

H_3^+ : from first principles to Jupiter

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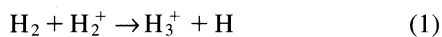
H_3^+ is the simplest polyatomic molecule and as such has always been the subject of extensive theoretical study. It has also long been known to be an important constituent of hydrogen plasmas that are prevalent in many locations in the Universe. This article traces the study of the spectrum of H_3^+ from the first principles quantum mechanical calculation to its observation in the ionosphere of Jupiter and beyond.

1. Introduction

H_3^+ was originally detected by J. J. Thomson. In a paper entitled 'Further experiments on positive rays' [1], he described using a technique, which was the precursor of modern-day mass spectroscopy, to find a particle with a mass-to-charge ratio of 3. H_3^+ violated all the then accepted rules of chemical bonding and Thomson's work gave no hint as to what structure the molecule might have.

Indeed, with the discovery of deuterium in the 1920s, the possibility that this species might have been HD^+ and not H_3^+ was canvassed and accepted by Thomson [2]. However, in the 1930s, a series of electronic structure calculations by Hirschfelder *et al.* [3] showed that H_3^+ was indeed a stable species. Of course, these calculations predated the computer era and all numerical integrals had to be solved by hand. They were thus a truly heroic piece of science involving the painstaking numerical evaluation of matrix elements that could today be done in a few seconds on any one of millions of computers world wide. Theory had made its first important contribution to the debate on H_3^+ , a problem Henry Eyring described as 'the scandal of modern chemistry' [4].

These early calculations actually failed to predict the correct equilibrium structure for H_3^+ but they did show that the reaction



favoured the formation of H_3^+ . In fact, it is now known that this reaction is exothermic by about 1.7 eV meaning that H_3^+ can be formed hot. The reaction is also very rapid. This is true even at low temperatures that act to suppress chemical activity between neutral species. As there is no energy barrier as H_2 and H_2^+ are brought together, the reaction is found to proceed at nearly every collision. One consequence of this is

that ionization of a gas of molecular hydrogen rapidly leads to the formation of H_3^+ . H_3^+ is thus easy to prepare in the laboratory using discharges. Astronomers realized that as molecular hydrogen is the dominant species in many different astrophysical environments, H_3^+ could also be important in them.

Early suggestions that H_3^+ made an important contribution to the opacity of the Sun have since been discounted. However, since Herbst and Klemperer [5], it has been widely accepted that H_3^+ is of vital importance in explaining the rich variety of molecules observed in the enormous, cold molecular clouds that occur in the vast regions of outer space between the stars known as the interstellar medium.

In order to detect H_3^+ in the interstellar medium, or elsewhere in space, it is important to understand its spectrum. Every molecule can absorb and emit light of specific frequencies giving a spectrum that is as characteristic of the molecule as fingerprints are of us. Molecular spectra are of three types; in order of increasing energy the transitions involve changes of rotational motion, vibrational motion and electronic motion. However, H_3^+ is spectroscopically unusual in that it has no known rotational or electronic spectrum. Furthermore, its vibrational spectrum, which lies in the infrared region of the electromagnetic spectrum, is highly irregular and does not conform to many rules built up from analysing the vibrational spectra of many other species. There were many failed attempts to observe the spectrum of H_3^+ covering more than a decade before part of it was recorded by Oka [6]. This success was aided by detailed theoretical predictions due to Carney and Porter [7].

This review traces the interplay between theoretical predictions of the spectrum of H_3^+ , laboratory observation of this spectrum and the accidental astrophysical observation of an H_3^+ spectrum not only in an unexpected location, but also in a spectral region in which no one had previously attempted such observations.

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2. Calculating a spectrum

The first principles (*ab initio*) calculation of molecular spectra has been a field of considerable activity over the past 2 decades. It has changed from the primary aim of providing qualitative but only semi quantitative understanding of spectra to one where predictions can be made with considerable accuracy and confidence. Thus, spectra are now routinely calculated for proving and developing potential energy surfaces (see below), predicting and assigning spectra, calculating transition intensities and generating data for the calculation of thermodynamic and emissivity parameters [8].

In 1929 Dirac [9] stated that ‘the underlying physical laws necessary for the mathematical theory for a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble’. The laws remain today but modern computers and the development of sophisticated (approximate) techniques for solving the equations has led to a radical advance in the accuracy with which theoretical predictions can be made. H_3^+ is a good example of this. The ion comprises three protons and two electrons. The Coulomb force between these particles are well known and it is therefore straightforward to write down the Schrödinger equation that any exact wavefunction of the system must satisfy.

However, this is merely to define the problem: how does one solve a 15-dimensional coupled differential equation when even the most powerful computers struggle to integrate directly in more than two dimensions simultaneously? In fact, there are two standard steps for reducing this dimensionality. First, the solutions we require are not sensitive to the overall motion of the system so it is possible to exactly factorize out three coordinates associated with the centre-of-mass motion. Second, a standard approximation is to note that the protons are nearly 2000 times as massive as the electrons and therefore can be assumed to move very slowly compared with the electrons. The Born–Oppenheimer approximation (see [10] for example) assumes that the electrons relax instantaneously to any change in nuclear geometry. This separates the problem into two sets of differential equations, one set for the electrons and one for the nuclei. For H_3^+ , each set is six-dimensional.

The energy obtained by solving the electronic problem at a fixed nuclear geometry gives the potential energy for the nuclei at that geometry. For a triatomic molecule, the potential is thus a three-dimensional function of the atom–atom distances. The nuclear motion problem is solved on a potential energy surface created by solving the electronic motion problem at many geometries. Figure 1 shows the steps that are necessary to obtain the spectrum of a molecule using first principles quantum mechanics.

The methods generally used to solve both electronic and

nuclear motion problems are substantially different in detail, but both rely on the same quantum mechanical theorem. The Variational Principle states that *any* correctly posed approximate wavefunction will always give an energy higher than the true ground state energy of the system [10]. By using a matrix formulation of the problem it is possible to extend this principle to give rigorous upper bounds for excited states as well as ground states. For both steps of the problem the desired wavefunctions, ψ , are expressed in terms of linear combinations of known functions, ϕ , which are usually referred to as basis functions:

$$\psi = \sum_i c_i \phi_i. \quad (2)$$

Appropriate basis set expansions are used which can be systematically improved to yield lower and hence better estimates of the energy. The final (best) approximation to the wavefunction is given by optimizing the coefficient vector c .

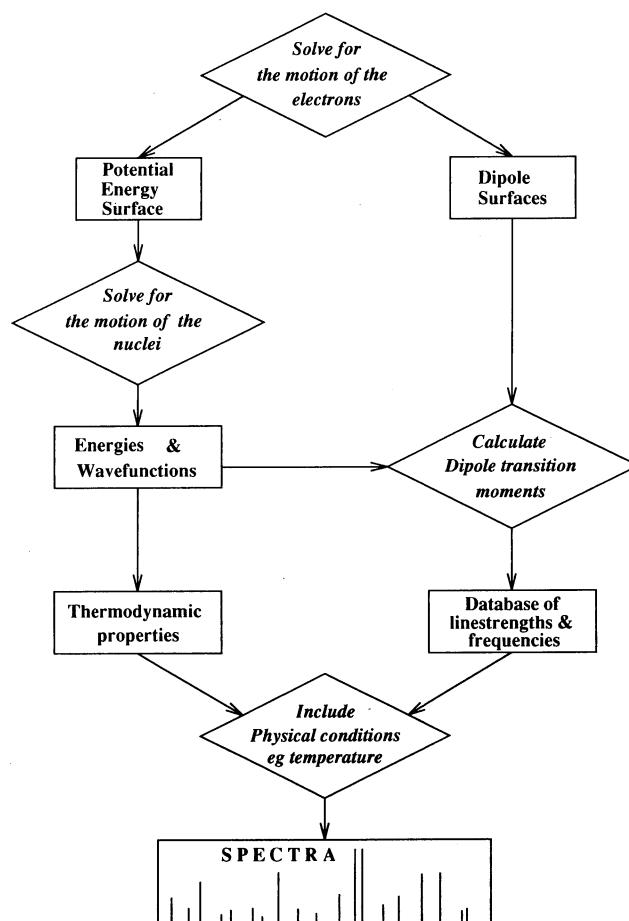


Figure 1. Flow diagram showing the steps (diamonds) and data (rectangles) involved in calculating an infrared spectrum using first principles quantum mechanics. Our program suite, TRIATOM [24], performs the calculation from the potential energy and dipole surfaces onwards.

In general c is obtained as a result of matrix diagonalization [10]. Such operations are ideally suited to modern computer architectures that, in part, explains the rapid advances made in both electronic structure and nuclear motion calculations. Below we briefly consider in turn how such calculations are performed for the electronic and nuclear motion.

The first step in the Born–Oppenheimer approximation involves finding electronic wavefunctions. In general, one has to consider two types of motion by the electrons. Approximate solutions to the problems can be obtained by considering the motion of each electron in the time-averaged field of the other electrons. These solutions, usually known as molecular orbitals, are generally constructed as linear combinations of atomic orbitals that are based on the known solutions to the hydrogen atom problem. The more challenging step of the calculation is to allow for the detailed electron–electron interactions that cause the actual motions of the individual electrons to be correlated. These correlations comprise a relatively small proportion of the total energy of a typical molecule but are vital if chemical or spectroscopic properties are to be obtained accurately.

The standard procedure for solving the correlation problem is via configuration interaction (CI). This involves expanding the wavefunction in terms of configurations that for an atom like He might be $1s^2, 2s^2, 2p^2, \dots$. For small molecules, CI lists containing billions of terms are not unknown. Meyer *et al.* constructed an H₃⁺ potential energy surface in this fashion [11]. They used 29 atomic orbitals on each H atoms and all possible configurations in their CI expansion. This type of calculation, known as a full CI calculation, is normally prohibitively expensive. However, H₃⁺ only has two electrons and we estimated that Meyer *et al.* only had to use about 1000 terms in their CI expansion.

Indeed, the electronic simplicity of the two-electron H₃⁺ system means that non-standard methods can be applied. It has long been known that wavefunctions, usually called Hylleras functions, that explicitly include electron–electron distances give a very good representation of the correlation energy. Explicit inclusion of electron–electron coordinates gives a problem that is numerically too difficult to solve except for systems with very few electrons. Recently, a Hylleras CI-based potential energy surface has been obtained for H₃⁺ by Lie and Frye [12].

For H₃⁺ it is also possible to attempt to solve the electronic Schrödinger equation directly using Monte Carlo integration techniques. The resulting solutions are not variational, but give an energy estimate *and*, unusually for *ab initio* calculations, an error bar. Anderson [13] used a quantum Monte Carlo calculation to obtain the energy of the equilibrium geometry of H₃⁺ to better than 0.5 cm^{-1} †.

A detailed comparison of >40 electronic structure calculations on H₃⁺ is given by Anderson [13]. Comparison with Meyer *et al.* and Lie and Frye shows that their calculations are 164 and 9 cm^{-1} respectively above the true minimum of the potential. These differences are very small by usual *ab initio* standards, but may appear large, perhaps hopelessly so, when compared with the typical accuracy of a high-resolution infrared experiment of $\leq 0.02 \text{ cm}^{-1}$. However, the feature that must be accurately reproduced if reliable rotation–vibration spectra are to be predicted is not the absolute energy but the location of the minimum and the shape of the potential in the region of the minimum. In this respect both Meyer *et al.* and Lie and Frye perform outstandingly well. This is because Lie and Frye’s potential is indeed of an accuracy perhaps only surpassed by calculations on molecular hydrogen, and because Meyer *et al.* took considerable, and unusual, care to obtain a potential of the correct shape.

All high-level electronic structure calculations on H₃⁺ show that its equilibrium geometry is an equilateral triangle. It displays a form of bonding that is sometimes found in carbon compounds, but is probably unique for hydrogen and each of the three nuclei share the two electrons equally. This high symmetry means that H₃⁺ has no permanent dipole moment, with consequences for its spectroscopy discussed below, and a number of other unusual properties.

Having obtained a potential energy function, it is now necessary to consider the nuclear motion problem. Two types of motion can be identified: vibration and rotation. These motions can be separately identified when an appropriate (body-fixed) Hamiltonian is used (see [14] for example). The basis functions required to represent the rotational motion exactly are well defined and unusually are finite in number. For states with rotational angular momentum quantum number J , a total of $2J + 1$ rotation matrices are required [15]. For the vibrational problem the situation is less clear cut. Usually the vibrational motions are represented by orthogonal polynomials that are solutions of appropriate model problems. Model problems whose solutions have been used include the harmonic oscillator (Hermite polynomials), the free rotor potential (Legendre polynomials) and the Morse and spherical oscillator problems (both Laguerre polynomials). Following Tennyson and Sutcliffe [16] it is usual for vibrational motion to be initially considered separately from rotational motion and then for the vibration–rotation (Coriolis) coupling to be included only in the final stage of the calculation. This procedure is computationally much more efficient than direct solution of the full problem.

We have performed a series of calculations [17–19] of the rotation–vibration spectrum of H₃⁺. Most of these calculations have used the potential energy surface due to Meyer *et al.* and vibrational basis functions based on the Morse oscillators and free rotor functions. Some of the results of these calculations will be discussed below.

†Infrared spectra are usually measured in a unit of wave-number denoted cm^{-1} ; as wave-numbers and energy correspond it is useful to remember that $1 \text{ eV} \approx 8065 \text{ cm}^{-1}$.

To predict a spectrum it is not sufficient to know at what wavelengths light will be absorbed or emitted. It is also necessary to know the intensity of each transition. This is particularly important if the spectrum is being used as a diagnostic, such as the astrophysical ones discussed below. It is from the transition intensities that physically important parameters such as the number of molecules undergoing the transition and their temperature can be obtained.

Most molecular spectra are driven by electric dipoles. As H_3^+ has no permanent dipole it has no pure rotational spectrum‡. For vibrational transitions the important property is the change in electric dipole upon a transition. To calculate this it is necessary to have a knowledge of the molecular dipole, μ , as a function of nuclear geometry. This is actually a by-product of most electronic structure calculations and the *ab initio* dipole surface of Meyer *et al.* is the one that has been widely used. The line-strength of a transition, S , is then given by

$$S = \left| \int \psi_i^* \mu \psi_f d\tau \right|^2, \quad (3)$$

where ψ_i and ψ_f are the vibration–rotation wavefunction for the initial and final state respectively. This method of calculating transition intensities, unlike simpler ones often employed, makes no assumption about which transitions are allowed and which forbidden [23]. This has proved to be an important feature of this approach for H_3^+ . Our program suite, TRIATOM [24], calculates spectra for triatomic molecules given only potential energy and dipole surfaces (Figure 1).

Before leaving the topic of first principles calculations, we should note that it is the *ab initio* H_3^+ line-strengths that are likely to be of enduring use for astronomers. Although the prediction of transition frequencies have been of immense use in assigning both laboratory and astronomical spectra, all astronomically observed transitions have been measured to very high accuracy in the laboratory [25]. However, as laboratory H_3^+ is produced in a plasma it is not in thermodynamic equilibrium. This means that it is very hard to determine populations of individual levels involved in a transition and no-one has ever measured the absolute line-strength of an H_3^+ transition. Thus all astronomical interpretation relies on *ab initio* estimates.

3. Attempts to detect H_3^+ in the interstellar medium

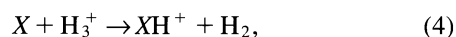
The enormous gaps between stars are not complete voids. Instead, regions of them are filled with mixtures of very diffuse plasmas and giant clouds. This is what is meant when astronomers talk of the interstellar medium (ISM).

The clouds in the ISM are cold, typical temperatures are 10–100 K, and very sparsely populated. Typical densities of 100–10 000 molecules cm^{-3} are much better vacuums than the usual ultrahigh vacuums produced in the laboratory. Although these clouds are 90% hydrogen, mainly in the form of H_2 , astronomers have observed spectra, mostly at radio frequencies, of around 100 molecules. These spectra include molecules with up to 13 atoms (see [26] for a full discussion of interstellar chemistry).

The diversity and complexity of interstellar chemistry was unexpected. On Earth typical gas phase chemical reactions involve the collisions of neutral species. Such reactions require the simultaneous collision of a third species to carry away excess energy if the first two species are to combine—seemingly a necessary first step in forming molecules from atoms. Furthermore, most neutral–neutral reactions actually contain activation barriers, which means that some initial energy is required to start the reaction even if the net result is energy release. Such reactions are strongly temperature dependent with reaction rates typically doubling with every 10 K rise in temperature.

The nature of the ISM is such that three-body reactions are very unlikely and there is insufficient energy available to overcome reaction barriers. Alternative reaction schemes are clearly required. The mechanism which astronomers hit upon was ion–molecule reactions. These two-body reactions often have no activation barrier and the long-range attraction between the species involved means that they actually go faster at low temperature.

Since Herbst and Klemperer [5] a series of ever more sophisticated models of the ISM have been built up on ion molecule reactions. A key step in these schemes is the formation of H_3^+ via the ionization of H_2 by cosmic rays. H_3^+ plays an important role in the chemistry of the ISM as a vigorous protonating agent:



where X is a stable species. For example when X is CO, this reaction converts the strongly bound and chemically inert CO species into the active ion HCO^+ , which then participates in further chemical reactions. Figure 2 shows chemical reactions involving oxygen bearing molecules in the ISM, with the role of H_3^+ emphasized.

The infrared spectrum of H_3^+ was first observed in the laboratory by Oka in 1980 [6] after many years of trying [4]. It was natural to try and use this spectrum to directly observe H_3^+ in the ISM. However this observation is fraught with difficulty.

As molecule forming regions of the ISM are generally very cold, H_3^+ cannot be expected to be seen in emission and detection must thus proceed via absorption. Absorption spectra require a light source so it is necessary to find a suitable molecular cloud between us and a star that emits strongly in the infrared. Furthermore, again because of the

‡Actually it is predicted to have a weak ‘forbidden’ rotational spectrum [20, 21] but this has yet to be observed.

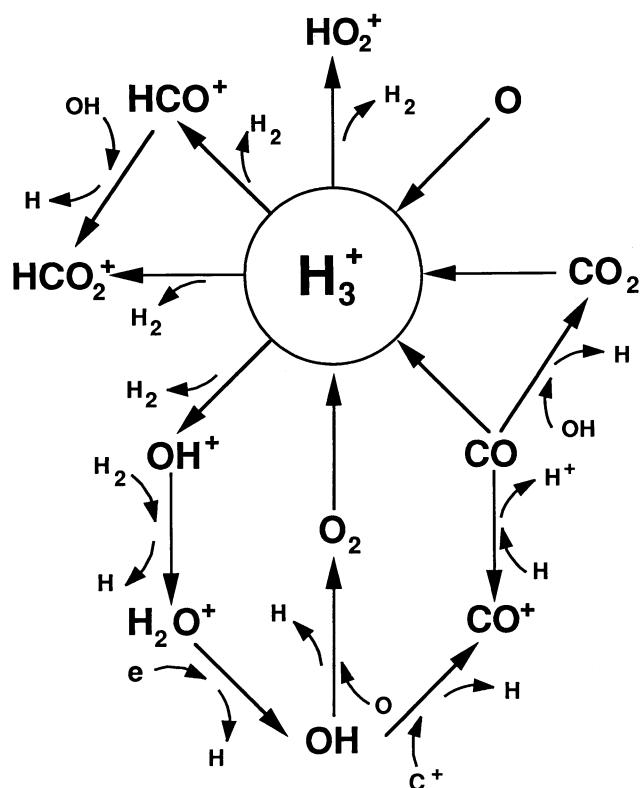


Figure 2. Reaction schemes involving oxygen-bearing species in interstellar medium. The scheme has been redrawn from [27] to emphasize the role of H_3^+ in these reactions.

low temperatures, there are only six candidate transitions [28] all of which lie in a difficult spectral region for observing because of absorption by water in the Earth's atmosphere. So far all attempts to detect H_3^+ in this fashion have proved negative [28–30].

4. Serendipitous detection of H_3^+ on Jupiter

Ground-based infrared astronomy is a constant struggle to observe through the Earth's atmosphere, especially where there is a lot of water vapour. The area made rapid advances in the 1980s due greatly to improved instrumentation and the opening up of high, dry, equatorial observing sites. One such site is an extinct volcano, Mauna Kea, in Hawaii (figure 3). The first ever astronomical detection of an H_3^+ spectrum made great use of these developments, but it also occurred by chance. H_3^+ was observed both in an object and at a wavelength that no one had thought to look in and by observations designed to detect another molecule.

Planetary astronomy is rather different from the rest of astronomy in that we have been there. At the very end of the 1970s the two *Voyager* spacecraft followed the earlier *Pioneer* missions and visited Jupiter as part of their grand tour of the Giant (Jovian) Planets. *Voyager* sent back a wealth of information on Jupiter including stunningly beautiful pictures (figure 4). Among many other scientific achieve-

ments (see NASA's *Voyage to Jupiter* [31]), the *Voyager* missions detected hot regions near both the north and south poles of Jupiter. As was later confirmed from Earth, these hot spots are not only hotter than the 200 K, which is typical for most of the planet, but also contain a number of hydrocar-bates (acetylene, ethylene, etc.) not observed elsewhere and signifying greater chemical activity.

Of course, Jupiter, like many astronomical objects, is substantially composed of hydrogen. Pierre Drossart *et al.* planned to study the infrared emission spectrum of molecular hydrogen in the hot polar regions of Jupiter while simultaneously using the satellite International Ultraviolet Explorer (IUE) to study the well known and much more energetic electronic transitions of H_2 that lie in the ultraviolet. H_2 infrared emissions had recently been seen in Jupiter at rather low resolution [32] but it was a difficult observation to attempt because H_2 emissions are *very* weak. Vibration–rotation transitions, which lie in the infrared, are usually driven by dipole moments but, like other homonuclear diatomic molecules, H_2 has no dipole in any of these states. This means that the spectrum consists of quadrupole transitions that are very much less favoured. For example the dipole transitions of H_3^+ are up to 10^9 times as strong as the H_2 quadrupole transitions sought by Drossart *et al.*

The strongest H_2 feature, the so-called S(1) transition, is at a wavelength of $2.122 \mu\text{m}$ (4713 cm^{-1}), which lies in a gap in the atmospheric water spectrum known to astronomers as the K window. In September 1988, Drossart *et al.* used the high-resolution Fourier transform infrared (FTIR) spectrometer on the Canada–France–Hawaii Telescope on Mauna Kea to observe the hot polar region in the south of Jupiter for a period of 5 h. They got considerably more than they bargained for. Besides getting the clear signature of the three molecular hydrogen transitions they hoped for [34], they observed some 33 other lines, several as strong or stronger than the H_2 emissions.

These features did not correspond to the spectrum of any species they knew, so they started to ask colleagues. In particular the list of unexpected emission lines was sent to the Herzberg Institute in Ottawa. There J. K. G. Watson recognized many of the features as corresponding to an unassigned spectrum obtained previously in his laboratory. This spectrum had been recorded by observing the emissions from a hot hydrogen discharge by his colleague Wotjeck Majewski. At that stage it was not known whether this spectrum was due to H_2 , H_3^* or H_3^+ . However, Watson was able to identify some of the lines as corresponding to H_3^+ and contacted us as we had recently predicted the spectrum of H_3^+ at this wavelength. Our *ab initio* data could be used to synthesize the Jovian spectrum (figure 5), make detailed assignments and, by fitting the spectrum, obtain an effective temperature for the rotational states involved in the emission. Remarkably this temperature proved to be $1050 \pm 100 \text{ K}$. After this spectrum was assigned [35], it became apparent



Figure 3. View of some of the infrared telescopes on Mauna Kea in Hawaii. On the right is NASA's Infra Red Telescope Facility (IRTF) and the Canada–France–Hawaii telescope is the large telescope on left. The UK InfraRed Telescope (UKIRT) is the silver domed telescope in the centre of the picture (Picture courtesy of NASA).

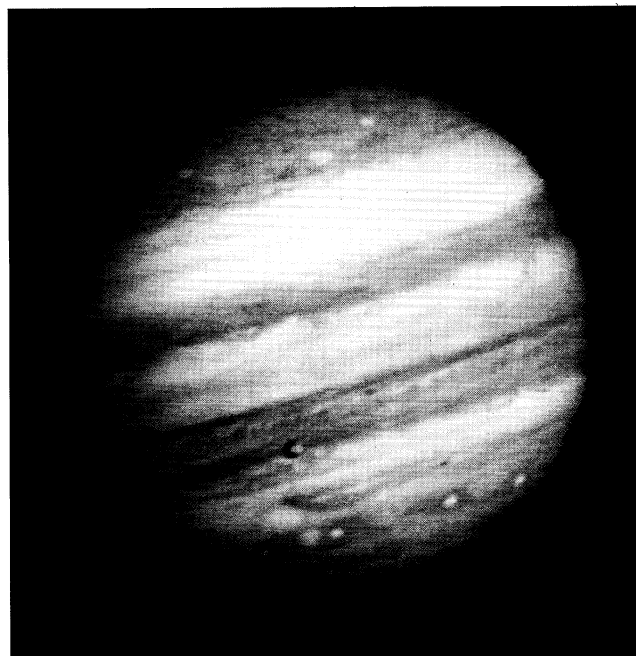


Figure 4. Jupiter as seen by the *Voyager* spacecraft. Similar, but less detailed, views can be taken using large optical telescopes from Earth (Picture courtesy of NASA).

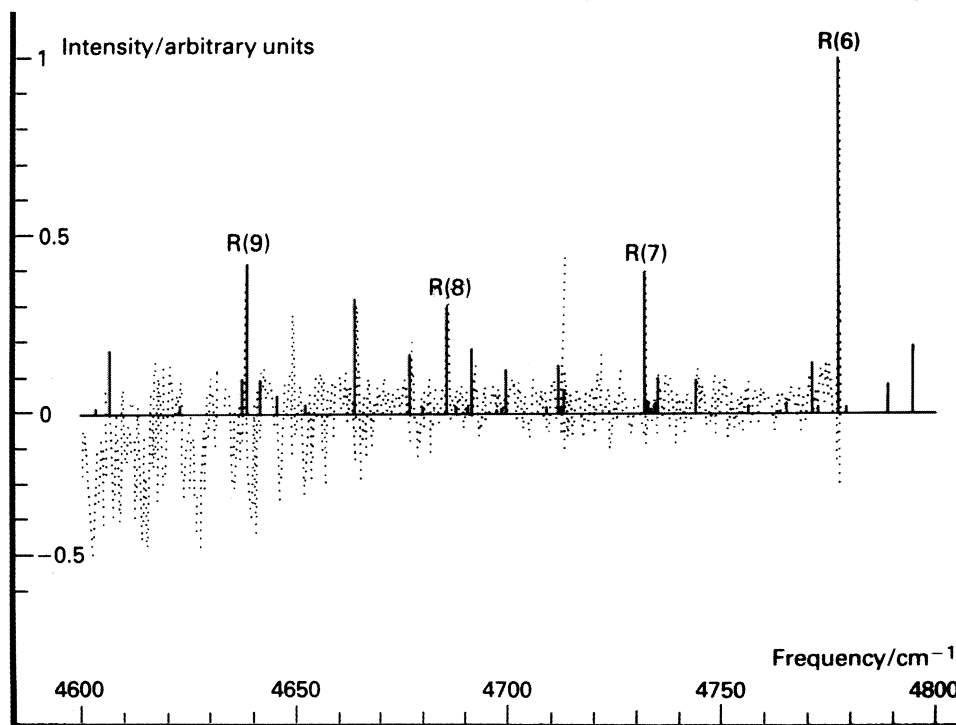


Figure 5. Infrared spectrum of the south polar region of Jupiter as recorded by Drossart *et al.* [35] using the Canada–Hawaii–France Telescope. The blue line is the observed spectrum and the red sticks are our first principles quantum mechanical predictions of the H_3^+ spectrum in this region. Our spectrum was synthesized assuming an H_3^+ (rotational) temperature of 1000 K. The line at 4713 cm^{-1} corresponds to the $\text{H}_2\text{S}(1)$ transition originally sought by Drossart *et al.* The line at 4649 cm^{-1} remains unidentified; if you have an assignment please contact us (Reproduced from 1990, *Chemistry in Britain*, 26, 1069).

that it had actually been observed previously by Trafton *et al.* [36]. They, however, had been unable to identify the cause of their observed emission features. In fact the spectrum is so irregular that they initially concluded that the emissions were caused by three separate molecules.

But was the observation of H_3^+ in Jupiter so surprising? At one level it was not: H_3^+ had already been detected in Jupiter by means of the low-energy, charged-particle instrument carried by the *Voyager* spacecrafts [37]. However, the observed H_3^+ emissions corresponded not to the fundamental band of H_3^+ observed previously by Oka [6] and others, but to an overtone band not even identified in the laboratory. This band involved a change of two in the vibrational quantum number of the H_3^+ bending mode and such bands are usually many orders of magnitude weaker than the fundamental. H_3^+ is not a usual molecule when it comes to spectroscopy however. Because of its very anharmonic behaviour, emission from $2\nu_2$ levels are of about the same strength as those from ν_2 levels (figure 6), a fact that had been predicted by theory.

An immediate question arose: was the hot rotational temperature obtained from the H_3^+ polar emissions a reflection of the true temperature of the environment or was it simply an artefact? As many transitions belonging to the fundamental ν_2 band also lie in a window in the Earth's atmosphere, the L window, observations of these transitions were soon undertaken [38]. Two groups [39, 40] independently recorded this spectrum and obtained a vibrational temperature close to the rotational temperature obtained previously. H_3^+ is clearly hot. This has recently been confirmed by use of ultrahigh-resolution spectroscopy to measure the broadening of H_3^+ transitions by translational motion and the Doppler effect. These observations also gave a translational temperature > 1000 K [41].

If H_3^+ is present on Jupiter and emitting strongly, should it not also be visible on the next largest and next nearest of the Giant Planets, Saturn? Initial attempts to detect H_3^+ emissions on Saturn saw nothing. It was therefore more in hope than in expectation that in April 1992, Larry Trafton, Tom Geballe and Steven Miller used the tail end of a night dedicated to observing Jupiter to look for H_3^+ in Uranus. The result (figure 7) was a strong clear spectrum showing H_3^+ emission. This spectrum suggests that H_3^+ has a rotational temperature of about 740 K [42], which can be compared with temperatures on the body of the planet of < 150 K.

Subsequently Geballe *et al.* [43] observed weak H_3^+ emission from Saturn. They found that while the flux of H_3^+ emission per unit area was similar for Jupiter and Uranus, that from Saturn was some two orders of magnitude weaker. Why Saturn has so much less H_3^+ activity is still not really understood. One suggestion is that its rings break up the flow of charge particles down the magnetic field lines and hence suppress auroral activity; another is that the hydrocarbons, particularly methane, in Saturn's upper atmosphere might act

to rapidly destroy H_3^+ . Which, if either, of these suggestions is correct will have to await further work.

5. H_3^+ as a probe of planetary ionospheres

Looking at Jupiter in the infrared at a range of frequencies, one sees (figure 8) structures on the planet very similar to those seen in visible light (figure 4). However at certain frequencies, sensitive to H_3^+ , the picture is very different.

Figure 9 shows a H_3^+ emission at $3.4 \mu\text{m}$ (2940 cm^{-1}) obtained using the camera, protoCAM, on NASA's Infrared Telescope Facility (IRTF). The picture, like figure 8, is actually a mosaic of nine separate pictures taken over a period of 40 min and then pieced together to give a single image. At this wavelength the majority of Jupiter is dark as all

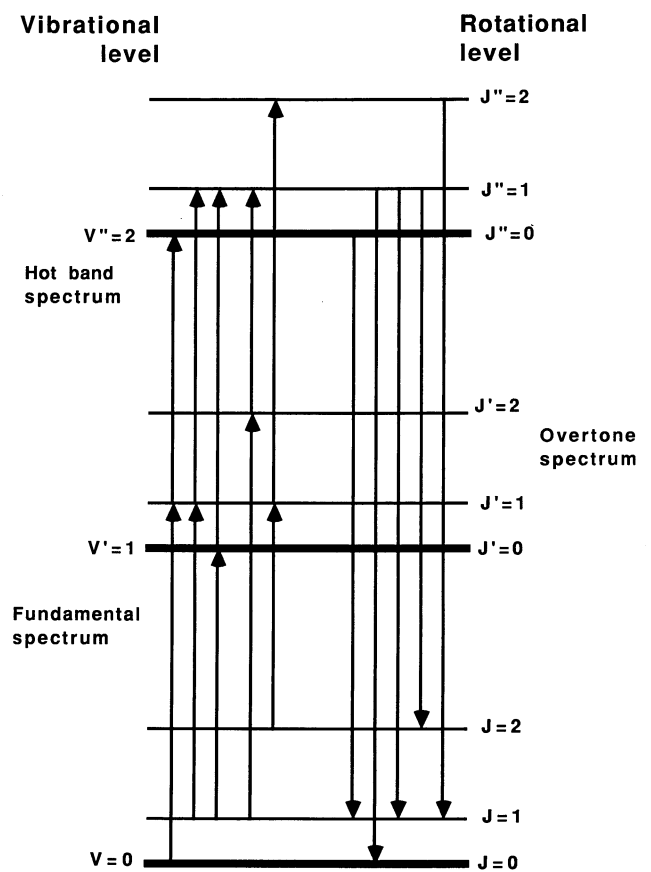


Figure 6. Simplified diagram of the vibrational levels of H_3^+ involved in the observed transitions on Jupiter. H_3^+ actually has two vibrational modes: a symmetric 'breathing' mode, ν_1 , and an infrared active bending mode, ν_2 . Only the fundamental (ν_2) and overtone ($2\nu_2$) levels of the bending mode are shown. Transitions on the left are in absorption and those on the right are in emission. It is possible to see fundamental, overtone and 'hot' ($2\nu_2 \leftrightarrow \nu_2$) bands in both absorption and emission. For clarity only a few rotational levels have been shown on the diagram and the splitting of the rotational levels has been neglected. Transitions involving states with rotational angular momentum, J , up to 9 have actually been observed on Jupiter.

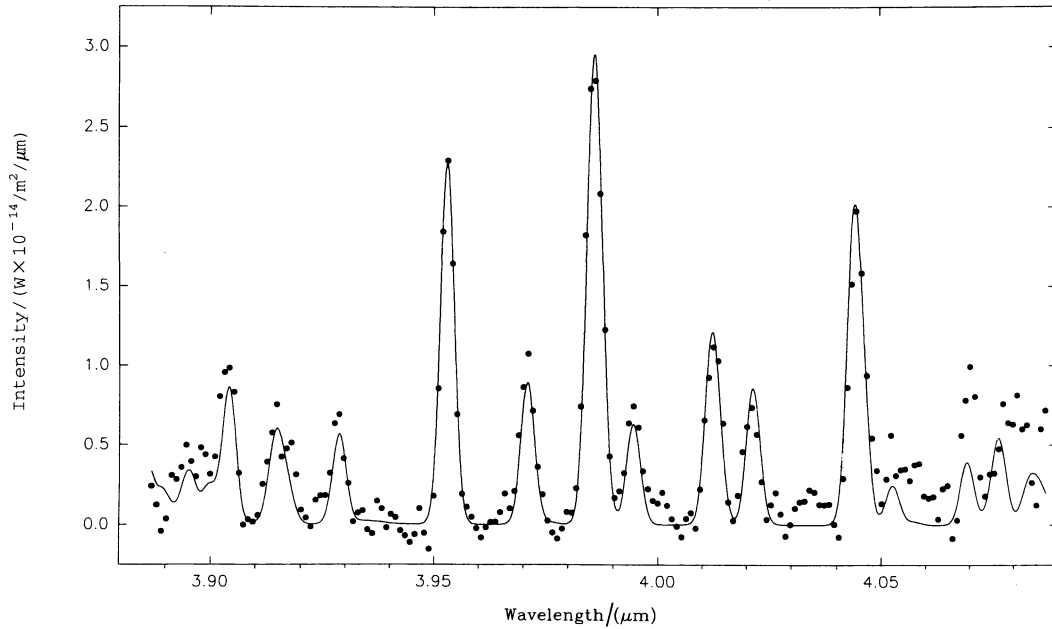


Figure 7. Emission spectrum of Uranus recorded by Trafton *et al.* [42] on 1 April 1992 using the UK Infrared Telescope (UKIRT). Dots represent the observed spectrum, and the continuous curve is a theoretical H_3^+ spectrum with a (rotational) temperature of 740 K at the resolution of the telescope. In fact most of the peaks are blends of several H_3^+ lines. Note the absence of any other features and almost total absence of any background emission.

incoming solar radiation is strongly absorbed in the dense Jovian atmosphere, particularly by methane. This means that the only bright features are due to the H_3^+ emissions near the poles. These are seen because the H_3^+ is high up in the atmosphere, well above any methane. The white spot apparently near the centre of the planet is actually due to Ganymede, one of Jupiter's moons, that happened to be passing while the picture was taken. Ganymede has no atmosphere and, like our Moon, simply reflects the incoming sunlight back.

What causes the H_3^+ emissions in the polar regions? What we are seeing here is an aurora, similar to the Aurora Borealis and Aurora Australis visible over the poles on Earth particularly during periods of high magnetic activity. Jupiter's magnetic field is some 10 000 times stronger than the Earth's field. This means that a huge region of space is strongly influenced by this field and that charged particles, which spiral down the magnetic field lines and into the poles, are travelling rapidly when they hit the Jovian atmosphere. It is generally assumed that the charged particles are fast electrons that collision-ionize molecular hydrogen leading to H_3^+ formation; however, it is possible that ionized atomic species are also present.

Where do these charged particles come from? There are two possible origins: one is the solar wind that is a steady stream of particles emitted by the Sun and that bombards all the planets. The other source is Jupiter's moon Io. Io is the nearest to Jupiter of its four large (Galilean) moons. Indeed, it is so near and Jupiter is so massive (it is more massive than

all the other planets put together) that gravitational friction melts Io's core. The result is that the surface of Io has a number of spectacular volcanos (figure 10). Io itself has so little gravity that atoms and molecules spewed out by these volcanos are simply lost in space. The result is a ring of particles surrounding Jupiter known as the Io plasma torus. Particles from the Io plasma torus will also get swept up in Jupiter's magnetic field.

By careful study of the morphology of the H_3^+ auroral emissions it should be possible to distinguish between the two sources of charged particles. This is because the particles follow different magnetic field lines and hence enter Jupiter's upper atmosphere at slightly different positions. Until recently all the evidence pointed to the auroral activity being associated with the solar wind. However, very recently Connerney *et al.* [44] analysed a series of mosaics similar to that shown in figure 8. While they found that the majority of H_3^+ was indeed associated with the solar wind they were able to identify separate emissions caused by the footprint of the Io itself on Jupiter's atmosphere.

Many astronomers have now studied these H_3^+ emissions and a number of interesting features are becoming apparent. Although the emissions appear to be thermal in origin, their temperature fluctuates between about 650 [38] and 1200 K [41]. Furthermore, the emissions are not uniformly spread about the poles but have pronounced structures that appear to vary in time [45]. It appears that by monitoring the H_3^+ emissions one gets detailed and up-to-the-minute information on the auroral activity on Jupiter. In addition, our

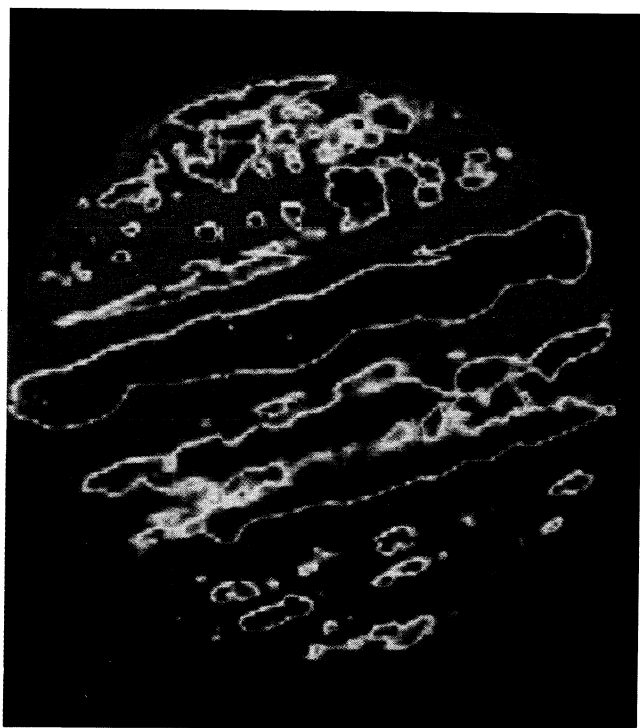


Figure 8. Image of Jupiter in the infrared. This picture is a mosaic of nine separate images recorded by Robert Joseph and Jonathan Tennyson within a 40-min period in February 1991 using protoCAM on NASA's Infrared Telescope Facility (IRTF). It was constructed using a broad-band filter that collected all the radiation in the M window (1920–2080 cm⁻¹). The false colour scheme actually represents intensity of radiation, not, as is usual with the visible, the wavelength of the radiation. The cloud structures depicted correspond to those that can be seen with better resolution in the visible (figure 3).

latest spectra show that H₃⁺ can actually be observed at all latitudes across Jupiter, but with greatly reduced intensity in the equatorial regions [46].

Attempts to look at the distribution of H₃⁺ on Uranus are much more difficult because the greater distance means that it is very difficult to distinguish clearly different regions of the planet. Initial attempts at imaging H₃⁺ emissions on Uranus (figure 11) suggest that these emissions are much more uniformly spread over the planet [47]. The magnetic pole of Uranus is at angle of about 60° to the geographic pole. Its exact position was determined by the *Voyager* mission, but uncertainties in Uranus' rotational period means that its position is no longer known. The region of strongest emission in figure 11 may correlate with the magnetic pole, but this has yet to be demonstrated.

Interestingly, back-of-the-envelope calculations suggest that if H₃⁺ is radiating some 10% of the entire energy arriving at Uranus, this energy is significantly larger than had been deduced from the data gathered by the *Voyager* fly-by in 1985 [42]. This may not be unreasonable as the *Voyager* fly-by

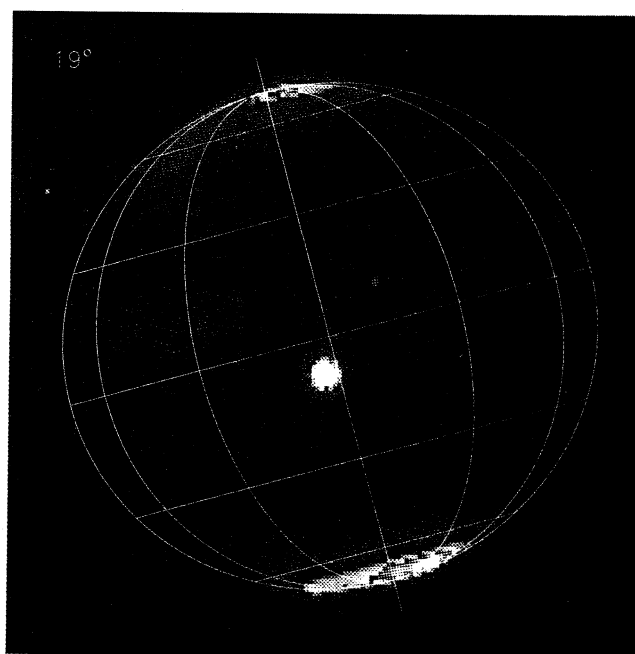


Figure 9. Jupiter with Ganymede passing at a wavelength sensitive to H₃⁺. The picture was recorded by Robert Joseph and Jonathan Tennyson in February 1991 using a 1% filter at 3.4 μm (2940 cm⁻¹) on the protoCAM imaging camera on NASA's Infrared Telescope Facility (IRTF). The central white spot is one of Jupiter's moon, Ganymede, that is simply reflecting sunlight. On Jupiter this radiation is absorbed by gases, particularly methane, in the atmosphere. As in figure 8, the colour scheme is used to denote the intensity of the emitted radiation. Lines of latitude and longitude have been superimposed on the raw image to show where the planet is situated.

took place during a period of relatively low solar activity, but in 1992 solar activity was close to its maximum.

6. H₃⁺ emission spectra outside the solar system

The observation of H₃⁺ in the planets emitting light rather than absorbing it led to the idea that maybe the way to detect H₃⁺ outside the solar system was to look for emission spectra in hotter regions. While searches for this spectrum have proved as frustratingly inconclusive as the attempts to observe its absorption spectrum (see § 3), there has been another interesting development.

In February 1987, astronomers world wide were highly excited by the sudden and spectacular death of a star in a nearby galaxy, the Large Magellanic Cloud. Explosions such as this, designated supernova 1987 *a*, only happen so close to Earth about once every 2 or 3 centuries. The star in question brightened greatly, so much so that it was visible to the naked eye, and a sudden burst of neutrinos was recorded on Earth. Meikle *et al.* [48] used the Anglo–Australian



Figure 10. An active volcano can be seen on the horizon of Jupiter's moon Io taken by the *Voyager* mission [31]. Particles ejected by volcanos on Io are one of the causes of the auroral activity and H_3^+ emissions on Jupiter (Picture courtesy of NASA).

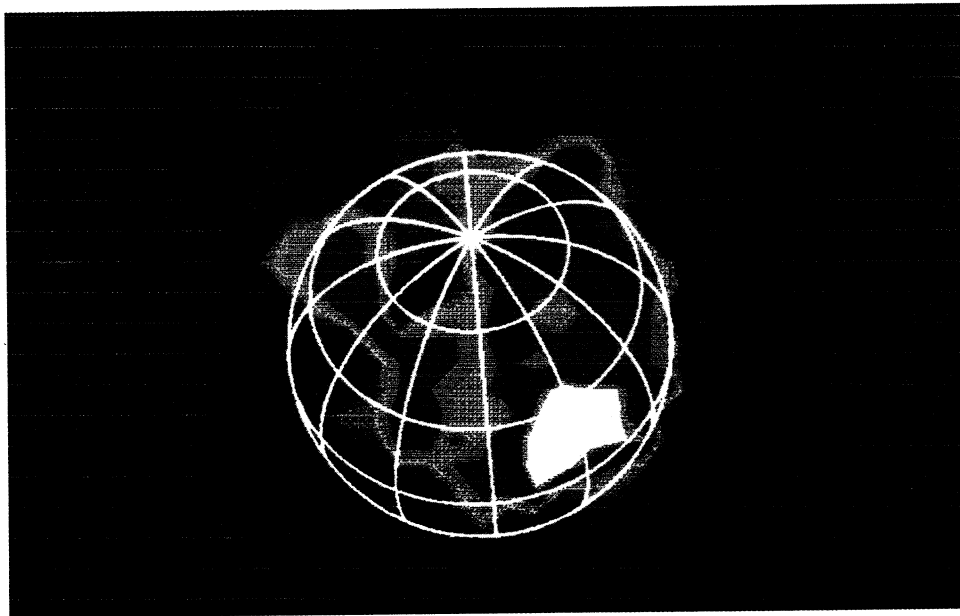


Figure 11. Image of Uranus at a wavelength ($3.99 \mu\text{m}$) sensitive to H_3^+ . The picture was taken by Hoanh Lam and Steven Miller on the 22 April 1993 using the protCAM imaging camera on NASA's Infrared Telescope Facility (IRTF). The intensity off the planet (which has been superimposed in white) is due to blurring of the image in Earth's atmosphere (the 'seeing'). The region of strongest emission, in white, may be located at Uranus's magnetic pole, but the position of this pole is not exactly known. The resolution is much worse than the corresponding Jovian image (figure 9) because Uranus is further from Earth (Picture from H. A. Lam, 1994, PhD thesis, University of London).

Telescope (AAT) to monitor supernova 1987 *a*'s infrared emissions over at regular intervals starting about 3 weeks after the explosion. These spectra show many features, some

of which are easily assigned to well known transitions of atomic hydrogen and He. Other features were harder to classify.

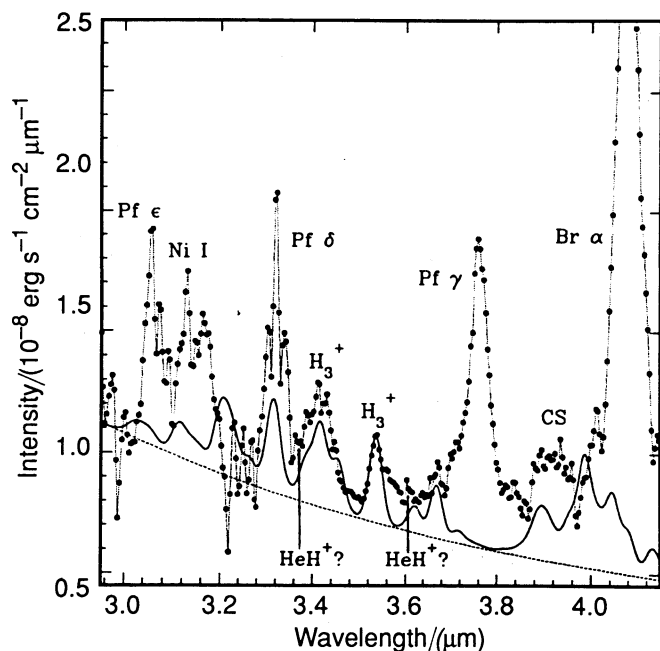


Figure 12. Infrared spectrum of supernova 1987 *a* taken 192 days after the initial explosion by Meikle *et al.* [48] using the Anglo–Australian Telescope (AAT). The raw spectrum is given by the filled circles and the computed H₃⁺ spectrum by the solid line. Assignments for many of the features are also given. Parameters: $T = 1000\text{ K}$; $M_c = 2.3 \times 10^{-8} M_\odot$; and $V_w = 3200\text{ km s}^{-1}$.

The spectrum of supernova 1987 *a* about 6 months after the initial explosion shows two features at 3.40 and 3.55 μm , wavelengths characteristic of H₃⁺. These features are too broad to be caused by a single atomic transition and we therefore set out to see whether they could be fit by blends of H₃⁺ transitions. Figure 12 shows one possible fit to these features using our H₃⁺ data. The fit, and other plausible ones we produced, is not perfect. However, in the absence of alternative explanations, and with corroborating evidence from the chemical model of Lepp and Dalgarno that suggests that it is possible to produce appropriate amounts of H₃⁺, our assignments seem likely to be correct [49].

This work has taken us into unfamiliar territory: the science of irreproducible results. Day 192 of supernova 1987 *a* is long past and in the absence of another nearby supernova explosion it is impossible to gather more observational evidence for or against the idea that these are H₃⁺ emissions.

7. Conclusions

The history of H₃⁺ thus far has been a fruitful interplay between first principles quantum mechanics, high-resolution laboratory spectroscopy and astronomy. These interactions have provoked considerable excitement within the specialist community and there are several review articles devoted to

this topic. Should the reader wish to learn about the subject at a more technical, and perhaps less partisan, level we can recommend references [4, 50–53]. In particular the last two references cited deal extensively with the intriguing and poorly understood photodissociation spectrum of H₃⁺ obtained by Carrington *et al.* [54].

Finally, as we write, Comet Shoemaker–Levy 9 is on a direct collision course with the planet Jupiter. This comet is now in 21 fragments after a previous close encounter with Jupiter that ripped it to pieces. What the exact effect of throwing dirty snowballs of between 1 and 5 km diameter at 60 km s⁻¹ into Jupiter will be is unclear. But it is inconceivable that this major injection of energy will have no effect on the planet's ionosphere or its infrared spectrum in general and the H₃⁺ emission lines, which have proved such a sensitive barometer of ionospheric activity, in particular. In common with many of the world's astronomers we will be watching this event with the greatest of interest.

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Steven Miller is a Senior Research Fellow in Astronomy and lecturer in Science Communication at UCL. Over the past few years he has pioneered the use of the H_3^+ molecular ion as a probe of planetary atmospheres and made the first identification of this species outside of the Solar System in the spectrum of Supernova 1987 *a*. He joined UCL in 1986, after 7 years as a political journalist. At UCL, together with Jonathan Tennyson, he carried out the first calculations on previously unknown transitions of H_3^+ , being sufficiently accurate to enable their detection by laboratory and astronomical spectroscopists. Dr Miller obtained both his BSc (1970) and PhD (1975) from the Chemistry Department at Southampton University, specializing in the physical chemistry of liquids. This research field was developed during fellowships at UMIST and Sheffield University. More recently, Dr Miller has been chosen to lead the observation team for the July 1994 impact of Comet Shoemaker-Levy 9 with Jupiter on the UK InfraRed Telescope in Hawaii and as part of NASA's team for the same event. His research on science communication centres on the reporting of astronomy in the British media.