1. The Infrared Spectrum of H$_3^+$ in Laboratory and Space Plasmas

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I always think that a great joy of being a scientist is meeting people with common interests. This must be the same for people of every profession; but for scientists, especially for spectroscopists, there exists a firm common ground and often similar temperament and personality that allow us to delve deeply into conversation, even with people whom we meet for the first time. I feel I am extremely lucky to have met Professor Rango Krishna Asundi in 1979 at the 87th IAU Symposium on Interstellar Molecules in Mont Tremblant near Montreal. Asundi was 84 years old then, but he was in excellent physical and mental condition. He had such good hearing and exceptionally keen perception that we could communicate very well even during a noisy reception. All through the conference we talked about science and scientists and the great Hindi epic Mahabharata. He was an unassuming person with enormous knowledge, and somehow I could speak very freely with him.

Some time later I received from him a reprint of his paper titled "Molecules in Interstellar Space," which turned out to be his last paper [1]. In this paper Asundi discusses the optical and microwave observation of interstellar molecules. His extensive description of cyanopolyacetylenes, which were discovered from 1976 to 1979 [2–4], and Douglas’ conjecture [5] (proposed in 1977) on the diffuse interstellar band as being due to carbon chain molecules, show that Asundi kept abreast with the most recent developments of molecular astrophysics throughout the last years of his life.

1. Molecules and Plasmas in the Universe
In this chapter I would discuss about the infrared spectrum of the protonated hydrogen molecule H$_3^+$, in laboratory and space plasmas, very much in the spirit of Asundi. First, I would like to emphasize the fact that molecules are everywhere in the universe. Compared with atoms, molecules are fragile. While atoms survive any number of ionizations most molecules fall apart
if more than one electron is removed. Therefore, molecules were initially thought not to be abundant in space because of photodissociation due to stellar ultraviolet radiation. As observational techniques progressed, however, it has become increasingly clear that this is not the case. The advent of optical molecular spectroscopy has revealed the existence of many diatomic radicals, both in stellar atmospheres and in interstellar space [6]. Since 1968, when Townes and his colleagues discovered NH$_3$ in Sgr. B2 [7], radioastronomers have observed about 100 stable molecules, free radicals and molecular ions, including many whose spectra were unknown in laboratories at the time of detection. Initially, molecules were thought to be concentrated in dense and diffuse clouds and circumstellar space subtending small solid angles, but later they were shown to exist continuously over much wider regions of space. Thaddeus and his colleagues observed the $J = 1 \rightarrow 0$ CO millimeter wave emission line over wide regions of Orion and Monoceros [8] and the Perseus-Taurus-Auriga complex [9]. They also detected CO emission from extreme outer regions of this galaxy outside the limit of star formation [10]. Millimeters and submillimeter wave CO emissions have been detected in many extragalactic objects. CO, CS, HCN, and HCO$^+$ emissions were reported in distant ultraluminous galaxies with $z = 0.008 - 0.042$ [11, 12] CO emissions from early epoch with $z$ as large as 2.2867 have been reported by Scoville, Yun, Brown, and Vanden Bout [13].

The enormous abundance of molecules, not only in our own galaxy but also in distant extragalactic objects, became even clearer with the development of infrared spectroscopic astronomy. Fig. 1 shows the extremely strong 2.23 $\mu$m quadrupole emission line of H$_2$ 6240 first reported by Joseph, Wynne-Williams [15], and Richer two years away with the spectral Doppler $S_1(1)$ line ($v = 1 \rightarrow 0$, $J = 3 \rightarrow 2$). The total luminosity of all H$_2$ lines exceeds that of the Sun and several percent of the total luminosity of all H$_2$ lines in the universe. Their identification of the Lyman series of H$_2$ has been reported by Cowie and Chaffee, and Black [20], and detection in galaxies in the early age of the universe [21].

Transition in Galaxies—Totally discussed that "large regions of gas and the molecular form following an increasing"

Second, I would like to emphasize the terrestrial atmosphere and the aurora; we see small fractions of ionized, auroral activity, are exceptional consist of plasma [22]. The high velocity of highly stripped metal ions are observed planetary nebulae, galactic halos, are all plasmas. Even inside the nucleus are weakly ionized plasmas because, through them and ionize atoms of TMC1 and the bright plasma spectroscopy. They look very different when it is concerned, they are comparable in order of $10^{-6} - 10^{-7}$. This allows us to probe by observing laboratory plasmas.

2. H$_3^+$

When hydrogen molecules are ionized by the ion-neutral reaction [24]

$$\text{H}_2 + \text{e}^- \rightarrow \text{H}_3^+ + \text{e}^-$$

This reaction is so efficient with $10^{-9} \text{cm}^3 \text{sec}^{-1}$ [25] and the excitations charges in hydrogen plasmas are ionization of H$_3^+$ [26] both in laboratory and in the equilateral triangle, is quite stable.
Therefore, molecules were initially
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techniques progressed, however,
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the existence of many diatomic
species in interstellar space [6]. Since
observed NH$_3$ in Sgr. B2 [7],
stable molecules, free radicals
whose spectra were unknown in
earily, molecules were thought to be
and circumstellar space subtending
area to exist continuously over
and its colleagues observed the
line over wide regions of Orion's
Auriga complex [9]. They also
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$\mu$m quadrupole emission line of H$_2$ from the ultraluminous galaxy NGC 6240 first reported by Joseph, Wright and Wade [14], Becklin, DePoy, and Wynn-Williams [15], and Rieke et al [16]. This object is 300 million light
years away with the spectral Doppler red shift of $z = 0.0254$. The strongest
$S(11)$ line ($v = 1 \rightarrow 0$, $J = 3 \rightarrow 1$) has a luminosity of $-3 \times 10^8$ L$_\odot$, and the total luminosity of all H$_2$ lines is $-3 \times 10^9$ L$_\odot$, equivalent to 3 billion suns and several percent of the luminosity of our galaxy [18]! A clear identification of the Lyman series from $v = 0 \rightarrow 0$ to $v = 4 \rightarrow 0$ in absorption
has been reported by Cowie and Songaila [19] at $z = 2.811$ in the Lyman forest of quasar PKS 0528−250, confirming the earlier report by Foltz, Chaffee, and Black [20], and demonstrating that that molecules also existed
in galaxies in the early age of the universe. All these results show molecular
are abundant in many varieties of galaxies. In a paper titled “The H to H$_2$
Transition in Galaxies—Totally Molecular Galaxies”, Elmegreen [21] has
discussed that “large regions of galaxies can spontaneously convert to
molecular form following an interaction or other event.”

Second, I would like to emphasize the fact that plasmas are everywhere.
Our terrestrial atmosphere and the atmospheres of the inner planets, where
we see small fractions of ionized gas in the ionosphere and during lightning
or auroral activity, are exception. More than 99% of the visible universe
consists of plasma [22]. The interiors of stars are fully ionized plasmas.
Highly stripped metal ions are observed in the solar corona [23]. Nebulae,
planetary nebulae, galactic halos, galactic coronas, diffuse clouds—they
are all plasmas. Even inside the most quiescent gaseous objects, dark clouds,
are weakly ionized plasmas because the ubiquitous cosmic rays penetrate
through them and ionize atoms and molecules. Fig. 2 shows the dark cloud of TMC1 and the bright plasma in my laboratory for molecular ion
spectroscopy. They look very different but, as far as the degree of ionization
is concerned, they are comparable, both having a charge fraction on the
order of $10^{-6}$ − $10^{-7}$. This allows us to study plasmas in astronomical objects
by observing laboratory plasmas.

2. H$_3^+$

When hydrogen molecules are ionized, protonated hydrogen H$_3^+$ is produced
by the ion-neutral reaction [24]

$$H_2 + H_3^+ \rightarrow H_3^+ + H$$

(1)

This reaction is so efficient with the large Langevin rate constant of $-2 \times 10^{-9}$ cm$^3$ sec$^{-1}$ [25] and the exothermicity of $-1.7$ eV that most positive
charges in hydrogen plasmas are in the form of H$_3^+$ “to the virtual exclusion
of H$_3^+$” [26] both in laboratory and in space plasmas. H$_3^+$, in which three
protons are bound by two electrons with the equilibrium structure of an
equilateral triangle, is quite stable if left alone. When it collides with other
The HX⁺ and X⁺ ions produced by ion neutral reactions leading to H⁺ neutral atoms by radioastronomers. This is the chemistry first proposed by Heisenberg and by Watson [28]. This process is an important step in star formation and other aspects of H₂⁺.

3. H₂⁺ in Laboratory Plasmas

Although a great many experiments were performed in the laboratory, it was not until 1980 when the first 15 spectral lines of H₂⁺ were discovered by J.J. Thomson in 1913. As a result, over 700 transitions have been identified.

\[
\text{H}_2^+ + X \rightarrow \text{H}_2 + \text{HX}^+ 
\]

since the proton affinity of H₂, 4.4 eV, is lower than that of most other atoms and molecules. The other abundant ion in space is the atomic helium ion He⁺. Since He has the highest ionization potential, 24.58 eV, of all atoms and molecules, it efficiently ionizes most atoms and molecules through the exchange reaction.
He$^+$ + X → He + X$^+$  \hspace{1cm} (3)

The HX$^+$ and X$^+$ ions produced by the reactions (2) and (3) initiate chains of ion-neutral reactions leading to the more complicated molecules observed by radioastronomers. This is the ion-neutral reaction scheme for interstellar chemistry first proposed by Herbst and Klemperer [27], chairman of this session, and by Watson [28]. The chemical evolution of molecular clouds is an important step in star formation and H$_3^+$ plays a fundamental role in the process. Several review papers [17, 29–37] have been published on this and other aspects of H$_3^+$.

3. H$_3^+$ in Laboratory Plasmas

Although a great many experiments had been reported [29] on H$_3^+$ since its discovery by J.J. Thomson in 1911 [38], the spectrum of H$_3^+$ was not obtained until 1980 when the first 15 spectral lines corresponding to the vibration-rotation transitions of the v$_2$ fundamental band were observed [39]. By now, over 700 transitions have been observed and assigned. Fig. 3 shows the
vibrational states of \( H_3^+ \) in which observed vibrational transitions are indicated by arrows. The assigned transitions are the fundamental \( v_1^0 \leftarrow 0 \) band; the first and second overtone bands \( 2v_1^0 \leftarrow 0 \) and \( 3v_1^0 \leftarrow 0 \); the first hot bands \( 2v_2^0 \leftarrow v_1^0, 2v_2^0 \leftarrow v_2^0, \) and \( v_1 + v_2^0 \leftarrow v_1; \) the second hot bands \( 3v_1^0 \leftarrow 2v_2^0, 3v_2^0 \leftarrow 2v_2^0, \) and \( 2v_1 + v_2^0 \leftarrow 2v_1; \) and forbidden bands \( v_1 \leftarrow 0 \) and \( v_1 + v_2^0 \leftarrow v_1 \), where superscripts indicate the vibrational angular momentum quantum number \( l \). For the observation of the fundamental band, overtone bands, and forbidden bands, liquid-N\(_2\) cooled pure hydrogen discharges were used while for the observation of hot bands, water or liquid N\(_2\) cooled He dominated discharges with \( 10\% \) H\(_2\) were used to increase the vibrational temperature. He atoms with their high metastable state ionize H\(_2\) efficiently through Penning ionization and keep H\(_2\) and H\(_3^+\) in high vibrational states. More details of the spectra obtained up to 1993 will be found in [32] and references exhaustively quoted therein.

Since the H\(_3^+\) emission spectrum observed in ionospheres of Jupiter and other outer planets demonstrate high excitation temperatures of H\(_3^+\) on the order of \( \sim 1100 \) K (see below), we attempted to observe H\(_3^+\) spectral lines corresponding to high rotational levels using a water cooled discharge cell and He dominated gas mixtures. Transitions starting from high rotational levels up to the rotational quantum number \( J = 15 \) and rotational energy of 5502.9 cm\(^{-1}\) have been observed [40]. Observed rotational levels are shown in Fig. 4. (Note that some rotational levels are higher than doubly excited vibrational states shown on the right.) Majewski, McKellar, Sadovskii and Watson reported observation and assignment of many H\(_3^+\) spectral lines in their high temperature hollow cathode emission [41]. We have obtained more spectral lines of the H\(_3^+\) second overtone band \( 3v_1^0 \leftarrow 0 \) using an external cavity controlled InGaAsP near infrared diode laser [42]. Experiments are being prepared to observe higher overtone bands \( 4v_2^0 \leftarrow 0 \) and \( 5v_2^0 \leftarrow 0 \) and the combination band \( v_1 + 2v_2^0 \leftarrow 0 \) using commercially available cavity controlled diode lasers and a Ti: Sapphire laser, and higher hot bands using high temperature plasma cells.

The analysis of the vibration rotation spectrum of H\(_3^+\) is not simple and right from the first observation I have relied on Jim Watson [39]. This might sound paradoxical, but spectroscopists know that the analysis of vibration rotation spectra of simple light polyatomic molecules is much more difficult than that of complicated heavy molecules. This is because (a) a spectra of light molecules span over a wide wave number region (the observed H\(_3^+\) \( v_1 \) fundamental band spans over nearly 2000 cm\(^{-1}\) [40, 43], and (b) the traditional perturbation or contact transformation treatment, which scales with the Born-Oppenheimer constant \( \kappa = (m_e/M)^{1/4} \) does not converge rapidly.

With the development of modern computers, the new variational method for the calculation of rovibrational levels came to the rescue. Sutcliffe and Tennyson [44], who noted that the simplification of the Wilson-Howard

Hamiltonian [45] by Watson [46] on the vibration-rotation spectrum method in which dynamics of the Hamiltonian was solved. A series of papers by Myhrvold [52] applied the variational method to the \( \textit{ab initio} \) potential of Myhrvold, a supercomputer, where indispensible to Watson's variational calculations, using a surface and the discrete variational squares procedure which in turn is Watson's variational calculations. His theoretical values agree with the third excited state. At 4\( v_1 \) the wave function barrier to inactivity and the variational

\[ E^* \] \[ \text{cm}^{-1} \] \[ \begin{array}{cccccc}
6000 & \ldots & \ldots & \ldots & \ldots & \ldots \\
4000 & \ldots & \ldots & \ldots & \ldots & \ldots \\
2000 & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 1 & 2 & 3 & 4 & 5 & 6
\end{array} \]
Vibrational transitions are indicated for the fundamental $v_1 \leftrightarrow 0$ band; the $0$ and $3v_1 \leftrightarrow 0$; the first hot band $v_2 \leftrightarrow v_1$; the second hot bands $2v_1$; and forbidden bands $v_1 \leftrightarrow v_2$ indicate the vibrational angular momentum of the fundamental band. Liquid-N$_2$ cooled pure hydrogen is used to study the spectra obtained up to 1993 and the spectra obtained therein.

Spectra of H$_3^+$ in ionospheres of Jupiter and Saturn indicate the presence of two bands starting from high rotational levels $J = 15$ and rotational energy of observed rotational levels are shown and are higher than those of doubly excited He$_2$ [41]. We have obtained the bands $3v_1 \leftrightarrow 0$ using an external diode laser [42]. Experiments are conducted on the bands $4v_2 \leftrightarrow 0$ and $5v_2 \leftrightarrow 0$ using commercially available cavity diode laser, and higher hot bands using a supercomputer, where indispensable during our assignment of hot bands [52] and overtone bands [53, 54]. More recently we have been relying on Watson’s variational calculations [55, 56] in which he uses a Morse potential based surface and the discrete variable representation method. By using observed spectral lines, Watson modifies the $ab$ initio potential by a least squares procedure which in turn leads to the prediction of still higher levels. Now his theoretical values agree with experiment to within 1 cm$^{-1}$ up to the third excited state. At $4v_2$ the vibrational energy approaches the top of the barrier to incoherence and the variational calculation may diverge. For this reason
measurements of the 4v_2 and 5v_2 states are particularly interesting. The ab initio work on H_3^+ has been summarized by Anderson [57]. In the last few years a considerable amount of work on the ab initio potential of H_3^+ and variational calculation of the vibration rotation energy levels has been published by Lie and Frye [58], Röhse, Klover, and Kutzelnigg [59] Henderson, Tennyson and Sutcliffe [60], Carter and Meyer [61], Bramley, Tromp, Carrington and Corey [62], Röhse, Kutzelnigg, Jacquet and Klover [63], Wolniewicz and Hinz [64] and Jacquet and Röhse [65].

4. H_3^+ in Space Plasmas

Searches for interstellar H_3^+ were initiated immediately after the discovery of its laboratory spectrum in 1980 [66]. Orion BN, IRC + 10216, and CIT were observed at the Kitt Peak National Observatory (KPNO). So far at least four groups of observers have attempted detection of H_3^+—in GL2591, LKHa101, BN, NGC2024/IRS, W33IR at the United Kingdom Infrared Telescope (UKIRT) [67], in NGC2264 and GL2591 at KPNO [68], in CRL618, IC443 and L1457 at UKIRT [69] and in GL2591 at the Canada France Hawaii Telescope [70]. While all these attempts failed, I believe that interstellar H_3^+ will be detected soon because of the recent great improvement in sensitivity and resolution of observational spectrometers using CCD detectors. Although H_3^+ is produced very abundantly in molecular clouds by cosmic ray ionization and the reaction (1), its steady state concentration is not very high because of the rapid reactions with CO, N_2, CO_2, C, O, etc. to produce their protonated species. Therefore, the deeply embedded protostars such as GL2136 [71] are most promising because most of these gases are frozen onto dust in such sources. With the equilibrium structure of an equilateral triangle, H_3^+ does not possess a dipole moment and thus has no rotational spectrum. The centrifugal distortion induced rotational spectrum [72] is sufficiently strong to effectively contribute to radiative thermalization of H_3^+ in space but seems too weak for detection, although Draine and Woods [73] advocated for it. The monodeuterated species H_3D^+, however, has the sizable effective dipole moment of 0.6 D due to the shift of the center of gravity from the center of charge [74]. Since deuterium fractionation [75] makes its concentration much higher than that expected from D natural abundance, the H_3D^+ rotational spectrum may be quite strong. A possible detection of the 1_{10} \rightarrow 1_{11} transition at 372 GHz was reported in NGC2264 [76], but it was later negated [77]. More recently Boreiko and Betz and reported detection of the lowest 1_{01} \rightarrow 0_{00} transition at 1370 GHz in M42 IRc2, which remains to be confirmed [78].

While the expected discovery of H_3^+ in interstellar space is still being attempted after 15 years since the initial attempt, the serendipitous discovery of the strong H_3^+ emission in the auroral regions of Jupiter came all of a sudden [79–81] and developed very quickly. The exciting story of the discovery and identification of H_3^+ has been described in my earlier review [17] and I shall not repeat it here. Figure 1 shows the strong H_3^+ emission spectrum (lower trace) using the FTIR spectrometer in the 2600 cm^{-1} to 2900 cm^{-1} region from 2400 m^{-1} to 2600 cm^{-1}, reflecting the high temperature gas. The red dashed line is opposed to the low H_3^+ rotational spectrum of the cooled laboratory plasma [39]. To [40] in Table 1, McNab [36]; he notes in his captions that "...the spectrum (in the lower trace) is a result of 54 days of scanning to locate the line with a delay time of 72 min."

\[ P(1) \]

2400 2500 2600

Wave Number (cm\(^{-1}\))
particularly interesting. The *ab initio* potential of $H_3^+$ and rotation energy levels has been calculated by Kupper and Kutzelnigg [59] and Carter and Meyer [61], Bramley, Kutzelnigg, Jaqueet and Kopper [65].

Immediately after the discovery of the reaction BN, IRC + 10216, and CIT Observatory (KPNO). So far ated detection of $H_3^+$—in GL2591, at the United Kingdom Infrared and GL2591 at KPNO [68], in Canada [70] and in GL2591 at the Canada these attempts failed, I believe in because of the recent great number of observational spectrometers placed very abundantly in molecular clouds by reaction (1), its steady state and the rapid reactions with CO, N$_2$, and species. Therefore, the deeply hydrogen [71] are most promising because each source. With the equilibrium does not possess a dipole moment and the centrifugal distortion induced strong to effectively contribute to it seems too weak for detection, needed for it. The monodeuterated effective dipole moment of 0.6 D from the center of charge [74].

Its concentration much higher than the $H_2D^+$ rotational spectrum of the $1_{10} \rightarrow 1_{11}$ transition at 2400 cm$^{-1}$ but it was later negated [77]. It was detected of the lowest $1_{01} \rightarrow 2_{01}$ which remains to be confirmed.

The interstellar space is still being discovered, the serendipitous discovery regions of Jupiter came all of a block. The exciting story of the discovery and identification of the $H_3^+$ spectrum as a result of a close collaboration of astronomers, laboratory spectroscopists, and theorists is in my earlier review [17] and shall not repeat it here. Fig. 5 shows the strong $H_3^+$ emission spectrum (lower trace) observed by Maillard et al [82] using the FTIR spectrometer in CFHT, together with a computer generated stick diagram (upper trace) of the $v_5$ fundamental band of $H_3^+$ observed in absorption in laboratory plasmas [39]. In R-branch region from 2600 cm$^{-1}$ to 2900 cm$^{-1}$, the two spectra are practically identical. In Q-branch region from 2400 m$^{-1}$ to 2600 cm$^{-1}$, the Jupiter spectrum shows more lines reflecting the high temperature of Jovian ionosphere ~1100 K [35, 83] as opposed to the low $H_3^+$ rotational temperature ~300 K in my liquid-N$_2$ cooled laboratory plasmas [39]. This figure is taken from the review by I.R. McNab [36]; he notes in his caption "It took 4½ years to locate the spectrum, and 54 days of scanning to locate all the lines shown (in the upper trace). ...the spectrum (in the lower trace) was recorded using a total integration time of 72 min.!

![Diagram of H3+ spectrum](image_url)

**Fig. 5**
The amazing aspect of the Jovian $H_3^+$ emission spectrum is that it is not only very intense, but it is so pure. The spectrum in Fig. 5 is completely free from spectral lines of other molecules, but it is also almost completely free from infrared background. Due to the relatively weak bonding in $H_3^+$ with $r_e = 0.87$ Å, this wave number region is lower than the typical hydrogen stretching vibration of the CH, NH and OH bonds, but is still higher than the typical heavy atom stretching of the CO, CN and NO bonds. Thus, the spectral lines of CH$_4$, NH$_3$, H$_2$O, CO, CO$_2$, N$_2$O, etc. are relatively weak in this region; this also gives the infrared L window where the terrestrial atmospheric interference is not severe. Nevertheless, spectral lines of CH$_4$ and NH$_3$ could appear in this region because of their enormous abundance; the infrared background due to the radiative cooling of Jupiter and to the reflection of the solar radiation could appear strongly and drown these beautiful lines. Here nature work its wonder and lets one of the problems kill the other. CH$_4$ and NH$_3$ exist abundantly at low altitude of Jovian atmosphere with high pressure and low temperature and their pressure broadened spectra wipe out the continuous infrared background. In other words, each of the enormous number of low temperature CH$_4$ and NH$_3$ molecules efficiently converts radiative energy into kinetic energy.

The purity of $H_3^+$ emission is even more clearly seen in higher resolution spectrum observed by Geballe et al [84] shown in Fig. 6. Here the quartet lines in Fig. 5 at −2830 cm$^{-1}$ were observed using the CGS4 grating spectrometer of UKIRT. Note that the spectrum is almost completely free of infrared background. In addition to the four lines (R(3, 2)$^-$ at 2832.197 cm$^{-1}$, R(3, 3)$^-$ at 2829.923 cm$^{-1}$, R(2, 1)$^+$ at 2826.113 cm$^{-1}$ and R(2, 2)$^+$ at 2823.138 cm$^{-1}$) which are visible in Fig. 5, we have two additional lines because of the high sensitivity of the spectrometer—R(3, 1)$^-$ at 2831.340 cm$^{-1}$ for the fundamental band $\nu_2^0 \rightarrow 0$ and R(8, 9) at 2821.518 cm$^{-1}$ for the hot band $2\nu_2^0 \rightarrow \nu_2^1$. The hot band line, together with many others since observed, is sensitive to the temperature of object and serves as a useful thermometer. The spectral image of Jupiter shown in the lower half of Fig. 6 demonstrates the power of modern spectrometers equipped with two dimensional multiple array detectors. After the horizontal dimension is used for wavelength resolution, the vertical dimension in Fig. 6 is used for the spatial resolution of the Jovian latitude by aligning the slit of the spectrometer along the direction from the north to the south pole of Jupiter which subtends the angle of sight of −40° and this is divided into −15 segments in Fig. 6. The picture clearly shows that the $H_3^+$ emission, which is a measure of plasma activities in Jupiter ionosphere, is maximum at the south pole (row 37) and the north pole (row 22) but it also covers the whole latitudes of Jupiter. Similar observations have been reported by other groups [85]. The $H_3^+$ emission serves as a useful ground based probe to monitor the plasma activities of Jupiter. The purity of the spectrum is so high that the $H_3^+$ emission can be monitored without using a spectrometer. Thus, morphology and temporal variations of the plasma emissions were monitored in two dimensions by using a narrow band filter [86, 87]. Results were reviewed by Miller [88] and Connerney et al [89] in which the author observed $H_3^+$ at the foot of the Io flux tube at mid-Jovian latitudes.

Soon after its discovery in Jupiter [89] and in Saturn [90]. The emission was considered of its smaller diameter and larger distance (−4) than Io $H_3^+$ allowing the monitoring of the Ulysses observatories. It has been observed...
Infrared Spectrum of H$_3^+$ in Laboratory and Space Plasmas

![Infrared Spectrum of H$_3^+$ in Laboratory and Space Plasmas](image)

The infrared spectrum is that it is not completely clear in Fig. 5 is completely clear in Fig. 6, but it is also almost completely clear. The relatively weak bonding in H$_3^+$ is lower than the typical hydrogen bonds, but is still higher than the H$_2$, N$_2$, O, CN and NO bonds. Thus, the L, P, Q, R, S, T, U bands are relatively weak in the L window where the terrestrial atmosphere is opaque. Nevertheless, spectral lines of CH$_4$ are of their enormous abundance; they can cool and condense on Jupiter and to the surface of the planet, and then appear strongly and remain clear during the observation of the satellite. Each one of the problems is essentially at low altitude of Jovian atmosphere and to their pressure, which is the dominant infrared background. In other words, low temperature CH$_4$ and NH$_3$ maintain their energy into kinetic energy.

The spectrum is clearly seen in higher resolution as shown in Fig. 6. Here the quartet of CGS4 grating spectrum is almost completely free of the four lines (R(3, 1) at 3.545 cm$^{-1}$, R(2, 1) at 3.543 cm$^{-1}$ and R(1, 0) at 3.555 cm$^{-1}$) in Fig. 5. In this case, we have two additional lines of the spectrometer—R(3, 1) at 3.543 cm$^{-1}$ and R(8, 8) at 3.546 cm$^{-1}$.

The hot band line, together with the two lines, is used to determine the temperature of Jupiter's atmosphere by aligning the slit of the spectrometer with the north pole of Jupiter. This is divided into −15 segments, which cover the entire H$_3^+$ emission, which is a measure of the temperature. This temperature is maximum at the south pole of Jupiter, which also covers the range of latitudes 0° to 60°. This is reported by other groups [85].

A ground based probe to monitor the H$_3^+$ in the atmosphere is so high that the spectrum can be obtained without using a spectrometer. Thus,
morphology and temporal variation of Jovian plasma activities can be directly monitored in two dimensions using infrared cameras with suitable narrow band filters [86, 87]. Results of such observations are summarized in an excellent review by Miller et al [35]. Particularly noteworthy is the work by Connerney et al [88] in which they clearly located the images of excited H$_3^+$ at the foot of the Io flux tube in Jupiter’s atmosphere.

Soon after its discovery in Jupiter, the H$_3^+$ emission was observed in Uranus [89] and in Saturn [90]. The emission from Uranus is remarkably strong considering its smaller diameter (−1/3), smaller magnetic moment (−1/410) and larger distance (−4) than Jupiter. The emission is very pure again, allowing the monitoring of the Uranian plasma activities from ground based observatories. It has been observed that morphology of its plasma is intricate
in spite of its featureless outlook. Searches for the H$_3^+$ emission in Neptune have been attempted without success indicating that Neptune, often considered as a twin planet with Uranus, is very different as far as its plasma activities are concerned. The H$_3^+$ emission from Saturn is two orders of magnitude weaker than that from Jupiter. Fig. 7 shows the H$_3^+$ emission spectral lines [90] R(1, 0)$^+$ at 2725.898 cm$^{-1}$ and R(1, 1)$^+$ at 2726.219 cm$^{-1}$. Clearly, Jupiter and Saturn are very different outer planets as far as their plasma activities are concerned. Much more will be learned on the magnetohydrodynamical activities of outer planets from more observation of the H$_3^+$ emission.

5. Other Molecular Ions

The observation of H$_3^+$ spectrum reveals that many of polyatomic molecular ions both of ions and radicals containing oxygen atoms that are abundant in space. Some examples are shown in Fig. 7.

CH$^+$   CH$_2^+$

CH   CH$_2$

NH$^+$   NH$_2^+$

NH   NH$_2$

OH$^+$   OH

A detection of H$_3^+$ spectrum in supernova SN1987A has been claimed [91]. While the detection is not as definitive as those in outer planets, this surprising observation keeps us hopeful to observe the spectra in other astronomical objects in which the presence of H$_3^+$ is unexpected. Also, although a supernova of the brightness of SN1987A may not come for many years, the ever-increasing observational capabilities should allow us to observe the spectrum of H$_3^+$.

*After the submission of this paper, Saykally and Amano also reported similar observations and anions containing oxygen atoms. Saykally and Amano also concentrated on molecular ions containing oxygen atoms. The authors have so far been identified in space, and the latter by submillimeter spectroscopy many more will be observed in the future.
The observation of \( \text{H}_3^+ \) spectrum marks the beginning of infrared spectroscopy of polyatomic molecular ions both in the laboratory and in space. We can consider a great many other molecular ions containing carbon, nitrogen and oxygen atoms that are abundant in the universe. Molecular ions containing one heavy atom are shown in Fig. 8. After many graduate-student-years of hard work, we have observed and characterized at least one band of all cations and anions containing one N or O atom. Laboratories of Lineberger, Saykally and Amano also contributed to the venture. We are now concentrating on molecular ions containing carbon [92–99]. We have observed and understood parts of the spectra of \( \text{CH}_3^+ \), \( \text{CH}_2^+ \) and \( \text{C}_2\text{H}_5^+ \), and we are now struggling with the spectrum of \( \text{CH}_4^+ \). Spectra of \( \text{CH}^+ \), \( \text{H}_2\text{O}^+ \) and \( \text{H}_3\text{O}^+ \) have so far been identified in space, the former two by their optical spectra and the latter by submillimeter spectrum. With the development of infrared spectroscopy many more will be observed in space*.

I wish to thank B.J. McCall for reading this article.

*After the submission of this paper, we detected \( \text{H}_3^+ \) in interstellar space using the \( \nu_2 \) fundamental band. The interstellar \( \text{H}_3^+ \) was detected toward young stellar object GL2136 and W33A using the 4m UKIRT telescope. The column density of \( \text{H}_3^+ \) has been measured to be \( 4 \times 10^{14} \text{ cm}^{-2} \) and \( 6 \times 10^{14} \text{ cm}^{-2} \) for GL2136 and W33A, respectively [100].
Reference