Infrared Spectrum of H₃⁺ as an Astronomical Probe

Takeishi Oka and Mary-Frances Jagod
Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637-1403, USA

According to the current theory of interstellar chemistry advanced in the early 1970s, the protonated hydrogen molecular ion H₃⁺ plays a crucial role in initiating a chain of ion–neutral reactions. The infrared spectrum of H₃⁺ was first observed in the laboratory in 1980 and has been extended greatly since. The spectrum has been observed as intense emission in polar regions of Jupiter, and very recently in Uranus and Saturn. Its detection has also been claimed in Supernova 1987A, and intense searching for the spectrum in interstellar space is in progress. We summarize the laboratory observation of the H₃⁺ spectrum and its use as an astronomical probe.

Hydrogenic Species

Since hydrogen is the most abundant element in the universe, spectra of hydrogenic species provide the most general probe with which astronomers can study a wide variety of gaseous objects in the cosmos. The electronic transitions of atomic hydrogen, initially observed by Fraunhofer in his solar spectrum1 (the C and the F lines), identified as due to hydrogen by Ångström,2 and expanded by Bohr,3 are used over the wide spectral region from the vacuum ultraviolet (Lyman series) all the way through to the radiofrequency (recombination lines). The 21 cm magnetic transition between the hyperfine levels of the hydrogen atom, initially observed in the laboratory by Rabi and co-workers4 and detected in our galaxy by Ewen and Purcell5 and by Muller and Oort,6 is the most universally intense radio signal with which we can observe deep into the galaxy. The spectrum of the negative ion of atomic hydrogen H⁻ causes the opacity of stars, as initially observed by Milne,7 suggested by Wildt,8 and explained by Chandrasekhar,9 and is a general probe for studies of circumstellar atmospheres.

With the advent of molecular astrophysics, the spectrum of the hydrogen molecule has come to play increasingly important roles in astronomical observations. The quadrupole-induced vibration–rotation spectrum of H₂, initially observed in the laboratory by Herzberg,10 has now been observed not only in planetary atmospheres,11 circumstellar space12 and interstellar space,13 in our galaxy, but also very strongly in extragalactic objects.14 The infrared emissions for the ν = 1 → 0 fundamental band from superluminous galaxies are extremely intense [∼10⁸ L₆₃;† for the S(1) line in NGC 6240],15–17 and pure rotational emissions show an extremely high temperature of gaseous hydrogen in certain regions. (Up to J = 17 → 15 has been observed in OMC,18 the energy of the upper state corresponds to a temperature of 21 600 K.)

The electronic transition of H₂ in the vacuum ultraviolet region, initially studied in the laboratory by Lyman19,20 and Werner,21 has been observed in interstellar space as strong absorption lines by a rocket spectrometer of Carruthers22 and the Copernicus satellite spectrometer of Spitzer and his colleagues.23 Even the VUV spectrum of HD is sufficiently strong to be clearly detected.24 Just as the presence of abundant H⁻ is detected through broad bound–free and free–free absorption, the abundant H₂ in Uranus and Neptune was first identified by Herzberg25 in the spectrum taken by Kuiper26 through the collision-induced, near-infrared spectrum of H₂. Note that this was the first detection of extraterrestrial H₂. More recently the abundant H₂ in Jupiter and Saturn was identified by McKellar27,28 in the spectrum by Gautier et al.29 through the H₂ dimer spectrum. The spectrum was also suggested in the mid-infrared region by Trafton and Watson.30

In all these cases hydrogenic species introduced something fundamentally new theoretically, experimentally and observationally. The impact of hydrogenic species on physics, astronomy and chemistry has been more thoroughly discussed in the two inspiring reviews of hydrogenic species by Herzberg.31,32

The purpose of this paper is to discuss yet another hydrogenic species, protonated hydrogen H₃⁺, whose spectrum was observed in the laboratory in 198033 and recently has been observed in space. It is likely that this spectrum plays a unique role in the study of the universe.

Thumbnail Sketch of H₃⁺

H₃⁺ is the simplest stable polyatomic system, in which three protons are bound by two electrons. It was discovered by J. J. Thomson34 in the early days of mass spectrometry, and since then a great many experimental and theoretical studies have been reported. Readers are referred to a review article for detail.35 We summarize below some fundamental properties of H₃⁺ needed for this discussion. (1) The H₃⁺ system is well bound. The proton affinity of H₂ (i.e., the dissociation energy of H₂ into H + H⁺) is 4.4 eV,† equal to the dissociation energy of H₂. (2) The three protons are equivalent, and the two electrons are paired. The equilibrium structure is an equilateral triangle. There is neither a permanent dipole nor an electronic magnetic moment. (3) While its ground state is stable, H₃⁺ has no stable electronic excited states, except for a triplet state very close to its second dissociation limit. Therefore its spectroscopic detection must be through either vibration–rotation transitions or rotational transitions induced by intramolecular interaction or isotopic substitution. (4) H₃⁺ is the most abundant ionic species in molecular hydrogen plasmas both in the laboratory and in space. This is because of the extremely efficient ion–neutral reaction

\[
H₂ + H₃⁺ \rightarrow H₃²⁺ + H
\]

(1)

which has a large Langevin rate (∼10⁻⁹ cm³ s⁻¹) and exothermicity (∼1.7 eV). (5) H₃⁺ is destroyed by wall collisions (in the laboratory), electronic recombination, and the proton–hole reactions,

\[
H₃⁺ + X \rightarrow H₂ + HX⁺
\]

(2)

This reaction is efficient for almost all molecules and atoms because of the relatively low proton affinity of H₂. Thus H₃⁺

† 1 eV ≈ 1.60218 × 10⁻¹⁹ J.

1 1 L₆₃ = 3.8 × 10²⁶ W; solar luminosity.
acts as the universal protonator in space and initiates interstellar chemistry. Once protonated, the reactions

$$HX^+ + Y \rightarrow XY^+ + H$$

proceed rapidly as opposed to the direct reactions

$$X + Y \rightarrow XY + h\nu$$

The great many papers that led to these conclusions are found in ref. 35.

### Spectrum in the Laboratory

#### Fundamentals

The normal vibrations of $H_2^+$ are shown in Fig. 1. The totally symmetric $v_1$ mode is infrared inactive, and the doubly degenerate $v_2$ mode is infrared active. The doubly degenerate mode has unit vibrational angular momentum $(\zeta_2 = -1)$ as initially shown by Teller. The vibrational states of $H_2^+$ are specified by two vibrational quantum numbers $v_1$ and $v_2$ and the vibrational angular momentum quantum number $l$. The vibrational energy structure of $H_2^+$ relevant for astronomical observations is shown in Fig. 2. The transitions observed in the laboratory are shown by upward-pointing arrows, while the emissions observed in astronomical objects are shown by bold downward-pointing arrows. The numbers in parentheses are $|l|$

The rotational energy levels are uniquely specified by three quantum numbers: the rotational angular momentum $J$ and its projection on the molecular axis $k$, and the vibrational angular momentum $l$. The last enters through the vibration-rotation interaction. The approximate rotational energy levels of $H_2^+$ are given by

$$E_J(J, K, l) = BJ(J + 1) + (C - B)k^2 - 2\zeta (Ckl + E_J(J, k, l))$$

(3)

where $B$ and $C$ are the rotational constants for the specified vibrational levels and $\zeta$ is the Coriolis coupling constant. $E_J(J, k, l)$ represents the higher-order centrifugal correction to the rotational energy which is treated in a variety of ways. There are many vibration-rotation coupling terms which have been treated by Watson in the traditional contact transformation formalism. The largest of them is the term

$$H_J = \frac{q^2 J_1^2 + q^2 J_2^2}{4}$$

(4)

where $q$ is the $l$-doubling constant, and $J_1$ and $J_2$ are the vibrational and the rotational ladder operators for $J$ and $k$, respectively. This term mixes levels ($J, K, l + 1$) and ($J, K - 1, l - 1$) and causes $l$-type doubling when the levels are degenerate and the $l$-type resonance otherwise. The effect of this term is universal and dominating in $H_2^+$ for the following reasons: (1) The value of $q$ is exceptionally large ($ca. -5.38 \text{ cm}^{-1}$) because of the large vibrational anharmonicity and small mass. (2) The relations $B \approx 2C$ and $C \approx -C$ cause the two interacting levels to always be nearly degenerate. For these reasons the two levels are completely mixed; $k$ and $l$ individually are no longer good quantum numbers, but $k - l$ is. It is for this reason that $|k - l|$ or $G$ has been used to specify the levels of $H_2^+$. In order to discriminate the two mixed levels with the same $G$, the labels I and II were used in the earlier papers in analogy with Fermi resonance. Watson introduced the $U = \pm 1$ label (+1 for the upper level), and this notation is currently used.

The analysis of the $v_1$ fundamental band was done using the traditional formalism for an ever increasing number of observed transitions. This formalism has met difficulties, however, in interpreting spectral lines related to higher energy levels because of the unusually large vibration-rotation interaction in $H_2^+$. Brute force variational calculations using supercomputers have taken its place. Readers are referred to ref. 43. It is nevertheless necessary to be versed in the traditional formalism to have understanding of, and insight into, the general energy structure, assignment of quantum numbers and selection rules.

In order to understand the selection rules, it is useful to identify three quantum numbers that stay good even after the levels are badly mixed; they are $J$, the parity $\pm$, and the total nuclear spin angular momentum $I$ ($I = I_1 + I_2 + I_3$). These quantum numbers are related to the invariance of the Hamiltonian with respect to rotation in space, to space inversion, and to (123) permutation. If we ignore the very small hyperfine interaction, they are good quantum numbers and follow the rigorous selection rules

$$\Delta J = 0, \pm 1$$

(5a)

$$\pm \leftrightarrow -$$

(5b)

and

$$\Delta I = 0$$

(5c)

for electric single-photon transitions. In the $H_2^+$-type molecules, parity is related to the evenness or oddness of $k$ as parity $= (-1)^k$, and the $J = 3/2$ (ortho) and the $l = 1/2$ (para) spin wavefunctions combine with the $G = 3n$ and the $G = 3n \pm 1$ coordinate wavefunctions, respectively. Thus the last two selection rules are equivalent to

$$\Delta k = \text{odd}$$

(6b)

and

$$\text{ortho} \leftrightarrow \text{para}$$

(6c)
In discussing the intensities of forbidden transitions, eqn. (6c) is more conveniently written as:

\[ \Delta g = 3n \quad (n \text{ integer}) \]  

(6d)

where \( g \equiv k - 1 \). Eqn. (5a) and eqn. (6) give the selection rules which are always followed. The strongest transitions are those with the smallest value of \( \Delta k \) (i.e., \( \Delta k = \pm 1 \)) and \( n \ U \) is not a quantum number, and it has no place in the selection rules.

\[ v_2 \text{ Fundamental Band} \]

The rovibrational transitions between the \( v_2 \) state and the ground state are the strongest and are best suited for astronomical observations. The laboratory observation of this band has been substantially extended \(^{33,39,40,41,46-50} \) since its initial discovery. Effort has continually been made to observe weaker transitions corresponding to higher rotational levels, in anticipation of their detection in hot astronomical objects. To date, 190 rovibrational transitions have been identified within the spectral range 3579–1798 cm\(^{-1} \). The highest rotational level so far observed is \( J = K = 15 \) with the energy of 5092 cm\(^{-1} \) (= 7327 K, 0.63 eV). A computer-generated stick diagram of the fundamental band is shown in Fig. 3 for assumed temperatures of \( T = 250, 500, 1000 \) and 2000 K. The first two temperatures correspond approximately to the rotational temperatures of \( \text{H}_2^+ \) in pure \( \text{H}_2 \) discharges in liquid-N\(_2\)-cooled and water-cooled plasma tubes, respectively. Likewise, 500 and 1000 K correspond approximately to the rotational temperatures of \( \text{H}_2^+ \) in He-dominated \( \text{H}_2 \) discharges in the respective plasmas. The experimental details may be found in the original papers. \(^{33,40,41,46} \) The values of individual frequencies, intensities, Einstein coefficients of spontaneous emission, etc., are listed in a table in ref. 51. This table has been revised considerably; new tables are available upon request.

Fig. 4 shows the energy structure and individual transitions for low rotational levels. The transitions are best specified by giving all labels \( (J, G, U) \leftarrow (J, K) \). Nevertheless, the traditional spectroscopist’s shorthand is sometimes useful. This may be done by looking at the actual energy level structure in the \( v_2 \) state. Thus, for example, \( (J, G, U) \leftarrow (J, K): \) \( (3, 2, +1) \leftarrow (2, 2), (3, 1, +1) \leftarrow (2, 1), (3, 0, +1) \leftarrow (2, 0) \) and \( (3, 1, -1) \leftarrow (2, 1) \) correspond to \( R(2, 2)' \), \( R(2, 1)' \), \( R(2, 0)' \) and \( R(2, 1)^{-1} \), respectively. Note that the \( K = 0 \) levels in the ground state with odd \( J \) are not allowed by the Pauli principle. \(^{44} \)

\[ \text{Hot Bands} \]

All three hot bands \( 2v_2(2) \leftarrow v_2, 2v_2(0) \leftarrow v_2 \) and \( v_1 + v_2 \leftarrow v_1 \) which are allowed from the first excited states of \( v_1 \) and \( v_2 \) have been identified. \(^{46} \) They are weaker than the fundamental bands, typically by a factor of ca. 50, owing to the Boltzmann factors for the vibrationally excited states in laboratory plasmas \( (T_e \approx 1000 \text{ K}) \). \(^{46} \) So far 112, 29 and 44 rovibrational transitions have been identified for each respective band. \(^{46,49} \)

Fig. 3 Computer-generated stick diagrams of the absorption spectrum of the \( v_2 \) fundamental band of \( \text{H}_2^+ \) at four different temperatures. Note the large number of lines at ca. 2500 cm\(^{-1} \) and Q branch transitions with the band origin at 2521.3 cm\(^{-1} \).

Fig. 4 Lower rotational energy levels of \( \text{H}_2^+ \) in the \( v_2 \) state and the ground state. They are specified by \( J, G, U \) and \( J, K \), respectively; see text. The allowed rovibrational transitions are shown by vertical lines.
Computer-generated stick diagrams of the observed transitions are given in Fig. 5.

During the preparation of this manuscript, we identified a hot-band transition in the Jupiter spectrum (see below). We believe the sensitivity of modern spectrometers is sufficient to observe many of them. These spectral lines will serve as a useful thermometer for astronomical objects.

Overtone Bands

Because of the small mass of the proton, the decrease of the transition dipole moment as we move to higher overtone bands of H\textsuperscript{3+} is not as drastic as in ordinary molecules. The band origins, transition moments, relative intensities and Einstein’s spontaneous emission probabilities theoretically calculated by Dinelli, Miller and Tennyson\textsuperscript{52} are listed in Table 1. Note that the value of A\textsubscript{j} is larger for the 2\textnu\textsubscript{2}(2) overtone band than for the \textnu\textsubscript{2} fundamental band because the \nu\textsuperscript{3} factor in the Einstein formula overrides the reduction of |\mu|\textsuperscript{2}. This explains the strong 2 \mum overtone emission observed in Jupiter.\textsuperscript{53,54}

In the laboratory, the 2\textnu\textsubscript{2}(2) first overtone band\textsuperscript{48} and the 3\textnu\textsubscript{2}(1) second overtone band\textsuperscript{55,56} have thus far been observed. The selection rules (6b) and (6d) require for this band \Delta k = \pm 1, \Delta \nu = \pm 2, i.e., \Delta \nu = \pm 3. Thus combinations

\[\textnu_1 + \textnu_2 \leftrightarrow \textnu_2\]

\[2\textnu_2(0) \leftrightarrow \textnu_2\]

\[2\textnu_2(2) \leftrightarrow \textnu_2\]

Fig. 5 Computer-generated stick diagrams of the three observed hot bands 2\textnu\textsubscript{2}(2) \leftrightarrow \textnu\textsubscript{2}, 2\textnu\textsubscript{2}(0) \leftrightarrow \textnu\textsubscript{2} and \textnu\textsubscript{1} + \textnu\textsubscript{2} \leftrightarrow \textnu\textsubscript{1} at a temperature of 1000 K.

Table 1 Intensities of fundamental, overtone and combination bands predicted by Dinelli, Miller and Tennyson\textsuperscript{52}

<table>
<thead>
<tr>
<th>bands</th>
<th>band origin</th>
<th>transition moment/D\textsuperscript{4}</th>
<th>relative intensity\textsuperscript{b}</th>
<th>A\textsubscript{j}/s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textnu\textsubscript{2}(1)</td>
<td>2521.3</td>
<td>0.160</td>
<td>1</td>
<td>129</td>
</tr>
<tr>
<td>\textnu\textsubscript{2}(2)</td>
<td>4997.4</td>
<td>0.009</td>
<td>1/7</td>
<td>145</td>
</tr>
<tr>
<td>\textnu\textsubscript{1} + \textnu\textsubscript{2}(1)</td>
<td>5553.7</td>
<td>0.0026</td>
<td>1/3900</td>
<td>0.35</td>
</tr>
<tr>
<td>\textnu\textsubscript{3}(1)</td>
<td>7003.5</td>
<td>0.0121</td>
<td>1/180</td>
<td>15.7</td>
</tr>
<tr>
<td>\textnu\textsubscript{1} + \textnu\textsubscript{2}(2)</td>
<td>7868.7</td>
<td>0.0097</td>
<td>1/270</td>
<td>14.4</td>
</tr>
<tr>
<td>2\textnu\textsubscript{1} + \textnu\textsubscript{2}(1)</td>
<td>8487.0</td>
<td>0.0028</td>
<td>1/3300</td>
<td>1.5</td>
</tr>
<tr>
<td>4\textnu\textsubscript{2}(2)</td>
<td>9107.6</td>
<td>0.0054</td>
<td>1/890</td>
<td>6.8</td>
</tr>
<tr>
<td>5\textnu\textsubscript{1}(f)</td>
<td>10870.0</td>
<td>0.0026</td>
<td>1/3800</td>
<td>2.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} D \approx 3.3356 \times 10\textsuperscript{-30} C m. \textsuperscript{b} This applies to laboratory absorption spectroscopy. \textsuperscript{c} J. K. G. Watson, personal communication.

of the sum of the \textnu\textsubscript{2} fundamental and the 2\textnu\textsubscript{2}(2)-\textnu\textsubscript{2} hot band (\Delta \nu = 0 for both) and the 2\textnu\textsubscript{2}(2) overtone band yield combination differences in the ground state between levels with different k (\Delta k = \pm 3) and allow us to determine their absolute energy values.

Forbidden Transitions

Weaker rovibrational transitions of \textnu\textsubscript{1} \binding 0 and of \textnu\textsubscript{1} + \textnu\textsubscript{2} \binding \textnu\textsubscript{2} have been observed in the laboratory\textsuperscript{62} based on the theoretical calculation of Miller et al.\textsuperscript{62} The \textnu\textsubscript{1} \binding \textnu\textsubscript{2} transition with the band origin at 600 cm\textsuperscript{-1} has yet to be observed. These transitions induced by various vibration-rotation mixing terms, are much weaker than the other transitions discussed so far and are not likely to be convenient astronomical probes. However, they will play important roles in the radiative thermalization of H\textsubscript{3}\textsuperscript{+} in interstellar space. For example, H\textsubscript{3}\textsuperscript{+} molecules produced in the \textnu\textsubscript{2} state will relax to the ground state via the cascading transitions \textnu\textsubscript{1} \binding \textnu\textsubscript{2} and \textnu\textsubscript{2} \binding 0.

Forbidden pure rotational transitions of H\textsubscript{3}\textsuperscript{+}, following the selection rules \Delta k = \pm 3, occur in the wide region from millimetre wave to mid-infrared.\textsuperscript{57,58} These transitions are caused by centrifugal distortions of the symmetric structure.\textsuperscript{45,59,60} No laboratory observation of them has been reported so far. These transitions are much weaker than the usual dipole-allowed rotational transitions in polar molecules, and their spontaneous emission rates range from ca. 10\textsuperscript{-9} s\textsuperscript{-1} to ca. 10\textsuperscript{-2} s\textsuperscript{-1}. Nevertheless, such weak transitions may be observable in low-density regions just like the H\textsubscript{2} quadrupole transitions. Also, the spontaneous emission lifetimes are short compared with the collisional time in low-density areas, making the forbidden rotational transitions important processes for cooling the rotational temperature of H\textsubscript{3}\textsuperscript{+}.

H\textsubscript{3}\textsuperscript{+} Spectrum in Astronomical Objects

Because of the efficient reaction (1), H\textsubscript{3}\textsuperscript{+} is expected to be produced in abundance in areas with (a) a large amount of H\textsubscript{2} and (b) a significant degree of ionization. Since both of these conditions are met by a great variety of gaseous astronomical objects, the H\textsubscript{3}\textsuperscript{+} spectrum may become a general means to probe weakly ionized areas. Searches for the spectrum in interstellar space have been attempted so far without success. In the meantime, strong infrared emission of H\textsubscript{3}\textsuperscript{+} has been observed in the planetary ionospheres of Jupiter, Uranus and Saturn. Its detection in Supernova 1987A has been claimed. Here we summarize these observations and possible future observations in various objects. Readers are referred to a review\textsuperscript{61} for a more informal summary.

H\textsubscript{3}\textsuperscript{+} in Interstellar Space

Recent work on ion-molecule reactions indicates that the molecular ion H\textsubscript{3}\textsuperscript{+} may also be expected in interstellar space.\textemdash It now appears desirable to consider the possibilities for detecting H\textsubscript{3}\textsuperscript{+} because this molecular ion may be present under some circumstances to the virtual exclusion of H\textsubscript{2}.


The H\textsubscript{3}\textsuperscript{+} molecular ion plays the pivotal role in the ion-neutral reactions scheme now generally believed to be the major mechanism for the chemical evolution of dense molecular clouds.\textsuperscript{53–57} H\textsubscript{3}\textsuperscript{+} is produced through cosmic ray ionization of H\textsubscript{2} followed by the ion-neutral reaction (1). Since the latter reaction is extremely fast, the rate-determining process for the production of H\textsubscript{3}\textsuperscript{+} is the cosmic ray ionization, whose rate is generally taken to be \zeta \approx 10\textsuperscript{-17} s\textsuperscript{-1}.\textsuperscript{63,64} The main destruction mechanism of H\textsubscript{3}\textsuperscript{+} is the proton-hop reaction (2).
Equating the rates of production and destruction, we obtain for the study-state number densities of $H_2^+$, $H_2$, and X.

$$n(H_2^+)/n(H_2) = \zeta/(\kappa n(X)) \tag{7}$$

where $k$ is the rate constant for reaction (2) which is the Langevin rate (ca. $10^{-9}$ cm$^3$ s$^{-1}$) or a little higher if $X$ is polar. Thus $n(H_2^+)/n(H_2) \approx 10^{-4} $ cm$^{-3}$/n(X). For $n(X) \approx 1$–100 cm$^{-3}$, we obtain $n(H_2^+)/n(H_2) \approx 10^{-6}$–$10^{-10}$. More detailed chemical model calculations gave $n(H_2^+)/n(H_2) = 1.1 \times 10^{-9}$, $9 \times 10^{-11}$ (Prasad and Huntress$^{68}$), $5.3 \times 10^{-10}$ (Millar and Freeman$^{71}$), $1.3 \times 10^{-10}$, $5 \times 10^{-11}$ (Watt$^{72}$), $6.3 \times 10^{-10}$ (Brown and Rice$^{73}$), $1.8 \times 10^{-9}$ (Herbst and Leung$^{74}$), and $3 \times 10^{-9}$ (Langer and Graedel$^{68}$). For the $H_2$ column density of $2 \times 10^{27}$ cm$^{-2}$ of Orion A(KL) and Sgr B2(OH), the last number gives the $H_2^+$ column density of $6 \times 10^{14}$ cm$^{-2}$.

Owing to the low temperature and quiescent conditions in dense clouds, the infrared spectrum of $H_2^+$ is expected in absorption. Thus some bright infrared object required behind the cloud containing $H_2^+$. Since $n(H_2^+)$ is inversely proportional to the concentration of the proton acceptor $X$ (which is mostly CO), de Jong, Dalgarno and Boland$^{74}$, and Lepp, Dalgarno and Sternberg$^{75}$ recommended searching for $H_2^+$ in carbon-depleted clouds. Thus obscured infrared objects, such as W33A where a strong solid CO spectrum was reported by Geballe$^{76}$, are more promising sources.

Because of the low temperature in dense molecular clouds and the high rotational constants of $H_2^+$, only the lowest few rotational levels are significantly populated. The lowest rotational level is $J = 1, K = 1$ which is para-$H_2^+$ and has the lower weight of the 2:1 spin statistics. (Note that the $J = 0, K = 0$ level is not allowed by the Pauli principle. The lowest ortho level $J = 1, K = 0$ is higher than the $J = K = 1$ level by 22.84 cm$^{-1}$. Thus, in the spin statistical weight, the $J = K = 1$ level is more populated for $T < 48$ K. The next lowest level $J = K = 2$ is higher by 105.18 cm$^{-1}$, and its population is negligible at the low temperatures of dense clouds. A computer-generated stick diagram for the $H_2^+$ spectrum at 30 K is given in Fig. 6. The assignments, frequencies and the squares of the transition moments are listed in Table 2. Each of these spectral lines has some nearby atmospheric interference which may be avoided by choosing the time of optimum Doppler shift. Oka$^{77}$ used lines 1 and 2, $\nu_2 = 0$ 30 K.

![Fig. 6](image-url)  
A computer-generated stick diagram of the $\nu_2$ fundamental band for $T = 30$ K. This simple spectrum should represent absorption in dense clouds.

| line no. | transition | frequency/cm$^{-1}$ | $|\mu |^2/10^{-7}$ cm$^2$ 

| 1 | 2, 1, +1 $\rightarrow$ 1, 1 | 2736.219 | 1.58 |
| 2 | 2, 0, +1 $\rightarrow$ 1, 0 | 2725.898 | 2.59 |
| 3 | 2, 1, $\rightarrow$ 1, 1 | 2691.444 | 1.41 |
| 4 | 1, 1, +1 $\rightarrow$ 1, 1 | 2545.418 | 1.28 |
| 5 | 1, 0, $\rightarrow$ 1, 0 | 2529.724 | 2.54 |
| 6 | 0, 1, +1 $\rightarrow$ 1, 1 | 2457.960 | 0.86 |

Geballe and Oka$^{77}$ 5 and 6, and Black et al.$^{78}$ 3. The standard formula$^{39,79}$ gives the peak absorption as

$$\alpha = \Delta l/I = 5.86 \times 10^{-14} N(H_2^+)/f_{jk}(T) |\mu_j|^2/\Delta v \tag{8}$$

where $N(H_2^+)$ is the column density of $H_2^+$ in cm$^{-2}$, $f_{jk}(T)$ is the temperature-dependent fraction of molecules in the given $J$, $K$ level, $|\mu_j|^2$ is the square of the transition dipole moment in D$^2$, and $\Delta v$ is the linewidth (HWHM) in km s$^{-1}$. If we apply this formula for line 5 at 30 K ($f_{jk} = 0.398$), and for a spectrometer with $\Delta v = 10$ km s$^{-1}$ and the minimum detectable absorption $\Delta n_{\text{min}}$ of 5%, we find the column density of $H_2^+$ needed for the observation to be $8 \times 10^{13}$ cm$^{-2}$, a value comparable to the predicted values given earlier. Compared with the recent infrared detection of more abundant neutral molecules such as CH$_4$ and C$_2$H$_2$ and HCN, the expected column density of $H_2^+$ is two to three orders of magnitude lower. However, the $H_2^+$ absorption should be comparable to those of $^{13}$C$_2$H$_2$ and OCS which were also reported because of the smaller rotational partition function and larger transition dipole moment.

So far, unsuccessful searches for $H_2^+$ in BN, GL 2591, LkH$_2$101, NGC 2024/IRS, W331R, NGC 2264 and AFGL 2591 have been reported. Black et al.$^{78}$ observed spectral lines of CO simultaneously with their search for $H_2^+$. The abundance of CO thus obtained together with the upper limit of the $H_2^+$ column density set a limit on the value of the cosmic ray ionization $\zeta$ through eqn. (7). van Dishoeck and Black have proposed on chemical grounds that the abundance of $H_2^+$ may be equally high in diffuse interstellar clouds.

Further increases in sensitivity and resolution of observational spectrometers will lead us to the detection of $H_2^+$ in interstellar space. If detected, the spectrum will give crucial information on the working of the ion–neutral recombination scheme for the chemical evolution of molecular clouds.

$H_2^+$ in Planetary Ionospheres

While the conscious search for the absorption spectrum of $H_2^+$ was being made in interstellar space over several years without success, the $H_2^+$ spectrum was found by chance as intense infrared emission in the auroral regions of Jupiter by two groups of astronomers. In 1989 Drossart et al. reported$^{53}$ vibrational transitions in the region 5000–4557 cm$^{-1}$ that were assigned to the $2v_2(2) \rightarrow 0$ first overtone of $H_2^+$, and Trafton et al.$^{54}$ reported five features comprising six transitions of the same band. Until then the overtone band was unknown to laboratory spectroscopists. For us (the authors), the intense spectrum from Jupiter, the strong overtone band and emission rather than absorption were all anticipated and were revelations. Readers are referred to ref. 61 for more information. A computer-generated stick diagram of the $2v_2(2) \rightarrow 0$ emission band is shown in Fig. 7. The full range of the spectrum which extends over 1500 cm$^{-1}$ may some day be employed for useful purposes.

After the observation of the 2 mm overtone emission band, even stronger emission for the 4 mm fundamental $\nu_2$ band was observed$^{83–85}$ The extensive Fourier-transform infrared emission spectrum reported by Maillard et al.$^{85}$ is shown in Fig. 8. This spectrum matches very well with the laboratory spectrum for $T = 1000$ K given in Fig. 3 (except for the intensity of the line corresponding to the 4, 3, $-1 \rightarrow 3, 3$ transition at 1289.923 cm$^{-1}$ which is stronger in Fig. 3; Telluric line absorption was mentioned by the authors as a possible cause for the anomaly$^{86}$). The observed emission spectrum given in Fig. 7 is remarkably free from Jovian background emission. Especially in the region 2900–2600 cm$^{-1}$, the background is almost non-existent. The infrared radiation from Jupiter is all absorbed by the pressure-broadened spectrum of CH$_4$ in the
Our most recent observation\textsuperscript{60} has added a new chapter to this already rich field. First we found that the H$_3^+$ emission is not limited to the polar regions but is observable over the entire planet. A spectral image of Jupiter is shown in Fig. 9. As we move from the polar regions to the equator, the emission decreases by one order of magnitude but is still clearly visible. The observation of H$_3^+$ emission will provide a useful means to study the Jovian ionosphere including its temporal variation. Secondly, we have detected a hot band transition 2v$_2$(0) → v$_2$ (9, 9 → 8, 9, 1), with an intensity of ca. 1/50 of neighbouring fundamental band lines. Unlike H$_2^+$ in the 2v$_2$(0) state which can radiatively relax directly to the ground state through Δν = 2 (overtone) transitions, H$_3^+$ in the 2v$_2$(0) state relaxes only through cascading Δν = 1 transitions. More observations of hot band lines including 2v$_2$(2) → v$_2$ and v$_1$ + v$_2$ → v$_1$ will enable us to determine temperatures directly and to acquire more knowledge about the dynamics of the Jovian ionosphere.

On April 1 1992 the 4 μm emission spectrum of H$_3^+$ was observed in Uranus by Trafton \textit{et al.}\textsuperscript{71} Twelve emission features comprising 21 Q branch transitions of the fundamental v$_2$ band have been detected between 2570 and 2545 cm$^{-1}$ with the resolution of ca. 1300. The emission lines are weaker than those from Jupiter by two orders of magnitude but were observed with a good signal-to-noise ratio because of the small background and of the high sensitivity of the spectrometer (CGS4). Considering the fact that Uranus has a smaller diameter (ca. 1/3) and much smaller magnetic moment (ca. 1/410) than Jupiter, and is four times further away from Earth, the emission is amazingly intense and suggests great plasma activity in this planet whose magnetic axis is tilted from the axis of rotation by 58.6°.

On July 18 1992, the H$_3^+$ emission spectrum was observed in Saturn. The emission is weaker than that of Jupiter by three orders of magnitude, but the doublet at 2725.898 cm$^{-1}$ (2, 0, 1 → 1, 0) and 2726.219 cm$^{-1}$ (2, 1, 1 → 1, 1) and the singlet at 2829.428 cm$^{-1}$ (4, 3, 1 → 3, 3) have been clearly identified. Observation of Q branch lines was hampered by a stronger background.

On the whole observation of H$_3^+$ emission has emerged as a useful ground-based observational method for the study of plasma activities in the outer planets.

\textbf{Other Astronomical Objects}

A most surprising paper appeared early this year in which Miller \textit{et al.}\textsuperscript{92} claimed detection of H$_3^+$ emission in the infrared spectrum of Supernova 1987A reported by Meikle \textit{et al.}\textsuperscript{93} The spectral features, that are most clearly noted in a spectrum 192 days after the event, are a blend of H$_3^+$ rovibrational transitions which are Doppler-broadened owing to the rapid expansion of the gas. Since the detailed fingerprint of the individual rovibrational lines is absent, the detection in Supernova 1987A is not very definitive, but their theoretically convoluted spectrum matches well with two observed strong emission features which had remained unidentified. Formation of molecular species within such a short period after the violent catastrophe seems difficult, but there is convincing spectroscopic evidence\textsuperscript{94} and a theoretical argument\textsuperscript{95} that CO exists abundantly after ca. 100 days. From a chemical-model calculation, Miller \textit{et al.}\textsuperscript{92} indeed show that formation of H$_3^+$ with the total mass of ca. 10$^{-7}$ M$_\odot$\textsuperscript{+} is possible. (This is approximately the amount of H$_3^+$ needed to explain the observed strong features.)

All those previous astrophysical studies related to H$_3^+$ suggest that no gaseous object should be neglected as a post-
sible source of the $\text{H}_2^+$ spectrum. The dense and diffuse clouds, planetary ionospheres and supernovae are widely different astronomical objects. The universal nature of the reaction (1) indicates that there always is the possibility that abundant $\text{H}_2^+$ exists as long as there are plenty of hydrogen gas and active plasmas. One guiding principle from the experience of detecting the $\text{H}_2^+$ emission in the Jovian ionosphere is to search for objects in which intense $\text{H}_2$ quadrupole emission is seen. Thus hot infrared objects, planetary nebulae, superluminous galaxies, and H–H objects are all possible candidates. The vibrational excitation of $\text{H}_2$ in these areas proceeds through collisional excitation due to hot gas in shockwave-heated areas; ultraviolet pumping by stellar radiation; or plasma excitation by charged particles in local magnetospheres. Stars, which are assumed to provide the vacuum ultraviolet radiation for the second mechanism in the wavelengths below 914 Å which excites the Lyman and Werner band of $\text{H}_2$, must also provide radiation for ionization. The existence of many vibrationally excited $\text{H}_2$ molecules also accelerates the ionization. However, such radiation will also photodissociate $\text{H}_2^+$ efficiently. $\text{H}_2^+$ will exist most abundantly in the areas with high magnetohydrodynamic activity where such UV photons do not penetrate.

Fig. 9 A spectral image of Jupiter from 2833 to 2821 cm$^{-1}$

It is our pleasure to acknowledge collaboration over many years with J. K. G. Watson, T. R. Gehalle and S. Miller. Many of their ideas have entered in this paper. This work has been supported by N.S.F. grant PHY-90-22647 and US Air Force Contract F33615-90-2035.

References
1 J. Fraunhofer, Denkschreiben der königlichen Akademie der Wissenschaften zu München, 1817, 5, 193.
3 N. Bohr, Philos. Mag., 1913, 26, 1.