

H₃⁺ in Space

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1 Introduction

SOMETIMES science is beautiful because something that is really complex turns out to have an inner simplicity. When Crick and Watson finally put together their double helix model of DNA, they just knew they had it; it was just so elegant. Other times, natural beauty lies in the ability of quite simple systems to carry out, and be responsible for, very complicated processes. The hydrogen molecular ion H₃⁺ is like that. In what follows, we hope to explain to you why, whatever else we might have done and might do, H₃⁺ will always have a special place in our scientific affections.

In 1912, J. J. Thomson wrote a paper called 'Further Experiments on Positive Rays'.¹ In it he drew attention to a track on the photographic plate he was using to record his hydrogen discharge experiments which had a mass to charge ratio of three. Carefully eliminating other possibilities, he came to the conclusion that the positive ray responsible for the track was H₃⁺. This was the discovery of this important molecular ion. But it was not as simple as that. Chemical theory at that time could not account for a stable triatomic molecule held together with just two electrons, and when deuterium was discovered Thomson was persuaded that he had seen HD⁺. It took further developments of chemical theory to explain that H₃⁺ really was a viable molecule and to elucidate its structure.² Indeed, the history of H₃⁺ shows that for this molecule in particular, theory has consistently led experiment.[†]

H₃⁺ is the simplest polyatomic molecule there is. The three protons that make up the individual hydrogen nuclei are held together by just two electrons. The molecule is an equilateral triangle at equilibrium. It can be thought of either as the first ionized state of H₃ or as protonated H₂. Chemists normally consider ions as being less stable than their parent molecules. This is not the case for the H₃/H₃⁺ system, however. For while the three electrons involved in H₃ make it intrinsically unstable,

removal of one of them leaves a pair of electrons in a strong bonding orbital. This gives H₃⁺ an energy of formation, from neutral H₂ and a proton, of 4.8 electron volts, making it 0.3 eV more tightly bound than H₂.

As a result of its simplicity, H₃⁺ has attracted a great deal of theoretical and experimental interest. Theoreticians have treated it as a test-bed for all sorts of problems from the calculation of very accurate electronic potential energy surfaces to studies of chaos and the relation between classical and quantum mechanics. One of the greatest challenges to our understanding of what happens to molecules when they start to break apart has been posed by a series of beautiful pre-dissociation spectra obtained by Alan Carrington and his co-workers.³

H₃⁺ is also something of a Holy Grail for astronomers interested not so much in stars but in the vast gas clouds that lie between them. The range of molecules detected in these clouds can only be explained by invoking H₃⁺ as an initiator of chains of chemical reactions. So far, however, all attempts to detect it in the interstellar medium – the general name given to these clouds – have failed.

2 Spectroscopy of H₃⁺

Transitions between the vibrational and rotational states of molecules give rise to line spectra of characteristic frequencies. Typically, pure rotational transitions are to be found at long – sub-millimetre to radio – wavelengths. Ro-vibrational transitions occur at shorter wavelengths, usually in the infrared, between one and ten microns (1 to 10 μm.) In the 'energy' units usually adopted by spectroscopists, rotational transitions are of the order of a few tenths to a few tens of a reciprocal centimetre (cm⁻¹) and ro-vibrational transitions are measured in the thousands of cm⁻¹.

Two of the most important centres for the study of the infrared spectra of molecular ions are the Herzberg Institute in Ottawa – named after the Nobel prizewinning spectroscopist – and the University of Chicago. Since its foundation in 1974, the Herzberg Institute has been a Mecca for spectroscopists. It was there that Takeshi Oka first measured the infrared spectral line of H₃⁺ on April 25, 1980 (Figure 1). Even at this early stage of H₃⁺ spectroscopy, what had been achieved owed much to accurate theoretical predictions.⁴ Over the next two weeks, Oka measured a further nine lines which were then analysed by theoretician Jim Watson, using his program developed for H₃ and D₃. The results were published later that year.⁵ At the time, Oka pointed out that the lack of an electronic spectrum meant that measuring 'the vibrational spectrum in the infrared region' was the only suitable probe of the properties of this fundamental ion. 'A beautiful jewel of nature, left for the laser spectroscopist,' was how Oka described it.

The interaction between electromagnetic radiation and a molecule can cause changes in the overall angular momentum *J*, or in the projection of *J* on the principal rotation axes, usually designated by *K*. Changes in *J* by – 1, 0, or + 1 give rise to P, Q, and R spectral branches. To a good first approximation, a molecule can only have a rotational spectrum if it has a

Steven Miller gained B.Sc. (1970) and Ph.D. (1975) degrees from Southampton University. Two years at UMIST as research fellow and two at Sheffield University were followed by seven years working as a political journalist before he joined the Molecular Physics Group at University College London to work on ro-vibrational transitions of triatomic molecules, including H₃⁺.

He has pioneered the use of H₃⁺ as an astronomical probe of planetary atmospheres and made the first identification of H₃⁺ outside the solar system (in Supernova 1987A) in 1990.

Jonathan Tennyson studied Natural Sciences at King's College Cambridge (B.A. 1977). In 1980 he completed a Ph.D. in Theoretical Chemistry at Sussex University under the supervision of Professor John Murrell. He then spent two years at the University of Nijmegen, The Netherlands, as a Royal Society Western Exchange Fellow followed by three years at the SERC Daresbury Laboratory where he worked on calculations of photo-ionization and electron molecule scattering. He moved in 1985 to the Department of Physics and Astronomy at University College London and was promoted to Reader in 1991.

His current research interests include calculating the ro-vibrational spectra of molecules, the consequences of classical chaos on molecular spectra, electron (positron) molecule collision calculations, and the calculation of molecular data for astrophysics (including observational studies).

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† A much fuller review of the historical aspects of the H₃⁺ molecular ion has been given by T. Oka in 'Molecular Ions: Spectroscopy, Structure, and Chemistry', ed. T. A. Miller and V. E. Bondybey, North Holland, 1983, p.73.

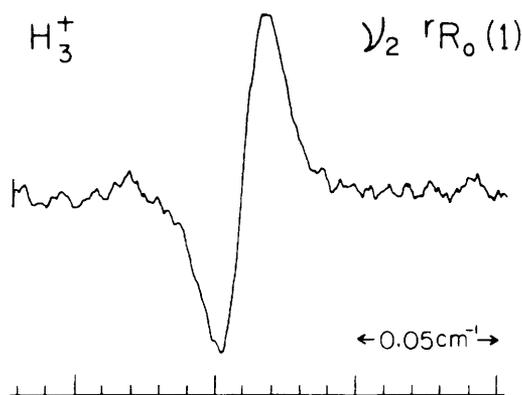


Figure 1 Spectrum of H_3^+ as measured by T. Oka. (Reproduced with permission from *Phys. Rev. Lett.*, 1980, 45, 531.)

permanent dipole. Ro-vibrational transitions are infrared active only if they involve a **change** in the dipole as a result of the vibration. As an equilateral triangle, with D_{3h} symmetry, H_3^+ has no permanent dipole and no 'allowed' rotational spectrum.

Of its vibrations, the symmetric stretch 'breathing' mode, ν_1 , is totally symmetric. Thus exciting ν_1 maintains the zero dipole. The other vibration, a doubly degenerate asymmetric stretch/bend, ν_2 , however, has a large transition dipole of 0.23 Debye. Associated with this stretch/bend mode is the quantum number l_2 , which represents a degree of **angular** motion associated with the mode. The quantum number l_2 can take on values of $-\nu_2, -\nu_2 + 2, \dots, \nu_2 - 2, \nu_2$, where ν_2 is the total number of ν_2 quanta of energy. The only truly allowed infrared spectra of H_3^+ are those which involve a change in the number of quanta ν_2 of the ν_2 vibration, and the strongest transitions tend to have $\Delta l_2 = \pm 1$ (see Figure 2). The transitions that Oka had measured belonged to the fundamental $\nu_2(l = \pm 1) \leftarrow 0$ band, usually abbreviated to ν_2 .

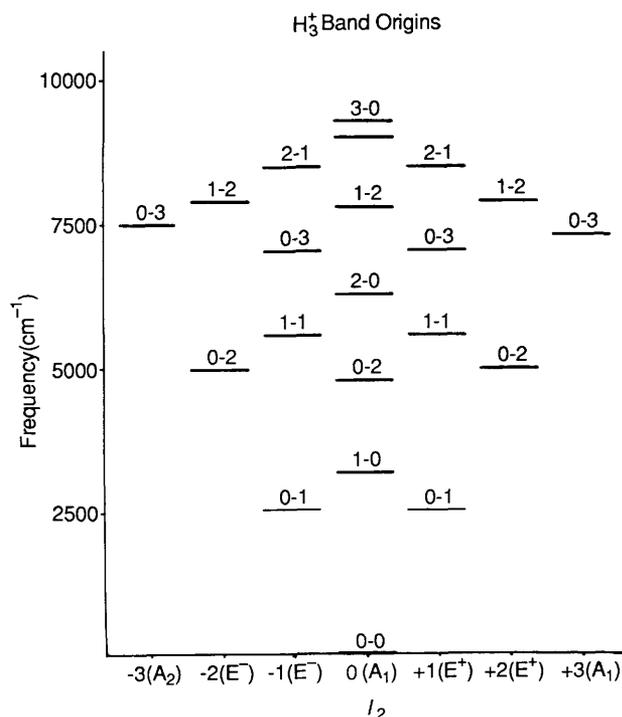


Figure 2 Energy level diagram of the hydrogen molecular ion, H_3^+ . The labels on the levels are ν_1 , the number of quanta in ν_1 , and ν_2 , the number of quanta in ν_2 . States with $l_2 = 1, 2$ are doubly degenerate E states. The others are A_1 or A_2 states. Allowed transitions involve $\Delta \nu_2 = 1$.

Soon after measuring the first H_3^+ spectrum, Oka left the Herzberg Institute to set up his own group in the Chemistry Department at the University of Chicago. In the half a decade that followed the first infrared measurements of H_3^+ , workers at the Herzberg and Chicago set about detailed studies of its spectroscopy and that of its deuterated cousins, H_2D^+ , D_2H^+ , and D_3^+ . Once the initial measurements had been made, one might have expected that progress on the spectra of so simple a molecule would have been rapid. But by 1987, only the fundamental bands of each molecule had been characterized. (In comparison, more than 60 vibrational bands of water have been measured.) One reason for this is that it is much more difficult to do ion spectroscopy than that of neutral molecules. Ions have to be made in electrical discharge cells and are easily destroyed because they are very reactive. But that is not the only difficulty where H_3^+ is concerned.

Normally, when spectroscopists are studying a new species, they measure a few transitions and from those work out the vibrational and rotational constants of the molecule involved. The usual starting point is to treat the vibrational modes of the molecule as harmonic oscillators involving small displacements from a well-defined equilibrium geometry. The rotating molecule is treated as a rigid rotor. Deviation from the harmonic oscillator ideal may be taken into account by allowing for varying degrees of anharmonicity, while rigid rotor constraint may be relaxed by allowing for centrifugal distortion. Coupling between the rotational and vibrational motions of the molecule are accounted for by Coriolis forces. These effects are generally treated using perturbation theory, with higher order approximations being required as the rotational and vibrational quantum numbers associated with the ro-vibrational states increase. Using computer programs which fit initial lines to a set of molecular constants it is then usually relatively easy to work out where to look for other lines.

H_3^+ , however, is what is known as a 'floppy' molecule; its vibrational modes are very anharmonic and it distorts rapidly due to centrifugal forces as it is rotationally excited. This makes it very difficult to use the traditional spectroscopic approach and thus to predict which frequencies to scan for H_3^+ transitions from higher vibrational (and rotational) states. The fact that it is a very light molecule adds to the problems; individual ro-vibrational transitions within a vibrational band are quite widely spaced, which means a spectroscopist has to scan a wide frequency range to find a reasonable number of lines with which to characterize the spectrum. Jim Watson, of the Herzberg Institute, and others were able to use perturbation theory⁶ to characterize the fundamental band, but were not able to make progress with higher vibrational levels.

To deal with the problems posed by floppy molecules, a number of groups – including our own Molecular Physics Group at UCL – have developed variational techniques to calculate ro-vibrational spectra (the subject of a previous article in this journal).⁷ Our technique makes **no a priori** assumptions about molecular geometry or about separating rotational and vibrational motions. To be useful, our approach requires an electronic potential energy surface which is an accurate approximation to that of the real molecule. The kinetic energy operators we use, developed by Brian Sutcliffe at the University of York, are exact; fully coupled ro-vibrational wavefunctions are built up either using model basis functions or a discrete variable representation (described elsewhere⁷). Transition intensities and frequencies are then computed from the wavefunctions generated and a dipole surface, which again has to be as accurate as possible. Once more, **no** assumptions about selection rules are made; we leave it to the intrinsic nature of the molecular wavefunctions and dipole surface to determine which transitions are experimentally observable.

In 1986, Wilfried Meyer and Peter Botschwina, from the University of Kaiserslautern in Germany, and Peter Burton, from the University of Wollongong in Australia, (MBB) published a very accurate potential energy surface for H_3^+ . They had calculated the surface *ab initio*, using thousands of interacting

atomic orbital configurations to account for the energy of the electrons in the system⁸ and then fitted their points to a global surface, adjusted to reproduce the ν_2 band frequency exactly. At UCL, we were able to use this surface to calculate the individual ro-vibrational frequencies, matching experiment to at least one part in 5000 and, on average, one part in 10000. The MBB dipole surface – which we had no reason to suppose is any less accurate – gave us additional information the experimental spectroscopists could not obtain *viz.* values for the intensities of the transitions and radiative lifetimes from the Einstein A-coefficients.⁹ Some examples are shown in Table 1.

Table 1 Dipole allowed ro-vibrational transitions for H₃⁺ in $\nu_2 \leftarrow 0$; sample results. Data from reference 9.

J' G' U'	J'' K''	ω_{if} (calc) (cm ⁻¹)	ω_{if} (obs) (cm ⁻¹)	S(f-i) (Debye ²)	A _{if} s ⁻¹
5 0 -1	5 0	2471.483	2471.210	.264(+0)	.114(+3)
5 1 -1	5 1	2471.901	2472.325	.254(+0)	.109(+3)
5 3 -1	5 3	2472.481	2472.846	.168(+0)	.723(+2)
5 2 -1	5 2	2472.838	2473.238	.222(+0)	.955(+3)
4 3 -1	4 3	2486.287	2486.559	.855(-1)	.458(+2)
4 2 -1	4 2	2491.438	2491.749	.162(+0)	.871(+2)
4 1 -1	4 1	2492.207	2492.541	.206(+0)	.111(+3)
3 2 -1	3 2	2503.117	2503.347	.850(-1)	.597(+2)
3 1 -1	3 1	2507.880	2508.131	.152(+0)	.107(+3)
3 0 -1	3 0	2508.815	2509.075	.174(+0)	.123(+3)
2 1 -1	2 1	2518.012	2518.207	.837(-1)	.838(+2)
1 0 -1	1 0	2529.554	2529.724	.761(-1)	.129(+3)

The success of the MBB surface and of our calculations of the fundamental frequencies encouraged us to go further and make some predictions as to where we expected lines belonging to overtone and 'hot' – transitions which start from a vibrationally excited level and go to an even higher level – bands might be found. During 1988, Mounji Bawendi and Brent Rehfuss at the Oka Ion Factory (as the group in Chicago is now known) succeeded in finding some lines belonging to the $2\nu_2 \leftarrow \nu_2$ hot bands, with frequencies very close to those predicted.¹⁰

With more calculations available, and the fundamental and hot band frequencies to check the accuracy of the predictions, the stage was set to take a big step forward in the spectroscopy of H₃⁺. But the measurement of the next important band of H₃⁺ came not from the laboratory. Instead – as sometimes happens in science – Fate stepped in from an unexpected corner to lend a helping hand. So, before going on with the spectroscopy of H₃⁺, we will have to take a diversion into astronomy.

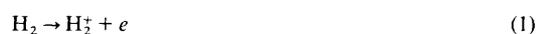
3 Attempts to Detect H₃⁺ in the Interstellar Medium

Between the visible, hot, bright, stars are vast clouds of generally cold, dark gas. Stars form from these clouds at the start of their lives. They return material that has been through the nuclear processing that goes on in stellar cores as they end their days, possibly as tranquil red giants or violent supernovas. Collectively, these clouds are referred to as the interstellar medium, or ISM. Reflecting normal cosmic abundance, the ISM is mainly composed of hydrogen with small amounts of heavier elements. Temperatures are typically between 10 and 100 K, except in regions where shocks caused by star formation or supernova explosions have heated the gas to a few thousand degrees. Densities vary from 100 particles per cubic centimetre, in diffuse clouds, to 10000 cm⁻³ in 'dense' clouds – densities which would be considered a hard vacuum in the laboratory.

In conditions like these, chemical reactions take place very slowly and almost invariably two-body processes dominate. But unlike laboratory chemists – astronomers have time; individual cloud lifetimes may be anything from 10⁵ to 10⁷ years. Even so, it is impossible to account for the range of molecules which have

now been detected assuming only reactions between neutral species; ions are required. Ions react relatively rapidly compared with neutral species in the ISM for two reasons: firstly, they **attract** neutral species by polarizing them; secondly, reactions between ions and neutral species do not have an activation energy – energy is not readily available at the low temperatures of the ISM. Typical ion–neutral reaction rates are 10⁻⁹ cm³ s⁻¹, several orders of magnitude faster than neutral–neutral reactions, but still requiring astronomical timescales to produce any appreciable molecular products at interstellar densities.¹¹

The ISM is continuously subject to ionizing radiation in the form of cosmic rays and photons. These interact initially to ionize molecular hydrogen:



which then reacts rapidly with more hydrogen:



H₃⁺ can then initiate chains of chemical reactions by protonating neutral species:



where X may be an atom, such as oxygen, or a molecule, such as CO. A typical reaction scheme is shown in Figure 3.

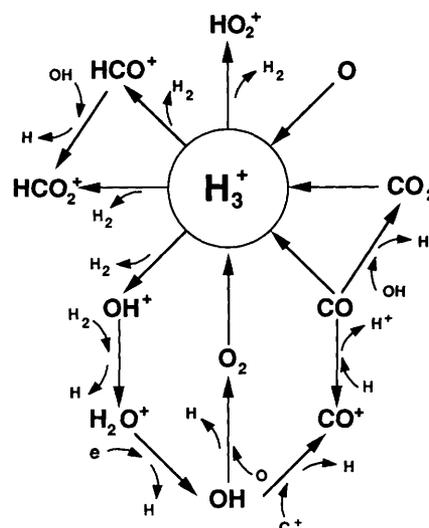


Figure 3 Chemical pathway for oxygen-bearing molecules in diffuse interstellar clouds (after Ewine van Dishoeck).

One reaction involving H₃⁺ is important for introducing deuterium into the interstellar chemical pathways. The ratio of D to H was established at the time of the Big Bang and is generally quoted at around 10⁻⁵. But the reaction



is slightly exothermic. This is for two reasons: firstly, the zero point energy of H₂D⁺ is less than H₃⁺ by more than that of HD is less than H₂; secondly, the $J = 0$ ground state of H₃⁺ is 'spin-forbidden' – the H₃⁺ energy level of lowest energy corresponds to $J = 1$ – and forming H₂D⁺ releases this rotational energy. The difference in energy between the reactants and products of reaction 4 is equivalent to 140 K. In cold clouds (T ~ 10 K), such as the Torus molecular cloud TMC-1, this is enough to bring the ratio of H₂D⁺ to H₃⁺ close to 1:10, four orders of magnitude more than the cosmic abundance. This effect is known as 'fractionation'. In subsequent reactions H₂D⁺ may hand on either a proton or a deuteron, and deuterium enters the chemical chain at enhanced concentrations.

There are good reasons for assuming that the chemistry outlined above is correct, and a number of astronomers have tried to detect H_3^+ in the interstellar medium by looking at infrared sources – such as newly forming stars – embedded in gas clouds in the hope of detecting $\nu_2 \leftarrow 0$ transitions in absorption. So far, however, all attempts have failed. There has been a putative detection of the deuterated species H_2D^+ in the cloud known as NGC2264, which is a cold ($T = 20\text{ K}$) cloud for which the fractionation effects are quite large.¹² But H_3^+ has not been seen there, or in TMC-1; nor in the warmer ($T \sim 70\text{ K}$) Orion molecular cloud, although many ionic and neutral species are known from these sources.^{13,14}

4 Spectroscopic Detection of H_3^+ in Jupiter

Molecules give rise to lines in the infrared region of the electromagnetic spectrum. But for ground based astronomical observations, infrared radiation from astronomical sources has to pass through the Earth's atmosphere, which absorbs much of it. Water is the principal culprit. There are, however, a number of useful 'windows': the M window around $5\ \mu\text{m}$, the L window around $3.5\ \mu\text{m}$, the K window around $2\ \mu\text{m}$, H around $1.6\ \mu\text{m}$, and J around $1.2\ \mu\text{m}$. Infrared radiation is affected much less in these windows than outside them, where it is almost totally absorbed.

Many of the searches for H_3^+ have been carried out using telescopes sited on the top of an extinct volcano in Hawaii called Mauna Kea. At the summit, 4200 metres above sea level, the air is very dry (and there is less of it to look through than in the valleys below). The place bristles with telescope domes, mostly dedicated to infrared astronomy. British astronomers run UKIRT, the three-metre* United Kingdom InfraRed Telescope, and the James Clerk Maxwell Telescope (a sub-millimetre telescope) jointly with partners from other countries. The new Keck ten-metre telescope – the largest in the world – is under construction there; NASA has its InfraRed Telescope Facility (IRTF), built from the small change out of the Voyager missions, and there is the Canada–France–Hawaii Telescope (CFHT), both of them three-metre telescopes.

In 1988, while the Oka Ion Factory was busy measuring the hot bands of H_3^+ , a group of astronomers was preparing to use the CFHT to monitor Jupiter. In particular, they wanted to look at the regions around the poles, where previous observations had suggested there were aurorae similar to the Aurora Borealis and Australis on Earth. Sang Kim, from the University of Maryland, had reasoned that it ought to be possible to see emission from the Jovian ionosphere in the K-window due to weak quadrupole transitions of molecular hydrogen. (Jupiter is basically a huge sphere of hydrogen, with small amounts of other elements; above a region known as the homopause, Jupiter's atmosphere consists entirely of hydrogen.)

On September 24, 1988, together with Pierre Drossart from the Observatoire de Paris-Meudon, Jean-Paul Maillard from the Paris Institut d' Astrophysique and John Caldwell of Canada's York University, Kim used a Fourier transform spectrometer fixed to the CFHT to search for the H_2 lines. The group found them. But they also found much more than they had bargained for. A score of other lines of comparable intensity to the H_2 lines showed up clearly against the background while they had the telescope pointed at the Jovian poles.

Back in Paris, Drossart asked colleagues what they thought the mystery lines could be. One proposed they might be due to H_3^+ , which mass spectrometer experiments on Voyager had suggested ought to be present in the Jovian ionosphere.¹⁵ So Drossart sent a copy of the spectrum to Jim Watson at the Herzberg Institute. Watson had seen something like it before; in one of the drawers at the Herzberg was a spectrum that had been obtained from one of their hydrogen discharge tubes some years earlier. But nobody had as yet been able to assign it.

As luck would have it Watson was not long back from a visit

to Chicago, where Takeshi Oka had shown him the new hot band spectra. Adding the hot band and the fundamental frequencies together gave transitions which matched some of the Jupiter frequencies – and those in the Herzberg unassigned spectrum – exactly. It was clear that both spectra were due to the first overtone transition of H_3^+ , and Watson was able to make a start on working out what was there. The problem, however, was that with the data he had available he could only fit the weakest of the Jupiter lines, corresponding to low values of angular momentum. Attempts to use perturbation theory to extrapolate to higher values of J just did not work out.

It was at this point, in the Spring of 1989, that Watson contacted us at UCL. The assignment of the Jupiter K-window spectrum is as much a testimony to the power of computer-based electronic mail (e-mail) as anything else. E-mail messages criss-crossed the Atlantic as UCL and the Herzberg exchanged spectral data and new calculations. Sometimes we were engaged in almost real-time computer conversations as our working days (extended into the evening at UCL and beginning early in the morning at the Herzberg) overlapped.

Eventually, calculations and spectra matched (almost) exactly. From the 23 fitted transitions observed on Jupiter, an excitation temperature around 1100 K was obtained, along with the column density and the ratio of *ortho* to *para*- H_3^+ . For the first time, H_3^+ had been positively identified outside of the laboratory (Figure 4).¹⁶

5 H_3^+ Astronomy on Jupiter

The Earth's Aurora Borealis and Aurora Australis are caused by particles from the Sun's (solar) wind interacting with the terrestrial magnetosphere, being accelerated and then colliding with the upper atmosphere. The energy deposited into the Earth's ionosphere from the solar wind to cause our aurorae is of the order of 10^9 watts. In comparison, Jupiter's auroral displays require 10^{14} watts of energy to account for their strength, as monitored in the ultraviolet region of the spectrum by the International Ultraviolet Explorer satellite (IUE). By the time the solar wind reaches Jupiter, however, it has only four per cent of its strength at the Earth. The enormously strong Jovian magnetosphere does have the energy to couple with the solar wind to produce the powers required for Jupiter's aurorae. Nonetheless, the present consensus of opinion is that this is not the main cause of the Jovian aurorae. Instead, it is believed that the source of energetic charged particles is what is known as the Io Plasma Torus.

Io, the nearest of Jupiter's large Galilean moons, is close enough to the giant planet to be inside its magnetosphere. Being so close to such a massive object means that Io is subject to very large gravitational tidal forces. These cause the centre of the moon to remain molten and cause widescale volcanic activity. Voyager pictures of Io show it to be a red and angry place, and the picture shown in Figure 5 is aptly nicknamed 'The Pizza'. As the volcanoes eject hot gases into the magnetosphere they become ionized by collisions. When this happens they are swept up by the Jovian magnetic field, which revolves along with the planet, to form a torus of charged particles which spreads out to be many times the diameter of Io and encircles Jupiter. From this torus, charged particles can follow the magnetic field lines towards the Jovian poles until they collide with particles from Jupiter's own upper atmosphere, initiating the aurorae.

The detection of H_3^+ in Jupiter has initiated a flurry of activity among planetary astronomers who had been modelling the Jovian upper atmosphere. Current models suggest that the ion is being formed as a result of charged particles, probably electrons with kinetic energies of few thousand electron volts, precipitating out of the Jovian magnetosphere. Measurements of ultraviolet spectra indicate that these particles are putting between 10 and 40 ergs per second through every square centimetre of the surface of Jupiter's ionosphere in the regions around the poles. The charged particles ionize molecular hydrogen (as in equation 1) and the reaction to form H_3^+ (equation 2) follows rapidly since

* This refers to the size of the primary collecting mirror.

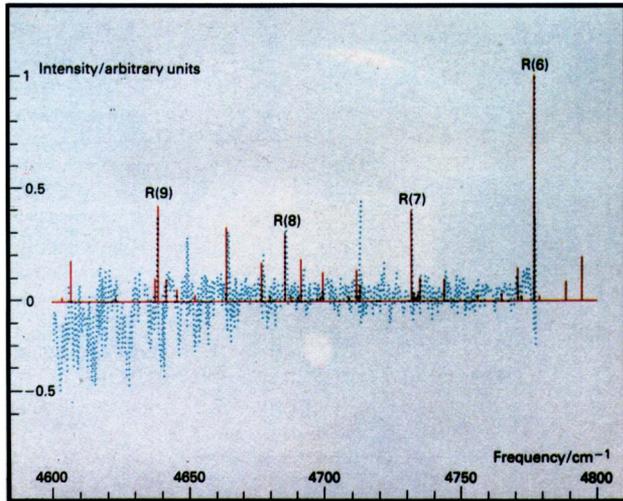


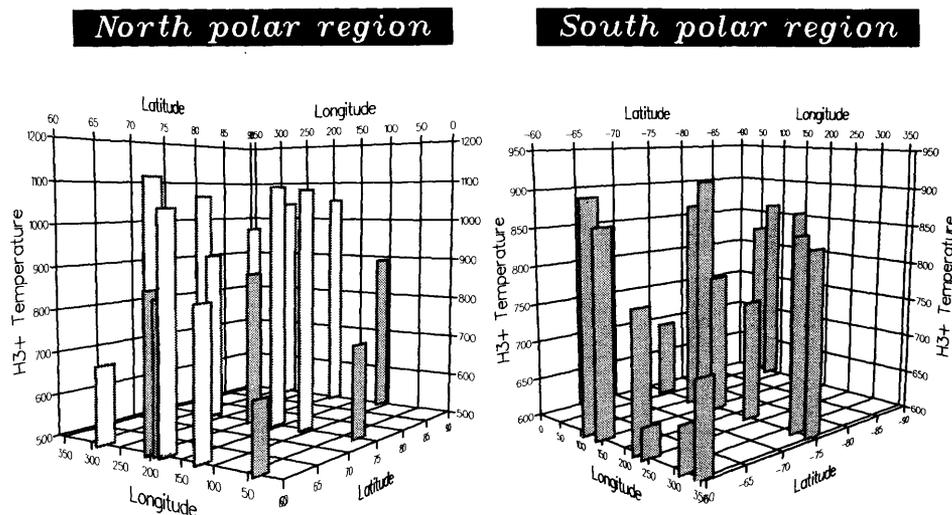
Figure 4 Spectrum of the southern auroral zone of Jupiter (dotted line) compared with that computed at UCL (solid line). (Reproduced with permission from *Chem. Br.*, 1990, 26, 1069.)

the number density of H₂ in the Jovian ionosphere is around 10¹¹ cm⁻³

This makes the H₃⁺ a very sensitive probe of the rate at which energy is deposited from the Jovian magnetosphere into the ionosphere. As a result, a number of collaborations are now using the ion to study auroral processes and the upper atmosphere of Jupiter. Our own collaboration involves UCL, Bob Joseph, Richard Baron, and Toby Owen at the Institute for Astronomy in Hawaii, and Gilda Ballester at the Department of Earth Sciences in Oxford.

From spectra we have taken on the NASA infrared telescope (IRTF) of both the overtone and the fundamental band, it has been possible to work out that the emitting H₃⁺ is being excited to vibrational temperatures around 1000 K.¹⁷ Since this is very similar to the derived rotational temperatures, we initially concluded that the H₃⁺ energy levels were in local thermal equilibrium. Other spectral measurements indicate that H₃⁺ temperatures and densities in the auroral regions vary considerably from place to place, and from night to night (Figure 6). The strength of the observed emissions indicates that H₃⁺ may be responsible for radiating back into space as much as a few tenths of the energy being deposited by the particles responsible for the aurorae, making this ion an important cooling agent.

Figure 6 A temperature 'map' of H₃⁺ in Jupiter's polar regions.



December 15/16 (unshaded) and December 16/17 (shaded) temperature profiles

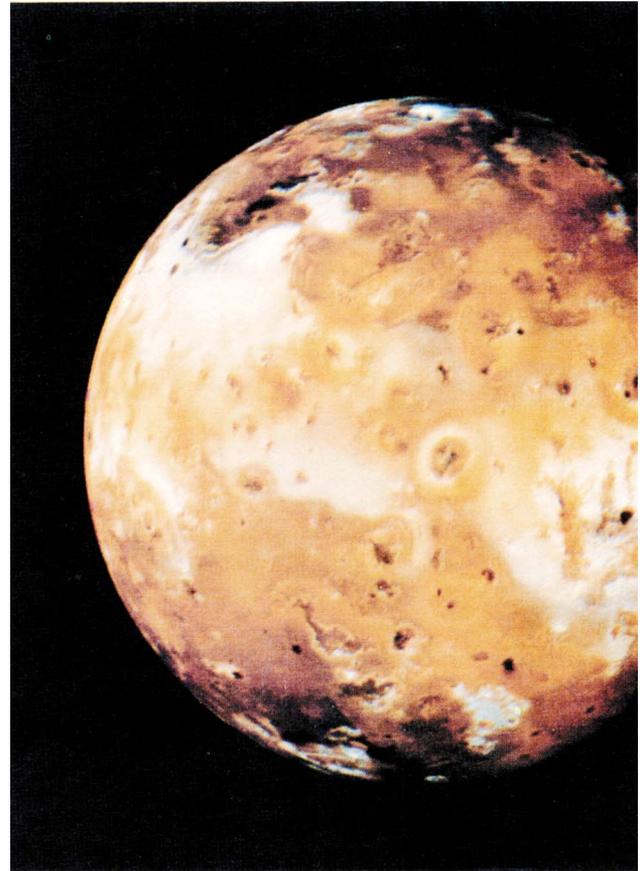


Figure 5 Voyager image of Jupiter's closest moon, Io. (Reproduced with permission from 'Voyage to Jupiter', NASA, Washington, 1980.)

Optical images of Jupiter, such as that shown in Figure 7, show up enormous detail of the weather systems in the Jovian atmosphere which give rise to bands and spots such as the Great Red Spot. The coloration of Jupiter results mainly from methane, ammonia, and phosphine. Recently, the IRTF has been fitted with an infrared imaging camera known as ProtoCAM. This has a 58 by 62 array of charge-couple detectors. A circular variable filter allows infrared radiation with a 1% bandwidth to pass from the telescope mirrors to the detector array. Some infrared images of Jupiter, such as the one shown in Figure 8, also show up the banded character of the planet.



Figure 7 Voyager image of Jupiter showing belts and Great Red Spot. (Reproduced with permission from 'Voyage to Jupiter', NASA, Washington, 1980.)

ProtoCAM has also been used to take the first images of Jupiter at wavelengths which are sensitive to H_3^+ . So far, we have found images taken at wavelengths corresponding to fundamental band transitions around 3.41 to $3.54\ \mu\text{m}$ to be most useful. At these wavelengths methane in the Jovian atmosphere below the homopause absorbs nearly all the incoming sunlight. This makes the body of the planet extremely dark. Emission from H_3^+ , by contrast, shows up strongly around the poles (Figure 9).

The images we have taken show that while the Jovian aurorae do extend to latitudes as low as 60° at some longitudes, they are mainly confined to latitudes above 75° , and seem to be centred

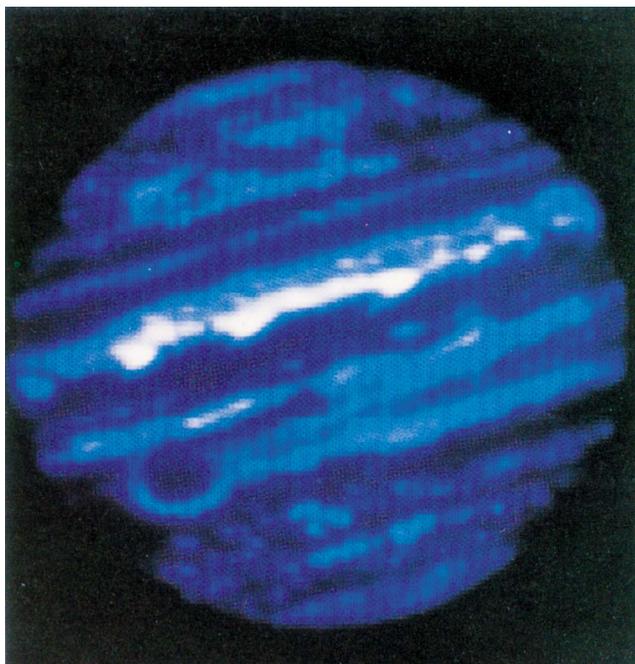


Figure 8 A $5\ \mu\text{m}$ M-window image of Jupiter taken using IRTF's ProtoCAM, showing the belt structure of the planet.

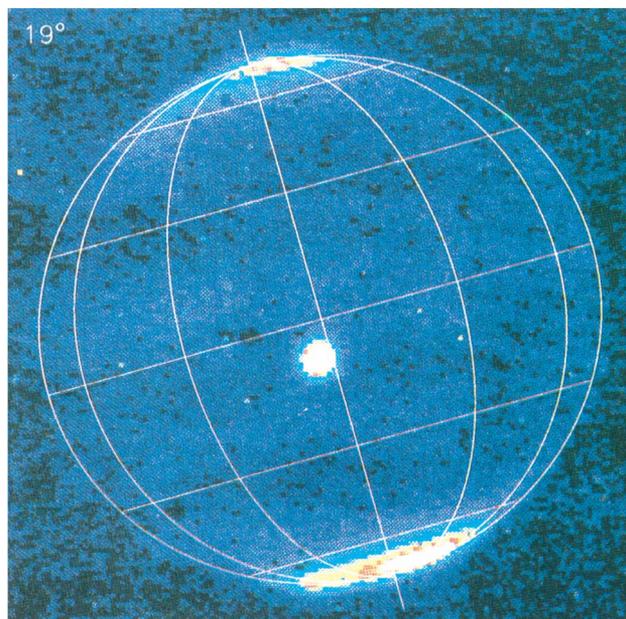
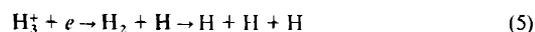


Figure 9 A $3.4\ \mu\text{m}$ image of Jupiter taken using IRTF's ProtoCAM, showing H_3^+ emission (light blue to white) around the Jovian poles. The rest of the planet is dark due to absorption of solar radiation by methane.

on the magnetic, rather than the rotational, poles. The structure is quite complicated, the northern aurora appearing to have the shape of a croissant or boomerang (depending on your preference), and there are strong suggestions that the displays vary on the timescale of an hour or less.¹⁸ (Jupiter's rotation period is roughly ten hours.) These are very early days of H_3^+ astronomy, and much work needs to be done just to extract more detailed information out of the spectra and images that are being obtained. It is hoped, however, that the data will be used as input into models of the Jovian atmosphere, particularly those that are interested in the coupling between the magnetosphere and the ionosphere.

H_3^+ may also have a role to play in what is happening to the atmosphere below the homopause. Already it appears there is some correlation – and equally significantly some **anticorrelation** – between the locations of H_3^+ emissions and regions where emission from various hydrocarbons have been observed. In the ISM, H_3^+ is thought to play an important role in chemical pathways as a protonating agent. In Jupiter, however, it may be as a provider of hydrogen atoms that it is most important. In the presence of electrons, H_3^+ undergoes a process known as dissociative recombination:



Hydrogen atoms are known to be important in Jovian chemistry involving such hydrocarbons as methane and acetylene. It is possible that the heating caused by the processes that are associated with H_3^+ formation may be enough to dredge up gas from below the homopause – which contains heavier elements – into regions where it can mix and react with ionic and atomic hydrogen species. Other mechanisms might be proposed which take atomic and protonated hydrogen **below** the homopause.

Sources

Before leaving the Solar System to look at the prospects for H_3^+ astronomy in other areas it is worth pointing out that this ion may also be important on the other Jovian planets, Saturn, Uranus, and Neptune. At first sight, in none of these do the

conditions for forming H₃⁺ seem likely to be so favourable. None of them has a plasma torus, if that is the source of the Jovian charged particle precipitation, and the strength of the solar wind decreases as the square of the distance from the Sun.

Several studies of Saturn have already been carried out. None of them has been successful, and so the outlook for Uranus and Neptune seemed even more bleak. But astronomy is full of surprises. On April 1, 1992, Larry Trafton of the University of Texas, Tom Geballe, the director of the United Kingdom Infrared Telescope (UKIRT), and our own group from UCL were successful in detecting the fundamental spectrum of H₃⁺ on Uranus.¹⁹ Once again, the figures obtained for the energy output from this remarkable little ion indicate it is a major cooling agent in the Uranian upper atmosphere; indeed, estimates of the amount of energy being put **into** Uranus have had to be revised upwards just to allow for the amount that H₃⁺ is radiating back **out** again.

7 Detection of H₃⁺ Outside the Solar System

On February 23, 1987 a supernova explosion was detected in the Large Magellanic Cloud, our own galaxy's next-door-neighbour. Supernova 1987A was caused when a hot, blue supergiant star underwent a catastrophic explosion. Being so close – astronomically speaking 150 000 light years is close – SN1987A gave astronomers the ideal opportunity to study the physics and chemistry of the supernova as it evolved. Our attention was drawn recently to some infrared spectra taken of SN1987A during the first few hundred days after the original explosion.²⁰ The spectra consist mainly of lines of atomic hydrogen – resulting from the recombination of hydrogen ions and electrons – and some heavier elements. But there were two unassigned emission peaks, most prominent around 200 days after the initial explosion, at 3.41 and 3.53 μm which caught our eye. These are precisely the fundamental band wavelengths we had been using to image H₃⁺ emissions on Jupiter.

Fitting to these peaks gave us a mass of around 0.5–1.0 × 10⁻⁷ solar masses of H₃⁺ and a temperature around 2000 K. A lower temperature 1000 K gave a fit consistent with the whole spectrum, allowing for a proposal that atomic sodium was also emitting around 3.4 μm (Figure 10). Stephen Lepp and Alex Dalgarno at the Harvard Center for Astrophysics then ran their model of the chemistry of the supernova and found that they could produce around 10⁻⁷ solar masses of H₃⁺ at Day 200, in good agreement with our findings.²¹

As a supernova explodes, light elements in the outer layers of the progenitor star (hydrogen and helium) are forced away ahead of the heavier elements which have been forming at the star's core. A supernova thus gives rise to two expanding concentric shells. The shells can, however, mix and it is of interest to astrophysicists to know how much mixing occurs. When H₃⁺ comes into contact with heavier elements, particular molecules such as CO, it is rapidly destroyed. The fact that we have been able to identify H₃⁺ in Supernova 1987A tells us that, at least in the first 200 days, this mixing is not significant, at least at a molecular level.

The detections of H₃⁺ in Jupiter, Uranus, and Supernova 1987A were all made as a result of **emission** spectra. All previous searches of molecular clouds had attempted to see H₃⁺ features in absorption against the radiation of an infrared source embedded in or behind the gas. This makes sense since at the cold temperature of the ISM nearly all the ions will be in the ground vibrational state. Unfortunately, the concentrations of H₃⁺ predicted by models of the cold ISM seem to be just too low for detection with the present astronomical instrumentation.

It may, however, be possible to detect this molecule in emission in regions that have somehow been heated to temperatures similar to that of Jupiter or Supernova 1987A. These could be regions of the ISM through which a shock wave was passing, or had 'just' passed. Regions where young stars are forming and blowing off the remnants of their parent gas cloud could be

Supernova 1987a

Day 192 (Meikle *et al.*)

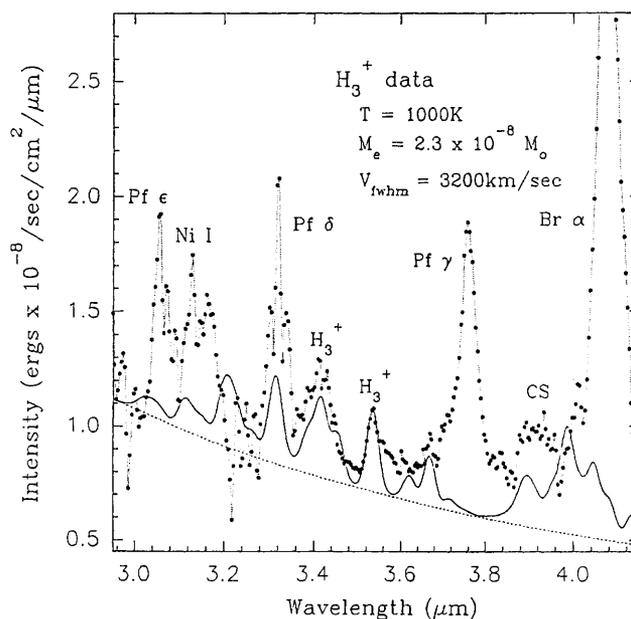


Figure 10 L-window spectrum of Supernova 1987A at Day 192 (dotted line) fitted with H₃⁺ emission spectrum (solid line). H₃⁺ accounts for the peak at 3.53 μm and most of the peak at 3.41 μm, and contributes to other features in the spectrum.

(Supernova spectrum, and identifications of features other than H₃⁺ from reference 20.)

candidates, as could regions affected by supernova explosions. Searches of this type are currently underway. With so much interest we feel confident that, one way or another, this fascinating molecule will be detected in the ISM by the end of this millennium. Just as atomic, then molecular, hydrogen transitions have provided astronomers with a rich store of data, H₃⁺ – at present only in its infancy as an astronomical tool – is sure to take its place alongside them.

8 Forbidden Transitions: Spectroscopy Revisited

In Section 2, we explained that only the degenerate asymmetric stretch/bend ν_2 vibration of H₃⁺ gives rise to infrared active transitions. All the work using the ion to monitor astronomical sources has made use either of the fundamental $\nu_2 \rightarrow 0$ or overtone $2\nu_2 \rightarrow 0$ emission spectra. It is because these are 'allowed' transitions, with large transition dipole moments, that H₃⁺ lines show up strongly in Jupiter when compared with the 'forbidden' quadrupole transitions of molecular hydrogen; although the abundance of H₃⁺ may only be 10⁻⁹ that of H₂, the individual lines are 10⁹ as intense.

Many molecules have been detected in the ISM through their rotational spectra which occur in the far infrared (submillimetre) region. Without a permanent dipole, however, H₃⁺ has no **allowed** rotational spectrum. But it can have a **forbidden** rotational spectrum, which can be thought of as being generated thus. At equilibrium, H₃⁺ is an equilateral triangle (D_{3h} symmetry). As it rotates about one of the in-plane (C₂) axes, centrifugal forces may cause the angle at the apex of rotation to open out. The molecule now resembles an isosceles triangle, with C_{2v} symmetry. A small dipole moment is produced by this effect, which can, in turn, give rise to a rotational spectrum. The effect is small, but obviously it will increase with increasing values of J .

Calculations by Oka's group²² using a formulation derived by Watson²³ and our own first principles, variational calcula-

tions²⁴ give close agreement for the order of magnitude of this effect, although the exact intensity of individual transitions depends on which approach is used. The effect is still a very weak one, however, and to date no forbidden rotational transitions of H_3^+ have been measured. (We are willing to have a small bet with the spectroscopy community that they will be detected **astronomically** first.)

Some forbidden transitions of H_3^+ have been measured, however. Not rotational transitions, this time, but ro-vibrational transitions belonging to the vibrational band $(\nu_1 + \nu_2) \leftarrow \nu_2$. Once more, the measurements have been made at the Oka Ion Factory following suggestions we made in 1990.²⁴ The spectroscopic notation of this band shows that the transitions involve a quantum of energy in the ν_1 symmetric stretch vibration. Such a change, however, ought not to give rise to an infrared spectrum because the ν_1 'breathing' mode does **not** alter the equilateral triangle 'shape' of the molecule, and thus does not give rise to a transition dipole.

It appears, however, that such is the 'floppiness' of the H_3^+ ion that merely putting one quantum of ν_2 vibrational energy into the molecule and starting the ν_1 transition from that state, rather than from the ground state, is enough to cause a breakdown in the normal spectroscopic selection rules. We were able to compute this effect because we do not start from preconceptions about what is, and what is not, an allowed transition in carrying out our calculations.

9 What of the Future?

In the first decade since its infrared spectrum was first measured, H_3^+ has truly come of age. As expected, Oka's jewel is providing a rich source of information about ion chemistry, planetary atmospheres, and unusual spectroscopic effects. By the end of its second decade, we expect this ion to be an important, if everyday, tool of astrophysics, its detection in astronomical sources aided both by the lessons we can draw from Jupiter, Uranus, and Supernova 1987A and improvements in telescopes and instrumentation.

There is clearly much more spectroscopy to be done. Progress has already been made in measuring transitions belonging to the second overtone.²⁵ The third overtone will take us to levels where the molecule can sample linear geometries, and we expect many novel effects to be encountered there. Calculations have already been made of **all** the bound vibrational band origins of the molecule.²⁶ Addition of rotational excitation, and the computation of quasi-bound states into which the molecule moves before dissociating puts us on course to interpret the fascinating Carrington spectra.³ Watch this space!

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