H$_3^+$: "A Beautiful Jewel of Nature"

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Existence of $H_3$.—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to $H_3$. 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. The polymeric modification of hydrogen seems to require special conditions for its formation, for it cannot be detected on many of the plates taken with hydrogen in the tube.
Arthur J. Dempster

- Discovered $^{235}\text{U}$
- Physics Prof. at U. Chicago
- Principal American authority on positive rays

$\rightarrow \text{H}_3^+$ formed in secondary reaction

A. J. Dempster,
Phil. Mag. 31, 438 (1916)
Charles A. Coulson

- First Ph.D. student of Lennard-Jones
- First ab initio calculation on a polyatomic molecule
- "It appears that the ion H$_3^+$ should exist in stable equilateral form with a nuclear distance about 0.85 Å, and that all excited levels are unstable."
- Prediction not accepted by Eyring, Hirschfelder, and others
- With advent of computers, prediction was confirmed (Christoffersen, Hagstrom, & Prosser 1964, Conroy 1964)

C. A. Coulson,
Proc. Camb. Phil. Soc. 31, 244 (1935)
ON THE POSSIBLE OCCURRENCE OF H₃⁺ IN INTERSTELLAR SPACE

The possibilities for detection of the molecular ion H₃⁺ by radio-astronomical techniques have recently received considerable attention, and theoretical predictions of the spectrum have been made by Mizushima (1961) and by Burke (1961). Recent work on ion-molecule reactions indicates that the molecular ion H₃⁺ may also be expected in interstellar space. In fact, with the presence of quantities of molecular hydrogen, H₂⁺ will react to form H₃⁺.

Formation of H₃⁺ through the reaction H₂⁺ + H₂ → H₃⁺ has been observed independently by Stevenson and Schissler (1958) and by Barnes, Martin, and McDaniel (1961). The cross-section for this reaction has been found to have a remarkably large value of the order of 10⁻¹⁴ cm² at normal thermal energies. This is much greater than the gas-kinetic cross-section for neutral hydrogen molecules. The cross-section for H₃⁺ formation by this reaction varies inversely with the relative velocity of the H₂⁺ ion and the hydrogen molecule (Stevenson and Schissler 1958; Lampe and Field 1959). The experimental work of Barnes, Martin, and McDaniel furthermore shows that H₃⁺ ions persist over very many subsequent collisions with hydrogen molecules. The H₃⁺ ion is stable against spontaneous dissociation. Its binding energy of 4.18 ev (Varney 1960) exceeds that of H₂⁺ (2.65 ev), so the formation reaction is exoergic (Hirschfelder, Curtiss, and Bird 1954).

Thus it may be expected that H₂⁺ will be converted to H₃⁺ upon encounter with a hydrogen molecule, and the population of H₃⁺ will be very strongly influenced by the density of neutral molecular hydrogen. It now appears desirable to consider the possibilities for detecting H₃⁺ because this molecular ion may be present under some circumstances to the virtual exclusion of H₂⁺.

D. W. MARTIN
E. W. McDaniel
M. L. Meeks

June 13, 1961
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA
Another important subclass of reactions are those involving $\text{H}_3^+$. This ion is produced by the well-studied reaction

$$4. \quad \text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H},$$

and then reacts with many neutral species according to the general formula

$$\text{H}_3^+ + X \rightarrow \text{XH}^+ + \text{H}_2,$$

where $X = \text{CO, N}_2, \text{H}_2\text{O}, \text{NH}_3$, etc. These reactions have been studied by Burt et al. E. Herbst & W. Klemperer, Astrophys. J. 185, 505 (1973) also: W. D. Watson Astrophys. J. 183, L17 (1973)

- $\text{H}_3^+$ “universal protonator”
  - $\text{H}_3^+ + \text{O} \rightarrow \text{H}_2 + \text{OH}^+$
  - $\text{OH}^+ + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}^+$
  - $\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H} + \text{H}_3\text{O}^+$
  - $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \text{H}$

- Origin of Earth's water (?)
Herzberg's Search for H$_3^+$

- 1967: with J. W. C. Johns, searched for emission in IR spectrum of discharge
- Looked for electronic transitions in VUV, found high rotational lines of Lyman bands
- Working in visible, stumbled onto H$_3$
Oka's Search for $H_3^+$

Allen Karabonik
Every morning, he transferred six 50 liter cans of liquid nitrogen to the laboratory!
The Long Search

• Four and a half years. Much of it assembling the DF system and discharge cell.

• Scanned from:
  – 6/12-8/3 (1978)
  – 12/18-1/26 (1978-79)
  – 4/24-12/18 (1980)

• R(1,0) April 25, 1980.
  – Oka and Allen Karabonik in lab
  – Keiko came in at 10 pm

• Watson assigned it overnight
The final spectrum
A Beautiful Jewel of Nature

Because of this stability $H_3^+$ is the most abundant hydrogenic ion in laboratory plasma and in dark molecular clouds. However there has previously been no spectroscopic observation of this species in any range. This is probably because $H_3^+$ is predissociated in electronic excited states and does not have a discrete optical spectrum. The vibrational spectrum in the infrared region seems to be the only way to study this ion spectroscopically. This is a beautiful jewel of nature left for the laser spectroscopist.

The Search Was On


Printed in Great Britain

A search for interstellar H$_3^+$

**BY T. OKA†**

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Based on the results of recent laboratory observation of the infrared $v_2$ fundamental band of the H$_3^+$ molecular ion, the possibility of observing this important ion in interstellar space is discussed. An observation of this spectrum has been attempted with the aid of the high-resolution Fourier transform spectrometer on the 4m Mayall telescope of the Kitt Peak National Observatory.

4. **Observation**

Observation was made for 2 days on 1981 March 23–25, with the coudé Fourier transform spectrometer with high resolution (ca. 0.041 cm$^{-1}$) on the 4m Mayall telescope of the Kitt Peak National Observatory. A liquid He cooled narrow band filter with the centre wavenumber of

Less than one year after first line was seen in laboratory!!!
Dear Dr. Geballe:

I enclose a copy of my preprint on an astronomical search for H_3^+ and my paper on laboratory spectra.

This is a very interesting species and I am extremely eager to search for this ion. I hope that you will read my preprint and find such an attempt worthwhile.

You said on the phone that you are in the process of moving. So am I. After the middle of July, my address will be in Chicago as specified on my preprint.

Looking forward very much to our collaboration,

Sincerely yours,

Takeshi Oka

TO: mpt
Encs:

Dear Professor Becklin:

It was nice to have seen you in Mauna Kea last month. This letter is to report our result briefly.

Our search (Eric Persson, Tom Geballe and I) for the IR spectrum of H_3^+ was done on the night of December 6-7. Unfortunately, neither the infrared spectrometer nor the weather was on our side on that night and we ended up with very inconclusive results.
H$_3^+$ on Jupiter!

- McDonald Observatory 2.7-m
- September 1987 – November 1989
- Study of H$_2$

After a month’s work J. K. G. Watson, who had earlier analyzed the first laboratory H$_3^+$ spectrum, came to the understanding of the Jovian spectrum as due to the $2\nu_2(2)\rightarrow0$ band of 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. Maillard), Ottawa (P. A. Feldman and J. K. G. Watson), and London (S. Miller), with recurring references to Bawendi, Dabrowski, Drossart, Herzberg, Majewski, Oka, Tarrasso, and Vervloet. The close collaboration of astronomers, laboratory spectroscopists, and theorists is characteristic of this field.
H$_3^+$ Fundamental Band

OBSERVATIONS OF THE 4 MICRON FUNDAMENTAL BAND OF H$_3^+$ IN JUPITER

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AND

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T. Oka and T. R. Geballe,
H$_3^+$ as a Diagnostic

J.E.P. Connerney and T. Satoh,
Phil. Trans. R. Soc. Lond. A358, 2471 (2000)

S. Miller, et al.,
Phil. Trans. R. Soc. Lond. A358, 2485 (2000)
Saturn and Uranus

T. R. Geballe, M.-F. Jagod, & T. Oka,

L. M. Trafton, et al.,
Continued Laboratory Work

• 17 lab studies
• Chicago & Ottawa
• over 800 transitions
• Overtones
  – $2\nu_2 \leftarrow 0$
  – $3\nu_2 \leftarrow 0$
• Hot bands
  – $2\nu_2^2 \leftarrow \nu_2$
  – $2\nu_2^0 \leftarrow \nu_2$
• Combination bands
  – $\nu_1 + 2\nu_2^2 \leftarrow 0$
  – $2\nu_1 + \nu_2 \leftarrow 0$
• Forbidden bands
  – $\nu_1 \leftarrow 0$
  – $\nu_1 + \nu_2 \leftarrow \nu_2$
Compilation Work

- Reassignment of all observed transitions
- Experimentally determined energy levels
  - utilize variety of band types observed
  - independent of theory
  - 526 energy levels
- Test for theory
- Reliable linelist

C. M. Lindsay & B. J. McCall, J. Mol. Spectrosc. 210, 60 (2001)
H$_3^+$ Above the Linearity Barrier

J. L. Gottfried, B. J. McCall, & T. Oka,

poster: Jennifer Gottfried
Back to the Interstellar Search

CSHELL on IRTF

CGS4 on UKIRT

Infrared array detectors
First detection!

LETTERS TO NATURE

Detection of $\text{H}_3^+$ in interstellar space

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Illinois 60637-1403, USA

T. R. Geballe & T. Oka,
Confirmed by Doppler Shift

Doppler shift confirms interstellar origin

reprocessed

H$_3^+$ as a Probe of Dense Clouds

- Spectrum gives $N(\text{H}_3^+) = 1-5 \times 10^{14}$ cm$^{-2}$

- Given $n(\text{H}_3^+)$ from model, and $N(\text{H}_3^+)$ from infrared observations:
  - path length $L = N/n \sim 3 \times 10^{18}$ cm $\sim 1$ pc
  - density $\langle n(\text{H}_2) \rangle = N(\text{H}_2)/L \sim 6 \times 10^4$ cm$^{-3}$
  - temperature $T \sim 30$ K

- Unique probe of clouds
- Consistent with expectations
  - confirms dense cloud chemistry

The Galactic Center

\[ N_{\text{para}} = 5.1(1.7) \times 10^{14} \text{ cm}^{-2} \]
\[ N_{\text{ortho}} = 2.4(1.1) \times 10^{14} \text{ cm}^{-2} \]
\[ N_{\text{broad}} = 17.5(3.9) \times 10^{14} \text{ cm}^{-2} \]

Cygnus OB2 12

$N_{\text{para}} = 2.4(3) \times 10^{14} \, \text{cm}^{-2}$

$N_{\text{ortho}} = 1.4(2) \times 10^{14} \, \text{cm}^{-2}$

Similar column density to dense clouds!!

Chemistry & Implications

Formation

\[ \text{H}_2 \xrightarrow{\text{cosmic ray}} \text{H}_2^+ + \text{e}^- \]
\[ \text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H} \quad \text{(fast)} \]

Rate = \( \zeta [\text{H}_2] \)

Destruction

\[ \text{H}_3^+ + \text{e}^- \rightarrow \text{H} + \text{H}_2 \text{ or } 3\text{H} \]

Rate = \( k [\text{H}_3^+] [\text{e}^-] \)

Steady State

\[
\frac{(3 \times 10^{-17} \text{ s}^{-1})}{(5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1})} \times (2400) = 10^{-7} \text{ cm}^{-3}
\]

\( \rightarrow \) path length \( L = N/n \sim 1 \text{ kpc} \)

\( \rightarrow \) density \( \langle n(\text{H}) \rangle = N(\text{H})/L \sim 20 \text{ cm}^{-3} \)
Other Diffuse Clouds, too!

- General problem with chemical model:
  - $\zeta$
  - $k_e$
  - $[e^-]/[H_2]$
H$_3^+$ toward ζ Persei

Rules out [e$^-$/[H$_2$]]

N(C$^+$) from HST

N(H$_2$) from Copernicus


H$_3^+$ Dissociative Recombination

- Laboratory values of $k_e$ varied by 4 orders of magnitude!
- Even worse: theory in infancy, way off...
- Big problem: not measuring H$_3^+$ in ground states
Storage Ring Measurements

- Complete vibrational relaxation
- Very simple experiment
- Control $H_3^+$ – e$^-$ impact energy
- Rotationally hot ions produced
- No rotational cooling in ring
Berkeley Supersonic Ion Source

- Supersonic expansion leads to rapid cooling
- Discharge from ring electrode downstream
- Skimmer to minimize arcing
CRYRING Results

- Considerable amount of structure (resonances) in the cross-section
- $k_e = 2.6 \times 10^{-7}$ cm$^3$ s$^{-1}$

McCall, et al.
Nature 422, 500 (2003)
Implications for ζ Persei

\[
\frac{N(H_3^+)}{L} = [H_3^+] = \frac{\zeta}{k_e} \frac{N(H_2)}{N(e^-)}
\]

\[
\zeta L = (2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}) \frac{N(H_3^+)}{N(H_2)} \frac{N(e^-)}{N(H_2)}
\]

\[
\zeta L = 8000 \text{ cm s}^{-1}
\]

Adopt ζ = 3 \times 10^{-17} \text{ s}^{-1}

\[
L = 85 \text{ pc}
\]

\[
\langle n \rangle = 6 \text{ cm}^{-3}
\]

Adopt L = 2.1 pc

ζ = 1.2 \times 10^{-15} \text{ s}^{-1}

(40x higher!)
CO and $\text{H}_3^+$ in the protoplanetary disk around the star HD141569

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Schawlow Thinking Disputed about Diatomic Molecules

In his very readable article “Chemistry: Blithe Sibling of Physics” (PHYSICS TODAY, April, page 11), Dudley Herschbach quotes the well-known remark attributed to Art Schawlow, “A diatomic molecule has one atom too many.”

My love affair with H$_3^+$ over many years, has led me to believe that some beautiful subtleties of physics do not appear until one faces a three-particle system. I suspect quantum chromodynamicists agree with this.

As for me, I say that a diatomic molecule has one atom too few.

Reference

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