate constants.

Full astrophysical information can be extracted only from the observed spectra *via* detailed models which consider the rates for the processes determining not only creation and destruction of the molecular species in question, but also the occupancy of the various levels in the system. Such modelling has recently been performed by Kim *et al.*[21] for the auroral regions of Jupiter. However, these workers lacked detailed information on H_3^+ radiative rates. These have since been calculated by Dinelli *et al.*[12] using a new method proposed by Le Sueur *et al.*[22] The results for states up to $2\nu_2$, the highest so far detected astrophysically, are given in Table 1.

The corresponding results for H_2D^+ are given in Table 2. We note that the lower symmetry of H_2D^+ means that many more transitions have to be considered. This is because of the splitting of the degenerate ν_2 mode and the loss of vibrational selection rules which means that all transitions are symmetry allowed.

Dinelli *et al.* treated all the vibrational states of H_3^+ up to $4\nu_2$. This is the highest vibrational state below the barrier to linear H_3^+. However, sufficient energy is generated in the formation of H_3^+ by reaction (1) for states above linearity to be populated. Le Sueur *et al.*[23] are presently extending the treatment of radiative rates to all the bound vibrational states of H_3^+ using wavefunctions obtained using a discrete variable representation (DVR).[24]

Thermalisation of H_3^+

Observations of several H_3^+ transitions can provide parameters relating to the environment of the molecule. Besides the column density, n, information on the temperature of the emitting levels and fraction of *ortho*/*para* H_3^+ can also be obtained. A typical emission spectrum in either the K or L window yields a rotation temperature, T_{rot}. Comparisons between the two windows can yield a vibrational temperature, T_{vib}. For Jupiter, observations[25] have found that $T_{rot} \approx T_{vib}$ suggesting that the emissions are thermal in origin. More detailed modelling has suggested that this distribution is only quasithermal because of the cooling effects on the vibrationally excited states of the infrared emissions.[21] The *ortho*/*para* ratio can be determined from the H_3^+ emission spectrum although experience has shown[26] that high resolution is required for a useful determination as otherwise *ortho* and *para* lines tend to blend.

The ro-vibrational states of H_3^+ can be classified using the S_3 permutation group as having either A_1, A_2 or E symmetry. Consideration of the nuclear spin couplings for H_3^+ show that

Table 2 Calculated band origins (in cm^{-1}) and Einstein, A, coefficients (in s^{-1}) for the low-lying bands of H_2D^+

		A_{if}					
(ν_1, ν_2, ν_3)	band origin	(0,0,0)	(0,1,0)	(0,0,1)	(1,0,0)	(0,2,0)	(0,1,1)
(0,1,0)	2206.24[a]	20.0					
(0,0,1)	2334.99[b]	179.2	0.001				
(1,0,0)	2992.94[c]	53.2	0.144	0.449			
(0,2,0)	4287.50	19.2	25.4	20.3	0.103		
(0,1,1)	4460.84	104.7	152.3	16.6	0.018	0.012	
(0,0,2)	4602.15	52.9	15.6	287.3	0.601	0.007	0.002

[a] Observed 2205.87.[41] [b] Observed 2334.45.[41] [c] Observed 2992.49.[42]

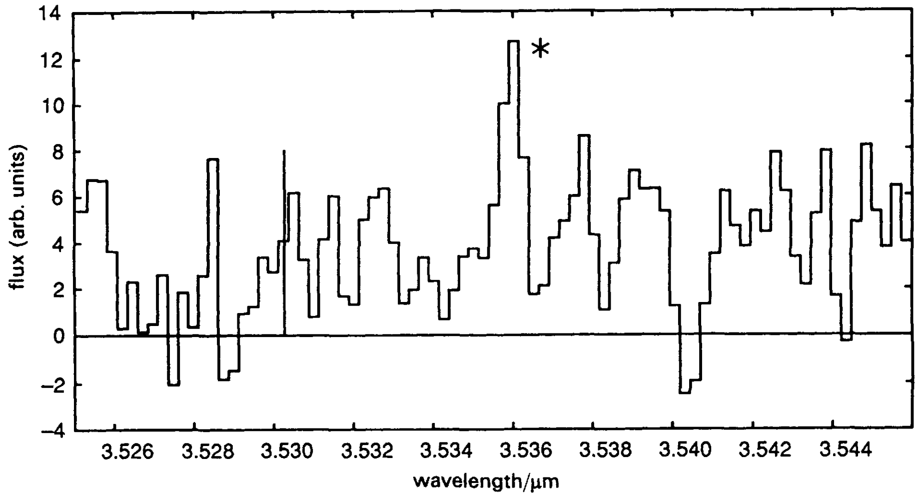

Fig. 3 Detection of an H_3^+ emission line in L1457? The starred feature can be attributed to a slightly redshifted H_3^+ $\nu_2 \rightarrow 0$ R(3) transition at $\lambda_0 = 3.534$ µm. The vertical line shows a typical error bar

these states have nuclear spin degeneracies of 0, 4 and 2, respectively. In the absence of states of A_1 symmetry, the remaining levels can be classified as *ortho* (A_2) or *para* (E). At high temperatures, there are twice as many occupied *para* E states as A_2, but because the E states have only half the spin weighting of the A_2 states, high-temperature equilibrium H_3^+ contains equal amounts of the *ortho* and *para* forms. At low temperatures, however, the situation changes. Since A_1 states are not allowed, the lowest available state is the para $J = 1$, $K = 1$ level. This is *ca.* 33 K lower in energy than the *ortho* $J = 1, K = 0$ level.

In Fig. 2 the inverted triangles show the mixture of *ortho*/*para*-H_3^+ to be expected in a self-thermalised gas as a function of temperature. At temperatures a little over 50 K, the *ortho*-H_3^+ fraction is *ca.* 0.5. (In fact, between 60 and 160 K there is a slight favouring of the *ortho* form.) However, searches for H_3^+ in the interstellar medium which use this self-thermalised curve to estimate relative abundances may seriously overestimate the relative abundance of the *ortho* form, for the following reasons: When H_3^+ is formed in reaction (1), the *ortho*/*para* ratio depends critically on the *ortho*/*para* ratio of the neutral H_2 from which it forms;[4] rules governing such a process have been given by Quack.[27,28] Stated briefly, they mean that *para*-H_2 can give rise only to *para*-H_3^+ and that *ortho*-H_2 produces 2/3 *ortho*-H_3^+ and 1/3 *para*-H_3^+.[6] At room temperature, the equilibrium *ortho* fraction of H_2 is 0.75, but at lower temperatures, once more it is the *para* form that predominates; the lowest available level of *para*-H_2 is *ca.* 170 K below that of *ortho*-H_2. The full curves in Fig. 2 show the fractional abundance of thermalised *ortho*- and *para*-H_2 and the circles that of *ortho*- and *para*-H_3^+ produced from such thermalised H_2.

In the interstellar medium, H_3^+ concentrations are typically of the order of 10^{-7} to 10^{-9} of that of molecular hydrogen. It has been widely assumed that the H_3^+ *ortho*/*para* ratio will thermalise *via* proton hopping:[2–4,29]

$$H_2 + H_3^+ \rightleftharpoons H_3^+ + H_2 \qquad (5)$$

As in the case of H_3^+ formation, [reaction (1)], it is the weaker ionic bond that breaks and a proton is transferred between hydrogen molecules.

The assumption that H_3^+ will thermalise seems to be based on laboratory measurements[2] almost certainly made above 150 K. At such temperatures, typical of most spectral measurements, it is clear from Fig. 2 the *ortho*-H_3^+ fraction is close to 0.5, with or without thermalisation. For temperatures up to *ca.* 150 K, however, there are marked differences in the *ortho*/*para*-H_3^+ ratios of the self-thermalised gas and that formed from thermalised H_2. At the temperature of a warm, 70 K, molecular cloud, such as are found in the Orion Molecular Cloud, self-thermalised gas would produce more than 50% *ortho*-H_3^+; H_3^+ freshly produced from H_2 thermalised at this temperature would have less than 30% of the *ortho* form. At lower tempertures, typical of cold clouds such as the Taurus molecular cloud, TMC-1, and NGC2264, the effect is even more dramatic. At 20 K the self-thermalised H_3^+ has 30% of the *ortho* form, the gas produced from H_2 has virtually none. Nor will the process of 'thermalisation' *via* proton hopping change this situation. Unless two bonds are broken during proton hopping, an extremely unlikely process even at room temperature, let alone at temperatures of 70 K or below, collisions between H_3^+ and *para*-H_2 involving the exchange of a proton can result only in *para*-H_3^+; these collisions cannot make up the deficit of *ortho*-H_3^+ noted above to bring the *ortho*/*para* ratio closer to the self-thermalised value, and collisions between *ortho*-H_2^+ and H_3^+ will once more result in the fraction of *ortho*-H_3^+ being equal to two-thirds that of *ortho*-H_2. A relative overabundance of *ortho*-H_3^+ might thus be brought down to a level reflecting the *ortho*/*para* ratio of H_2, but the fraction of *ortho*-H_3^+ cannot be increased. This argument leads to the conclusion that the *ortho*/*para* ratio of H_3^+ in the interstellar medium ought to follow the circles in Fig. 2 rather than the triangles.

This does not necessarily mean that *ortho*/*para* ratio of H_3^+ directly reflects the temperature of the ambient molecular hydrogen. Even in cold regions of the ISM, H_2 is thought to be formed on grains in its high-temperature form with an *ortho* fraction of 0.75, thermalising slowly thereafter.[30] Equilibration times are typically of the order of 10^6 years, and Flower *et al.* have suggested that using ammonia maser activity to probe the *ortho*/*para* ratio of H_2 might be a useful way of determining the age of molecular clouds.[31] Analogously, one might argue that measurements of the *ortho*/*para* ratio of H_3^+ would also be useful for dating molecular clouds, given that it is possible to detect H_3^+ at all in the ISM.

Recent Observations

Although previous searches for H_3^+ in the ISM have concentrated on looking for absorption lines against an infrared

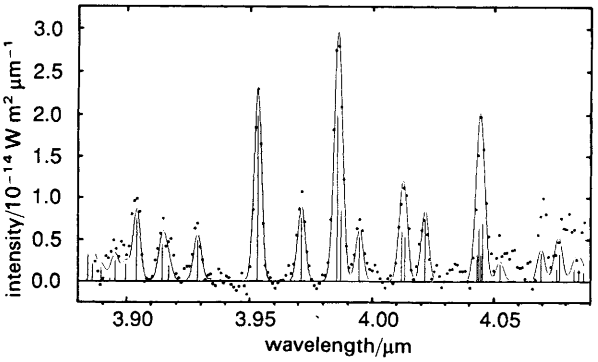

Fig. 4 Spectrum of Uranus between 3.89 and 4.09 μm by Trafton *et al.*[7] (filled circles) compared to a fit using calculated H_3^+ parameters (full line). The sticks give the position and relative intensity of the H_3^+ transitions included in the fit, $T = 740$ K; $f_0 = 0.51$; $\rho = 6.5 \times 10^{10}$ cm^{-2}

source,[2–4] the first detections of this ion outside of the laboratory involved emission features. It is therefore plausible that regions of the ISM which have conditions favourable for H_3^+ emission may be the best targets for future searches. We have recently been involved in two separate sets of observations using the United Kingdom Infrared Telescope (UKIRT) for studying H_3^+ emissions. The first run on February 2–4 1992 (UT) which was awarded time specifically for the search for H_3^+ emission in shock and X-ray-excited molecular gas, was adversely affected by bad weather. The second run (April 1–3, 1992) was awarded time for continuing work mapping and monitoring H_3^+ emissions from Jupiter (results of which will be presented elsewhere[32]), but, because Jupiter is not visible all night, allowed some time for observing other objects.

The detection of H_3^+ beyond the solar system (with the exception of SN1987a) has continued to prove more difficult than expected. We concentrated our efforts to observe emissions in the Q and R branches of H_3^+ in the K and L bands. Astrophysical sites most likely to emit this radiation are shock-excited molecular clouds, where the local temperature can reach several thousand degrees, or X-ray-excited molecular gas, where as model calculations have shown H_3^+ concentrations may be very high.[33] Shocks in the interstellar medium are very common and are usually produced by stellar ejecta impinging on a molecular cloud or by collisions between different molecular clouds, *i.e.* in merging galaxies. Stellar ejecta can be due to stellar winds from young stellar objects (Herbig Haro objects), winds from OB stars (star-forming regions like Orion, starburst galaxies) or supernova ejecta.

During our observations in February 1992 we seached five starburst or merging galaxies for H_3^+ emission with a negative result. Galactic targets included the proto-planetary nebula CRL 618, parts of the supernova remnant IC443, and the dark cloud L1457. The best candidate for a possible H_3^+ detection among these was L1457. Fig. 3 shows the result of a 23 min observation of this object. It shows an emission feature (starred) at the 2σ level which can be attributed to a slightly redshifted H_3^+ $\nu_2 \rightarrow 0$ R(3) transition at $\lambda_0 = 3.534$ μm. Unfortunately, poor weather prevented us from confirming this tentative detection.

Dark clouds consist of molecules and dust. The latter absorbs visible light but is transparent to infrared light. L1457 is, however, a special object in two respects with both factors facilitating the possibility of a H_3^+ detection. First, L1457 is the nearest object of this type at a distance of only 65 pc from the Sun[34] and secondly it seems to contain a hard X-ray source[35]. The exact nature of this X-ray source is unclear but the most likely candidate would be a luminous T Tauri star.

Even more recently, H_3^+ has been detected in the atmospheres of Uranus[7] and Saturn.[36] Fig. 4 shows an emission spectrum of Uranus taken on the 1st April 1992[7] using 1 h integration on CGS4 with a 150 lines mm^{-1} grating and 150 mm focal length camera which gives a resolving power of $R = 1150$ (or a resolution of *ca.* 0.0035 μm). The spectrum was fitted to calculated line frequencies and intensities[18] with no background. This gives a temperature of 740 ± 40 K for the rotational levels of the emitting ν_2 level of H_3^+. The sticks in Fig. 4 represent the positions and, on an arbitrary scale, intensities of the individual lines used in fitting the spectrum. These demonstrate that at this resolution many of the features actually comprise blends of H_3^+ transitions.

Conclusions

Since the first spectra of H_3^+ in 1980,[37,38] first-principles calculations have played an important role in the search for an assignment of laboratory spectra. With the observation of an H_3^+ emission spectrum in Jupiter,[6] this role has now extended to astrophysics. Furthermore, these calculations are now being used to generate chemical reaction[20] and radiative[12] data useful for modelling.

Despite the success of observing[6,7] and assigning[8] H_3^+ emission spectra, H_3^+ has yet to be observed in cool interstellar clouds. Attempts to observe cold H_3^+ in absorption have used transitions of both *ortho* and *para*-H_3^+, the lower levels of which have been assumed to be in thermal equilibrium. We suggest that the proposed thermalisation mechanism, proton-hopping, may not actually function in environments where *para*-H_2 is the dominant species. Under these circumstances there may be an overabundance of *para*-H_3^+ relative to *ortho*-H_3^+.

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