

16. Molecular Ions and Fractionation

1. Review of Gas Phase Chemistry
2. Molecular Ions
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References

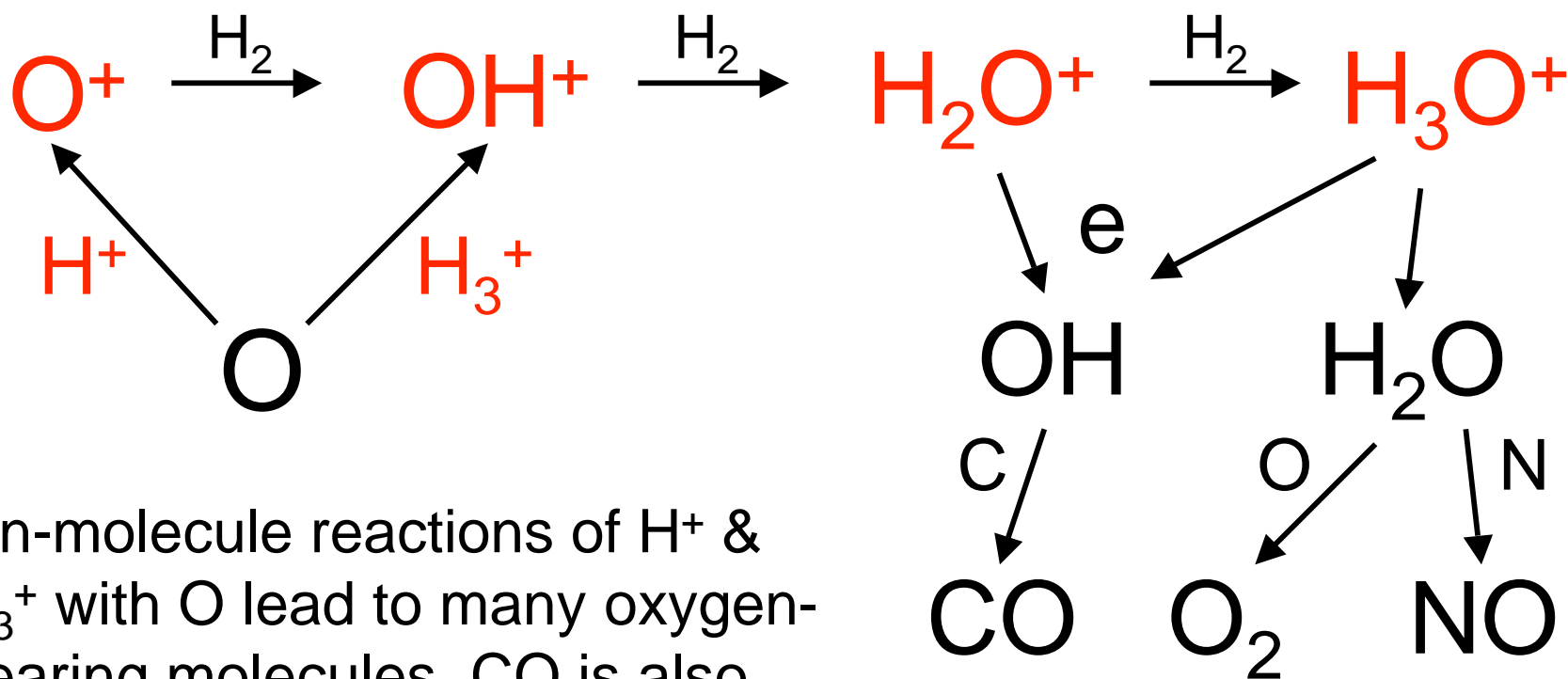
Tielens, Secs. 8.8, 10.2, 10.4.4

Bergin & Tafalla, ARAA 45 339 2007, Sec. 4.4

T. Oka, Proc. NAS 103 12235 2006

A. Dalgarno, NAS 103 12269 2006

The Ion-Molecule Reaction Oxygen Paradigm

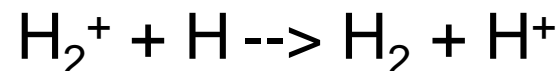
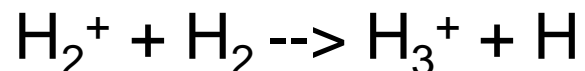


Ion-molecule reactions of H^+ & H_3^+ with O lead to many oxygen-bearing molecules. CO is also formed by C^+ interacting with OH and H_2O to form HCO^+

Similar schemes starting with C & N end prematurely at CH_3^+ and NH_3^+

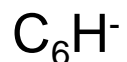
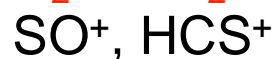
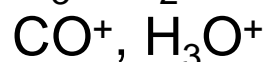
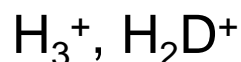
2. Molecular Ions

The “first” *molecular ion* produced by cosmic ray ionization is H_2^+ , but it is rapidly destroyed by reactions with H and H_2 :



This occurs because the proton is better bound by H_2 than by H. But there are many species which can do this even, and the original H_2^+ is transformed into a set of molecular ions that are the essential characteristic of the ion-molecule chemistry.

Detected interstellar molecular ions



Ions marked in red are particularly useful diagnostics.

Not all isotopic variants are shown.

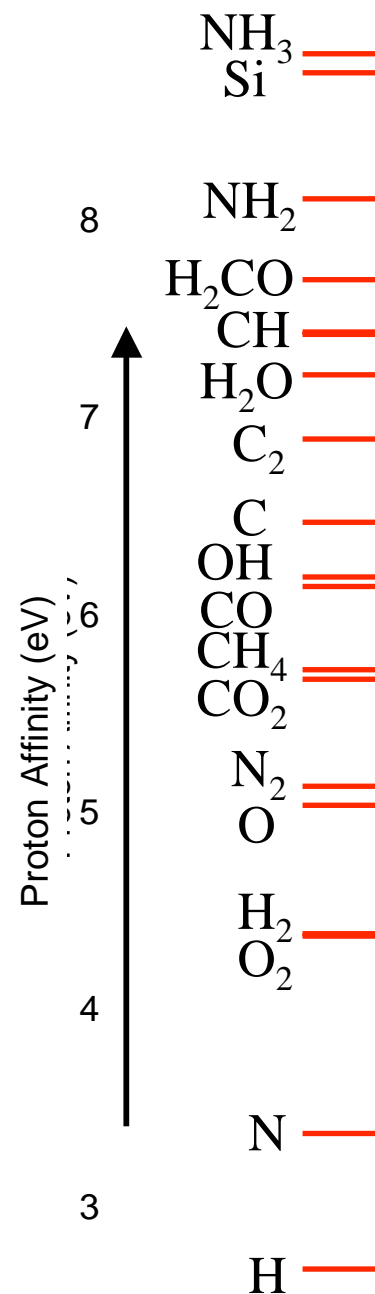
Molecular Ions and Proton Affinity

A molecular ion AH^+ will usually transfer its proton from A to B if it gets better bound. The essential quantity is the **proton affinity** or proton binding energy. The energy yield (difference between initial and final energies) in a proton transfer reaction is,

$$\Delta E(AH^+ + B \rightarrow BH^+ + A) = [pa(B) - pa(A)]$$

CR ionization is passed upward in the diagram to other ions by proton transfers to higher binding species, generating many molecular ions.

NB: The first entry at the bottom of the table for H gives the binding energy of H_2^+ as 2.65 eV. From the entry for H_2 , one sees that H_3^+ has a binding similar to H_2 itself.



Most Useful Interstellar Molecular Ions

The abundance is determined by that of the capturing species and whether other species with higher proton affinities are available.

Thus, HCO^+ is abundant because CO is, and because well-bound molecules like H_2O and NH_3 (with larger proton affinities) are not.

Observability depends on the frequency band and the dipole moment (or A -value).

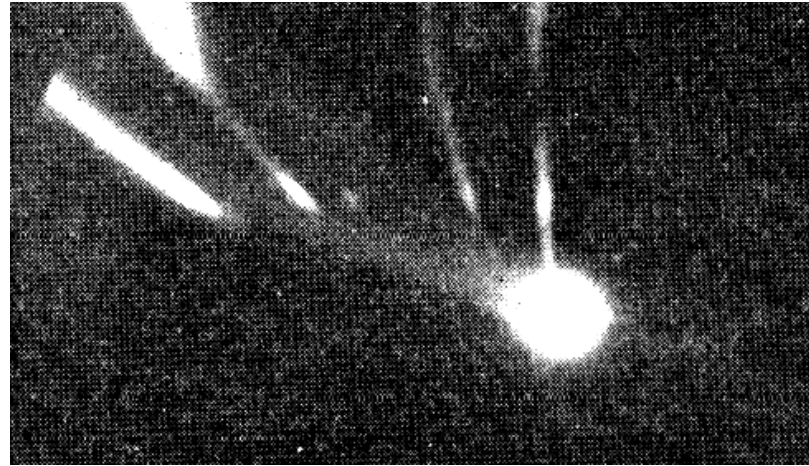
Molecule	$\mu(\text{D})$	$\nu_{10}(\text{GHz})$
HCO^+	3.93	89.19
N_2H^+	3.4	93.18

$$A_{ul} = \frac{64\pi^4}{3hc^3} \mu_{ul}^2 \nu_{ul}^3$$
$$= 1.16 \times 10^{-5} \text{ s}^{-1} \left(\frac{\mu_{ul}}{D} \right)^2 \left(\frac{\nu_{ul}}{100 \text{ GHz}} \right)^3$$

The first molecular ion discovered in the ISM was HCO^+ (Snyder et al. 1970, Klemperer 1974). It served as a surrogate for H_3^+ and the signature for ion-molecule chemistry until H_3^+ was discovered in the ISM in 1995.

3. The Astronomical Detection of H_3^+

Discovered by J. J. Thomson (Phil. Mag. 21 225 1911)

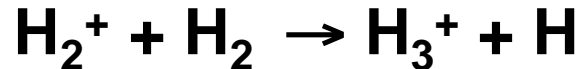


Existence of H_3 .—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to H_3 . The existence of this substance is interesting from a chemical point of view, 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.

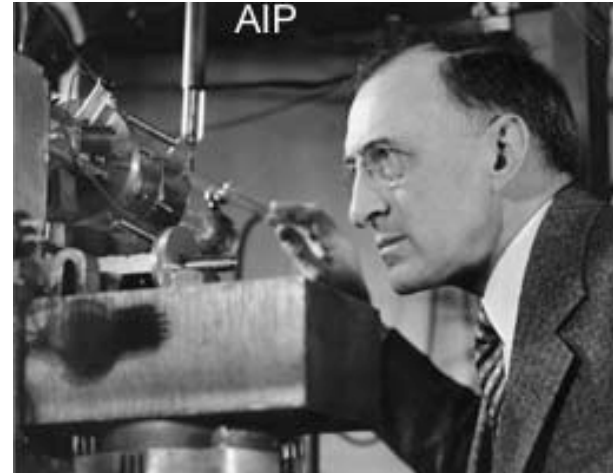
H_3^+ in Laboratory Hydrogen Plasmas

A. J. Dempster (discoverer of ^{235}U) established that H_3^+ is abundant in lab plasmas (Phil Mag 31 438 1916)

H_3^+ is produced in the reaction



Hogness & Lunn (Phys Rev 26 44 1925)



The exothermic nature and rate of this reaction had been known since the 1930's, but appreciation of its interstellar role had to wait 30 years for a 1/2 page note in ApJ (Martin et al., ApJ 134 1012 1962), 10 more years for serious consideration and 25 more to be detected in the ISM.

See Oka (Rev Mod Phys 64 114 1992) for the history.

ON THE POSSIBLE OCCURRENCE OF H_3^+ IN INTERSTELLAR SPACE

The possibilities for detection of the molecular ion H_2^+ 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 H_3^+ may also be expected in interstellar space. In fact, with the presence of quantities of molecular hydrogen, H_2^+ will react to form H_3^+ .

Formation of H_3^+ through the reaction $H_2^+ + H_2 \rightarrow H_3^+$ 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 H_3^+ formation by this reaction varies inversely with the relative velocity of the H_2^+ ion and the hydrogen molecule (Stevenson and Schissler 1958; Lampe and Field 1959). The experimental work of Barnes, Martin, and McDaniel furthermore shows that H_3^+ ions persist over very many subsequent collisions with hydrogen molecules. The H_3^+ ion is stable against spontaneous dissociation. Its binding energy of 4.18 ev (Varney 1960) exceeds that of H_2^+ (2.65 ev), so the formation reaction is exoergic (Hirschfelder, Curtiss, and Bird 1954).

Thus it may be expected that H_2^+ will be converted to H_3^+ upon encounter with a hydrogen molecule, and the population of H_2^+ will be very strongly influenced by the density of neutral molecular hydrogen. It now appears desirable to consider the possibilities for detecting H_3^+ because this molecular ion may be present under some circumstances to the virtual exclusion of H_2^+ .

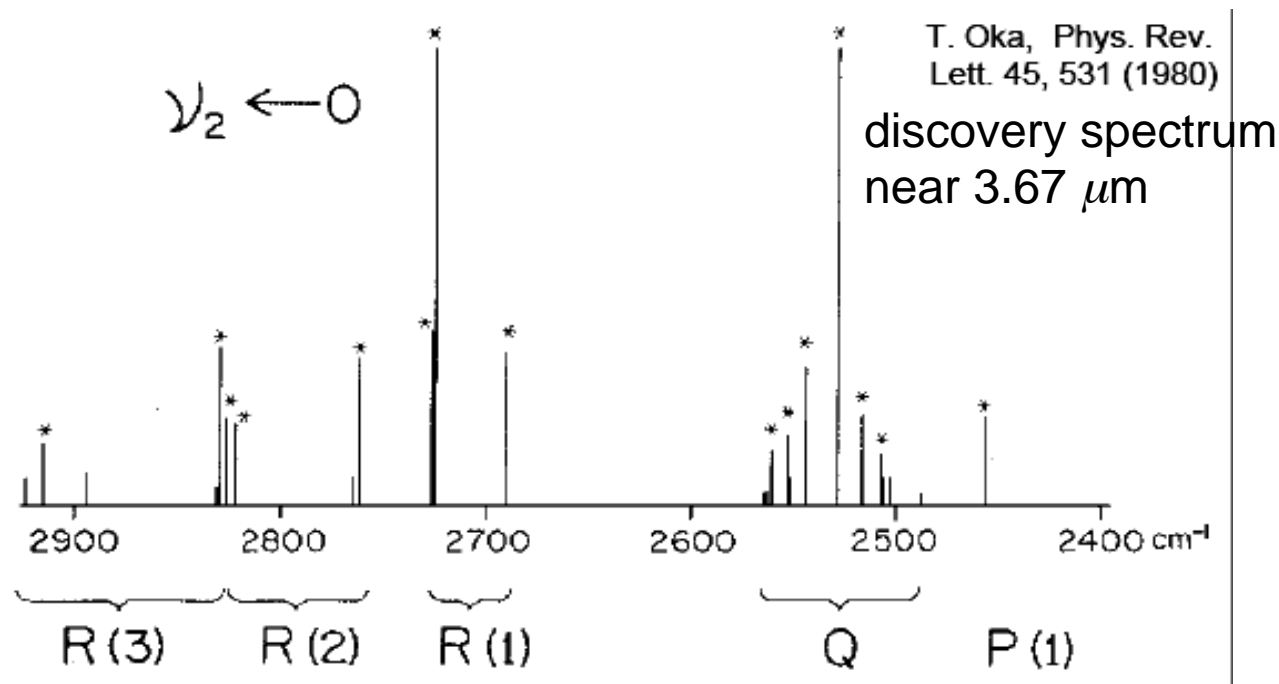
D. W. MARTIN
E. W. MCDANIEL
M. L. MEEKS

June 13, 1961
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

ApJ 134 1012 1961

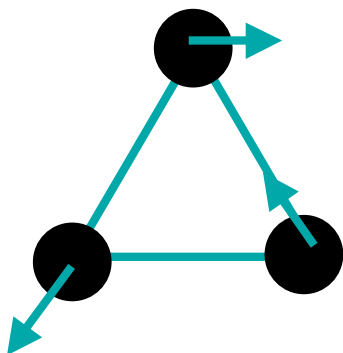
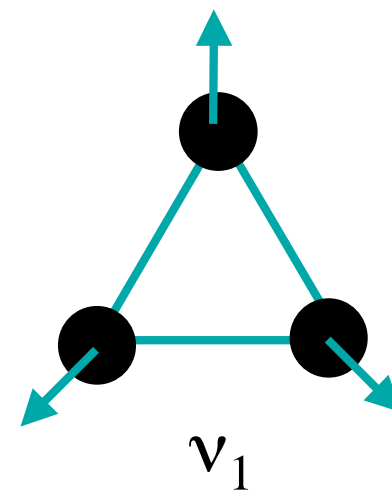
The Spectrum of H_3^+

- Equilateral triangle symmetric rotor
- Forbidden pure rotational spectrum
- No electronic states or spectrum
- NIR ro-vibrational transitions the only tool
(for both lab and astronomical study)
- Nuclear spins: 1/2 (para) & 3/2 (ortho)

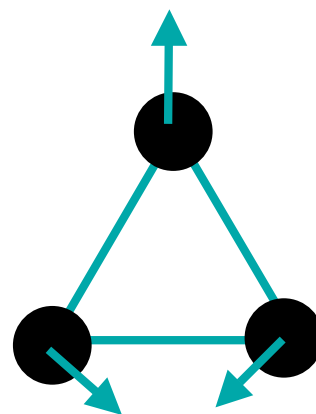


Vibrational Modes of H_3^+

- One combination is the totally symmetric ν_1
 - Breathing mode $r_1 + r_2 + r_3$
- Two other combinations are the ν_2 mode
 - $r_1 + \varepsilon r_2 + \varepsilon^2 r_3$
 - $r_1 + \varepsilon^2 r_2 + \varepsilon r_3$
 - $\varepsilon = e^{2\pi i/3}$



ν_2



H₃⁺ Rotational Structure

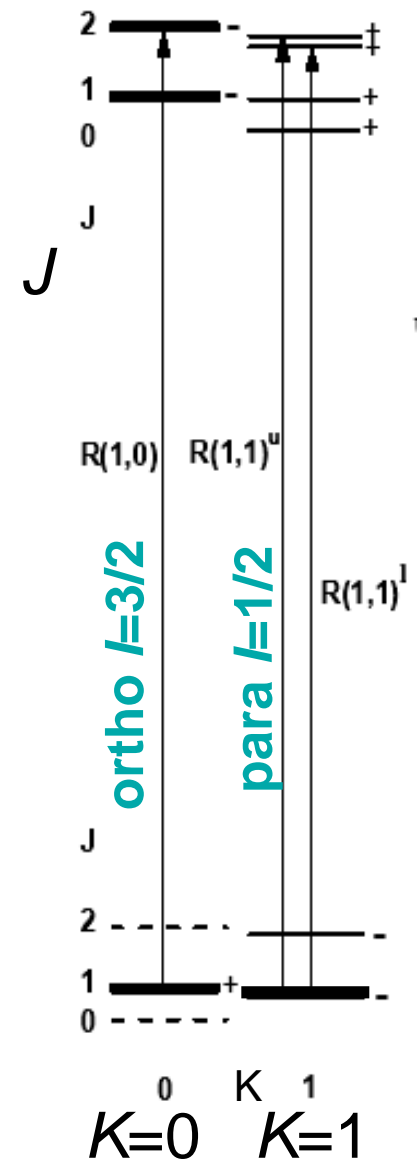
Energy levels are those of a symmetric top:

$$E = B J(J+1) + (C-B) K^2$$

$$B = 43.56 \text{ cm}^{-1} \quad C = 20.61 \text{ cm}^{-1}$$

Observed $\nu_2 = 1-0$ transitions

- $J=K=0$ state is forbidden by the exclusion principle
- The $J = 1, K = 1$ state of *para* H₃⁺ is the lowest rotational state
- The $J = 1, K = 0$ state of *ortho* H₃⁺ is 32.9 K higher.
- No other states are populated for $T \approx 5 - 50$ K.
- They have ~ equal populations since the higher statistical weight of ortho ($I = 3/2$) compared to para ($I = 1/2$) compensates approximately for the Boltzmann factor.
- The first two transitions reading from the left in the figure are referred to as the “ortho-para” doublet



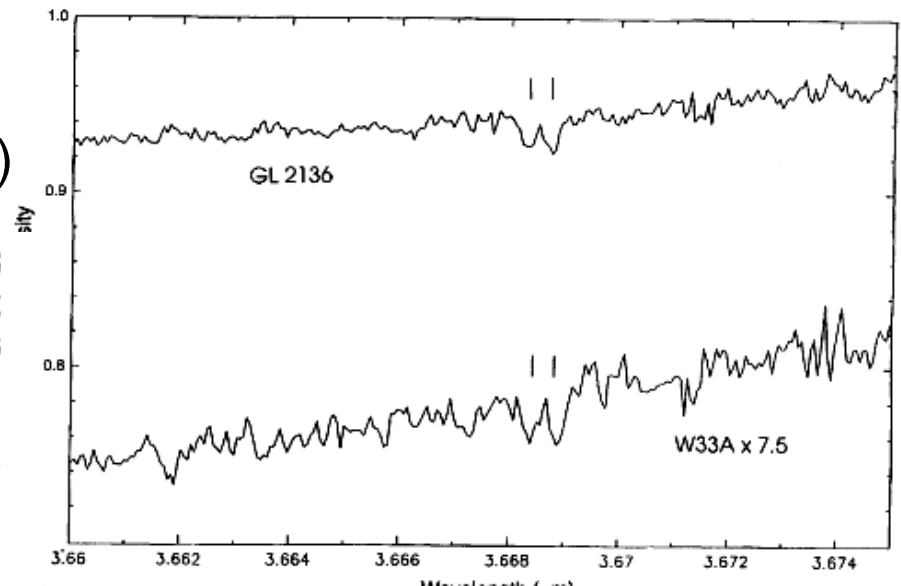
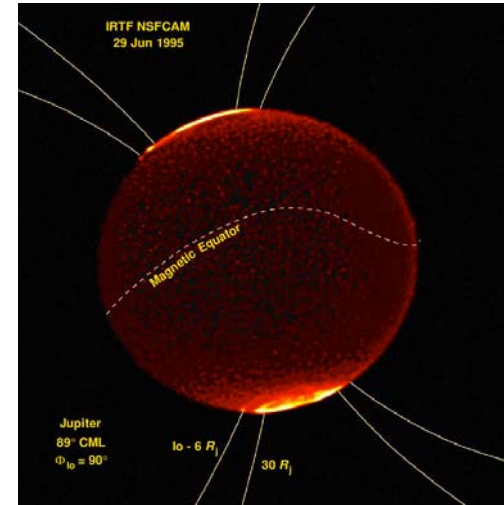
Discovery of Extraterrestrial H_3^+

First detection of H_3^+ in space was in the aurora of the Jovian planets (Trafton et al. ApJ 343 L17 1989).

First interstellar detections towards massive, IR-bright, deeply embedded YSOs, W33A and AFGL2136, in the ortho-para doublet.

$N(\text{H}_3^+) \approx 4 \times 10^{14} \text{ cm}^{-2}$, $T = 30\text{-}35 \text{ K}$
(Geballe & Oka Nature 384 334 1996)

FIG. 1 Spectra of GL2136 and W33A ratioed by BS6378 (A2V), in the vicinity of the H_3^+ ortho-para doublet at $3.668 \mu\text{m}$. The doublet, indicated by vertical lines, consists of the $\text{R}(1,0)$ transition of *ortho* H_3^+ at $2,725.898 \text{ cm}^{-1}$ ($3.66852 \mu\text{m}$, right-hand line of doublet) and the $\text{R}(1,1)^+$ transition of *para* H_3^+ at $2,726.219 \text{ cm}^{-1}$ ($3.66808 \mu\text{m}$, left-hand line of doublet).



ISM Detections of H_3^+

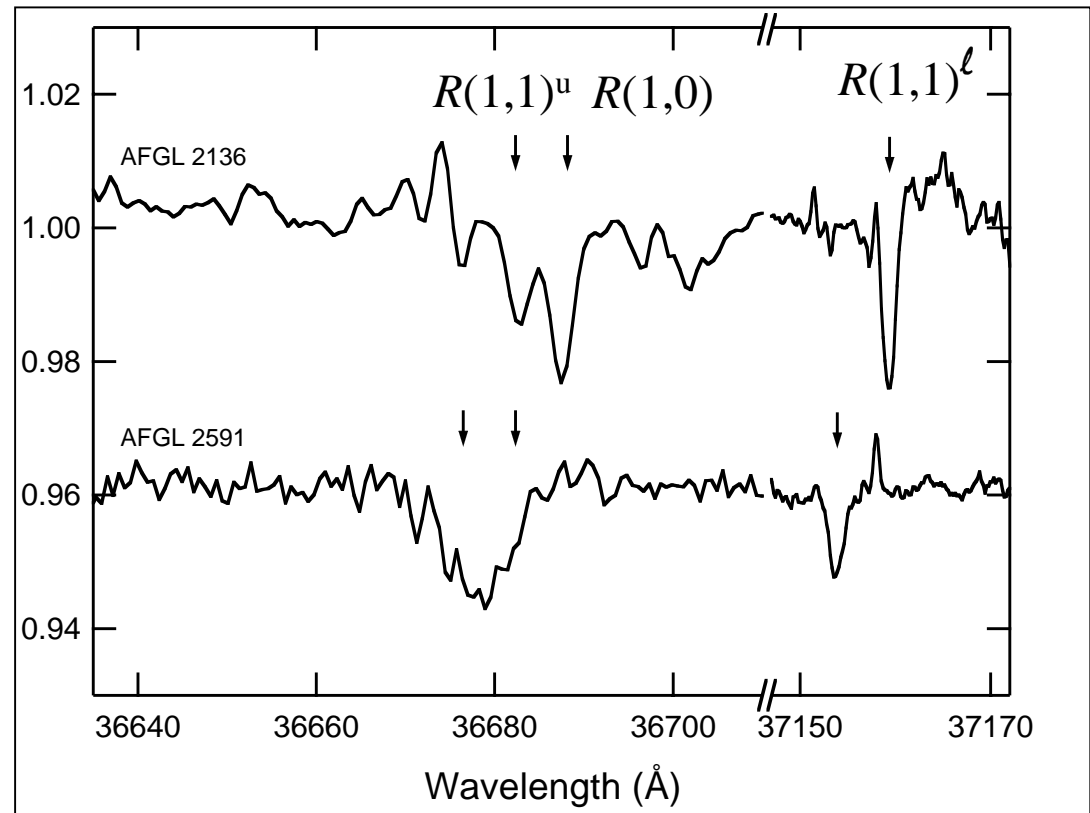
Geballe, Hinkle, McCall, & Oka detected H_3^+ along several lines of sight, originally towards distant IR-luminous embedded YSOs and more recently towards nearby bright stars for which extensive UV observations are available.

- McCall et al. Nature 279 1910 1998 Cyg OB2 #12 – “diffuse”
- Geballe et al. ApJ 510 251 1999 Galactic center – “diffuse” and “dense” (also Cyg OB2 #12)
- McCall et al. ApJ 522 338 1999 luminous embedded YSOs – “dense”
- McCall et al. ApJ 567 391 2002 – diffuse clouds
- McCall et al. Nature 422 500 2003 ζ Per – diffuse cloud

Quotation marks have been used for some of the diffuse & dense designations where the lines of sight are long and very likely involve inhomogeneous gas.

H_3^+ in “Dense” Clouds

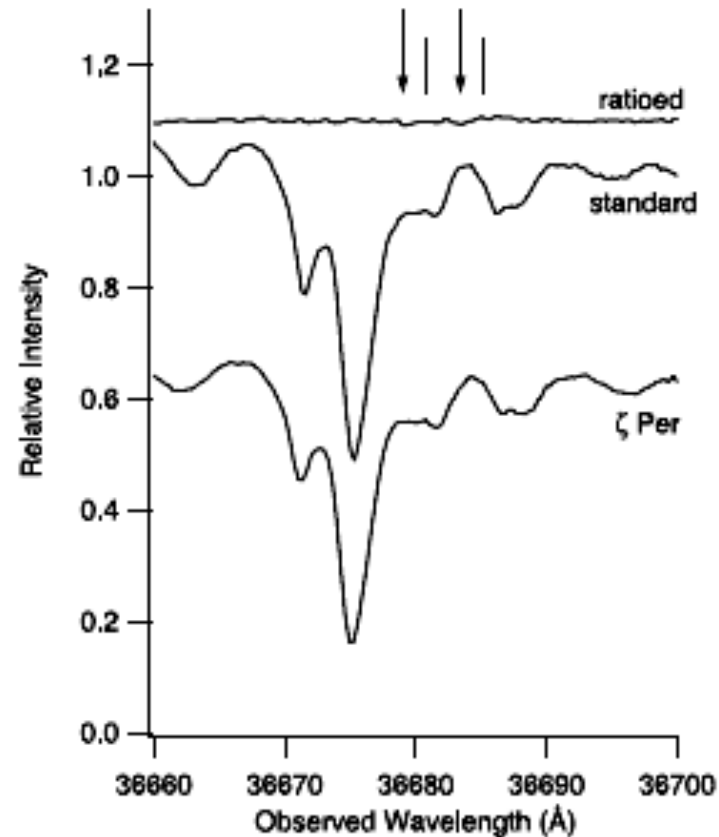
McCall, Geballe, Hinkle, & Oka, ApJ 522 338 1999



Notice the small depths of the features ~ few %

H₃⁺ in Diffuse Clouds

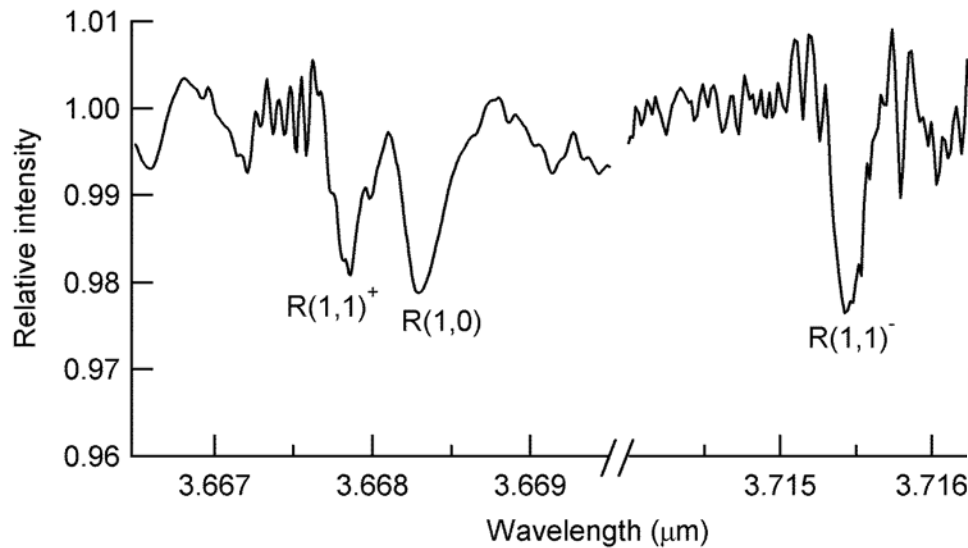
- Diffuse cloud observations with the cooled grating spectrometer at UKIRT
- The weak lines are blended with atmospheric methane
- Many instrumental and atmospheric corrections are required
- The figure shows how the observed spectrum is corrected with (divided by) that of a standard star.
- Arrows shows the expected location of the ortho-para doublet of H₃⁺; vertical lines are the rest frequencies.
- As shown in the following slide the absorption in ζ Per depth is only 1%.



Indriolo et al., ApJ 671 1376 2007

Eight out of twenty detections in the range $0.6 - 3.9 \times 10^{14} \text{ cm}^{-2}$

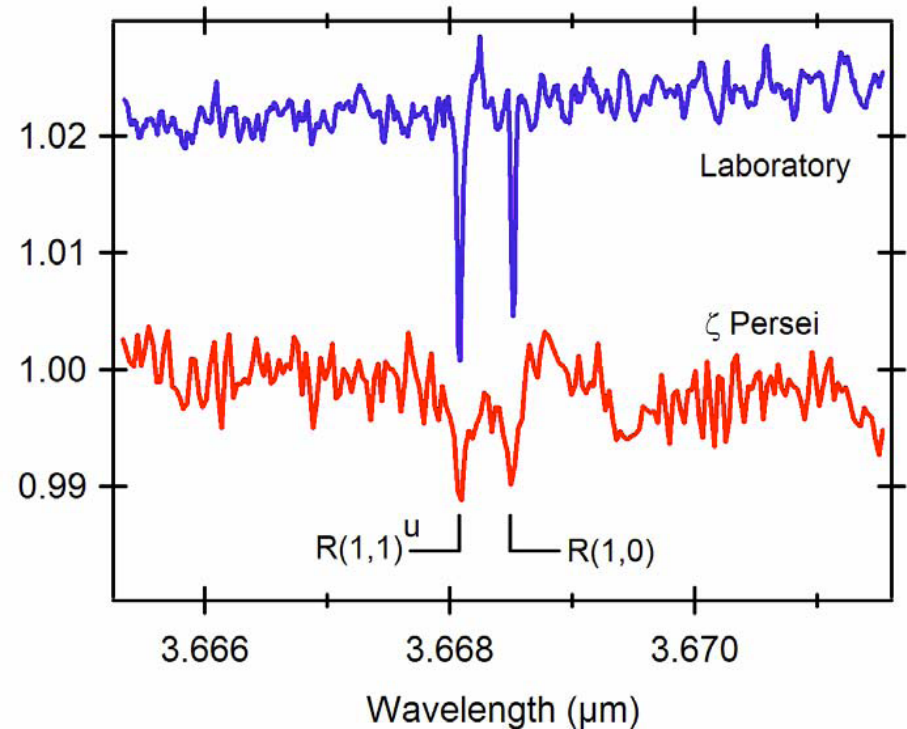
Cygnus OB2 12 and ζ Per



$N(\text{H}_3^+) \approx 3.8 \times 10^{14} \text{ cm}^{-2}$
similar to columns for
“dense” clouds

$$N(\text{H}_3^+) \approx 7 \times 10^{13} \text{ cm}^{-2}$$

ζ Per is a well studied cloud that nicely exemplifies the supposed conundrum posed by the observations of H_3^+



Analysis of the Observations

The local abundance of H_3^+ can be estimated as the ratio of production to formation rates

$$x(\text{H}_3^+) = \frac{\zeta_2}{n_{\text{H}}} \frac{x(\text{H}_2)}{\beta x_{\text{e}} + kx_{\text{O}}}$$

where ζ_2 is the CR ionization rate of H_2 ,

β is the dissociative recombination rate of H_3^+ ,

k is the rate coefficient for its reaction with oxygen-bearing species

- H_2 is near the bottom of the proton-affinity ladder, and H_3^+ can be destroyed by abundant neutrals species like CO, N_2 , O, H_2O etc., with large rate coefficients $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Thus **$kx_{\text{O}} \sim 10^{-13} \text{ cm}^3 \text{ s}^{-1}$** .
- $\beta \sim 2\text{-}3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ in the 20- 60 K range.
- For diffuse clouds, dissociative recombination dominates (large x_{e})
- For dense clouds, particle reactions dominate (small x_{e}).

Estimates of the H_3^+ Abundance

For a **dense cloud** with $n_{\text{H}} = 2000 \text{ cm}^{-3}$, $T = 20 \text{ K}$ and $\zeta_2 = 10^{-16} \text{ s}^{-1}$, then $x(\text{H}_3^+) \sim 2.5 \times 10^{-7}$. To achieve the measured column of H_3^+ requires a linear dimension of $8 \times 10^{17} \text{ cm}^{-2}$, typical of a clump in a large molecular cloud.

For the **diffuse cloud** towards $\zeta \text{ Per}$, the UV observations (Copernicus, Savage et al. ApJ 216 291 1977; HST Cardelli et al. ApJ 467 334 1996) give :

$$\begin{array}{ll} N_{\text{H}} = 1.6 \times 10^{21} \text{ cm}^{-2} & n_{\text{H}} \sim 215 \text{ cm}^{-3} \\ L \sim 7.4 \times 10^{18} \text{ cm} & 2N(\text{H}_2)/N_{\text{H}} = 0.6 \\ T = 28 \text{ K} & N(\text{C}^+)/N_{\text{H}} = 10^{-4} \end{array}$$

Taking $x_{\text{e}} = 10^{-4}$, $\zeta_2 = 10^{-16} \text{ s}^{-1}$ and using column densities as local densities, then $x(\text{H}_3^+) \sim 5 \times 10^{-9}$. To achieve the measured column of H_3^+ requires a requires a length $\sim 20 \text{ pc}$, much larger than required by the hydrogen, and suspiciously large.

This is one way of stating the difficulty in understanding the H_3^+ measurements of diffuse clouds posed by the work of McCall et al.

More Detailed Analysis for ζ Per

Measured column densities need to be converted into local quantities with a realistic model. To illustrate this problem, we integrate the above local formula for $x(\text{H}_3^+)$ to obtain:

$$N(\text{H}_3^+) = \varsigma_2 \int ds \frac{x(\text{H}_2)}{\beta x_e + kx_0} \cong \varsigma_2 \int ds \frac{x(\text{H}_2)}{\beta x_e} \quad (\text{for diffuse clouds})$$

or

$$N(\text{H}_3^+) \approx \varsigma_2 L \left\langle \frac{1}{\beta} \frac{x(\text{H}_2)}{x_e} \right\rangle$$

If we further assume that β is roughly constant, we can solve for the CR ionization rate of H_2 in terms of the measured H_3^+ column

$$\boxed{\varsigma_2 \approx \frac{\beta N(\text{H}_3^+)}{L} \left\langle \frac{x(\text{H}_2)}{x_e} \right\rangle^{-1}}$$

Analysis for ζ Per

This expression highlights the fact that the cloud average of the abundance ratio of H_2 to electrons is likely to be variable, one increasing and the other decreasing, so that the ratio increases rapidly going into a cloud (or into a dense inhomogeneity of the cloud). What McCall et al. do is to replace these abundance by *column density ratios*:

$$\zeta_2 \approx \frac{\beta N(H_3^+)}{L} \frac{N(C^+)/N_H}{N(H_2)/N_H}$$

Substituting the measured column densities for ζ Per (using the parameters in Indriolo et al.) leads to:

$$\zeta_2 \approx 6.4 \times 10^{-16} \text{ s}^{-1}$$

This is $\sim 1/2$ the value given by McCall et al. (Nature 422 500 2003), and close to the result of Le Petit et al. (A&A 417 993 2004), who use a complex two-component model with shocks.

Summary of H_3^+ in Diffuse Clouds

Indriolo et al. have made additional observations of diffuse clouds and analyzed them carefully. They recognize that H_3^+ measures the ionization rate ζ_2 for H_2 , and not the primary rate to ionize atomic H (without consideration of heavy elements), a factor of 2.3.

The well publicized puzzle about the large cosmic ray ionization rate from H_3^+ measurements in diffuse clouds seems now to be only a factor of a few disagreement with the value deduced from the demodulated measurements of the local CRs.

Some issues that still need to be considered:

- (1) Why is H_3^+ not detected in so many other diffuse clouds, e.g., towards the well studied cloud towards ζ Oph?
- (2) Should not the net ionization rate in any case be somewhat larger due to Galactic soft X-rays, as maintained by Wolfire et al. (2003) In their treatment of the two-phase model?

4. Isotope Fractionation

The replacement of an element by a heavier isotope lowers the energy of a molecule through the reduction of the zero-point vibrational energy. If there is a reaction that can accomplish this replacement, it will be slightly *exothermic*, i.e., allowed energetically, whereas the reverse reaction will be endothermic. Thus, at low temperature, the heavier isotope is favored. This possibility was first suggested by Watson et al. (1976) for CO:



The rate coefficient is fairly large, $\sim 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, so the $^{13}\text{CO}/^{12}\text{CO}$ ratio will be increased for low T . The measured ISM ratio is ~ 70 , smaller than the terrestrial ratio of 89. Some of the reduction could be due to the fractionation of CO by this ion-molecule exchange reaction, but fractionation tends to be countered by the fact that ^{13}CO is more easily dissociated by interstellar UV radiation than ^{12}CO (because it is less well self-shielded). Moreover, galactic nucleosynthesis may well be more important, since ^{13}CO is generated by the CNO and ^{12}CO by the triple- α process (Wilson & Rood ARAA 32 191 1994).

Deuterium Fractionation

Deuterium fractionation can be strong because of the relatively large isotope mass difference. The basic reaction is:



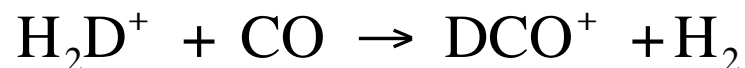
Thermodynamic considerations might suggest that the backward reaction is almost completely shut down at low temperature, since at 10K, $\exp(-23) = 10^{-10}$. However, laboratory experiments (e.g., Gerlich et al. Plan Sp. Sci. 50 1275 2002), show that the rate coefficients depend on the rotational properties of the molecules and thus on the nuclear spin state of H_3^+ . The measured rate coefficients at 10 K are:

$$k(\text{forward}) = 3.5 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$$

$$k(\text{backward}) = 4.9 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \quad \text{for nuclear spins in equilibrium}$$

$$k(\text{backward}) = 7.3 \times 10^{-13} \text{ cm}^3\text{s}^{-1} \quad \text{for the para state}$$

Nonetheless, fractionation can still occur because, once formed, H_2D^+ interacts strongly with other molecules and deuterates them, e.g.



Other Deuteration Reactions

A remarkable result on deuterated molecules is the detection of > 1 D in cold molecular cloud cores, e.g., D_2H^+ , D_3^+ , NH_2D , NHD_2 , $HDCO$, etc. These species are believed to result from the reactions:

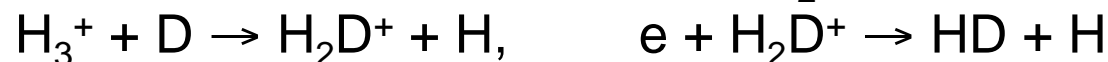


followed by interaction of D_2H^+ and D_3^+ with NH_3 and H_2CO .

To deuterate complex molecules, HD must be present. There are two to synthesize HD:

Grain formation: $D + (Gr + H) \rightarrow (Gr + H + D) \rightarrow Gr + HD$

Ionic reactions: $H^+ + D \rightarrow D^+ + H - 41K$, $D^+ + H_2 \rightarrow H^+ + HD$



The ionic reactions are fast, except the first which has a small barrier. Destruction of HD is by photodissociation and by reaction with H_3^+ .

See Tielens Sec.10.4.4 and Dalgarno (2006) for estimates of the CR ionization rate from the abundance of HD and other products of ion-molecule reactions.