

## 22. Molecular Ions and Fractionation

1. Review of Gas Phase Chemistry
2. Introduction to Molecular Ions
3. The Detection of  $\text{H}_3^+$  and the Cosmic-Ray Ionization Rate
4. Isotope Fractionation

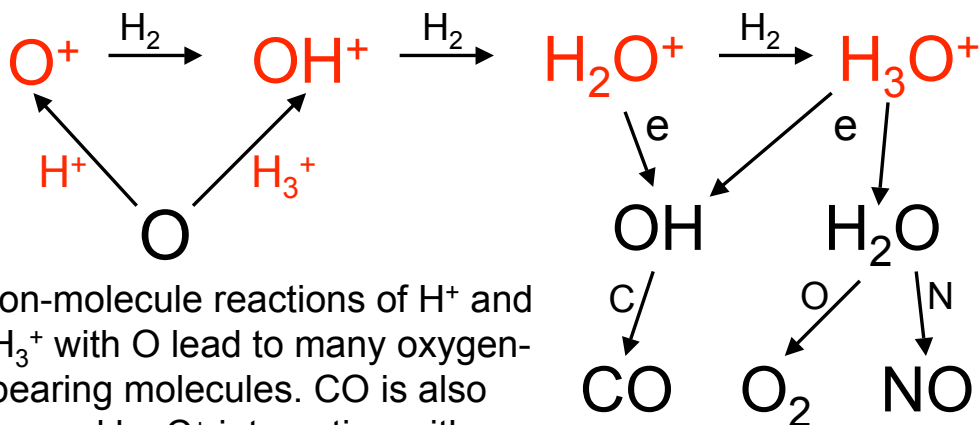
### References

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, Proc. NAS 103 12269 2006

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### The Ion-Molecule Oxygen Molecule Paradigm



Ion-molecule reactions of  $\text{H}^+$  and  $\text{H}_3^+$  with  $\text{O}$  lead to many oxygen-bearing molecules.  $\text{CO}$  is also formed by  $\text{C}^+$  interacting with  $\text{OH}$  and  $\text{H}_2\text{O}$  to form  $\text{HCO}^+$ , which is not shown here.

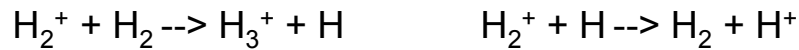
**N.B.** Similar schemes starting with  $\text{C}$  and  $\text{N}$  end prematurely at  $\text{CH}_3^+$  and  $\text{NH}_3^+$

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## 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 that can do this, and the original  $H_2^+$  is transformed into a set of molecular ions that define ion-molecule chemistry.

### Detected interstellar molecular ions

$H_3^+$ ,  $H_2D^+$   
 $H_3O^+$   
 $CO^+$ ,  $HCO^+$ ,  $DCO^+$ ,  $HOC^+$ ,  $HOCO^+$ ,  $H_2COH^+$   
 $N_2H^+$ ,  $N_2D^+$ ,  $HCNH^+$ ,  $HC_3NH^+$   
 $SO^+$ ,  $HCS^+$   
 $C_6H^+$

Ions marked in red are particularly useful diagnostics.  
 Most isotopic variants are not shown.

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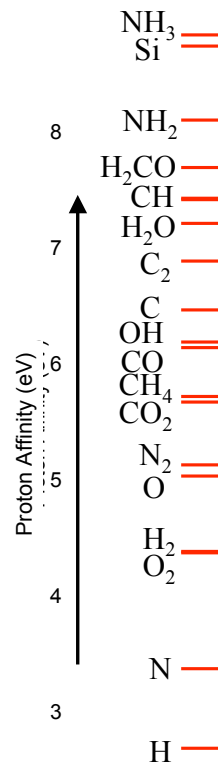
## Molecular Ions and Proton Affinity

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.



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## 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.

HCO<sup>+</sup> is abundant because CO is, and because well-bound molecules like H<sub>2</sub>O and NH<sub>3</sub> (with larger proton affinities) are not.

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

Molecule	$\mu$ (D)	$\nu_{10}$ (GHz)
HCO <sup>+</sup>	3.93	89.19
N <sub>2</sub> H <sup>+</sup>	3.4	93.18

$$A_{ul} = \frac{64\pi^4}{3hc^3} \mu_{ul}^2 \nu_{ul}^3$$

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

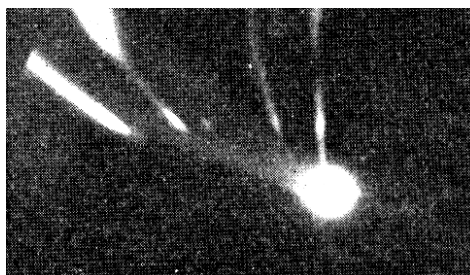
The first molecular ion discovered in the ISM was HCO<sup>+</sup> (Snyder et al. 1970, Klemperer 1974). It served as a surrogate for H<sub>3</sub><sup>+</sup> and as the signature for ion-molecule chemistry. H<sub>3</sub><sup>+</sup> was discovered in the ISM in 1995.

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## 3. The Astronomical Detection of H<sub>3</sub><sup>+</sup>

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



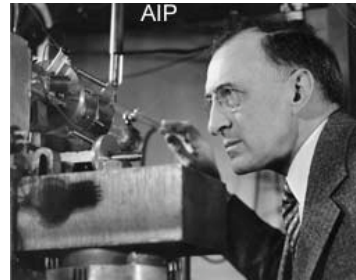
*Existence of H<sub>3</sub>.*—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which  $m/e = 3$  has been detected. There can, I think, be little doubt that this line is due to H<sub>3</sub>. The existence of this substance is interesting from a chemical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

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# H<sub>3</sub><sup>+</sup> in Laboratory Hydrogen Plasmas

A. J. Dempster (discoverer of <sup>235</sup>U) established that H<sub>3</sub><sup>+</sup> is abundant in lab plasmas (Phil Mag 31 438 1916)



H<sub>3</sub><sup>+</sup> is produced in the reaction  
$$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$$
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 (1/2 page note by Martin et al., ApJ 134 1012 1962), 10 more years for serious consideration (T. Oka) and 25 more to be detected in the ISM.

**See Oka, Rev Mod Phys 64 114 1992 for more history.**

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## ON THE POSSIBLE OCCURRENCE OF H<sub>3</sub><sup>+</sup> IN INTERSTELLAR SPACE

The possibilities for detection of the molecular ion H<sub>3</sub><sup>+</sup> 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<sub>3</sub><sup>+</sup> may also be expected in interstellar space. In fact, with the presence of quantities of molecular hydrogen, H<sub>2</sub><sup>+</sup> will react to form H<sub>3</sub><sup>+</sup>.

Formation of H<sub>3</sub><sup>+</sup> through the reaction H<sub>2</sub><sup>+</sup> + H<sub>2</sub> → H<sub>3</sub><sup>+</sup> 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<sup>-14</sup> cm<sup>2</sup> at normal thermal energies. This is much greater than the gas-kinetic cross-section for neutral hydrogen molecules. The cross-section for H<sub>3</sub><sup>+</sup> formation by this reaction varies inversely with the relative velocity of the H<sub>2</sub><sup>+</sup> 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<sub>3</sub><sup>+</sup> ions persist over very many subsequent collisions with hydrogen molecules. The H<sub>3</sub><sup>+</sup> ion is stable against spontaneous dissociation. Its binding energy of 4.18 eV (Varney 1960) exceeds that of H<sub>2</sub><sup>+</sup> (2.65 eV), so the formation reaction is exoergic (Hirschfelder, Curtiss, and Bird 1954).

Thus it may be expected that H<sub>2</sub><sup>+</sup> will be converted to H<sub>3</sub><sup>+</sup> upon encounter with a hydrogen molecule, and the population of H<sub>2</sub><sup>+</sup> will be very strongly influenced by the density of neutral molecular hydrogen. It now appears desirable to consider the possibilities for detecting H<sub>3</sub><sup>+</sup> because this molecular ion may be present under some circumstances to the virtual exclusion of H<sub>2</sub><sup>+</sup>.

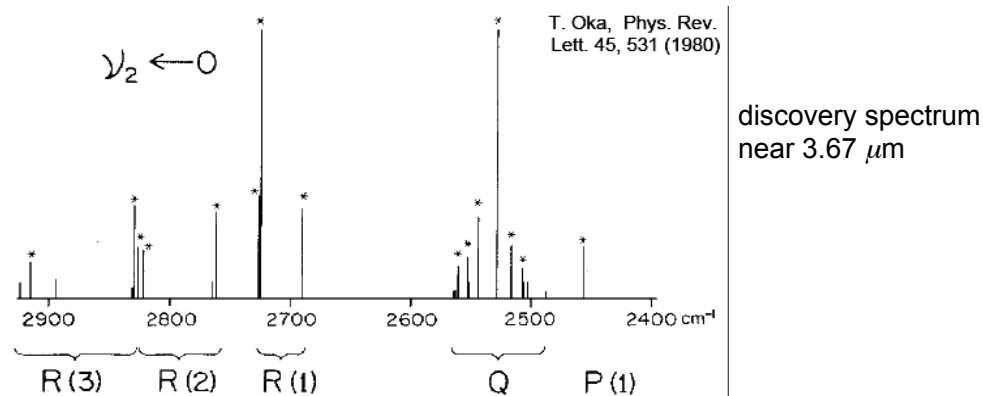
D. W. MARTIN  
E. W. MCDANIEL  
M. L. MEEKS

June 13, 1961  
GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA

ApJ 134 1012 1961

## The IR Spectrum of $\text{H}_3^+$

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



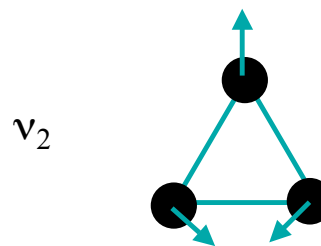
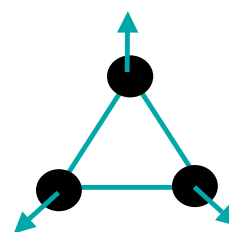
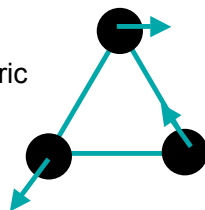
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## Vibrational Modes of $\text{H}_3^+$

- One combination is the totally symmetric  $\nu_1$ 
  - Breathing mode  $r_1 + r_2 + r_3$
- Two other combinations are the  $\nu_2$  mode
  - $r_1 + \varepsilon r_2 + \varepsilon^2 r_3$
  - $r_1 + \varepsilon^2 r_2 + \varepsilon r_3$ 
    - $\varepsilon = e^{2\pi i/3}$

The degeneracy of the asymmetric stretch and bending modes is removed in the deuterated molecules  $\text{H}_2\text{D}^+$  and  $\text{HD}_2^+$



Reference on the spectroscopy of  $\text{H}_3^+$ : MacNab, Adv Chem Phys 84 1 1995

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# H<sub>3</sub><sup>+</sup> Rotational Structure

Energy levels are those of a symmetric top:

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

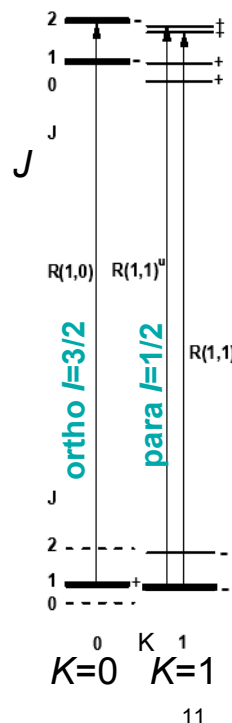
$$B = 43.56 \text{ cm}^{-1} \quad C = 20.61 \text{ cm}^{-1}$$

Pure rotational transitions in H<sub>3</sub><sup>+</sup> do not occur, but the isotope H<sub>2</sub>D<sup>+</sup> is observable near 1mm.

## Discovery $\nu_2 = 1-0$ Rovib Transitions

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

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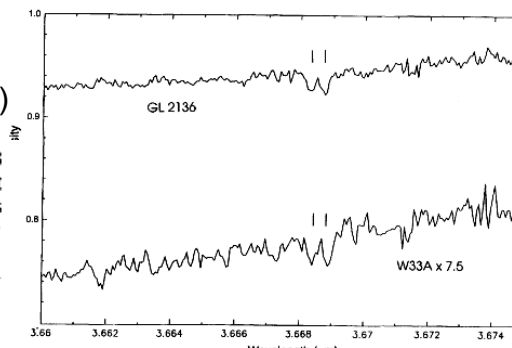
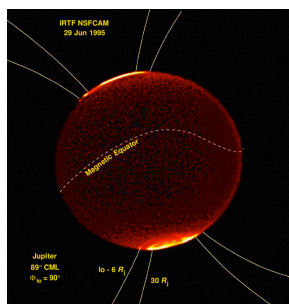
## Discovery of Extraterrestrial H<sub>3</sub><sup>+</sup>

First detection of H<sub>3</sub><sup>+</sup> 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.

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

FIG. 1 Spectra of GL2136 and W33A ratioed by BS6378 (A2V), in the vicinity of the H<sub>3</sub><sup>+</sup> ortho-para doublet at 3.668  $\mu\text{m}$ . The doublet, indicated by vertical lines, consists of the R(1,0) transition of *ortho* H<sub>3</sub><sup>+</sup> at 2,725.898  $\text{cm}^{-1}$  (3.66852  $\mu\text{m}$ , right-hand line of doublet) and the R(1,1)<sup>+</sup> transition of *para* H<sub>3</sub><sup>+</sup> at 2,726.219  $\text{cm}^{-1}$  (3.66808  $\mu\text{m}$ , left-hand line of doublet).



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## 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  $\zeta$  Per – diffuse cloud
- Indriolo et al. ApJ 671 1376 2007 - many lines of sight to diffuse clouds

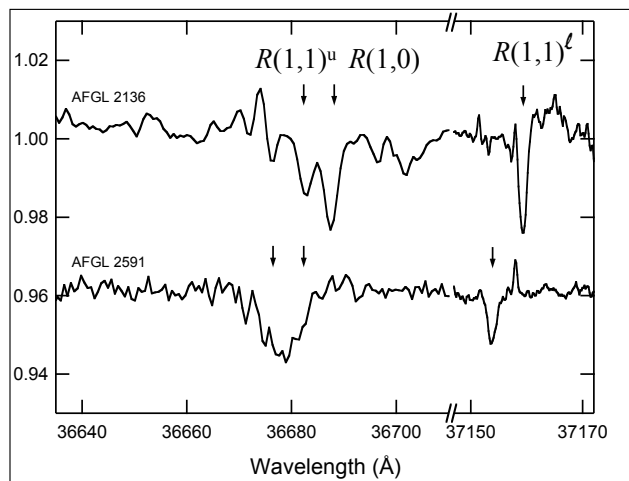
N.B. Quotation marks have been used for some of the diffuse and dense designations with long sight lines which are likely to involve inhomogeneous gas.

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## $H_3^+$ in “Dense” Clouds

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



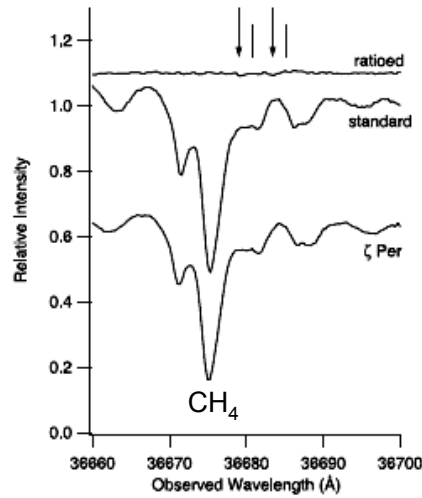
Notice the small depths of the features ~ few %

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# H<sub>3</sub><sup>+</sup> 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 H<sub>3</sub><sup>+</sup>; vertical lines are rest frequencies.
- As shown in the next slide the absorption in ζ Per depth is only 1%.



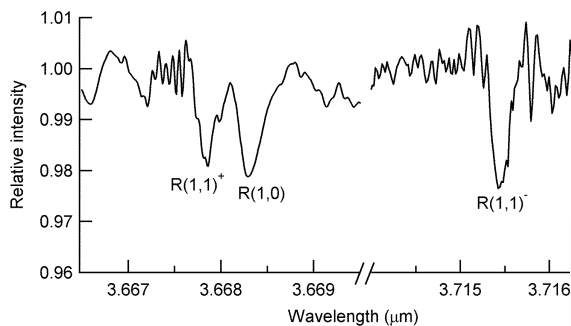
Indriolo et al., ApJ 671 1376 2007

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

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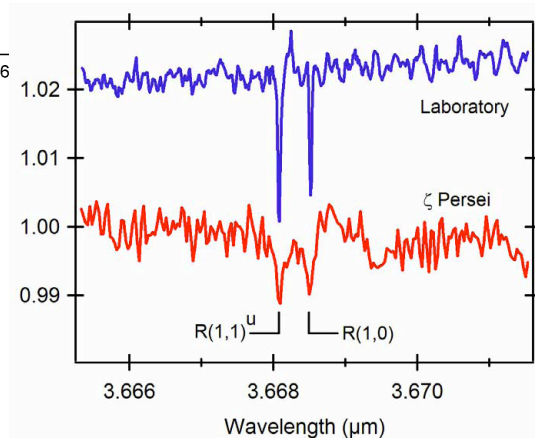
# Cygnus OB2 12 and ζ Per



$N(\text{H}_3^+) \approx 3.8 \times 10^{14} \text{ cm}^{-2}$   
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 advertized conundrum posed by the observations of H<sub>3</sub><sup>+</sup>



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## Analysis of the Observations

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

$$x(H_3^+) = \frac{\zeta_2}{n_H} \frac{x(H_2)}{\beta x_e + kx_O}$$

where  $\zeta_2$  is the CR ionization rate of  $H_2$ ,

$\beta$  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  $kx_O \sim 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .
- $\beta \sim 2\text{-}3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  in the 20 - 60 K range.
- For diffuse clouds, dissociative recombination dominates (large  $x_e$ )
- For dense clouds, particle reactions dominate (small  $x_e$ ).

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## Estimates of the $H_3^+$ Abundance

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

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

$$\begin{array}{ll} N_H = 1.6 \times 10^{21} \text{ cm}^{-2} & n_H \sim 215 \text{ cm}^{-3} \\ L \sim 7.4 \times 10^{18} \text{ cm} & 2N(H_2)/N_H = 0.6 \\ T = 28 \text{ K} & N(C^+)/N_H = 10^{-4} \end{array}$$

Taking  $x_e = 10^{-4}$ ,  $\zeta_2 = 10^{-16} \text{ s}^{-1}$  and using column densities as local densities, then  $x(H_3^+) \sim 5 \times 10^{-9}$ . To achieve the measured column of  $H_3^+$  requires a length  $\sim 20 \text{ pc}$ , which is inconsistent with the hydrogen measurement.

**This is one way of stating the difficulty in understanding McCall's  $H_3^+$  measurements for diffuse clouds.**

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## More Detailed Analysis for $\zeta$ Per

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

$$N(\text{H}_3^+) = \zeta_2 \int ds \frac{x(\text{H}_2)}{\beta x_e + kx_o} \cong \zeta_2 \int ds \frac{x(\text{H}_2)}{\beta x_e} \quad (\text{for diffuse clouds})$$

or

$$N(\text{H}_3^+) \approx \zeta_2 L \left\langle \frac{1}{\beta} \frac{x(\text{H}_2)}{x_e} \right\rangle$$

If we further assume that  $\beta$  is roughly constant, we can solve for the CR ionization rate of  $\text{H}_2$  in terms of the measured  $\text{H}_3^+$  column

$$\zeta_2 \approx \frac{\beta N(\text{H}_3^+)}{L} \left\langle \frac{x(\text{H}_2)}{x_e} \right\rangle^{-1}$$

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## Analysis for $\zeta$ Per

This expression highlights the fact that the local ratio of the  $\text{H}_2$  and electron densities is likely to be variable, one increasing and the other decreasing. The ratio increases rapidly going into a cloud (or into a dense inhomogeneity of the cloud). However, McCall et al. replace local density ratios by *column density ratios*:

$$\zeta_2 \approx \frac{\beta N(\text{H}_3^+)}{L} \frac{N(\text{C}^+)/N_{\text{H}}}{N(\text{H}_2)/N_{\text{H}}}$$

Substituting the measured column densities for  $\zeta$  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.

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# Summary of $H_3^+$ in Diffuse Clouds - 2008

Indriolo et al. made additional observations of diffuse clouds in 2007 and analyzed them carefully. They recognize that  $H_3^+$  measures the ionization rate  $\zeta_2$  for  $H_2$ , and not the primary rate to ionize atomic H (without consideration of heavy elements), a factor of 1.5 (c.f. Lecture 9-08).

The well publicized puzzle about the large cosmic ray ionization rate from  $H_3^+$  measurements in diffuse clouds would seem to be reduced to less than a factor of 10 (and maybe even less) disagreement with the value deduced from the demodulating local measurements.

Some other issues that still need to be considered:

- (1) Why is  $H_3^+$  not detected in many other diffuse clouds, e.g., towards the well studied cloud towards  $\zeta$  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?

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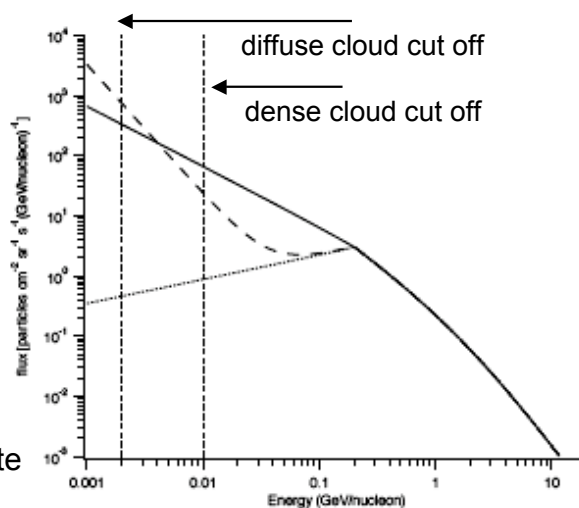
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## Possible Role of Low Energy Protons - 1

Model cosmic ray spectra  
 solid - standard above 0.2 GeV  
           + low-energy extrapolation  
 dotted - leaky box model  
 dashed - another extrapolation

Rapidly rising spectra towards low energies give a large ionization rate in diffuse gas and a small rate in dense gas, but low-energy cut offs are needed.

Suggest these spectra are generated in local shocks rather than in SNR.

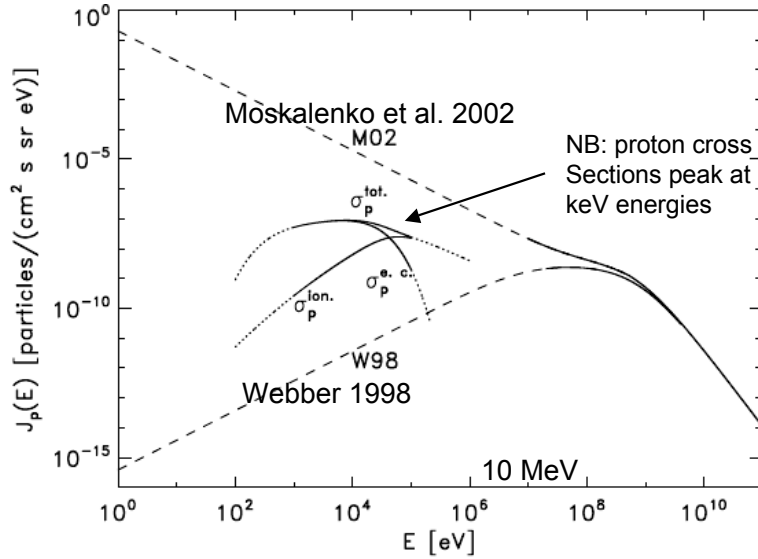


Indriolo et al. arXiv 0901.1143

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## Possible Role of Low Energy Protons - 2



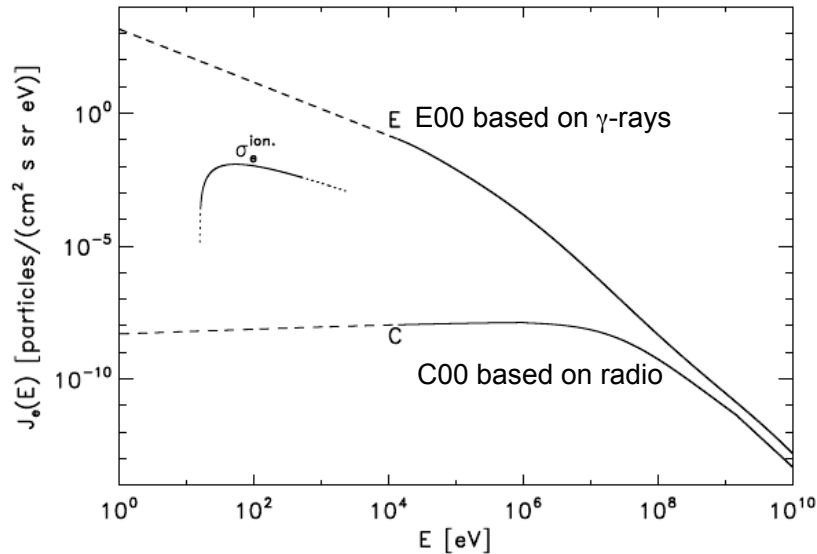
**Padovani et al. A&A in press 2009**

Two extrapolations of the local cosmic ray proton intensity by cosmic ray physicists.

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## Possible Role of Low Energy Electrons



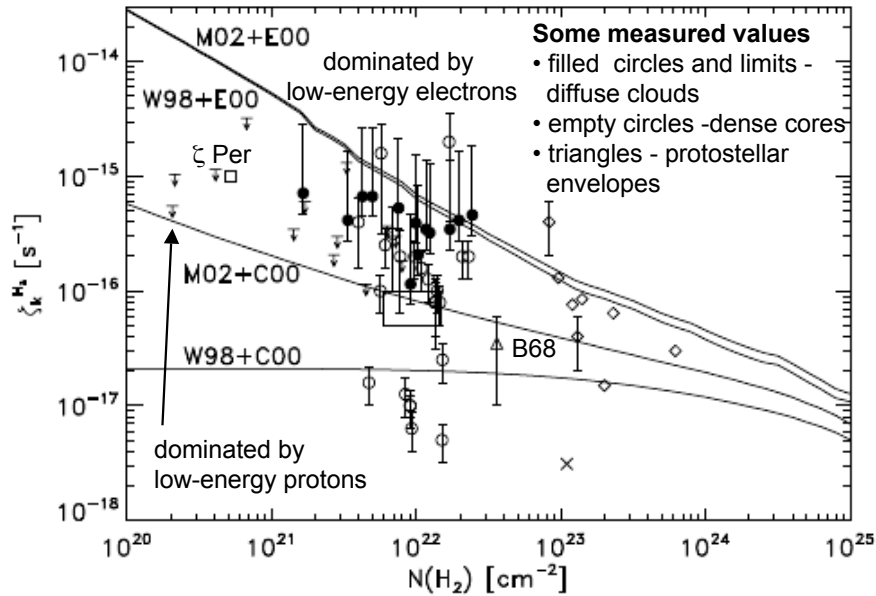
**Padovani et al. A&A in press 2009**

Two extrapolations of the local cosmic ray electron intensity by The Cal Tech cosmic ray group (Strong et al. ApJ, 537, 763, 2000)

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## Ionization Rates: Trying to Put it All Together



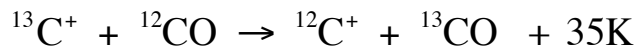
Padovani et al. A&A in press 2009  
**The story is unfinished!**

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## 4. Isotope Fractionation

The replacement of an element by a heavier isotope lowers a molecule's energy by reducing the zero-point vibrational energy. Reactions that accomplish this are slightly *exothermic* (energy producing), whereas the reverse reaction will be endothermic. At low temperatures, the heavier isotope will be favored. This possibility was first suggested by Watson et al. (1976) for CO:



- The rate coefficient is fairly large,  $\sim 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and the  $^{12}\text{CO} / ^{13}\text{CO}$  ratio can be increased for low  $T$ .
- The measured ISM ratio is  $\sim 70$ , less than the terrestrial ratio 89.
- This could be due to fractionation, but the ratio is affected by the fact that  $^{13}\text{CO}$  is more easily dissociated by interstellar UV radiation than  $^{12}\text{CO}$ , i.e., it is less well self-shielded.
- Galactic nucleosynthesis may be more important:  $^{13}\text{CO}$  is produced by the CNO cycle and  $^{12}\text{CO}$  by the triple- $\alpha$  process (Wilson & Rood ARAA 32 191 1994).

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## Deuterium Fractionation

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



Simple thermal considerations suggest that the backward reaction is shut down at low temperature: at 10K  $\exp(-230/T) = 10^{-10}$ .

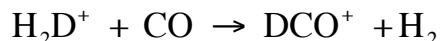
Laboratory experiments (e.g., Gerlich et al. *Pl. Sp. Sci.* 50 1275 2002), show that the rate coefficients depend on the rotational properties of the molecules and thus on the nuclear spin state of  $\text{H}_3^+$ . At 10 K rate:

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

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

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

Nonetheless, fractionation does occur. Once formed,  $\text{H}_2\text{D}^+$  interacts strongly with other molecules and deuterates them, e.g.



**DCO<sup>+</sup> J= 2-1 is observed at 144 GHz etc.**

**See Caselli et al. ( AA 492 703 2008) for a survey of dense cores in the 372 GHz line of ortho  $\text{H}_2\text{D}^+ 1_{10}-1_{11}$ .**

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## Other Deuteration Reactions

Remarkably, molecules with more than one D are observed in cold molecular cloud cores, notably  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$  and even  $\text{ND}_3$ .

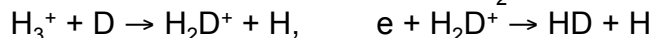
This is believed to occur by reactions with multiply-deuterated  $\text{H}_3^+$ :



There are several ways to synthesize HD:

**Grain formation:**  $\text{D} + (\text{Gr} + \text{H}) \rightarrow (\text{Gr} + \text{H} + \text{D}) \rightarrow \text{Gr} + \text{HD}$

**Ionic reactions:**  $\text{H}^+ + \text{D} \rightarrow \text{D}^+ + \text{H} - 41\text{K}$  and  $\text{D}^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{HD}$



The ionic reactions are fast, except the first which has a small barrier. Destruction of HD is by photodissociation and by reaction with  $\text{H}_3^+$ .

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.

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# The HD Molecule

Basic facts:

reduced mass =  $2/3 m_H$   
finite permanent electric dipole ( $5.85 \times 10^{-4}$  D)  
low abundance ( $x_D = 2 \times 10^{-5}$ )

- With the same number of electrons as  $H_2$  and with non-identical nuclei (spins  $1/2$  and  $1$ ), the *electronic levels* are very similar to  $H_2$ . Expect transitions analogous to the Lyman and Werner bands and line photodissociation, but with little self-shielding
- The *vibration frequencies* are decreased by  $(3/4)^{1/2} = 0.866$ , and rotational frequencies decreased by  $3/4$ .
- The most profound difference with  $H_2$  is the absence of the effects of the Exclusion Principle on the *rotational spectrum*: HD has an ordinary rotational ladder with  $E(J) = BJ(J+1)$ . The lowest rotational transition is  $E(1-0) = 2B(HD)$ , in contrast  $6B(H_2)$  for  $H_2$ , which means

$$\lambda(1-0, HD) = (4/3) \times 3 \lambda(1-0, H_2) = 112 \text{ microns.}$$

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## Observations of HD Electronic Transitions

Discovered by the first UV satellite observatory *Copernicus* (UV absorption line spectroscopy) and more recently by FUSE with a line at  $1105 \text{ \AA}$ . See the recent and most complete study by Snow et al. (ApJ 688 1124 2008) of 41 lines of sight towards hot stars with visual extinction up to  $A_V = 3$ .

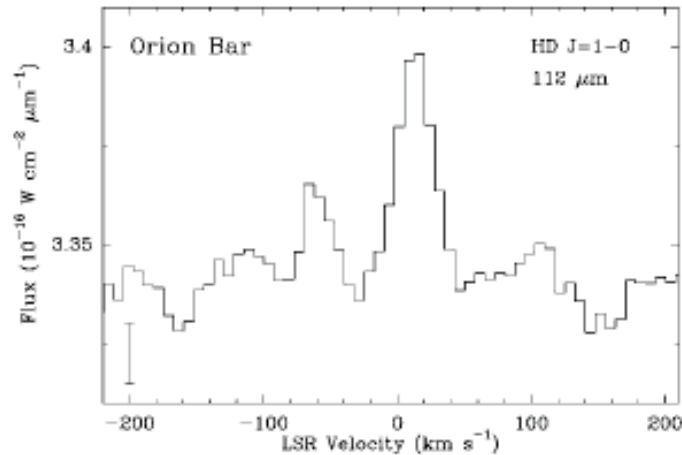
The main conclusion is that the abundance of HD is less than that of atomic D, specifically  $x(HD) \sim 10^{-7} - 10^{-6}$ .

Conclusion: The abundance of HD is determined by local conditions of density and temperature that affect its formation and destruction, and not by Big-Bang cosmology (except that's the origin of deuterium).

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## Discovery of the 112 $\mu\text{m}$ Line of HD



Wright et al. ApJ 515 L29 1999 using ISO LWS  
HD/H<sub>2</sub>  $\sim 10^{-5}$

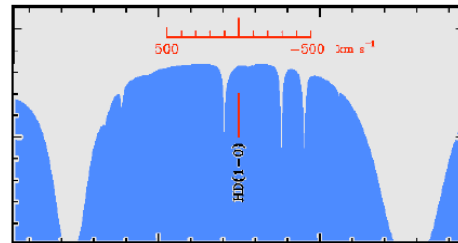
*Spitzer* detected the  $J = 5-4$  and  $4-3$  rotational lines at 23.0 and 28.5  $\mu\text{m}$  in the SNR IC443 with similar abundances (Neufeld et al. ApJ 617 L33 2006)

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## SOFIA Perspective Cold Molecular Hydrogen Using the 112 $\mu\text{m}$ of HD

- Without the restrictions of the Exclusion Principle, the  $J = 1-0$  transition at 63 K will be available to new generation FIR systems like *Herschel* and SOFIA.
- The rotational constant of HD is  $\sim 3/4$  that of H<sub>2</sub>
- The permanent electric dipole moment of HD is  $5.85 \times 10^{-4}$  D



80% atmospheric transmission  
for the HD line at 40,000 feet

### Eric Becklin's View (2007)

The lower excitation temperature and finite dipole moment almost compensate for the low abundance of HD relative to H<sub>2</sub>.

The 112  $\mu\text{m}$  of HD could be mapped much like the HI 21cm line but for cold molecular gas.

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