

# The infrared spectrum of $\text{H}_3^+$ in laboratory and space plasmas

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Protonated hydrogen,  $\text{H}_3^+$ , composed of three protons and two electrons, is the simplest stable polyatomic system. It is the most abundant ionic species in molecular hydrogen plasmas, and it is assumed to play a central role in the chemical evolution of molecular clouds, the birthplace of stars. The existence of this species has been known since its discovery by J. J. Thomson in 1912, but its first spectrum was observed only in 1980. The infrared spectrum has since been extended to higher vibrational and rotational states. The existence of a large amount of  $\text{H}_3^+$  in Nature was first demonstrated in the serendipitous discovery of its infrared emission bands in the polar auroral regions of the Jupiter ionosphere. The spectrum is extremely intense and pure and can be used to monitor the morphology and temporal variation of the dynamic Jovian plasmas. Early this year, an identification of  $\text{H}_3^+$  emission was claimed in Supernova 1987A. In April strong  $\text{H}_3^+$  infrared emission was detected in Uranus. These developments are reviewed and the future is projected.

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## I. INTRODUCTION

From my point of view one of the most inspiring developments in recent science has been the unification of astronomy and chemistry. When I was a student, molecules had hardly any place in astronomy. Most of the matter in the Universe was believed to be condensed in hot stars, where nuclear physics dominates; interstellar space was viewed as a vast vacuum with an extremely low density of atoms and dust. The existence of a few unstable diatomic radicals had been reported (with hindsight, they were just the tip of the iceberg), but by and large it was assumed that stable molecules could not exist in the harsh conditions of interstellar space.

This understanding was drastically changed when Townes and his colleagues discovered the microwave emission spectrum of interstellar ammonia in Sagittarius B2, a molecular cloud located towards the center of our galaxy (Cheung *et al.*, 1968). This discovery induced an avalanche of radio-astronomical observations of many familiar molecules and also of many that were unfamiliar even to chemists, e.g.,  $\text{HC}_n\text{N}$  ( $n=5,7,9,11$ ). These discoveries and subsequent studies have created a new discipline, molecular astrophysics. Once a novel concept, the "molecular cloud" is now well established as being

the birthplace of stars; the chemical evolution of these clouds is recognized as a step in star formation.

The entry of molecules into the astrophysics not only of our own galaxy, but also of distant extragalactic objects, is best demonstrated by the infrared emission of quadrupolar transitions of molecular hydrogen. These transitions, initially observed by Herzberg (1949) in the laboratory, are extremely weak, but intense emissions appear in a variety of astronomical objects because of the enormous abundance of hydrogen in molecular form at low densities and at high temperatures. Figure 1 shows the extremely strong  $2\ \mu\text{m}$  infrared emission of  $\text{H}_2$  from the enigmatic superluminous galaxy-merger system NGC

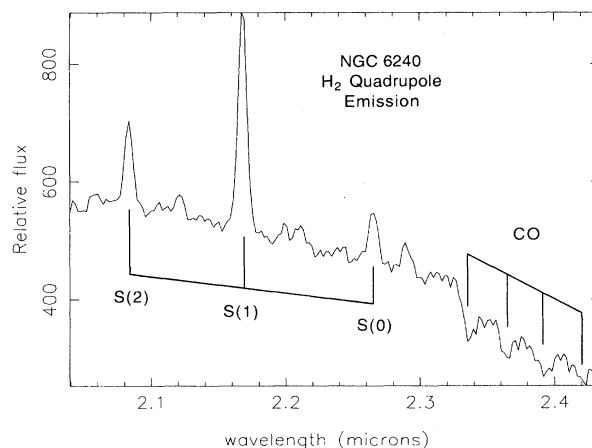


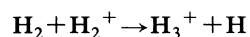
FIG. 1.  $\text{H}_2$  quadrupole emission spectrum from the superluminous galaxy NGC 6240. The single line  $S(1)$  ( $\nu=1\rightarrow 0$ ,  $J=3\rightarrow 1$  of ortho- $\text{H}_2$ ) carries the total brightness of a hundred million solar luminosities, as initially reported by Joseph, Wright, and Wade (1984). There are also weaker features corresponding to the hot band emission  $\nu=2\rightarrow 1$  [ $S(1)$  at  $2.28\ \mu$ ,  $S(2)$  at  $2.20\ \mu$ , and  $S(3)$  at  $2.12\ \mu$ ]. This spectrum was recorded by Geballe, Momose, and Oka using the CGS4 grating spectrometer at the United Kingdom Infrared Telescope. Note that the spectrum is Doppler shifted by  $Z=0.0254$  (redshift of  $\sim 0.05\ \mu\text{m}$ ) due to the expansion of the universe.

6240, one of the most luminous known infrared objects, some 300 million light years away. These extremely strong molecular features correspond to the vibration-rotation transitions  $v=1\rightarrow 0, J+2\rightarrow J$  of  $\text{H}_2$ . They are easily visible after a few minutes of integration with a modern high-resolution infrared spectrometer. The luminosity of the strongest  $\text{H}_2$  emission line  $S(1)$ , initially reported in that source by Joseph, Wright, and Wade (1984), amounts to  $\sim 1 \times 10^8 L_\odot$  ( $L_\odot$ =one solar luminosity). Can you imagine—the total luminosity of one hundred million suns in one molecular spectral line! The absorption due to the  $R$ -branch bandheads of carbon monoxide first-overtone bands ( $\Delta v=2$ ) and its hot bands are also visible in Fig. 1. Remember these spectral lines because we shall come back to them later.

In dense clouds where a vast number of molecules at low temperature ( $\sim 30$  K) are shielded from stellar radiation, the main chemical reaction scheme is believed to be ion-neutral kinetics. The ubiquitous cosmic rays ionize  $\text{H}_2$  and He, and the subsequent ion-neutral reactions govern the chemical evolution of the clouds, as initially advocated by Klemperer (Herbst and Klemperer, 1973), Watson (1976), Dalgarno (Dalgarno and Black, 1976), and their colleagues. The theory was strongly influenced by the radio-astronomical discovery by Buhl and Snyder (1970) of the strong emission of protonated carbon monoxide  $\text{HCO}^+$  (Klemperer, 1970). Recognition of such a chemical scheme and subsequent studies on interstellar chemistry revealed a major void in our knowledge of molecular spectroscopy, a void that had previously been known to a few specialists but was not widely felt. The spectrum and thus the quantum-mechanical information on protonated hydrogen  $\text{H}_3^+$ , the simplest and the most fundamental polyatomic system, was totally absent. It is this ion which is initially produced in molecular clouds and which plays the universal role of protonator in interstellar chemistry.

## II. HISTORICAL BACKGROUND<sup>1</sup>

The existence of  $\text{H}_3^+$  has been known since the early days of mass spectroscopy. It was none other than J. J. Thomson (1912) who discovered  $\text{H}_3^+$  in his “positive rays” and noted “the existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with the ordinary conceptions about valency, if hydrogen is regarded as always monovalent.” Dempster (1916) soon showed that  $\text{H}_3^+$ , rather than the primary ion  $\text{H}_2^+$ , is most abundant in hydrogen discharges, a fact which applies both to laboratory and to space plasmas. Hogness and Lunn (1925) identified the celebrated reaction



<sup>1</sup>See Oka (1983) for more details.

as the origin of the production and dominance of  $\text{H}_3^+$ . This reaction, with its large Langevin rate ( $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) and exothermicity ( $\sim 1.7$  eV), is extremely efficient. Thus the  $\text{H}_2^+$  ions initially produced in molecular clouds by the cosmic ray flux are immediately converted to  $\text{H}_3^+$ . One can interpret this reaction as “proton hopping” from an H atom (with proton affinity  $\sim 2.7$  eV) to the  $\text{H}_2$  molecule (P.A.  $\sim 4.4$  eV). More recent experiments, however, have demonstrated that this naive picture is not quite right; approximately 50% of the reaction is due to hydrogen abstraction (i.e., an H atom hopping from H to  $\text{H}_2^+$ ). The true nature of this most fundamental reaction is still under study experimentally and theoretically (see Pollard *et al.*, 1991, and references therein). The  $\text{H}_3^+$  ion thus produced acts as the universal protonator through the proton-hopping reaction  $\text{H}_3^+ + X \rightarrow \text{HX}^+ + \text{H}_2$  and initiates interstellar chemistry. This reaction is generally efficient for most molecules and atoms whose proton affinities exceed that of  $\text{H}_2$  (notable exceptions are He, Ne, Ar, N, and  $\text{O}_2$ ). Once protonated, reactions such as  $\text{HX}^+ + Y \rightarrow \text{XY}^+ + \text{H}$  proceed efficiently (contrary to the reactions  $X + Y \rightarrow \text{XY} + h\nu$ , which are extremely slow). The late Hiroko Suzuki (1989) coined the phrase “ $\text{H}_3^+$  chemistry” for these chemical processes.

For many years after its discovery, the true nature of  $\text{H}_3^+$  remained an enigma. Experiments could not tell much about  $\text{H}_3^+$  other than that it existed. Eyring was quoted<sup>1</sup> as having said that the  $\text{H}_3^+$  problem was “the scandal of modern chemistry.” Being the simplest polyatomic system,  $\text{H}_3^+$  presented a major challenge to quantum chemistry. It is a historical curiosity that Niels Bohr (1919) was the first to publish a theoretical paper on triatomic hydrogen. From 1936–1938 Eyring, Hirschfelder, and others published a series of five papers, concluding in Part V (Hirschfelder, 1938) that the triangular structure is more stable than the linear structure. With the advent of modern computers, the quantum mechanics of the three hydrogen system has become a major battlefield for theorists (Porter, 1982). It was shown that the equilateral configuration has the minimum energy (Christoffersen *et al.*, 1964; Conroy, 1964) and that  $\text{H}_3^+$  (protonated  $\text{H}_2$ ), like  $\text{H}^-$  (deprotonated  $\text{H}_2$ ), does not have any stable excited electronic state except for a triplet state very close to its second dissociation limit. These results indicated that the vibration-rotation spectrum associated with the infrared active degenerate vibrational mode,  $\nu_2$ , is the only possible vehicle for laboratory and astronomical observation except for weaker distortion-induced rotational transitions (Pan and Oka, 1986). Carney and Porter (1974, 1976) published classic papers predicting the frequency of the  $\nu_2$ -fundamental band to be  $2516 \text{ cm}^{-1}$ , a value found to be only  $5 \text{ cm}^{-1}$  off the real value. Their predictions on the electrical properties of  $\text{H}_3^+$  and on some crucial vibration-rotation constants (unpublished but made available to Oka and J. K. G. Watson) were of great help in planning the laboratory spectroscopy and in its identification. Close collabora-

tion of theorists and experimentalists has been an essential ingredient of this field ever since. Today brute force variational calculations using supercomputers predict individual vibration-rotation levels with an accuracy of  $\sim 1 \text{ cm}^{-1}$ . This truly remarkable development, in a series of many papers by Miller, Tennyson, and Sutcliffe (1990 and references therein), based on an *ab initio* potential of Meyer, Botschwina, and Burton (1986), has played a major role in the recent studies of the  $\text{H}_3^+$  spectrum in the laboratory and in space.

### III. THE $\text{H}_3^+$ SPECTRUM IN THE LABORATORY

Several papers claimed observation of the  $\text{H}_3^+$  spectrum in the early days. The spectral lines reported in the optical region, however, were subsequently all ascribed to transitions between excited electronic states of  $\text{H}_2$ . Since theory indicated that no discrete optical spectrum was likely to exist, the search for the  $\text{H}_3^+$  spectrum was shifted to the infrared region. Herzberg (1967) described his plan to find the spectrum in infrared emission. His effort over many years culminated with his discovery (Herzberg, 1980; Herzberg *et al.*, 1981; Herzberg, 1982) of a Rydberg spectrum of the important and beautiful neutral species  $\text{H}_3$ . The observation of the  $\text{H}_3^+$  spectrum, however, had to wait for the high sensitivity of laser spectroscopy.

#### A. The $\text{H}_3^+$ $\nu_2$ fundamental band<sup>1,2</sup>

The infrared absorption spectrum of  $\text{H}_3^+$  was observed using a liquid-nitrogen-cooled hydrogen plasma (Oka, 1980). Crucial for this observation were two recent technological advances: (1) the development of a widely tunable laser infrared source by Pine (1974) and (2) the use of a long positive column glow discharge introduced to microwave spectroscopy by Woods and his colleagues (Woods *et al.*, 1975). Figure 2 shows a stick diagram of the 15 observed lines. Unlike the usual vibration-rotation spectra of simple molecules, this spectral pattern shows no obvious symmetry or regularity. This is because of the large interaction between vibration and rotation, which makes the perturbation treatment difficult. J. K. G. Watson looked at this enigmatic spectrum and analyzed it overnight; his name should have appeared as a coauthor.

The most telltale feature of this spectrum is the absence of any line over an interval of more than  $100 \text{ cm}^{-1}$  at  $\sim 2600 \text{ cm}^{-1}$ . This indicates that the carrier of this spectrum cannot occupy the lowest rotational state with no angular momentum ( $J=K=0$ ), called an *S* state by physicists of other disciplines. This is the fingerprint of a system composed of the three identical fermions with

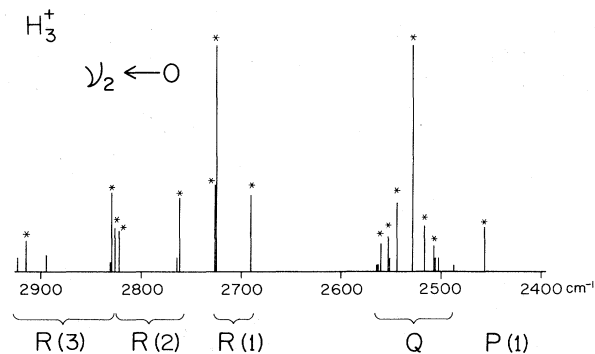


FIG. 2. Stick diagram of the first 15 lines of the  $\nu_2$  fundamental band of  $\text{H}_3^+$  observed in the laboratory (Oka, 1980). Observed lines are shown with asterisks.

spin  $\frac{1}{2}$ . An *S*-state eigenfunction is symmetric under both the odd permutation (12) and the even permutation (123) of nuclei and thus cannot satisfy the Pauli principle for the two operations simultaneously, regardless of the associated spin function. [An extra dimension of *color* was introduced in quantum chromodynamics to overcome this dilemma (Han and Nambu, 1965).]

Since the first observation of the  $\text{H}_3^+$  spectrum, which was made in a most primitive way, the sensitivity of molecular ion spectroscopy has been increased by at least three orders of magnitude by a variety of techniques. In particular, the velocity modulation method introduced by Gudeman, Saykally, and others (1983) has made an enormous impact on the field. A table recently published by Kao *et al.* (1991) lists 129 lines of the fundamental band, along with many more lines of other bands. Efforts are continually being made to reach higher rotational levels, anticipating their observation in some hot astronomical objects. By now we have reached the rotational state  $J=K=15$  ( $J$  and  $K$  are quantum numbers for rotational angular momentum and its projection to the  $\text{C}_3$  molecular axis) at  $5092 \text{ cm}^{-1}$  (0.63 eV) above the lowest rotational level.

One noteworthy independent development has been the laboratory observation of the  $\text{H}_3^+$  emission spectrum, which was made possible by use of a high-temperature hollow-cathode discharge ingeniously designed by Majewski, and of a high-resolution Fourier-transform spectrometer. The emission from such a discharge is dominated by the  $\text{H}_2$  emission spectrum, but Majewski, Watson, and others (1987) discriminated the  $\text{H}_3^+$  and  $\text{H}_3$  emissions through their intensity dependence on gas pressure. Majewski's spectrum contained not only the fundamental band but also overtone bands of  $\text{H}_3^+$ , and would play an important role in deciphering the  $2\text{-}\mu\text{m}$  Jovian emission spectrum (Majewski *et al.*, 1989).

#### B. Hot, overtone, and forbidden bands

The second phase of  $\text{H}_3^+$  laboratory spectroscopy was initiated in late 1987 as an attempt to detect other bands

<sup>2</sup>For an account from a different viewpoint, see Herzberg (1982).

of  $\text{H}_3^+$  which are weaker than the fundamental band by orders of magnitude. This project was motivated purely by our curiosity about the quantum mechanics of the excited vibrational states and about the dynamical behavior of  $\text{H}_3^+$  in plasmas. However, its results played a crucial role in the analysis of the then totally unexpected 2- $\mu\text{m}$  emission spectrum of Jupiter.

The vibrational energy-level structure of  $\text{H}_3^+$  is shown in Fig. 3; various observed transitions are shown by arrows. The normal vibrations of a triatomic equilateral triangle molecule are a textbook case, composed of the totally symmetric infrared-inactive  $\nu_1$  mode and the doubly degenerate infrared-active  $\nu_2$  mode. Bawendi, Reh-fuss and Oka (1990) observed the hot bands  $2\nu_2(2)\leftarrow\nu_2$ ,  $2\nu_2(0)\leftarrow\nu_2$ , and  $\nu_1+\nu_2\leftarrow\nu_1$ . These bands are weaker than the fundamental band by a factor of about 50 because of the Boltzmann factor for the excited vibrational states. Xu, Gabrys, and others observed the first-overtone band  $2\nu_2(2)\leftarrow 0$  (Xu *et al.*, 1990) and the forbidden bands  $\nu_1\leftarrow 0$  and  $\nu_1+\nu_2\leftarrow\nu_2$  (Xu *et al.*, 1992), and Lee, Ventrudo, and others (1991) observed the second-overtone band  $3\nu_2(1)\leftarrow 0$ . These bands span the wavelength range of 5 to 1.4  $\mu\text{m}$ , requiring various laser technologies for their observation. The first principle calculations of Miller and Tennyson (Miller *et al.*, 1990, and references therein) have been indispensable for the analysis of the observed spectrum corresponding to high vibrational states.

The  $\text{H}_3^+$  emissions observed in Jupiter, corresponding to the overtone band  $2\nu_2(2)\rightarrow 0$  and to the fundamental band  $\nu_2\rightarrow 0$ , are also indicated in Fig. 3 with bold arrows. Usually the overtone band is much weaker than the fundamental because of its smaller transition moment. The  $\text{H}_3^+$  ion is special in that, because of the large vibrational

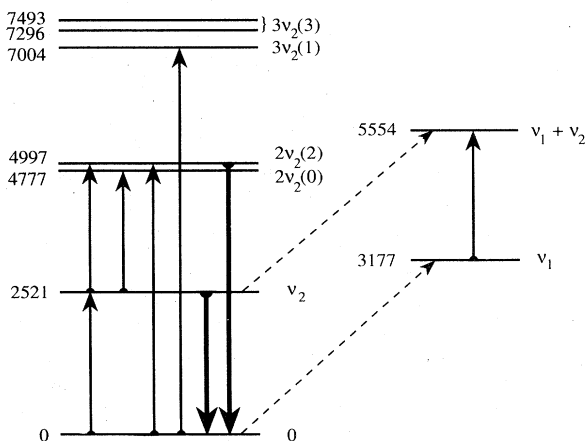


FIG. 3. Energy diagram showing the lower vibrational states of  $\text{H}_3^+$ . The bands observed in the laboratory are shown by arrows pointing upwards. The broken lines show observed forbidden transitions. Transitions observed in astronomical objects are shown by bold arrows pointing downwards. The numbers beside the levels give their energy in  $\text{cm}^{-1}$ . For example,  $3\nu_2(1)$  signifies  $\nu_2=3$  (vibrational quantum number) and  $l=1$  (vibrational angular momentum).

amplitude of its protons, the decrease of the transition moment is modest and it is compensated by the  $\nu^3$  factor in the Einstein coefficients for spontaneous emission, so much so that the value of  $A_{ij}$  for the overtone band (174  $\text{s}^{-1}$ ) is actually larger than that for the fundamental band (124  $\text{s}^{-1}$ ).

Experimental and theoretical efforts are being made to reach even higher vibrational and rotational states. Carrington, Buttenshaw, Kennedy, and others have observed a great many transitions of  $\text{H}_3^+$  near its dissociation limit. Their observations and many associated theoretical papers are outside the scope of this article (see Carrington and McNab, 1989, for a review).

#### IV. THE $\text{H}_3^+$ SPECTRUM IN SPACE

Immediately after the laboratory observation of the  $\text{H}_3^+$  spectrum, I attempted to detect it in absorption in the Orion Molecular Cloud and in other clouds that contain bright infrared objects (Oka, 1981). The euphoria induced by the laboratory detection made me neglect the theoretical prediction (Herbst and Klemperer, 1973) that, although the production rate of  $\text{H}_3^+$  is very high, its high reactivity, especially with CO, lowers the steady-state concentration. I was also hoping that the strong mysterious emission feature at 3.4  $\mu\text{m}$  reported by Merrill, Soifer, and Russell (1975) had something to do with  $\text{H}_3^+$ . (How naive of me; this feature is still unexplained.) The search for  $\text{H}_3^+$  in molecular clouds has continued to this day without success (Geballe and Oka, 1989; Black, van Dishoeck, and Woods, 1990). The possible detection of the submillimeter-wave rotational spectrum of  $\text{H}_2\text{D}^+$  (Phillips *et al.*, 1985) remains unconfirmed and controversial. However, the great increase in the sensitivity of spectrometers brought about by the use of multiple-diode detection arrays makes us optimistic that the discovery of  $\text{H}_3^+$  in molecular clouds is just around the corner. (Our next observation session is in July of this year. Perhaps . . .) Many theoretical papers (see Geballe and Oka, 1989, for a summary) predict  $\text{H}_3^+$  column densities on the order of  $\sim 10^{14} \text{ cm}^{-2}$ , which should be just detectable by the modern infrared spectrometer.

In the meantime the first detection of the  $\text{H}_3^+$  spectrum in Nature came from serendipitous discoveries in emission on an entirely unexpected object.

##### A. The $\text{H}_3^+$ emission from the Jovian auroral regions

Retrospectively, the first Jovian spectrum of  $\text{H}_3^+$  was recorded by Trafton and others using the McDonald Observatory infrared grating spectrometer. Their spectrum on the night of September 21, 1987 (Trafton, Lester, and Thompson, 1989) already showed the clear emission feature at 2.093  $\mu\text{m}$  which would later be assigned to the  $(J, G, U=7, 9, +1)\rightarrow(J, K=6, 6)$  transition of the  $2\nu_2(2)\rightarrow 0$  overtone band of  $\text{H}_3^+$ . Their spectrum, pub-

lished in 1989 as still unidentified, is shown in Fig. 4. Note the  $\text{H}_2$   $S(1)$  quadrupole emission line at  $2.121 \mu\text{m}$  (remember the strong line in Fig. 1). These authors were primarily studying this  $\text{H}_2$  emission from Jupiter and accidentally stumbled on the rich emission features due to  $\text{H}_3^+$ .

The same emission features were observed more extensively in higher resolution at the Canada-France-Hawaii Telescope with the Fourier transform infrared spectrometer (FTIR) during the night of September 24, 1988 (Drossart *et al.*, 1989). This observation was made as a part of a systematic study of Jovian auroral activity (Kim and Maguire, 1986) during the International Jupiter Watch Week. The emission was observed only in the auroral regions at the northern and southern poles. The results were reported at the Austin DPS meeting in October 1988 (Kim *et al.*, 1988), and the possibility of emission from hydrocarbon free radicals or  $\text{H}_3^+$  was suggested. A list of the strange emission lines was sent to the Herzberg Institute of Astrophysics in late October and caused quite a sensation (which I witnessed when I gave seminars at the Institute on November 3 and 4). Majewski had recorded an extensive FTIR emission spectrum from a laboratory  $\text{H}_2$  plasma in the same wavelength region, and this spectrum contained extremely rich spectra of  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_3^+$ , which are all good candidates. After a month's work J. K. G. Watson, who had earlier analyzed the first laboratory  $\text{H}_3^+$  spectrum, came to the understanding of the Jovian spectrum as due to the  $2\nu_2(2) \rightarrow 0$  band of  $\text{H}_3^+$ . Crucial to his solution were the laboratory data of the  $2\nu(2) \rightarrow \nu_2$  hot band provided by Bawendi *et al.* (1990), the analysis of which is based on the theoretical calculations of Miller and Tennyson (1989). The initial guesses, uncertainties, heated discussions, and the sudden final solution are vividly recorded in extensive E-mail correspondences between Paris (J.-P.

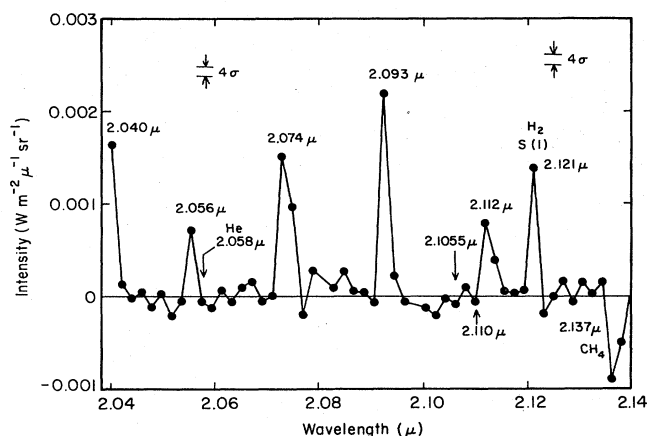


FIG. 4. The  $2\text{-}\mu\text{m}$  Jovian emission spectrum reported by Trafletton, Lester, and Thompson (1989). They were studying the  $S(1)$   $\text{H}_2$  quadrupole emission line at  $2.121 \mu\text{m}$  (also shown in Fig. 1) and accidentally observed the other emission lines due to  $\text{H}_3^+$ . The spectrum was recorded using the McDonald Observatory infrared grating spectrometer.

Maillard), Ottawa (P. A. Feldman and J. K. G. Watson), and London (S. Miller), with recurring references to Bawendi, Dabrowski, Drossart, Herzberg, Majewski, Oka, Tarrago, and Vervloet. The close collaboration of astronomers, laboratory spectroscopists, and theorists is characteristic of this field.

After the  $2\text{-}\mu\text{m}$  emission was attributed to the  $2\nu_2(2) \rightarrow 0$  overtone band of  $\text{H}_3^+$ , it was natural to expect the fundamental band  $\nu_2 \rightarrow 0$  to appear even more strongly. The observation of this band was made at the United Kingdom Infrared Telescope (UKIRT) in the morning on September 14–19, 1989 using the grating spectrometer CGS2 (Oka and Geballe, 1990). Ten strong emission lines of  $\text{H}_3^+$  corresponding to the  $Q(\Delta J=0)$  branch of the fundamental band were observed in the  $4\text{-}\mu\text{m}$  region. The previously detected  $2\text{-}\mu\text{m}$  emission was not detected, in spite of our efforts during September 9 and 10, indicating significant temporal variations of the Jovian plasmas. The much higher observed intensity of the  $4\text{-}\mu\text{m}$  fundamental band compared to that of the overtone band suggested that the observed emission does not originate from freshly produced  $\text{H}_3^+$  but from  $\text{H}_3^+$  in thermal equilibrium at temperatures of 1100 K (Drossart *et al.*, 1989) to 670 K (Oka and Geballe, 1990), collisionally excited to high vibrational states by  $\text{H}_2$  and He. This was established by Miller, Joseph, and Tennyson (1990) in their subsequent observations of the  $2\text{-}\mu\text{m}$  and the  $4\text{-}\mu\text{m}$  emissions.

The beautiful FTIR results on the  $\text{H}_3^+$  fundamental band observed by Maillard *et al.* (1990) give the best panoramic view of the band (Fig. 5). The advantage of the wide-frequency coverage due to the Fourier-transform method is clearly demonstrated. All of the stronger observed lines are assigned to the fundamental band of  $\text{H}_3^+$ . The amazing characteristic of this spectrum is that its background infrared emission is almost nonexistent. In particular, in the region of  $2600$  to  $2900 \text{ cm}^{-1}$ , the background is almost completely flat and virtually zero. Jupiter is still cooling and is radiating much of its heat in the infrared. It is also reflecting the solar radiation. However, the infrared radiation in this wavelength region is almost completely wiped out by the pressure-broadened absorption of  $\text{CH}_4$  (see, for example, Larson *et al.*, 1980).  $\text{CH}_4$  molecules exist abundantly in the low-altitude, low-temperature Jovian atmosphere and convert radiative energy to kinetic energy. Only the  $\text{H}_3^+$  emission occurring at the high altitudes of the ionosphere reaches us unabsorbed! When comparing the  $2600\text{--}2900 \text{ cm}^{-1}$  in Fig. 5 with the laboratory spectrum of Fig. 2, the agreement is breathtaking.

## B. The colossal Jovian plasma

The infrared emission from Jupiter is so intense that a brief integration suffices to see it very strongly. None of us was sufficiently imaginative to think about this possibility until it was discovered accidentally, providing yet

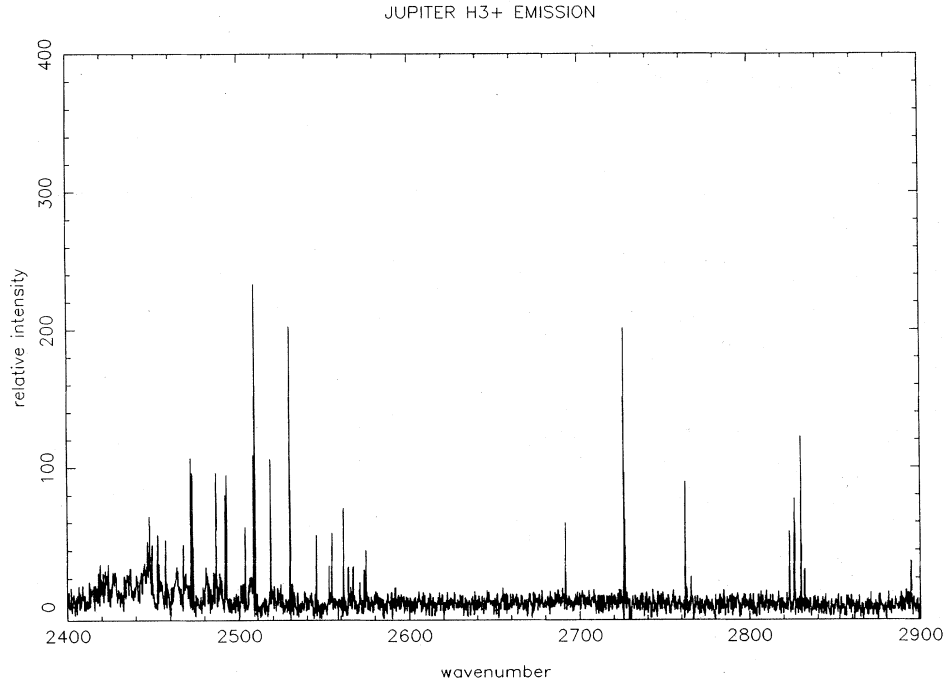


FIG. 5. The apodized  $\text{H}_3^+$  emission spectrum from the southern auroral zone of Jupiter recorded by Maillard *et al.* (1990) using the Canada-France-Hawaii Telescope Fourier-transform spectrometer. The spectral lines from 2600 to 2900  $\text{cm}^{-1}$  match perfectly with the laboratory spectrum of Fig. 2. The spectral lines in the region of 2400  $\text{cm}^{-1}$  have different relative intensities because of the higher temperature in Jupiter plasmas (1100 K) compared to the liquid-nitrogen-cooled laboratory plasmas (200 K).

another example of how we are all nitwits up against Nature. For nearly ten years I had been searching for the spectrum in objects that are thousands of light years away while the strong signal was waiting to be observed in an object only 40 light minutes away! As usual it is obvious after the fact that the auroral regions of the Jovian ionosphere provide ideal conditions for  $\text{H}_3^+$  plasmas (see Dessler, 1983). In fact,  $\text{H}_3^+$  ion had been detected *in situ* in the Jovian magnetosphere by the low-energy-charged-particle instrument on the two *Voyager* spacecraft. (Hamilton *et al.*, 1980; Krimigis and Roelof, 1983). The theoretical chemical model by McConnell and Majeed (1987) had predicted an  $\text{H}_3^+$  column density on the order of  $10^{13} \text{ cm}^{-2}$  in the Jovian ionosphere, which approximately matches the observed values (Oka and Geballe, 1990).

Jupiter is a big blob (mean radius  $\sim 70\,000$  km) of supercritical fluid composed of hydrogen and helium. Because of the high gravitational pressure, hydrogen at a depth of 25 000 km from the surface into the core is believed to be metallic fluid with good electrical conductivity. Perhaps because of this (see, for example, Levy, 1989), the magnetic field of Jupiter is very high. Its magnetic moment is established (Dessler, 1983) to be  $4.3 \text{ GR}_J^3$  ( $1.4 \times 10^{30} \text{ gauss cm}^3$ ), more than four orders of magnitude higher than that of the Earth. This large magnetic field rotates along with Jupiter with a relatively short period ( $\sim 10$  h), sweeping charged particles around. The charged species are trapped by the magnetic field

and corotate with Jupiter at great speed. This magnetic field not only rotates but also wobbles because the Jovian rotation axis is  $10^\circ$  off from the magnetic dipole axis. To this gigantic plasma, the ejecta from the moon Io add fuel (Fig. 6). Io's rotational period is 1.8 days, and thus Io is overtaken by the rotating field and its trapped species. The differential speed,  $v \sim 57 \text{ km s}^{-1}$  at Io ( $\sim 400\,000$  km from Jupiter), for a proton corresponds to the energy of  $\sim 16 \text{ eV}$ , sufficient to ionize ejecta from Io which are mostly oxygen and sulfur. The magnetic field  $B$  ( $\sim 20$  mG) moving with respect to Io induces a relativistic electric field  $\mathbf{E} = (\mathbf{v} \times \mathbf{B})/c$  of  $\sim 0.11 \text{ V/m}$  along the direction from Jupiter to Io. This electric field, amounting to a potential difference of 400 kV across Io, accelerates the ion-

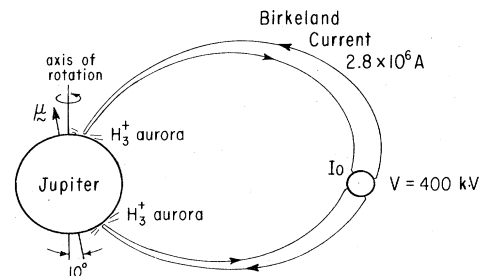


FIG. 6. Simplified schematic picture of the Jupiter-Io plasma power induction (Piddington and Drake, 1968). The diameter of Io is magnified by a factor of 10 for clarity. Other relative distances are to scale.

ized species. The ions and electrons thus accelerated move along the magnetic field and reach Jupiter (Pidington and Drake, 1968). The field-aligned electric current has been estimated from the *Voyager 1* observation to be  $2.8 \times 10^6$  A (Acuña, Neubauer, and Ness, 1981). This enormous Birkeland current is focused onto the magnetic poles of Jupiter, flows through the ionosphere, and then returns back to Io along the magnetic field. Such a colossal Jupiter-Io plasma activity, amounting to a total power dissipation of  $\sim 1 \times 10^{12}$  W, was initially suggested from the Jovian decametric radio emission and was later observed more directly by the *Voyagers* during their close encounters with Jupiter (Dessler, 1983).

We can now monitor the infrared aurora thus produced through the  $\text{H}_3^+$  spectrum from ground-based observatories. As mentioned earlier, the Jovian infrared emission in a certain wavelength region is almost purely due to  $\text{H}_3^+$ . Thus a high-resolution spectrometer is not needed for such observation; a narrow-band filter and an infrared camera suffice. Two such papers have appeared showing detailed morphology and the fast temporal variation of the auroral activity (Kim *et al.*, 1991; Baron *et al.*, 1991).

### C. $\text{H}_3^+$ in Supernova 1987A (!?)

A most surprising paper appeared early this year in which Miller, Tennyson, Lepp, and Dalgarno (1992) claimed identification of  $\text{H}_3^+$  emission in the infrared spectrum of Supernova 1987A reported by Meikle *et al.* (1989). A comparison of the observed spectrum of SN 1987A on day 192 and a computed  $\text{H}_3^+$  fundamental spectrum is shown in Fig. 7. Here the observed spectrum is Doppler broadened by the high speed of materials in the ejecta, and it is impossible to rely on the clear fingerprint of rotational structure. Therefore the identification is nowhere near as definitive as in the Jovian spectrum discussed previously or in the Uranus spectrum to be discussed below. Nevertheless, the agreement between the observed and calculated spectrum is quite remarkable, especially for the feature at  $3.54 \mu\text{m}$  dominated by the strongest  $4,3,1 \rightarrow 3,3$  transition. The agreement in the other wavelength region is not as impressive. Since the spectroscopic evidence is not as definitive as in other cases, other circumstantial evidence is called for: (a) no known atomic spectrum can explain the observed features, and (b) it is indeed possible that a large amount ( $\sim 1 \times 10^{-7} M_\odot$ ) of  $\text{H}_3^+$  is produced in a type-II supernova in  $\sim 100$  days.

The appearance of abundant molecular species in a supernova in such a short time interval is certainly incredible but has good observational support in the characteristic *R*-branch head of the  $\Delta v = 2$  CO overtone bands in emission reported by Spyromilio *et al.* (1988; remember the same bands in Fig. 1). Molecules are definitely there in 192 days. Studying the chemical evolution of a supernova in 100 days is somewhat like doing the same for the

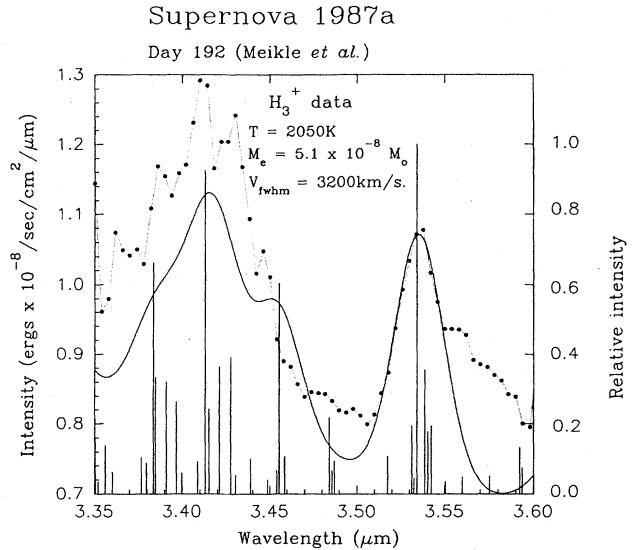


FIG. 7. Emission spectrum of Supernova 1987A on day 192: filled circles, observed results of Meikle *et al.* (1989); solid curve, computer-convoluted  $\text{H}_3^+$   $\nu_2 \rightarrow 0$  spectrum calculated by Miller *et al.* (1992).

big bang in 10 billion years. Lepp and Dalgarno applied their theory of molecular formation in primordial molecular clouds, coming up indeed with  $\text{H}_3^+$  of mass  $\sim 1 \times 10^{-7} M_\odot$  in 100 days.

One disturbing aspect of this identification is the glaring mismatch between the assumed low rotational temperature (2050 K, 1000 K) and the high kinetic temperature expected from the high expansion velocity ( $3200 \text{ km s}^{-1}$ ). The infrared and far-infrared emission through forbidden rotational transitions with lifetimes on the order of minutes to hours (Pan and Oka, 1986) will lower the rotational temperature, but whether this process is efficient enough to explain the observed results remains to be seen. Now, five years after the event, the supernova remnant is diffuse and much of the  $\text{H}_3^+$  is dissociated. The identification of  $\text{H}_3^+$  in SN 1987A will probably stay somewhat controversial. The arrival of the next bright supernova radiation (which must be on its way) is awaited. Infrared astronomers of the world, stay tuned.

### D. The $\text{H}_3^+$ emission from Uranus

On April 1 of this year, extremely strong emission of  $\text{H}_3^+$  was detected in Uranus by Trafton, Geballe, and Miller (Geballe, private communication) using the UKIRT CGS4 spectrometer. The twelve observed features between  $3.90$  and  $4.07 \mu\text{m}$  comprise 21 *Q*-branch transitions of the  $\nu_2$  fundamental band. Uranus has a smaller diameter than Jupiter ( $\sim \frac{1}{3}$ ) and is farther from Earth ( $\sim 4 \times$ ). Despite those facts, the intensity of the

$\text{H}_3^+$  spectrum is very high and suggests tempestuous plasma activity in Uranus, whose magnetic dipole axis is tilted from the axis of rotation by  $58.6^\circ$ . This is amazing in view of the small magnetic moment of Uranus ( $\sim 1/410$  that of Jupiter). By the way, the search for  $\text{H}_3^+$  emission in Saturn produced negative results in spite of good integration over two nights (Geballe and Oka, unpublished). Results of the search in Neptune are also negative thus far.

## V. FINAL REMARKS

I conclude this article with a rough projection for the future.

(1) Molecular astrophysics will grow further and will provide crucial information for our understanding of star formation. Observational infrared spectroscopy will play a major role in its development. The increasing sensitivity of spectrometers in the last few years has been phenomenal.

(2) With the new tunable-laser sources (InGaAsP communication diode, Ti-sapphire laser), laboratory  $\text{H}_3^+$  spectroscopy will reach high vibration-rotation states near or above the barrier for linearity. A new theoretical formulation will be needed to account for such states.

(3) The  $\text{H}_3^+$  spectrum will be observed in many astronomical objects and will become a common astronomical probe for the study of ionized regions. Past experience has shown that it is almost impossible to predict in precisely which object  $\text{H}_3^+$  will appear. The proposal to attempt  $\text{H}_3^+$  observation in NGC 6240 is thrilling (Draine and Woods, 1990).

(4) Following the laboratory observation of the  $\text{H}_3^+$  spectrum, spectra of many other fundamental molecular ions such as  $\text{CH}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3^+$ ,  $\text{NH}_4^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{H}_3\text{O}^+$  have been observed, all of which are key ingredients in interstellar chemistry. Their infrared spectra will also be detected in astronomical objects.

Finally, a word of caution. Space constraints and the limitations of my own training have forced me to simplify some complex subjects in this colloquium—perhaps, from the viewpoint of a specialist, to oversimplify. The reader is advised to consult the references in infrared astronomy, interstellar chemistry, theoretical astrophysics, ion kinetics, planetary science, and plasma physics for more detailed treatments of the many subfields that contribute to the fascination of this topic.

*Note added in proof.* After submission of this manuscript, we have detected the  $\text{H}_3^+$   $\nu_2$  band emission in Saturn (Geballe, Jagod, and Oka, unpublished). The emission observed in Saturn's polar regions is weaker than that from Jupiter by a few orders of magnitude, but the great improvement in the sensitivity of our spectrometer has led us to a clear detection of three vibration-rotation transitions:  $pR(1,0)$  at  $2725.898\text{ cm}^{-1}$ ,  $rR(1,1)$  at  $2726.923\text{ cm}^{-1}$ , and  $rR(3,3)$  at  $2829.923\text{ cm}^{-1}$ .

## ACKNOWLEDGMENTS

I wish to thank M. G. Bawendi, S. Chandrasekhar, U. Fano, P. A. Feldman, C. M. Gabrys, T. R. Geballe, G. Herzberg, M.-F. Jagod, T. Kawai, W. Klemperer, J.-P. Maillard, S. Miller, Y. Nambu, H. Sasada, K. Shimoda, K. Takagi, C. H. Townes, L. Trafton, J. K. G. Watson, and D. P. Weliky for reading this paper. Our work in this article has been supported by NSF Grants PHY-81-13097, PHY-84-08316, PHY-87-07025, PHY-90-22647 and partially also by Air Force Grants F04611-86-K-0069 and F33615-90C-2035.

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