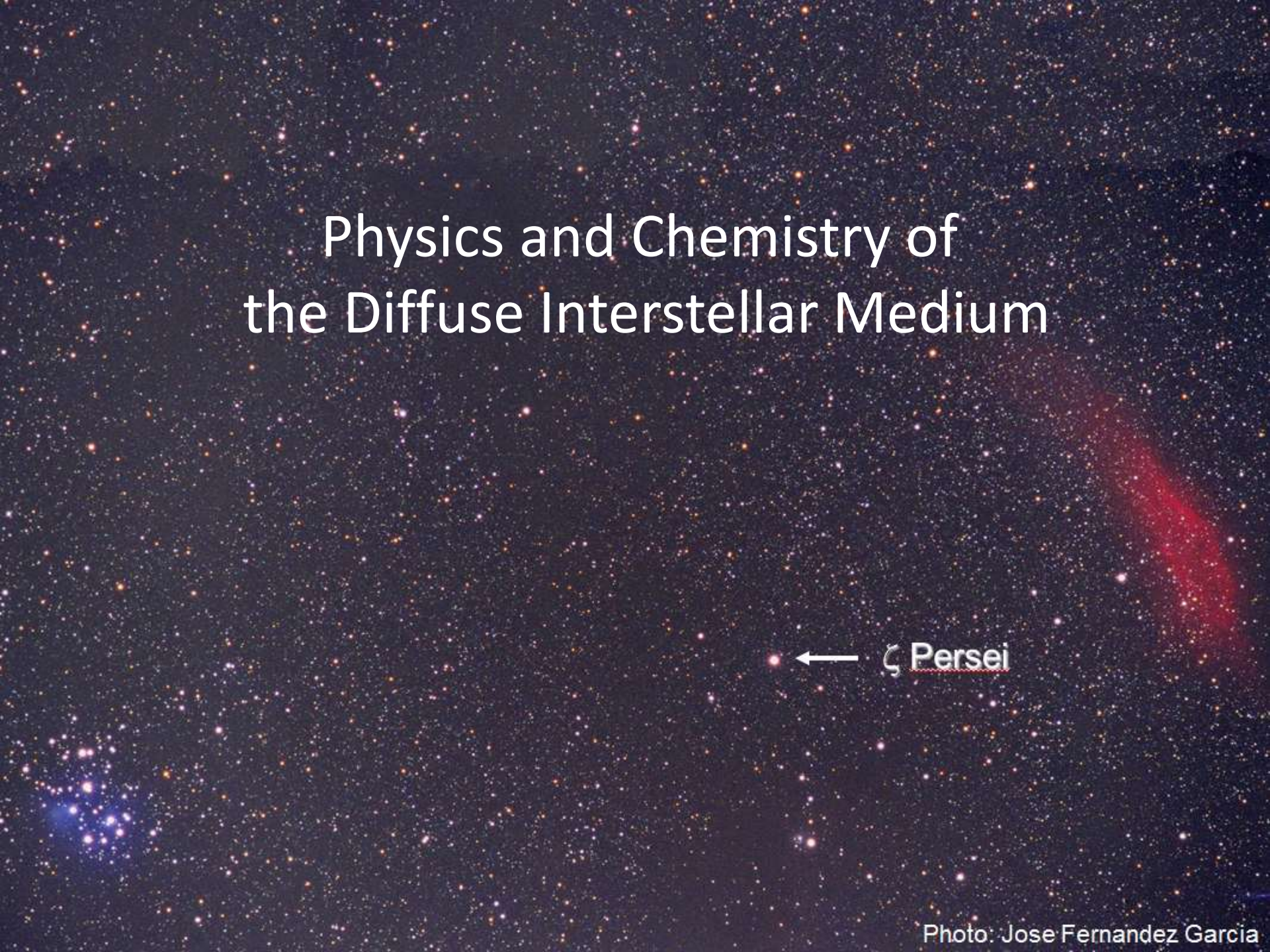
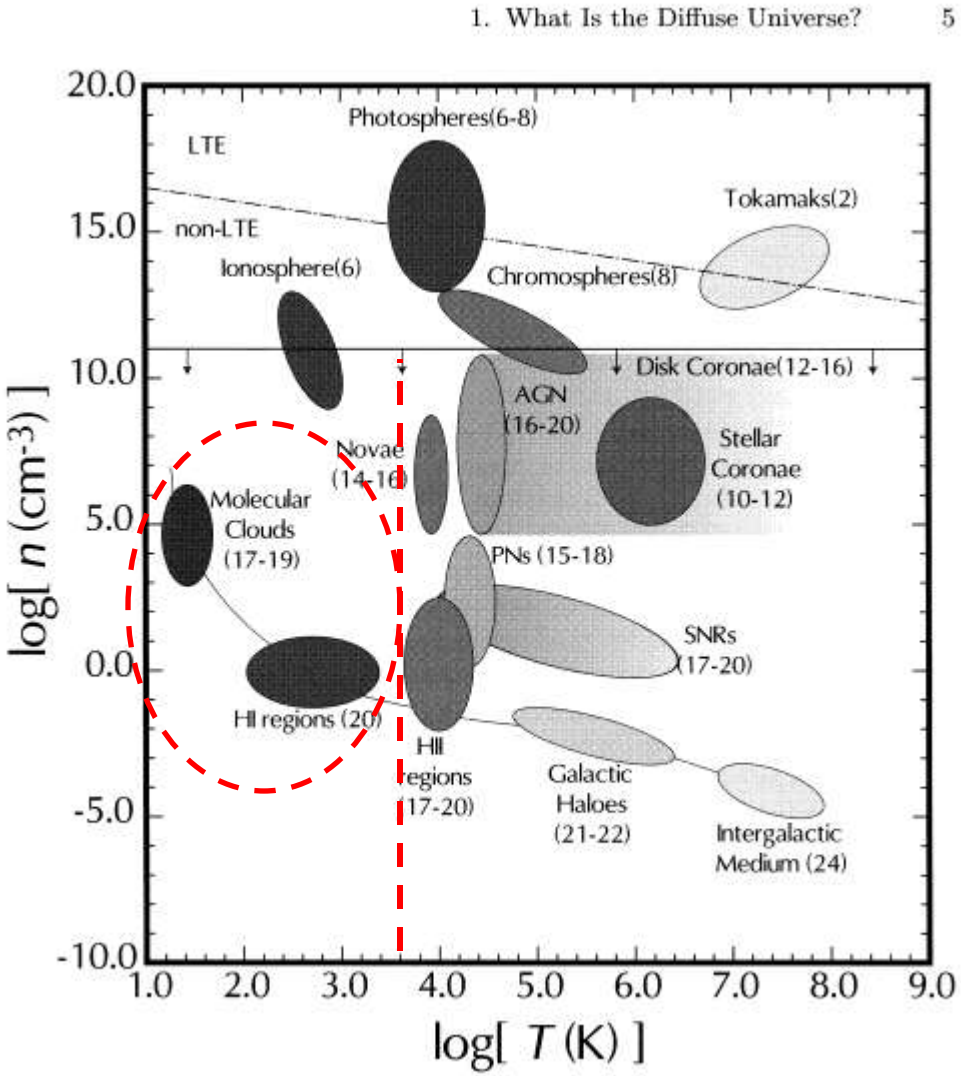
Physics and Chemistry of the Diffuse Interstellar Medium



What is the Diffuse Interstellar Medium?

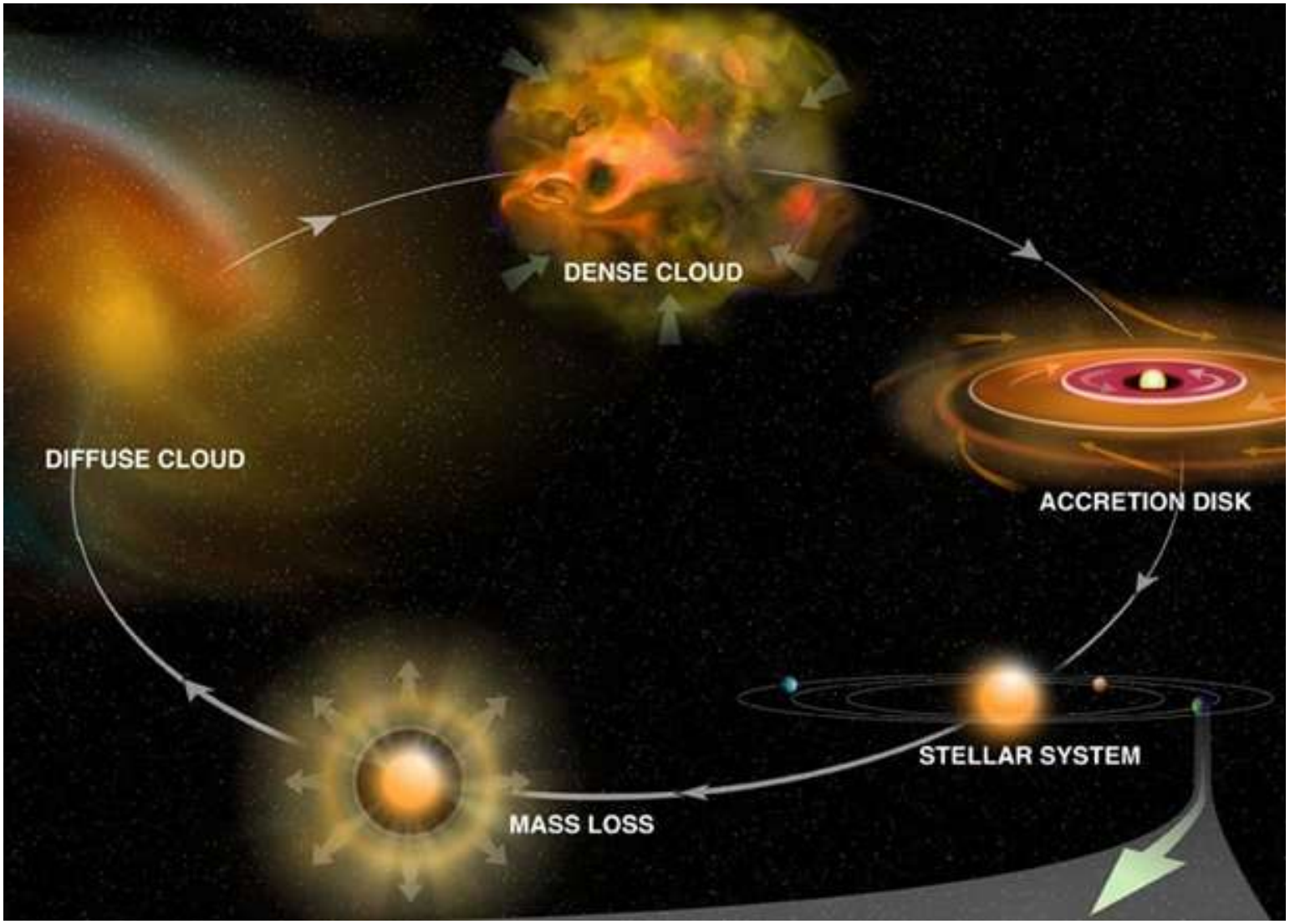


Picture from Dopita / Sutherland, “Astrophysics of the Diffuse Universe”, Springer

HII regions

- in Astronomy “HII” stands for ionized hydrogen atoms H^+, “HI” stands for neutral hydrogen H, “FeIV” would stand for Fe^{3+}, etc …
- consequently, HII regions are characterized by all hydrogen being ionized,
- Temperatures are on the order of 10 000 K,
- HII regions are low density clouds of gas where star formation recently happened,
- too hot and violent for molecules to exist,
- Precursors are Giant Molecular Clouds -> star formation

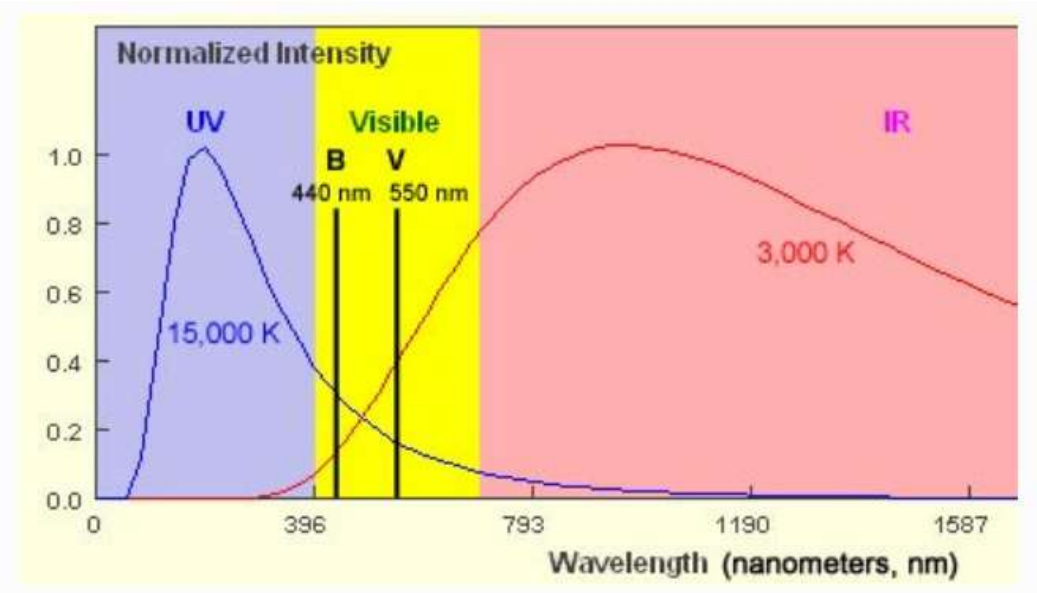
The Cosmic Chemistry Cycle

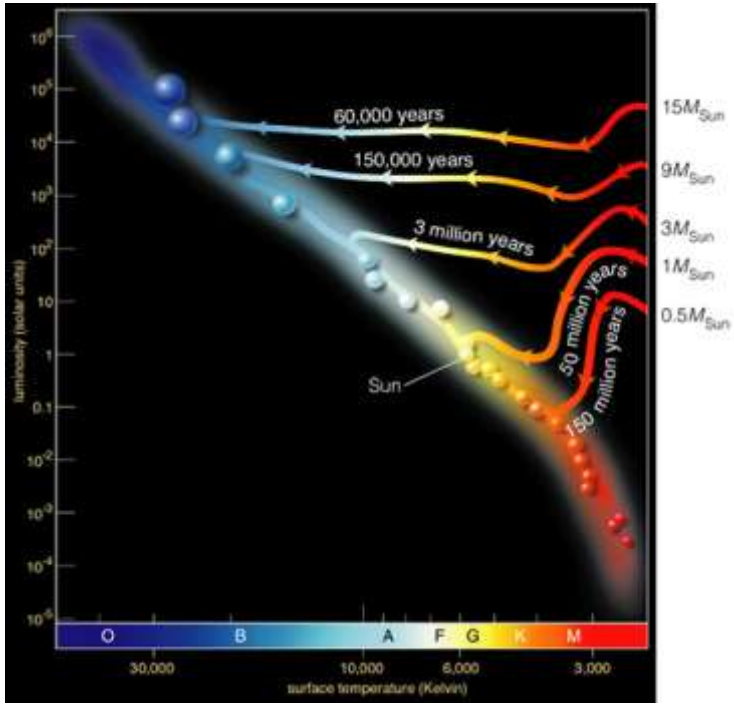


Credit: NRAO

Spectral classes of stars

Spectral Class	O	B	A	F	G	K	M
Temperature (K)	50,000 - 28,000	28,000 - 10,000	10,000 - 7,500	7,500 - 6,000	6,000 - 4,900	4,900 - 3,500	3,500 - 2,000
Colour	Blue	Blue-white	White	White-yellow	Yellow	Orange	Red





Young, massive stars shine in the UV

HII regions and the attenuation of Extreme UV light (EUV)

Photons with $E_\gamma > 13.6$ eV directly photoionize H atoms

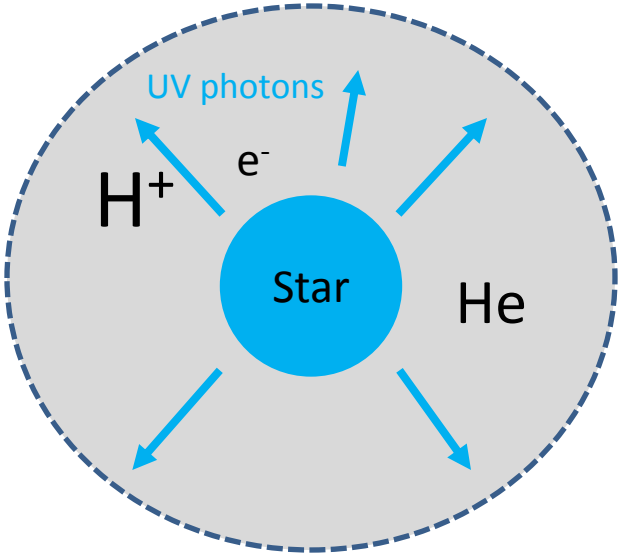
$$H + \gamma \longrightarrow H^+ + e^- \qquad (+\,\Delta E)$$

Recombination between electrons and H^+ can occur into any atomic level, followed by photon emission:

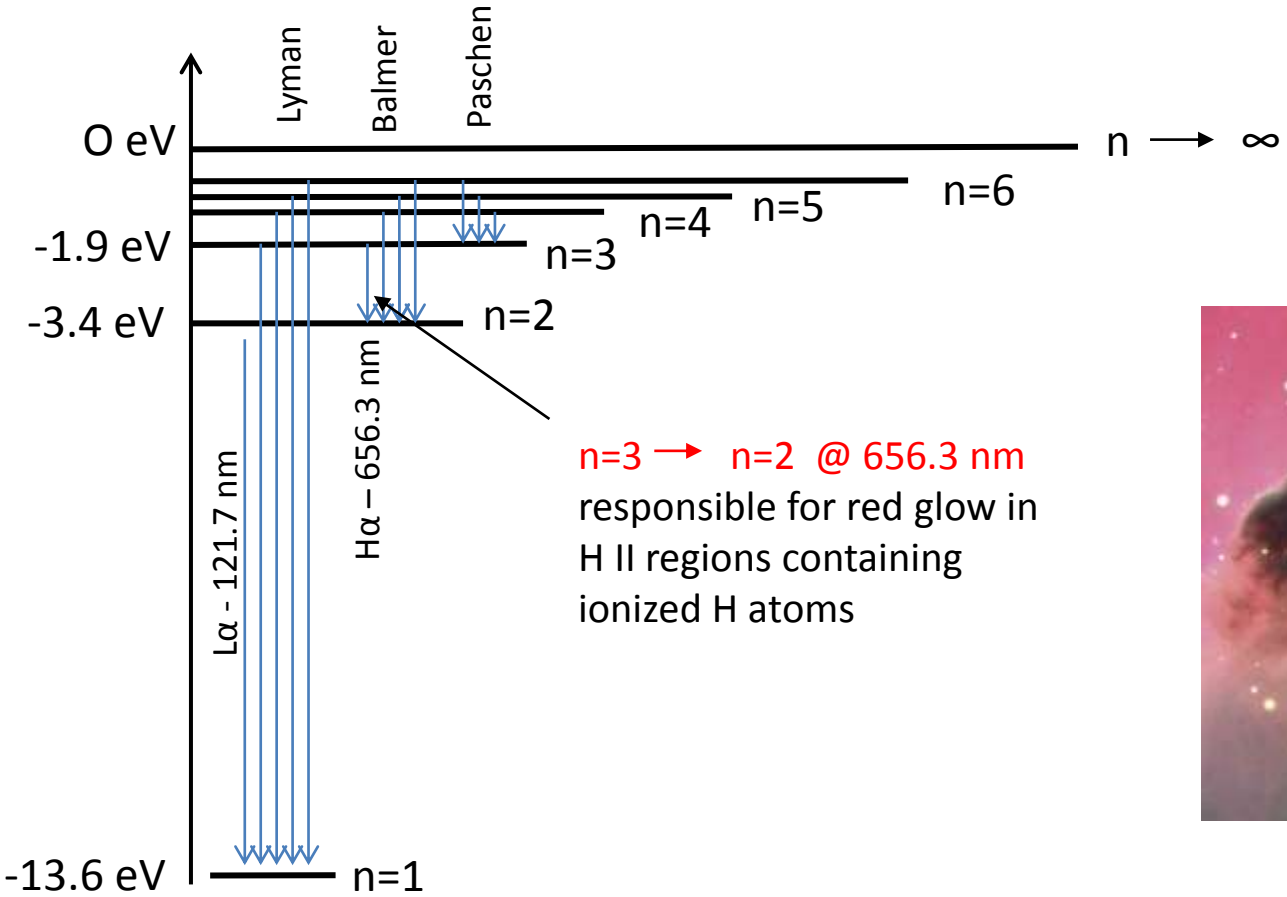
$$H^+ + e^- \longrightarrow H(n)$$

$$H(n) \longrightarrow H(n') + \gamma \qquad (n' < n)$$

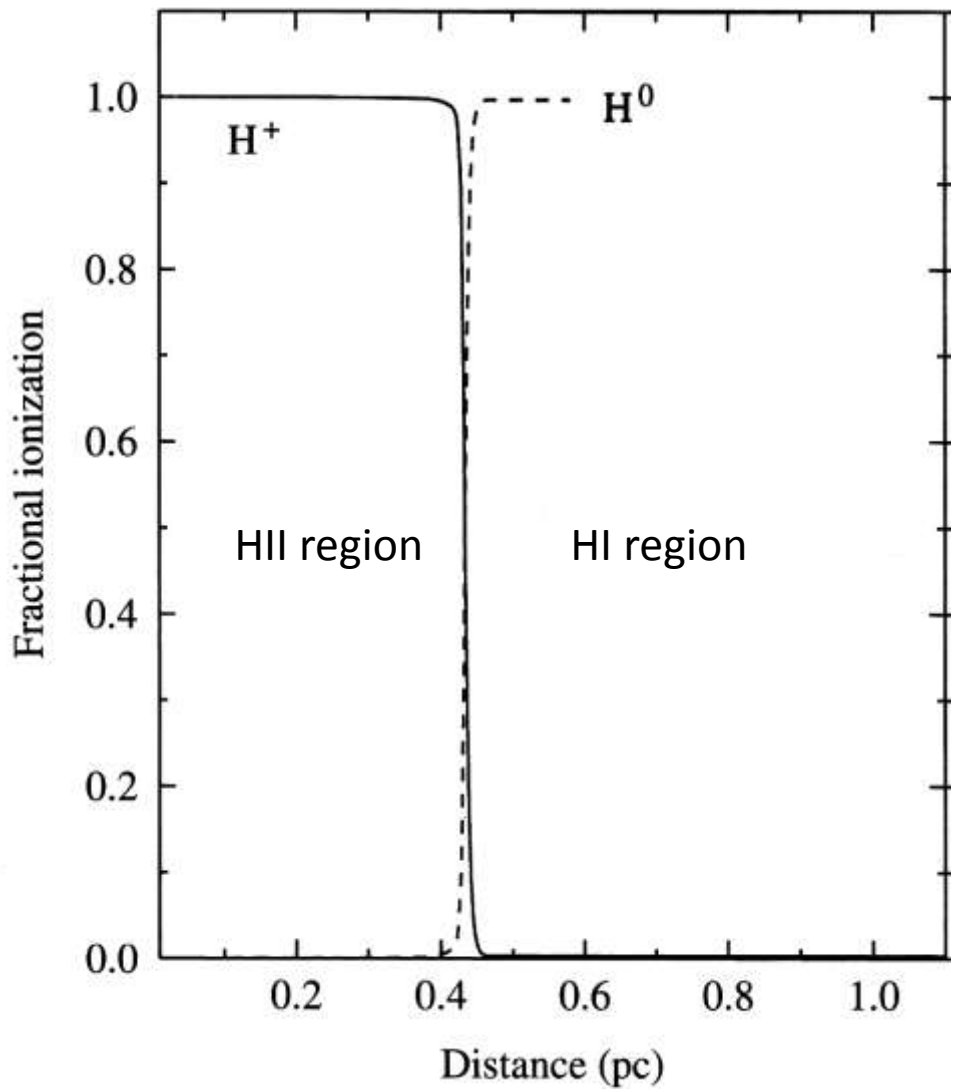
Except for a direct capture into n=1, the emitted photon has an energy of < 13.6 eV, insufficient to ionize neutral H, therefore the UV radiation field is weakened



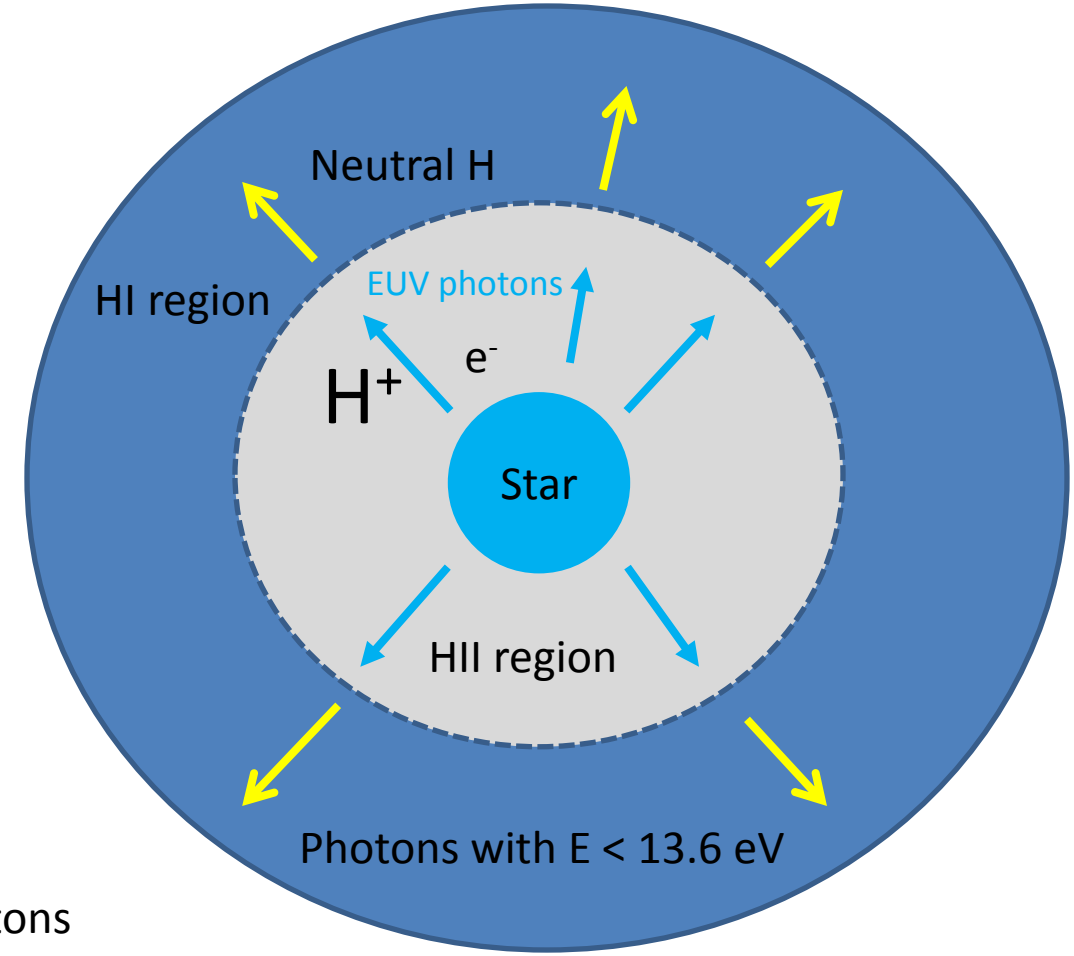
HII regions and the attenuation of Extreme UV light (EUV)



Transition between HII and HI region

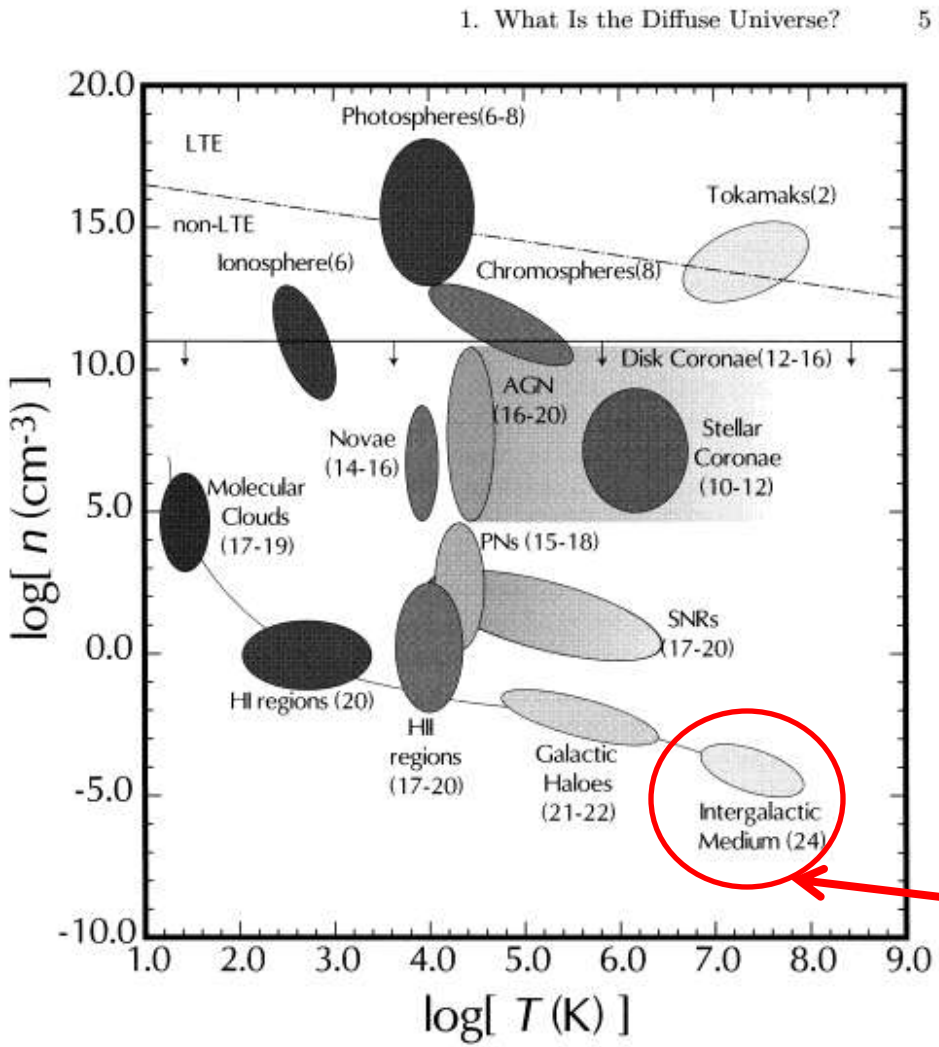


From A.G.G.M. Tielens: “Interstellar Medium”, Cambridge press



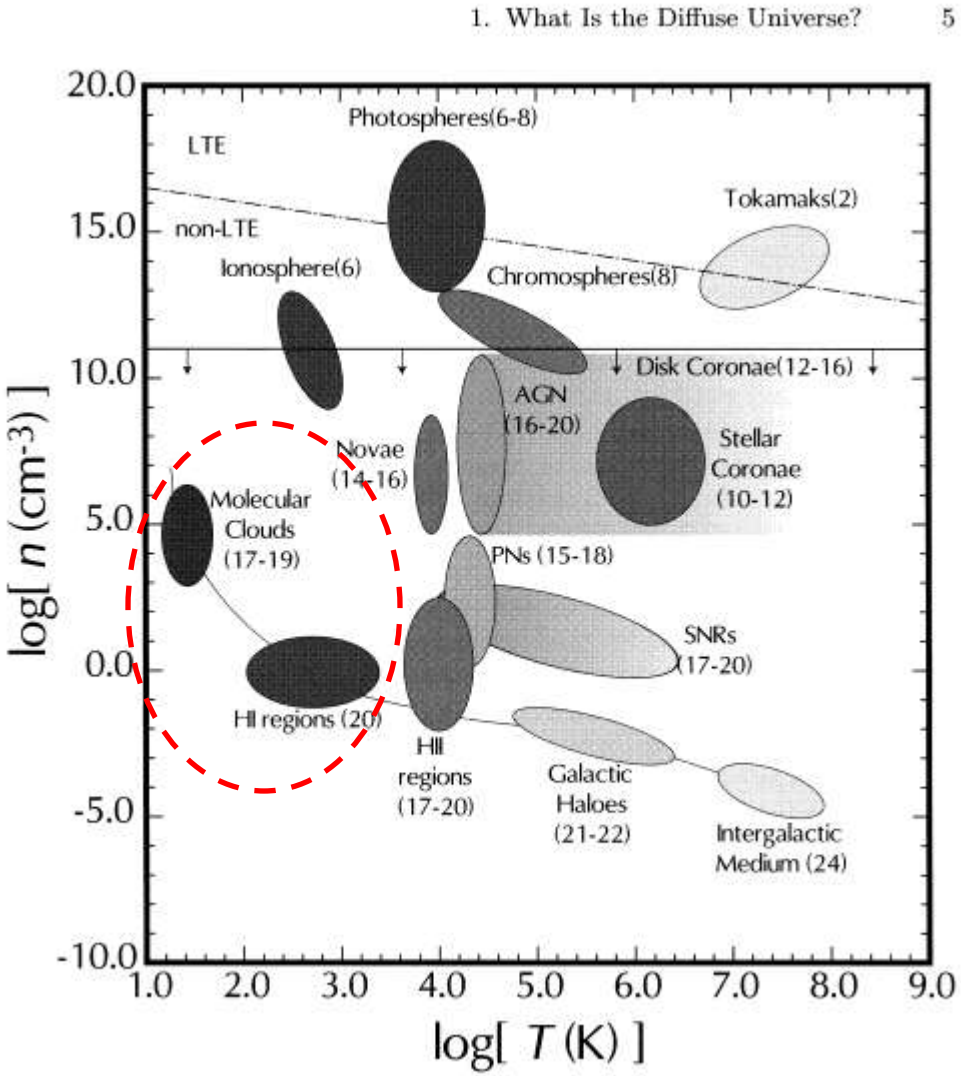
HII regions around young stars act as filters for EUV photons with E > 13.6 eV

For completeness: the Intergalactic Medium



Very dilute,
hydrogen fully ionized,
Very hot: 10^4-10^7 K.

What is the Diffuse Interstellar Medium?

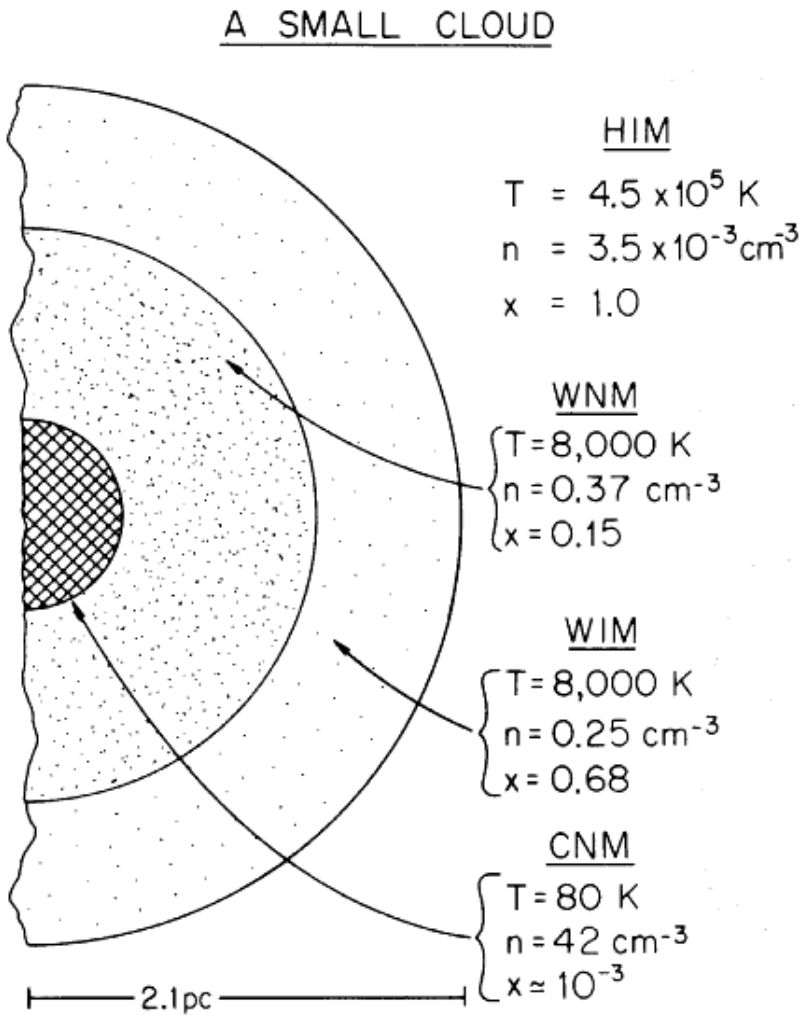


Picture from Dopita / Sutherland, “Astrophysics of the Diffuse Universe”, Springer

Diffuse medium vs. terrestrial conditions

	Earth's atmosphere	Interstellar Medium
Density	10^{19} cm^{-3}	10^{2} – 10^{6} cm^{-3}
Collision time scale	nanoseconds, 3-body collisions likely	hours – years for binary collisions, no 3-body collisions
statistics	Boltzmann $\frac{N_j}{N_1} = \frac{g_j}{g_1} \exp\left(\frac{-\Delta E_m}{kT}\right)$	Often local thermodynamic equilibrium is not reached, radiative lifetimes can be much shorter than average collision times $\longrightarrow$ many species in ground state, irrespective of kinetic temperature

Traditional Classification of the diffuse ISM



x: ionization fraction

The ISM is complex in it's structure, probably clumpy, therefore most sightlines probably consist of a mixture of different phases.

HIM: hot ionized medium

WIM: warm ionized medium

WNM: warm neutral medium

CNM: cold neutral medium

McKee & Ostriker, ApJ 218, 148 (1977)

Modern Classification of Interstellar Cloud Types

Snow & McCall, Annu. Rev. Astron. Astrophys. 2006. 44:367-414

Definitions:

Number density of species X: $n(X)$ $[cm^{-3}]$

Column density: $N(X)$ $[cm^{-2}]$

Integral of n(X) along sightline

Total nuclei number density: n_X $[cm^{-3}]$

example: $N_H = n(H) + 2n(H_2)$, $n_C \approx n(C^+) + n(C) + n(CO)$

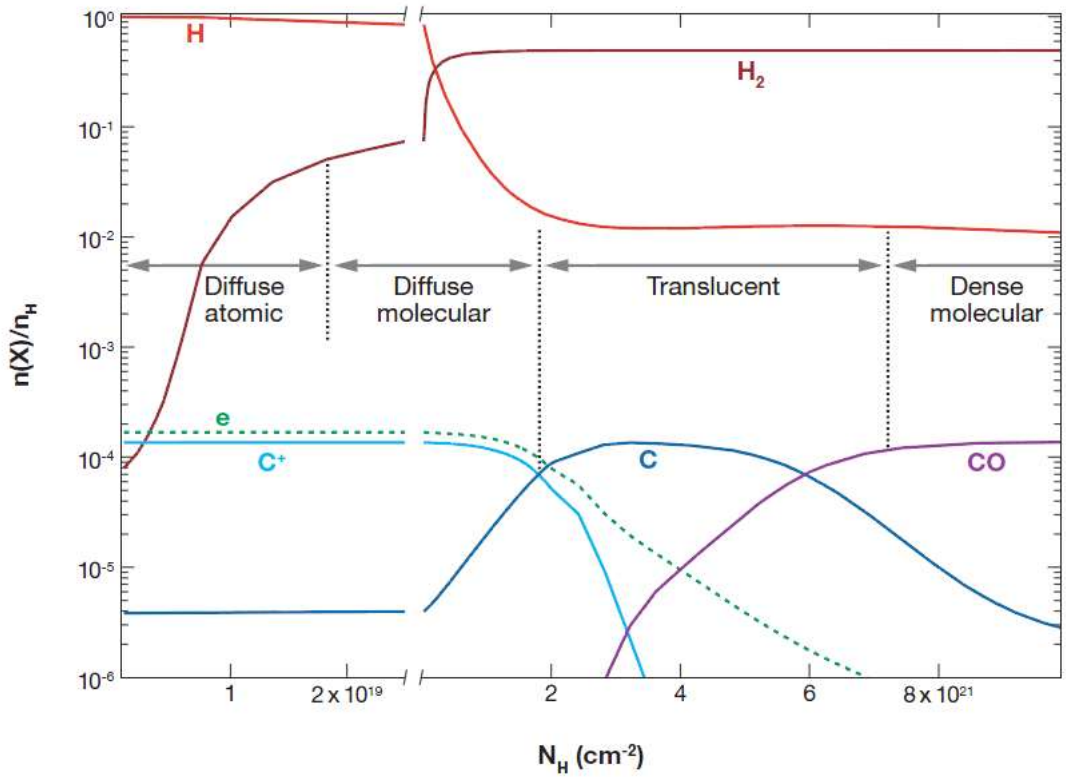
Local fraction: f^n

example: $f^n_{H2} = 2n(H_2)/n_H$, $f^n_{CO} = n(CO)/n_C$, etc …

	Diffuse Atomic	Diffuse Molecular	Translucent	Dense Molecular
Defining Characteristic	$f^n_{H_2} < 0.1$	$f^n_{H_2} > 0.1$ $f^n_{C^+} > 0.5$	$f^n_{C^+} < 0.5$ $f^n_{CO} < 0.9$	$f^n_{CO} > 0.9$
A_V (min.)	0	~0.2	~1–2	~5–10
Typ. n_H (cm^{-3})	10–100	100–500	500–5000?	$>10^4$
Typ. T (K)	30–100	30–100	15–50?	10–50
Observational Techniques	UV/Vis H I 21-cm	UV/Vis IR abs mm abs	Vis (UV?) IR abs mm abs/em	IR abs mm em

The diffuse ISM can be explored by Visible and UV observations!
Easy to study? Still a lot of problems …

Transition between Cloud Types

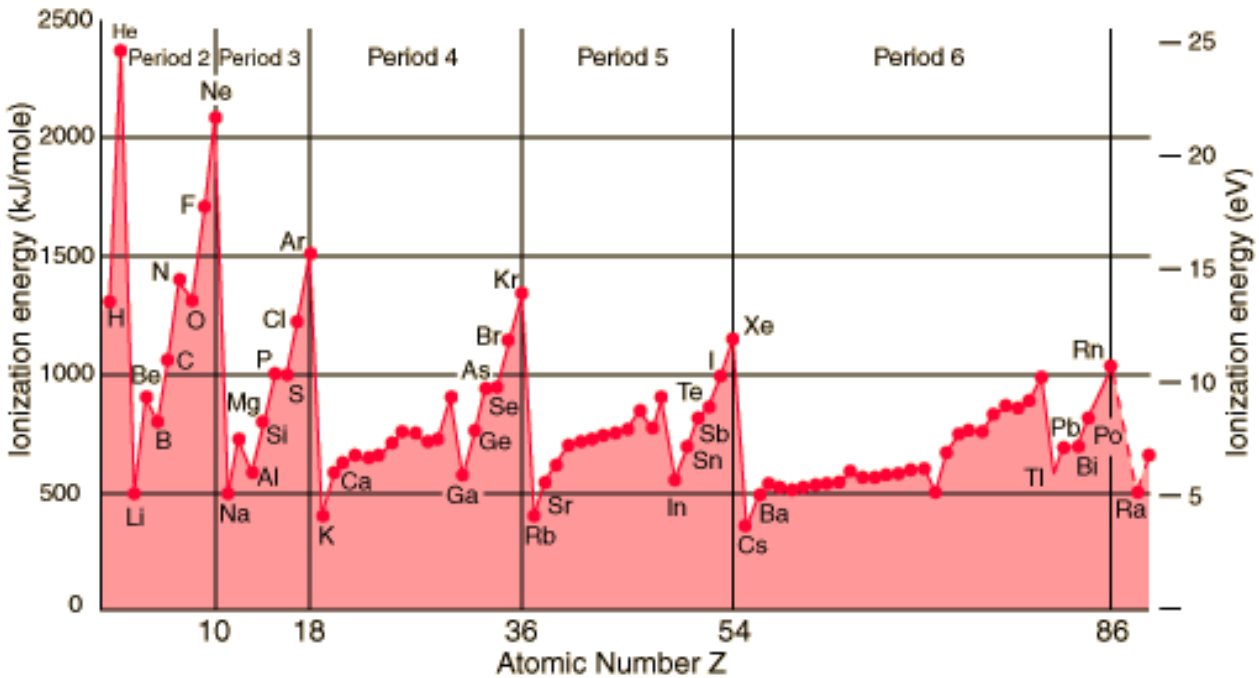


	Diffuse Atomic	Diffuse Molecular	Translucent	Dense Molecular
Defining Characteristic	$f^n{}_{H_2} < 0.1$	$f^n{}_{H_2} > 0.1$ $f^n{}_{C^+} > 0.5$	$f^n{}_{C^+} < 0.5$ $f^n{}_{CO} < 0.9$	$f^n{}_{CO} > 0.9$
A_V (min.)	0	~0.2	~1–2	~5–10
Typ. n_H (cm^{-3})	10–100	100–500	500–5000?	$>10^4$
Typ. T (K)	30–100	30–100	15–50?	10–50
Observational Techniques	UV/Vis H I 21-cm	UV/Vis IR abs mm abs	Vis (UV?) IR abs mm abs/em	IR abs mm em

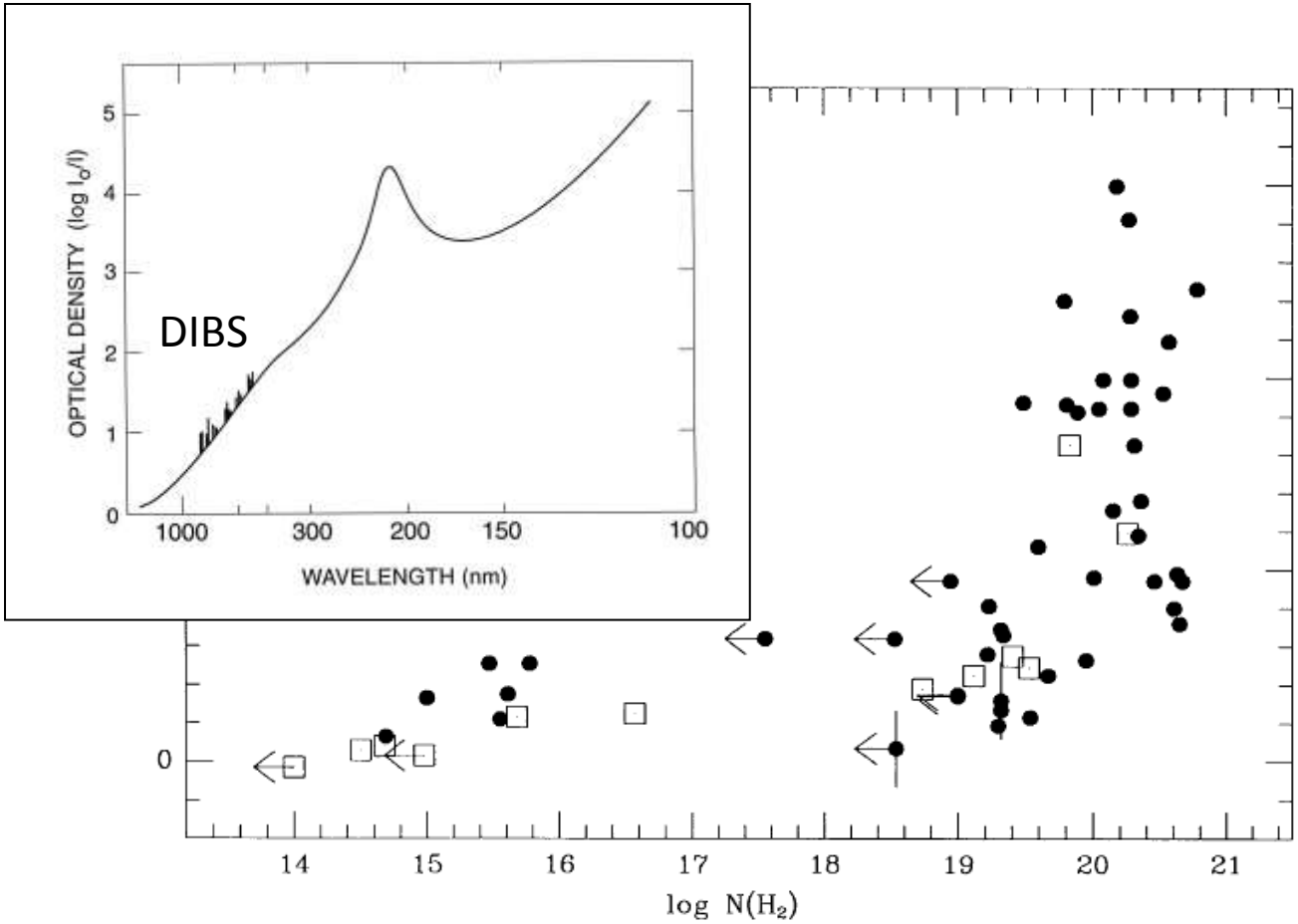
Snow & McCall, Annu. Rev. Astron. Astrophys. 2006. 44:367-414

Diffuse Atomic Clouds

- Part of the diffuse interstellar medium that is fully exposed to radiation field
- Nearly all molecules quickly destroyed by photodissociation
- Hydrogen in neutral atomic form (H).
- Elements with Ionization potential < 13.6 eV almost fully ionized (e.g. C -> C^+)



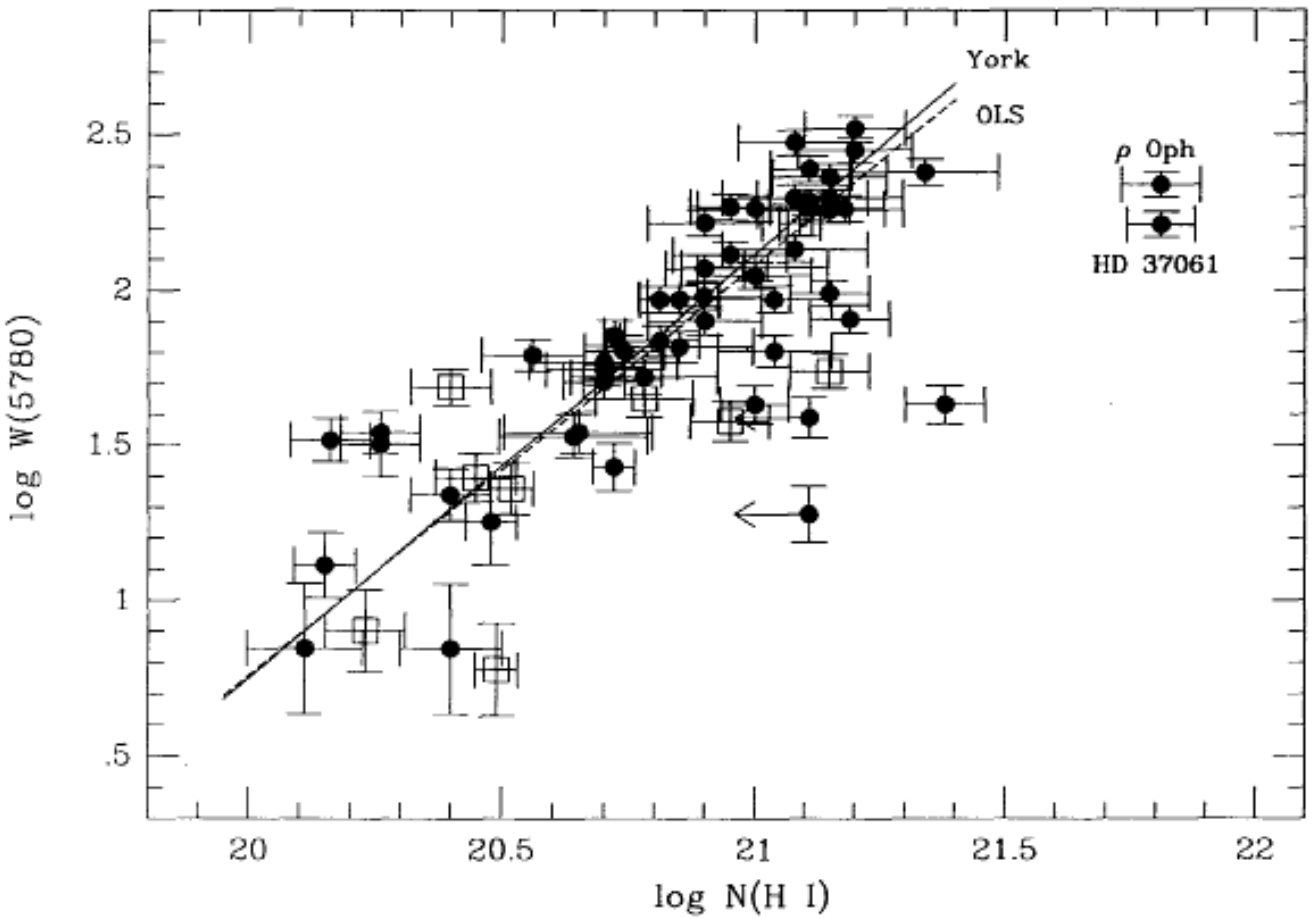
Diffuse Interstellar Bands: Dependence on $N(H_2)$



- There seems to be no correlation between N(H2) and the strength of the DIB features.
- DIBS exist even when $N(H_2)$ gets very small.
- **This suggests that H_2 is not involved when the DIB carriers are formed!**

Herbig ApJ 407, 142 (1993)

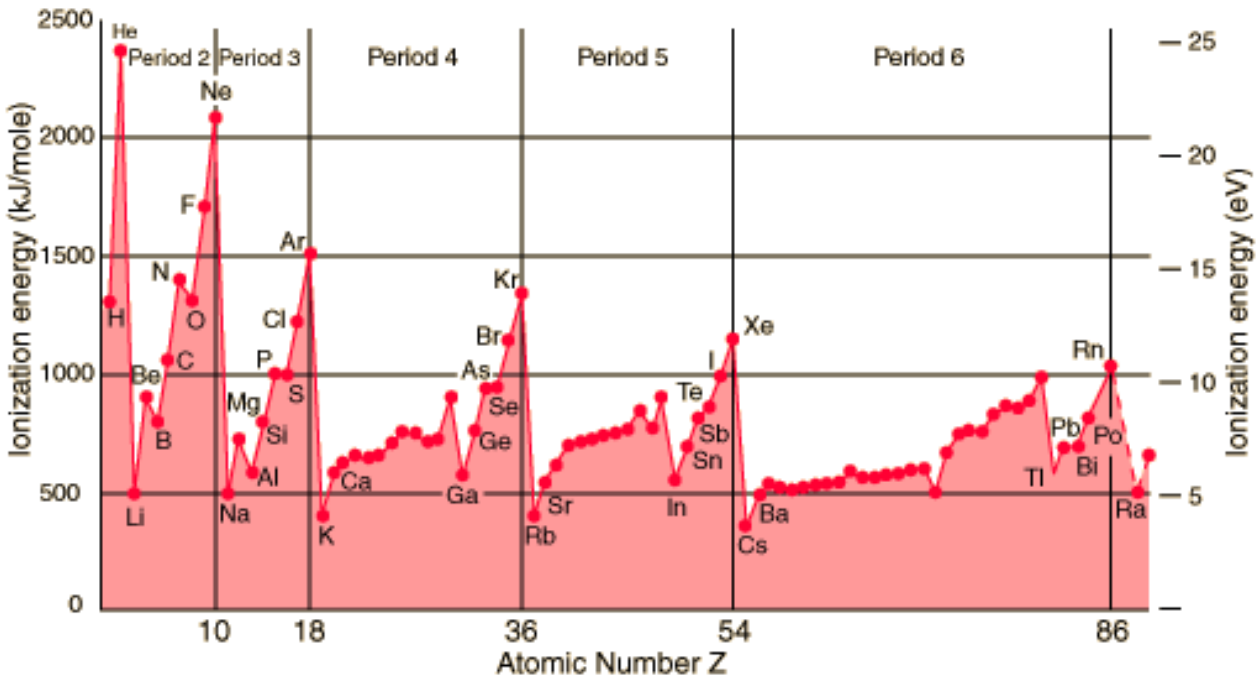
Diffuse Interstellar Bands: Dependence on N(H)



Herbig ApJ 407, 142 (1993)

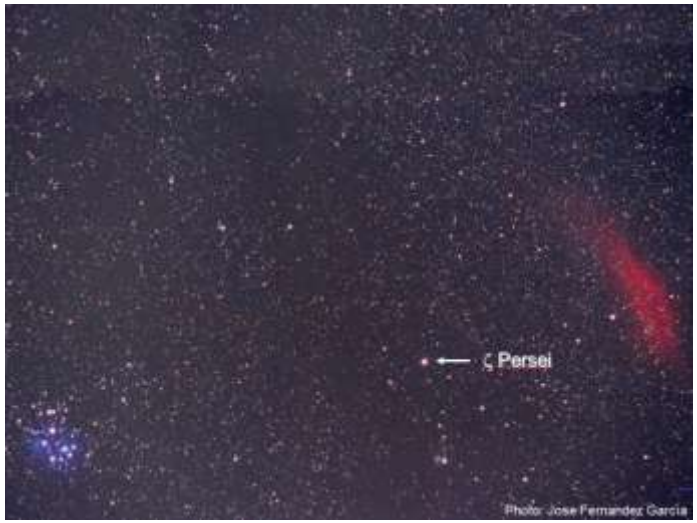
Diffuse Atomic Clouds

- Part of the diffuse interstellar medium that is fully exposed to radiation field
- Nearly all molecules quickly destroyed by photodissociation
- Hydrogen in neutral atomic form (H).
- Elements with Ionization potential < 13.6 eV almost fully ionized (e.g. C -> C^+)
- Hardly any molecules, **but strong Diffuse Interstellar Bands (Mystery!)**



Diffuse Molecular Clouds

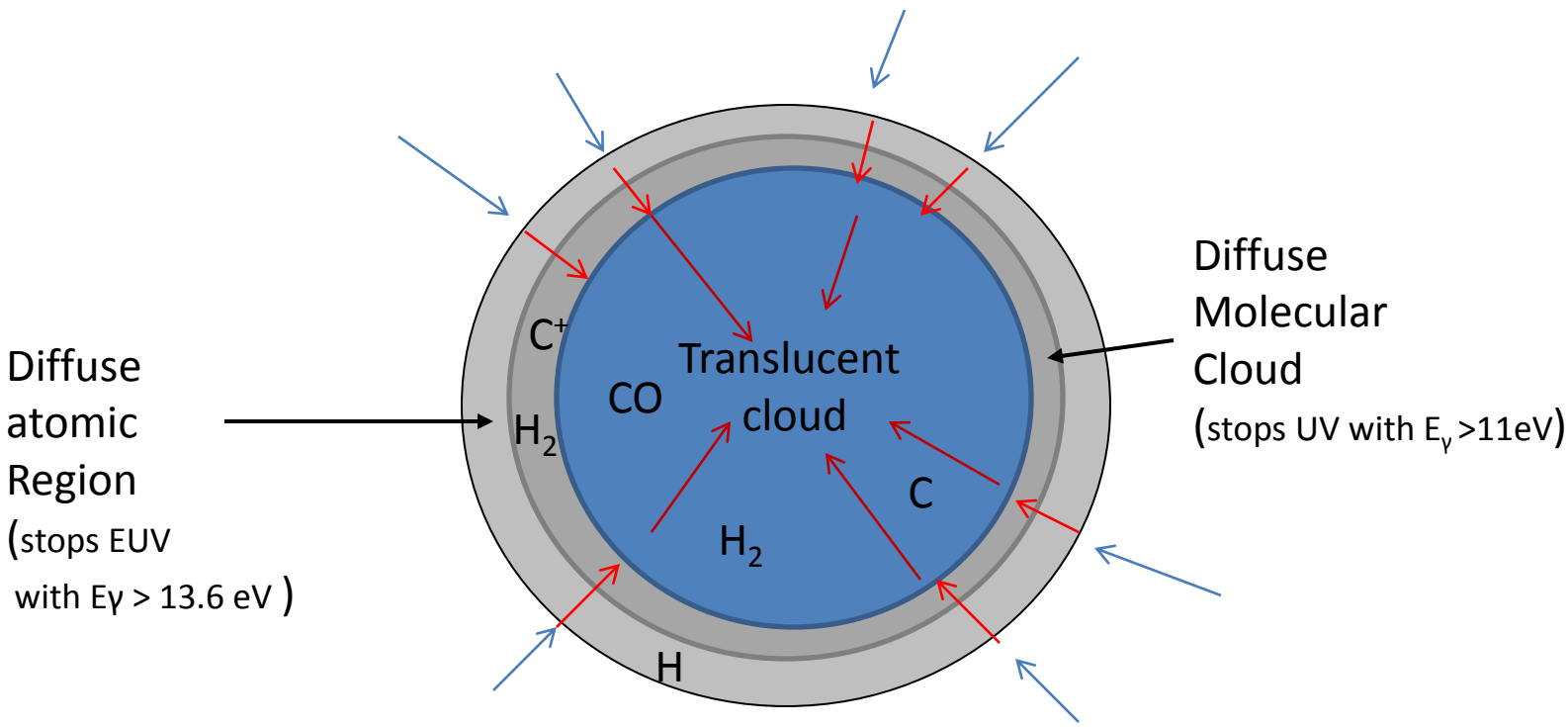
- Interstellar radiation field is sufficiently attenuated in the UV regime for H_2 to survive,
- typically surrounded by diffuse atomic gas,
- Most diffuse molecular sightlines will also cross atomic sightlines,
- densities 100-500 cm^{-3},
- temperature 30-100 K,
- Almost all carbon ionized (C^+)
- High ionization fraction, $n(C^+) \approx n(e)$
- Electron recombination dominant destruction route for many ions



Translucent Clouds

- Characterized by the transition from ionized C^+ to neutral C and CO
- Introduced by Van Dishoeck and Black (1989),
- Translucent regime not well understood,
- Lack of observational data,
- Chemical models do not agree in the C, Co transition regime,

- Interstellar radiation field is sufficiently attenuated at energies <13.6 eV that carbon becomes neutral (C) or molecular (CO)
- Typically surrounded by diffuse molecular gas,



Dense Molecular Clouds

- With increasing extinction, carbon becomes completely molecular (CO),
- No longer observable in the visible or UV regime,
- Much lower ionization fraction than diffuse medium,
- Electron recombination is much less important due to lack of electrons,
- Main source of ionization: Cosmic rays!
- Most of the detected interstellar molecules are observed in dense clouds,
- Places of star formation.

Key Species in Diffuse Molecular Clouds: H_2

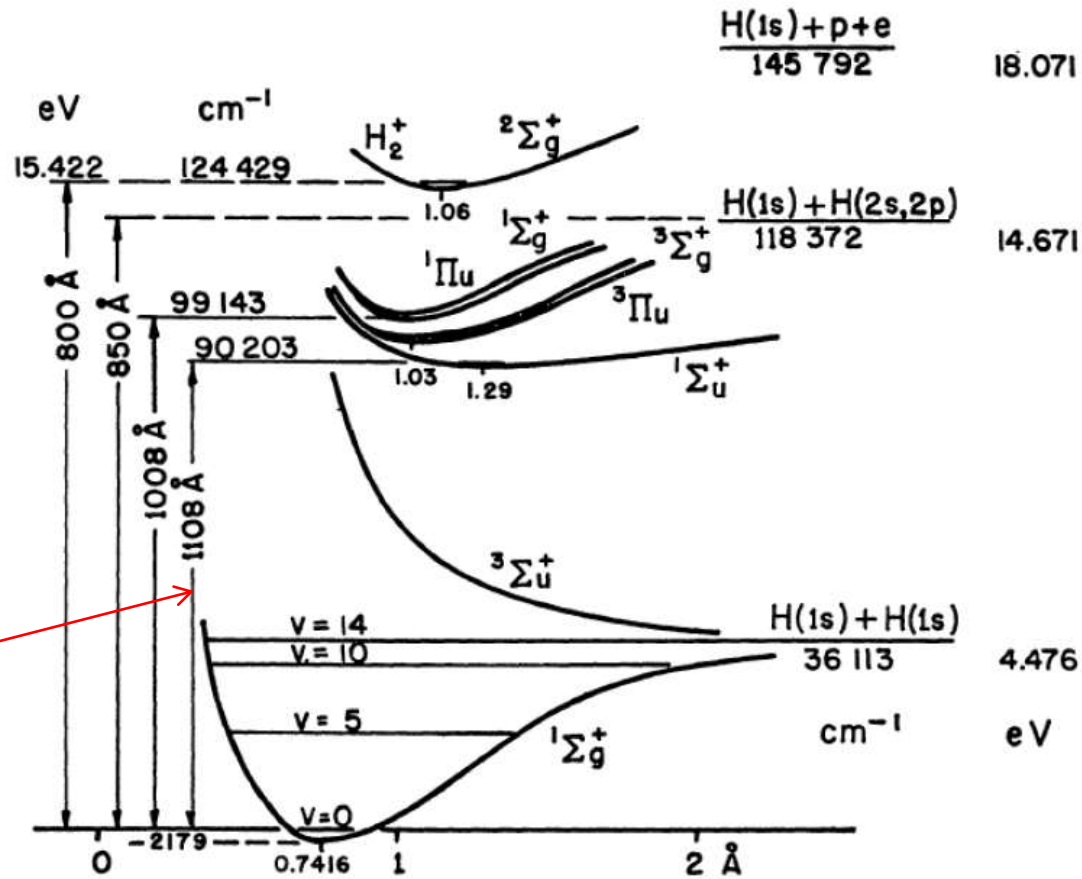
- No dipole moment, homonuclear
  → no allowed vibrational or rotational transitions
- Space-based far-UV spectrographs needed for observations

Werner bands
E_γ >12.3 eV
λ < 100.8 nm

$$X^1\Sigma_g^+ \rightarrow C^1\Pi_u$$

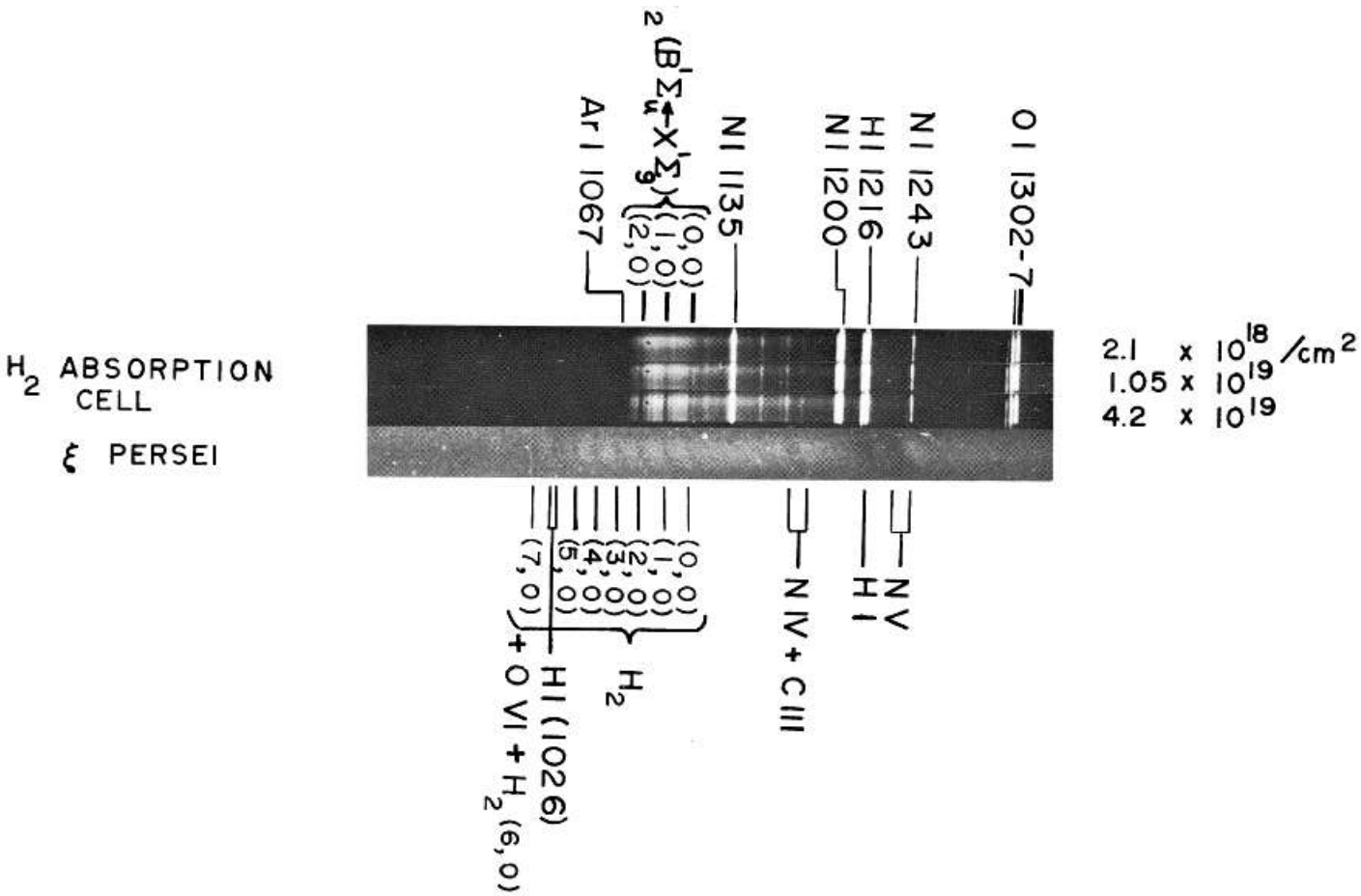
Lyman bands:
E_γ >11.2 eV
λ < 110.8 nm

$$X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$$



Electronic states of H_2, from Field, Somerville & Dressler (1966)

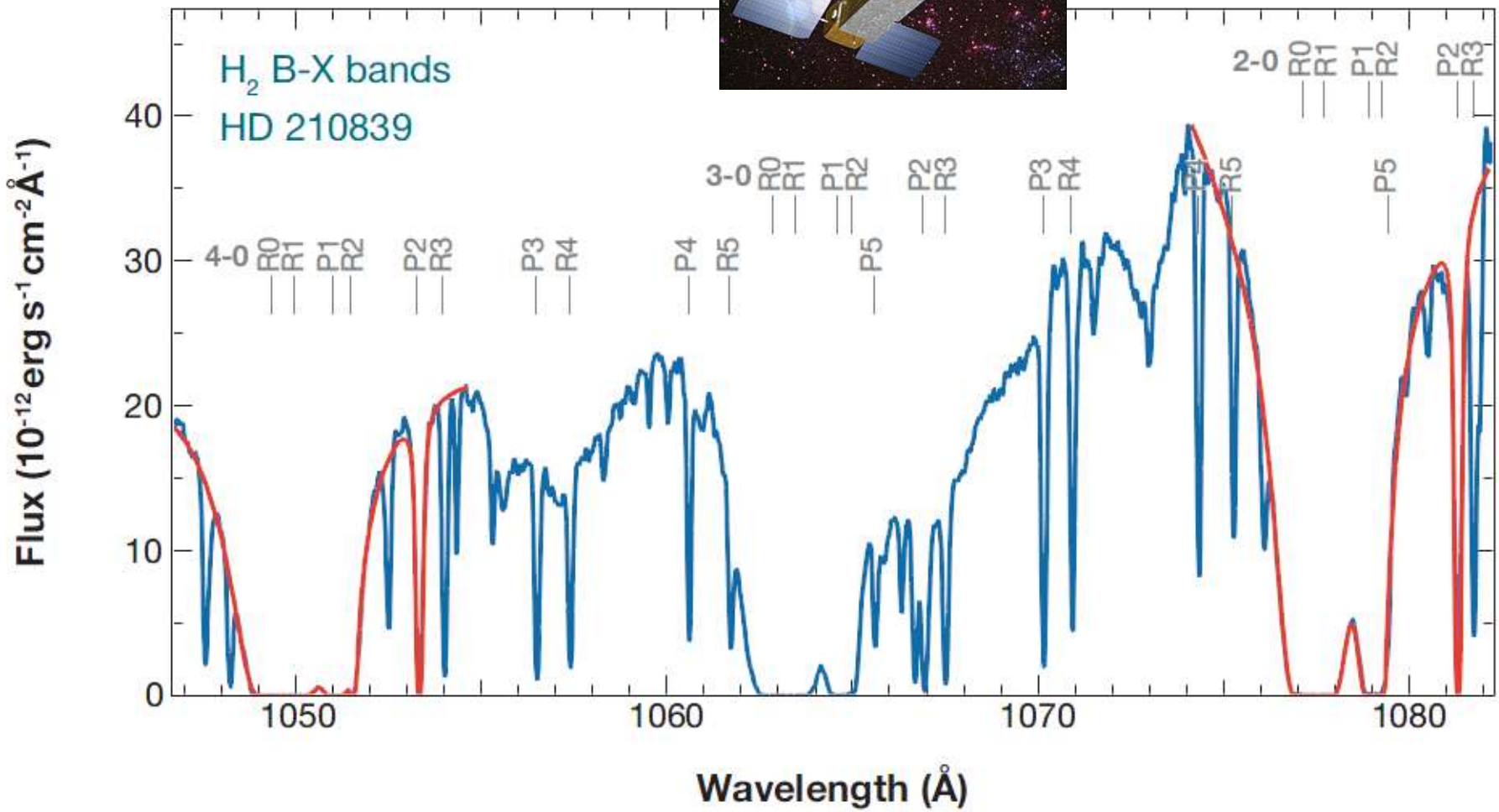
First Interstellar H_2 Absorption spectrum



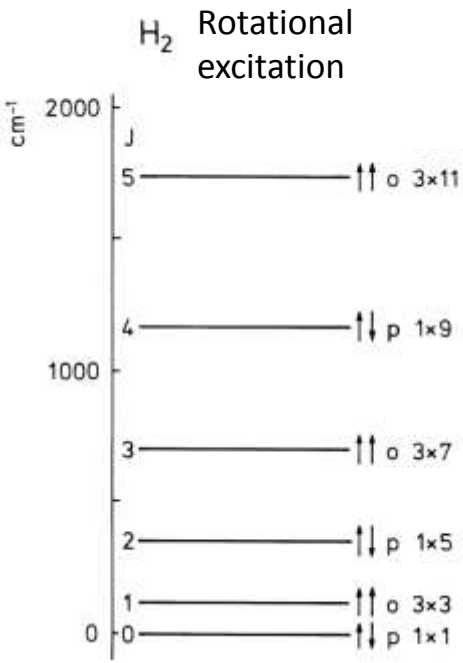
- Rocket experiment : Carruthers, ApJ 1970, 161 L81
- H_2 and H column densities comparable

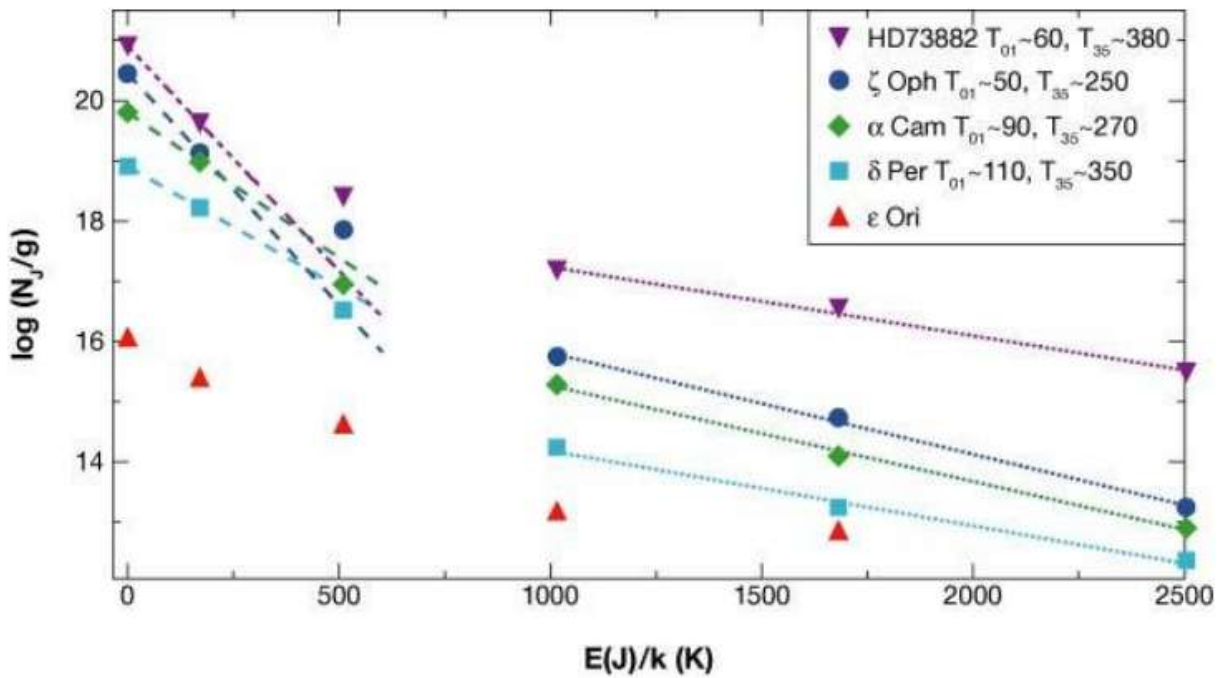
H_2 UV observations with FUSE

Far Ultraviolet Spectroscopic Explorer



Observed H_2 rotational population





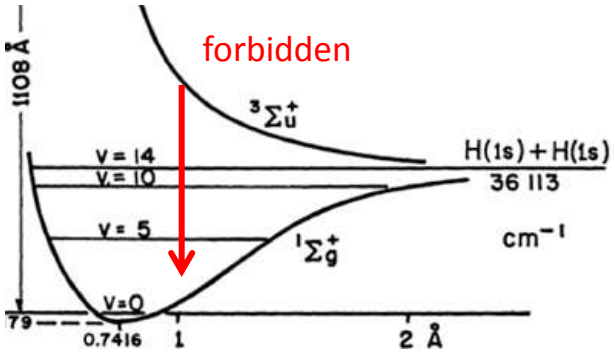
Snow TP, McCall BJ. 2006.
Annu. Rev. Astron. Astrophys. 44:367–414

Boltzmann law: $$N_J \sim g_J \, e^{\frac{E_J}{kT}}$$

Key Species in diffuse clouds: H_2 Formation

Direct radiative association:

$$H + H \longrightarrow H_2 + \gamma$$



Radiative transitions between the lowest states of H_2 forbidden, fraction of atoms in 2p states negligible

→ Radiative association extremely inefficient

The H_2^+ pathway:

$$H + H^+ \longrightarrow H_2^+ + \gamma \qquad \alpha < 10^{-16}\ \text{cm}^3\ \text{s}^{-1}$$

$$H_2^+ + H \longrightarrow H_2 + H^+ \qquad \alpha \approx 10^{-9}\ \text{cm}^3\ \text{s}^{-1}$$

→ The 1. step is rate-limiting, renders H_2^+ path negligible

The H^- pathway:

$$H + e^- \longrightarrow H^- + \gamma$$

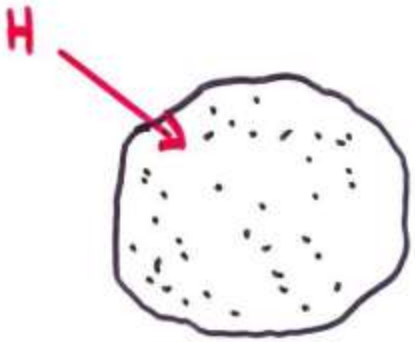
$$H^- + H \longrightarrow H_2 + e^-$$

H^- binding energy 0.75 eV

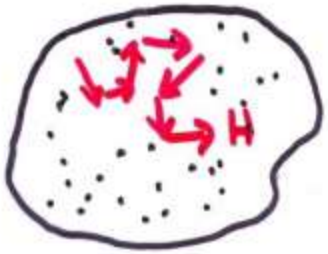
→ Without shielding of visible light, H^- does not live long enough

→ Only formation on dust grains remains

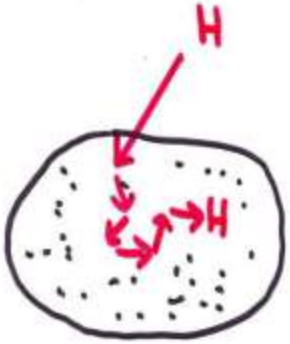
H_2 formation on grains



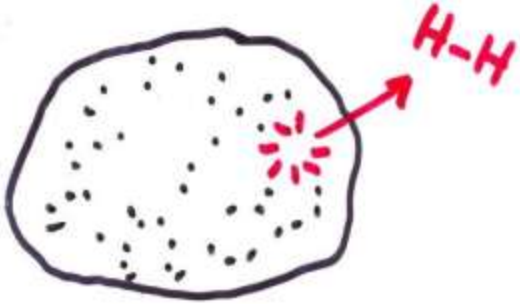
1. H collides with grain



2. H explores grain until either
{ (encounter with another H)
immobilized at enhanced binding site



3+4. second H atom collides with grain: explores surface and encounters first H atom



5. H_2 formation on surface
H_2 ejected from surface

E. Van Dishoeck / Lecture notes

H_2 observations vs. dust grains

(NGC 6720 plantery nebula)

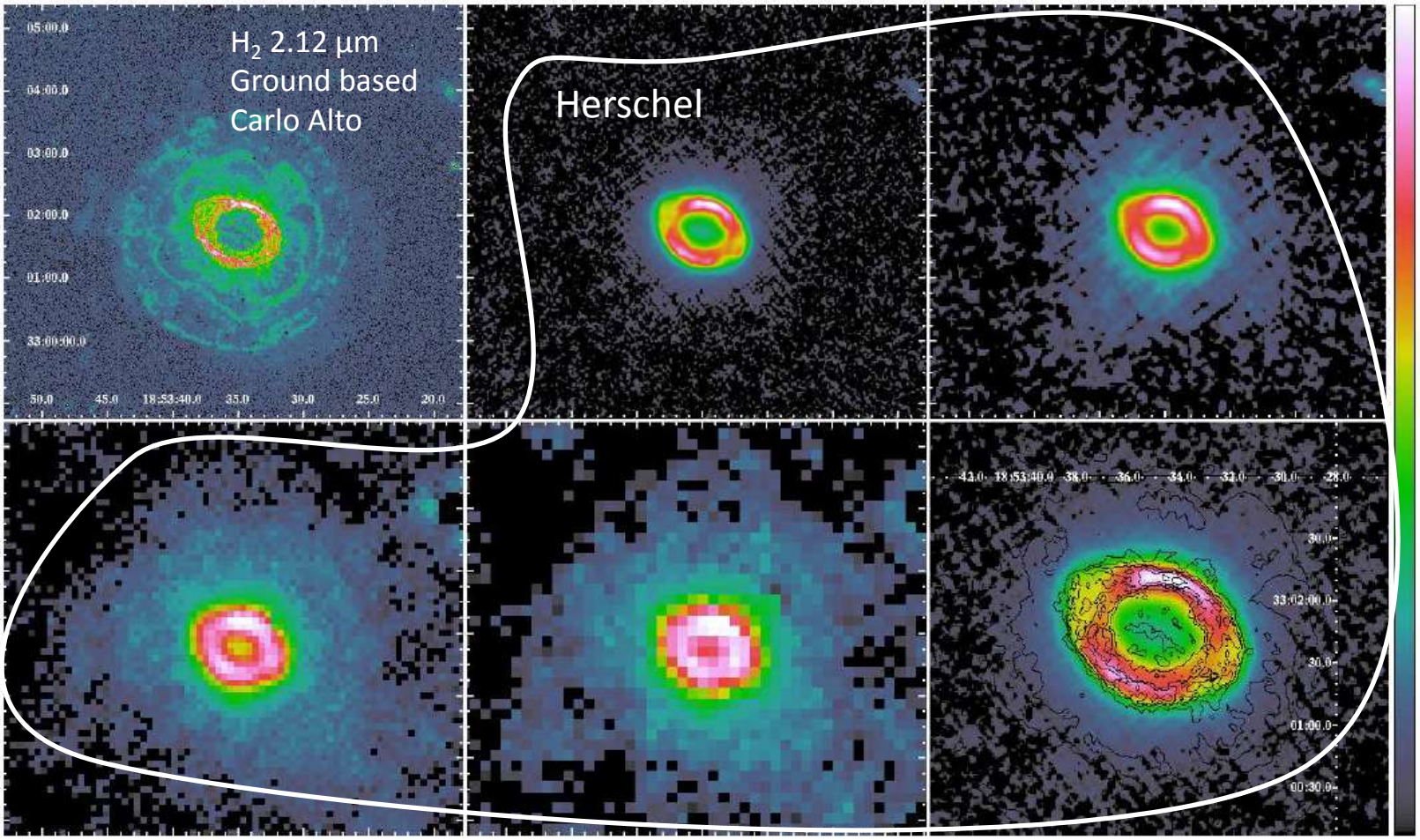
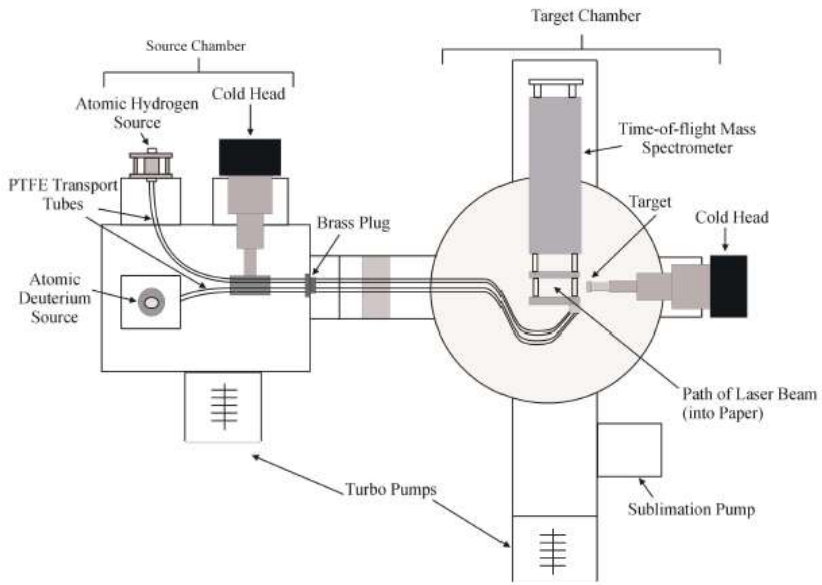
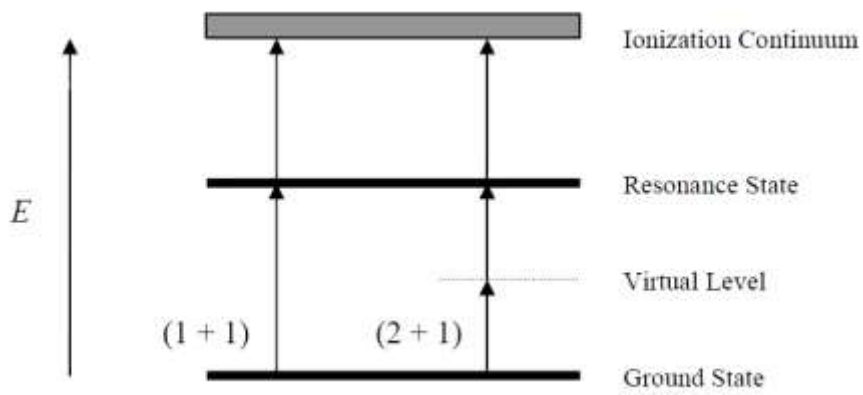


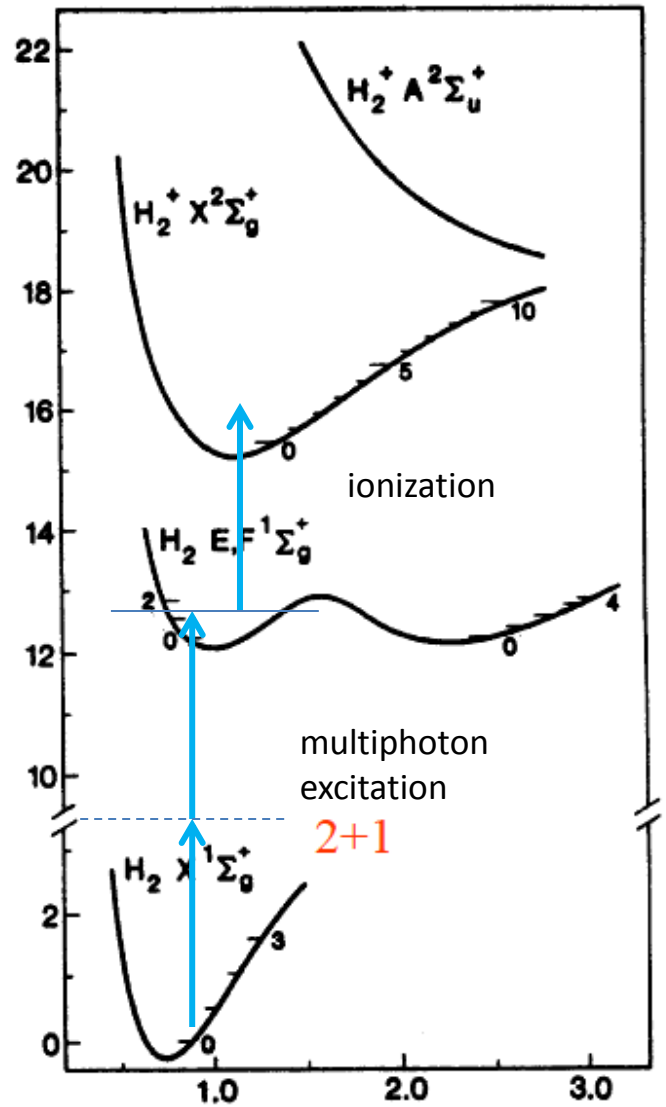
Fig. 1. NGC 6720 in five photometric bands. Top row from left to right: H_2 2.12 μm, PACS 70 μm, PACS 160 μm. Bottom row from left to right: SPIRE 250 μm, SPIRE 350 μm, and an overlay of the Calar Alto H_2 contours on the PACS 70 μm image. The H_2 image is not flux calibrated. The maps have standard orientation (N to the top, E to the left).

Van Hoof et al., A&A 2010

Ro-vibrational excitation in HD formation detected by Resonantly Enhanced Multiphoton Ionization (REMPI)

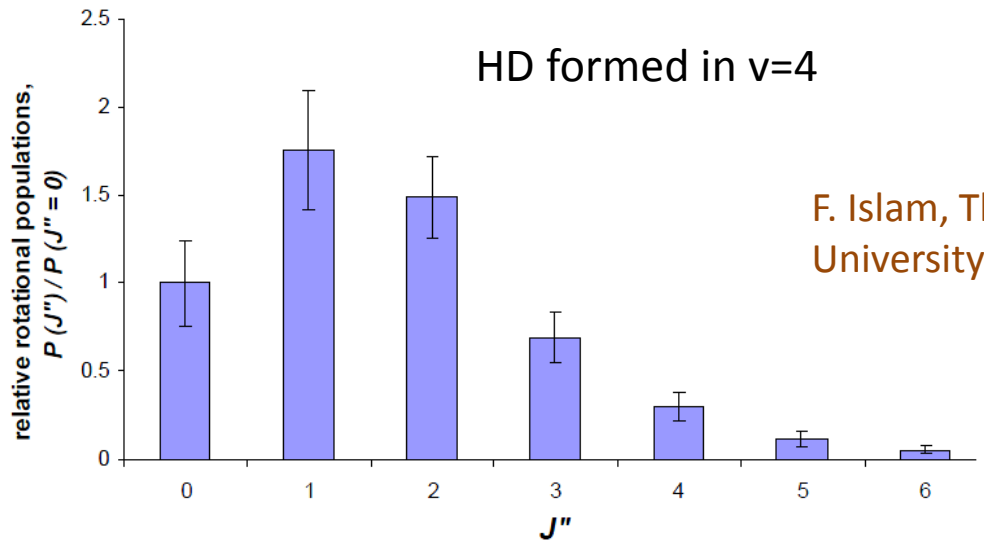






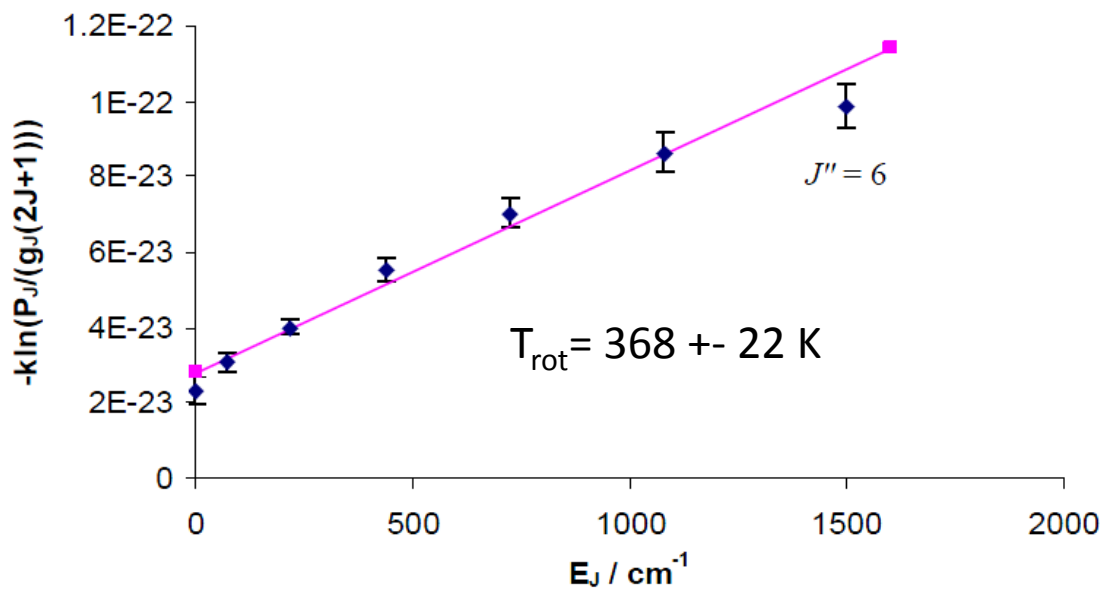
F. Islam, Thesis 2009 University College London

HD Formation and Ro-vibrational excitation



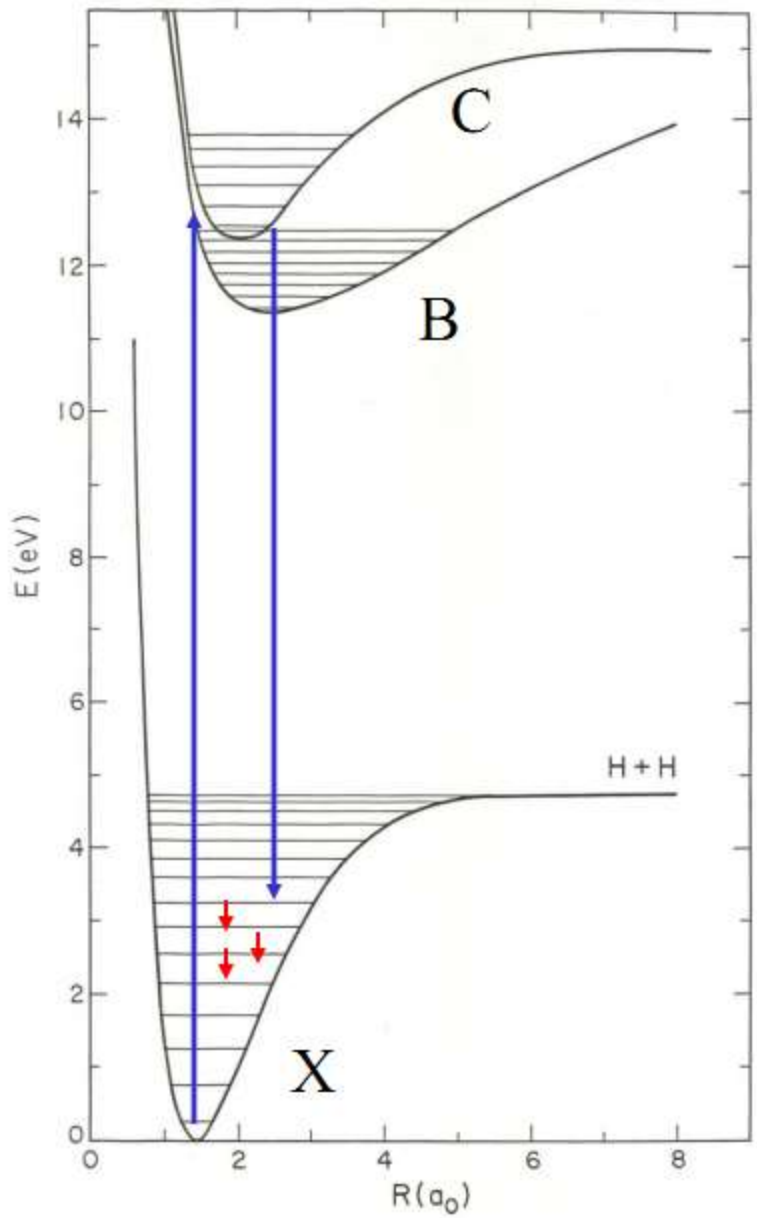
F. Islam, Thesis 2009
University College London

Energy released in the Dust grain formation may contribute to the non-thermal H_2 distribution observed in diffuse clouds

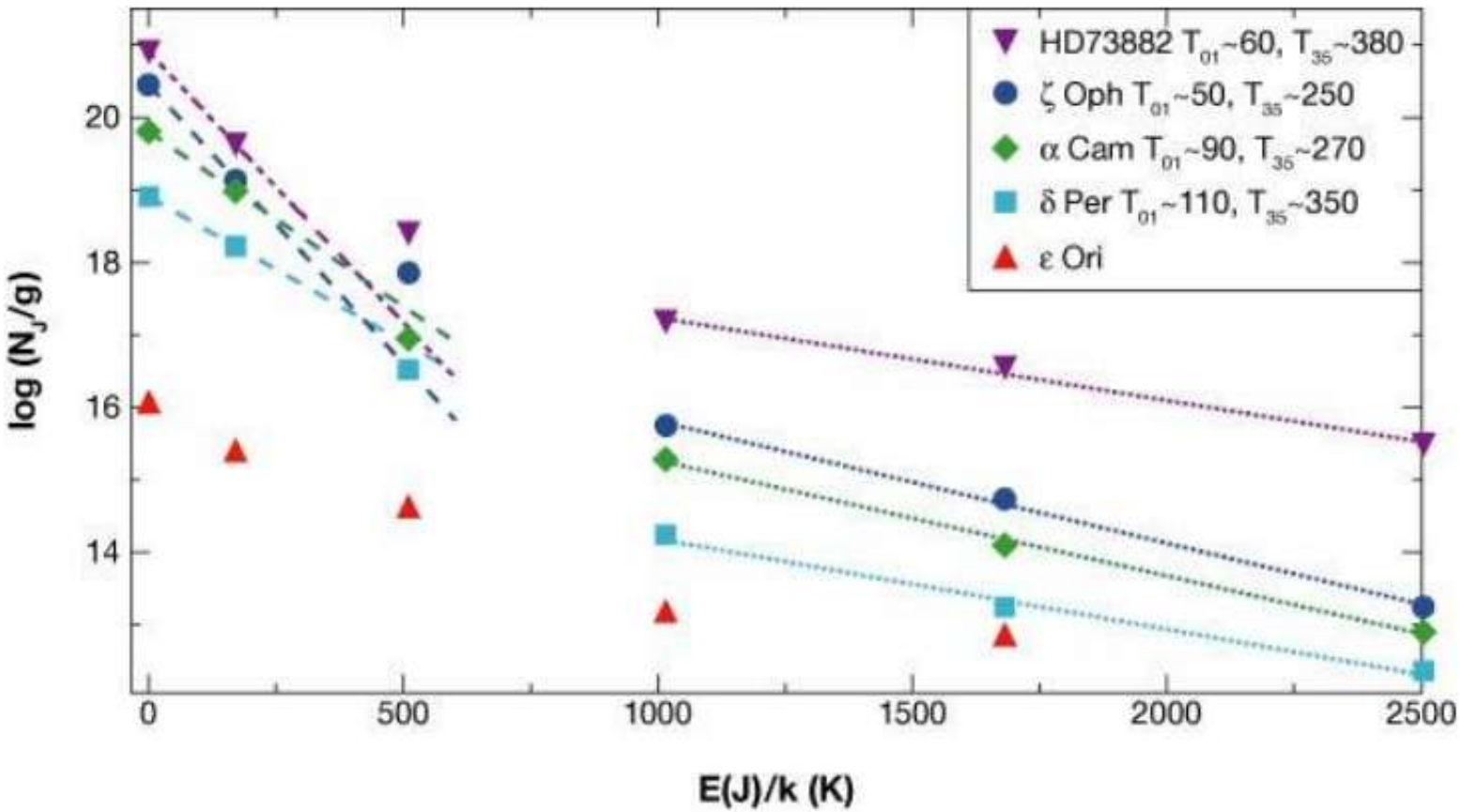


H_2 optical pumping

B-X: Lyman system
C-X: Werner system



Observed H_2 rotational population



Snow TP, McCall BJ. 2006.
Annu. Rev. Astron. Astrophys. 44:367–414

Rotational excitation of H_2 kinetic temperature and optical pumping

H_2 lines up to J = 7 detected with Copernicus + FUSE
Population distribution non-thermal, **2 temperature regimes!**

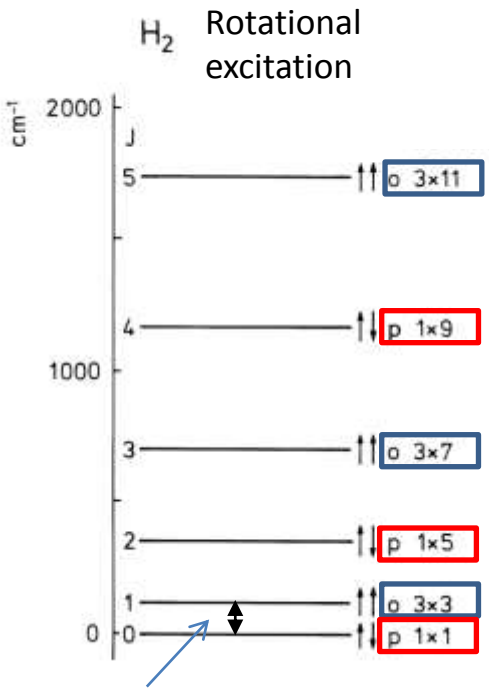
Low J: excitation dominated by collisions

- sensitive to T and nH
- abundance H^+ large enough that ortho/para exchange rapid and J=1/J=0 gives T_{kin}

High J: energy levels lie very high (> 1000 K)

- not populated by collisions at T = 40 - 80 K
- populated by optical pumping
- process through B <- X and C <- X systems
- proportional to radiation field
- possibly contribution from dust grain formation process

H_2 nuclear spin and kinetic cloud temperature



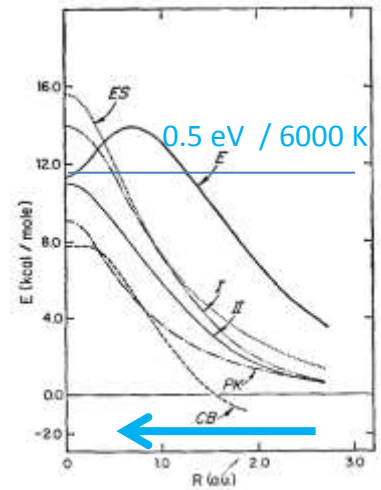
ΔE (J=0, J=1) = 170.9 K

Ortho – para exchange reactions

1)

$H + o\text{-}H_2 \longleftrightarrow H + p\text{-}H_2$

→ Activation barrier too high



2)

$H^+ + o\text{-}H_2 \longleftrightarrow H^+ + p\text{-}H_2$

- No activation barrier
- Requires some ionized atomic H fraction

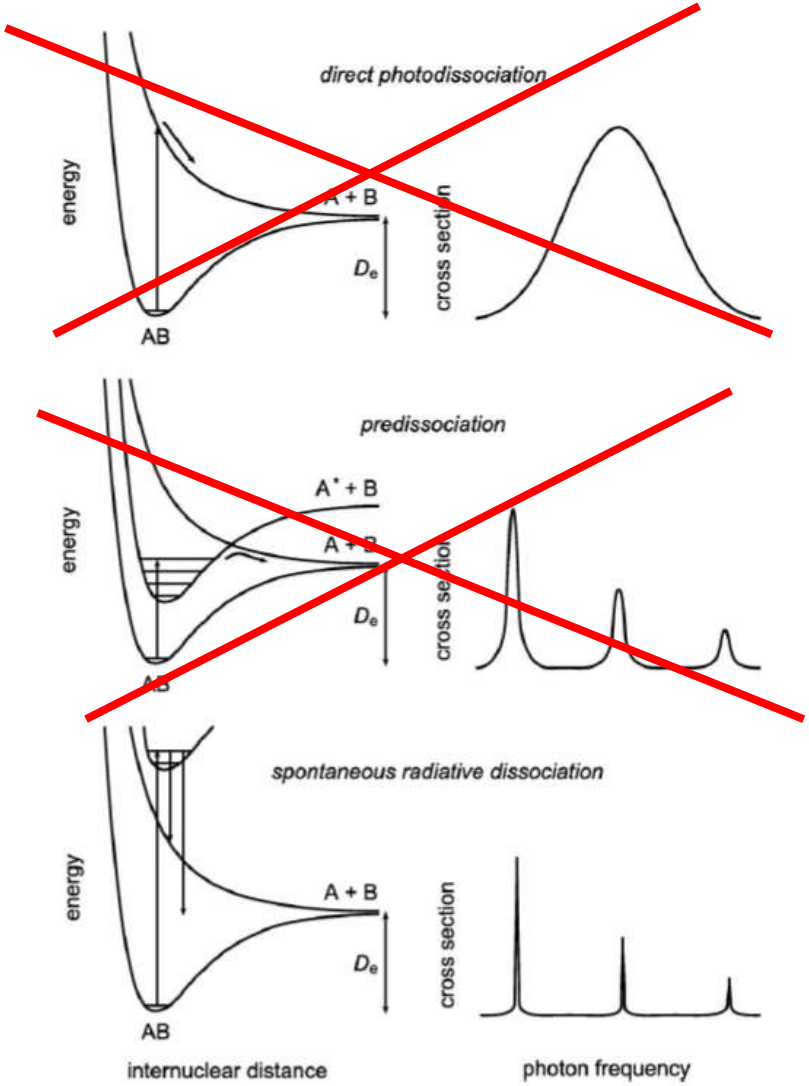
Due to high efficiency of 2), H_2 ortho / para fraction should reflect kinetic cloud temperature

H_2 destruction: possible processes

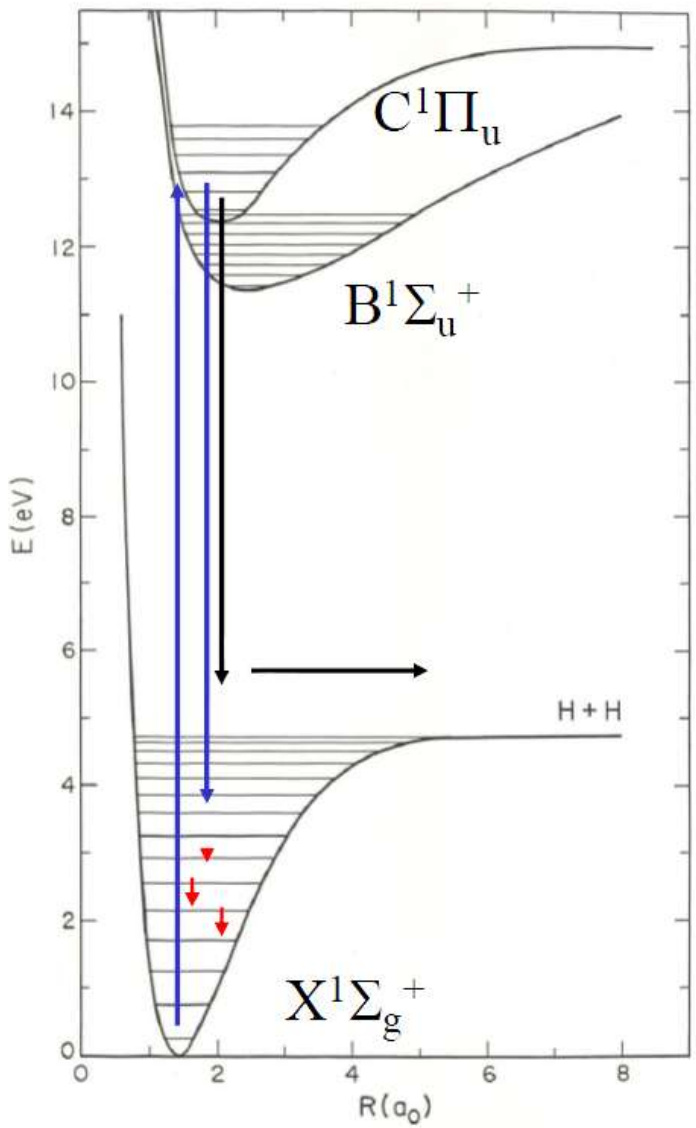
For direct photodissociation
photons with Eγ > 15 eV
are needed, which are already
Depleted by the atomic outer layers

There is no bound state in
the right energy regime for H_2

Major H_2 destruction
mechanism in the diffuse ISM



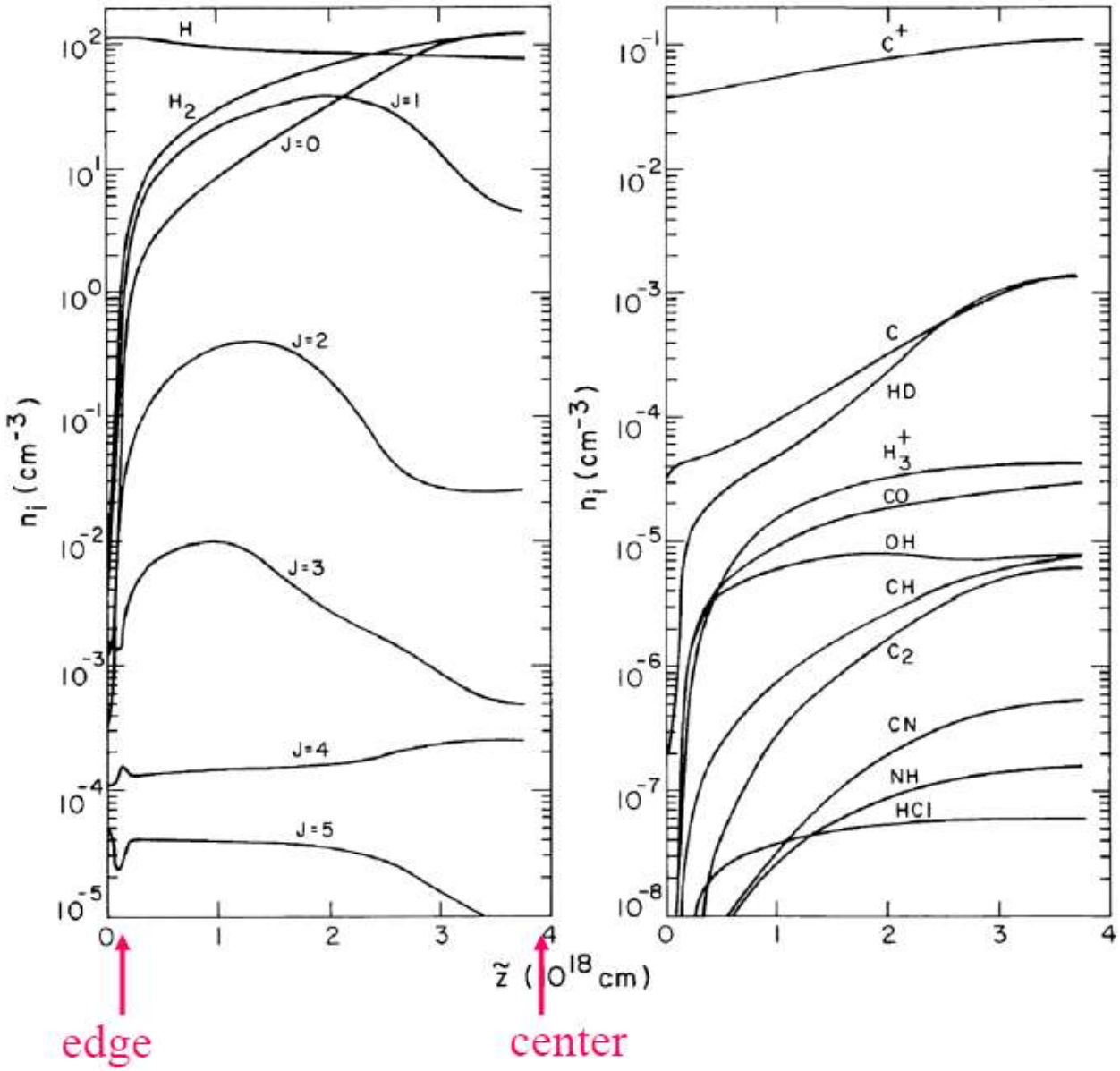
H2 destruction by radiative dissociation through Lyman and Werner Bands



90% of the flux returns back to the electronic ground state (contributing to the observed optical pumping of rotational states)

10% of the flux leads to spontaneous dissociation

Depth dependence of various species

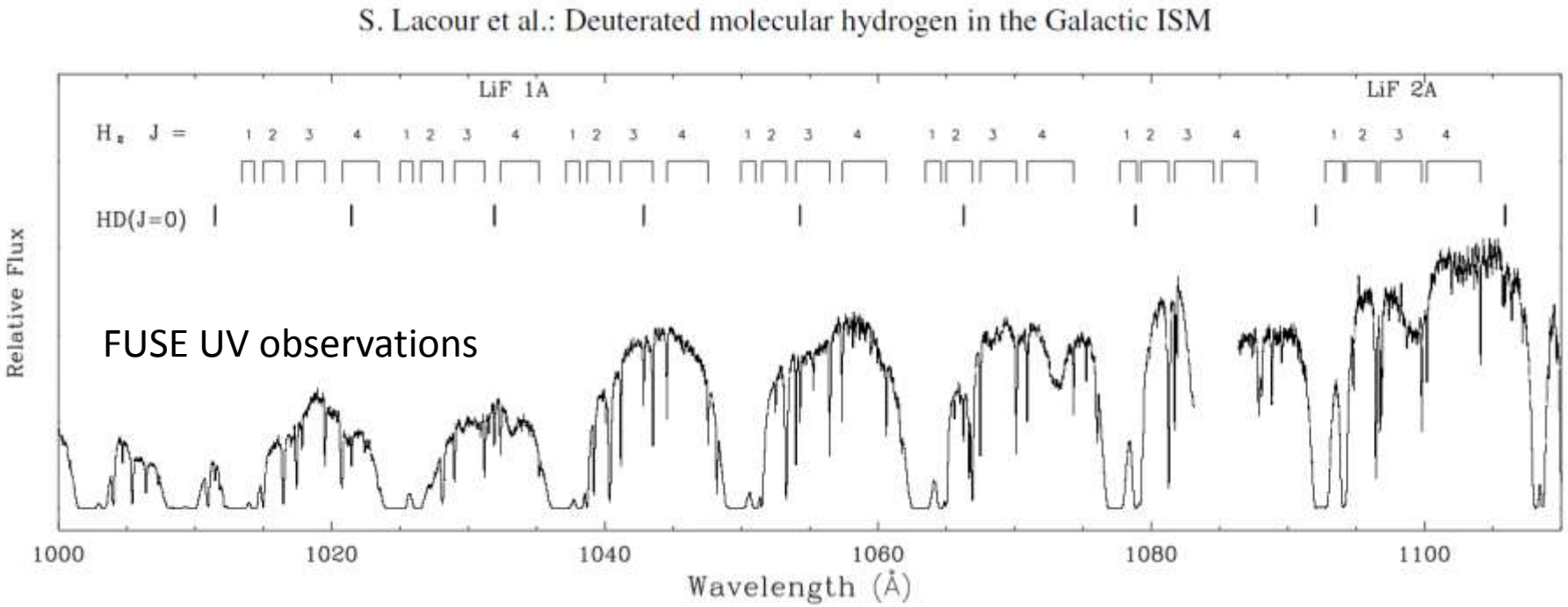


Note: overall density increases with depth

Van Dishoeck & Black 1986

HD observations in the diffuse medium

Can we use N(HD) to constrain cosmic D/H ?



- Even most HD lines are fully saturated
- Obscured by H2 and other molecular lines
- Difficult analysis

HD fraction in diffuse clouds

Star	$E_{(B-V)}$	$f(H_2)$ [a]	N(H I) [cm^{-2}]	$N(H_2)$ [cm^{-2}]	N(HD) [cm^{-2}]	Ref.	$N(HD)/2N(H_2)$	N(CH) [cm^{-2}]	Ref.
HD 27778	0.38	0.57	$9.5^{+9.5}_{-4.8}$ (20)	$6.2^{+0.9}_{-0.8}$ (20)	$3.2^{+3.2}_{-1.7}$ (15)	1	$2.6^{+2.6}_{-1.4}$ (-6)	3.0 ± 0.3 (13)	2
HD 73882	0.72	0.67	$1.3^{+0.5}_{-0.4}$ (21)	$1.3^{+0.3}_{-0.2}$ (21)	$5.8^{+3.7}_{-3.4}$ (15)	1	$2.2^{+1.6}_{-1.3}$ (-6)	3.5 ± 0.4 (13)	2
HD 110432	0.40	0.55	$7.1^{+2.9}_{-2.1}$ (20)	$4.4^{+0.4}_{-0.4}$ (20)	$1.9^{+0.7}_{-0.6}$ (15)	1	$2.2^{+0.9}_{-0.7}$ (-6)	1.5 ± 0.3 (13)	3
HD 185418	0.51	0.47	$1.3^{+0.5}_{-0.4}$ (21)	$5.8^{+0.7}_{-0.6}$ (20)	$4.3^{+1.9}_{-1.1}$ (15)	1	$3.7^{+1.7}_{-1.0}$ (-6)	1.3 ± 0.3 (13)	2
HD 192639	0.66	0.32	$2.1^{+0.7}_{-0.5}$ (21)	$4.9^{+0.6}_{-0.5}$ (20)	$1.5^{+0.9}_{-0.7}$ (15)	1	$1.5^{+1.0}_{-0.7}$ (-6)	2.8 ± 0.5 (13)	2
HD 206267	0.52	0.42	$2.0^{+0.8}_{-0.6}$ (21)	$7.2^{+0.7}_{-0.6}$ (20)	$2.1^{+1.5}_{-1.0}$ (15)	1	$1.4^{+1.0}_{-0.7}$ (-6)	3.0 ± 0.2 (13)	2
HD 207538	0.64	0.42	$2.2^{+0.7}_{-0.5}$ (21)	$8.1^{+0.8}_{-0.7}$ (20)	$5.0^{+5.1}_{-2.4}$ (15)	1	$3.1^{+3.2}_{-1.5}$ (-6)	4.3 ± 0.2 (13)	2
HD 21278	0.10	0.10 [b]	5.5 (20) [b]	$3.0^{+2.1}_{-1.2}$ (19)	$1.5^{+0.1}_{-0.1}$ (14)	4	$2.5^{+1.7}_{-1.0}$ (-6)		
o Per	0.30	0.50	8.0 ± 2.4 (20)	$4.0^{+1.6}_{-1.2}$ (20)	$3.0^{+3.0}_{-1.5}$ (15)	4	$3.8^{+4.4}_{-2.0}$ (-6)	2.1 ± 0.2 (13)	5
ζ Per	0.33	0.59	6.4 ± 0.6 (20)	$4.7^{+2.4}_{-1.6}$ (20)	4^{+4}_{-2} (15)	4	$4.3^{+5.3}_{-2.4}$ (-6)	2.2 ± 0.2 (13)	5
ϵ Per	0.09	0.21	2.5 ± 0.5 (20)	$3.3^{+2.7}_{-1.5}$ (19)	6^{+2}_{-1} (13)	4	$9.1^{+8.7}_{-4.9}$ (-7)	< 2.0 (12)	6
ξ Per	0.33	0.35	1.3 ± 0.3 (21)	$3.4^{+1.4}_{-1.0}$ (20)	$2.5^{+0.5}_{-0.5}$ (14)	4	$3.7^{+1.8}_{-1.2}$ (-7)	1.3 ± 0.3 (13)	5
α Cam	0.32	0.35	8.0 ± 1.6 (20)	$2.2^{+0.9}_{-0.6}$ (20)	8^{+2}_{-2} (14)	4	$1.8^{+0.9}_{-0.7}$ (-6)	6.9 ± 1.6 (12)	5
139 Tau	0.15	0.12	8.0 ± 1.6 (20)	$5.4^{+3.1}_{-2.0}$ (19)	8^{+2}_{-2} (13)	4	$7.4^{+5.0}_{-3.1}$ (-7)		
ζ Oph	0.32	0.63	5.2 ± 0.3 (20)	$4.4^{+0.9}_{-0.8}$ (20)	6^{+6}_{-3} (14)	4	$6.8^{+7.2}_{-3.5}$ (-7)	2.5 ± 0.2 (13)	5
59 Cyg	0.18	0.19	1.8 ± 0.4 (20)	$2.0^{+1.0}_{-0.7}$ (19)	8^{+2}_{-2} (13)	4	$2.0^{+1.2}_{-0.8}$ (-6)		
10 Lac	0.11	0.06	5.0 ± 1.5 (20)	$1.7^{+0.5}_{-0.4}$ (19)	3^{+2}_{-1} (13)	4	$8.8^{+6.9}_{-3.4}$ (-7)	2.5 ± 0.8 (12)	7

N (HD) does not seem to represent cosmic H/D fraction (≈ 10^{-5}). Why?

Processes that influence the HD fraction

- H_2 is protected by self shielding of narrow resonances
- HD self-shielding sets in much later

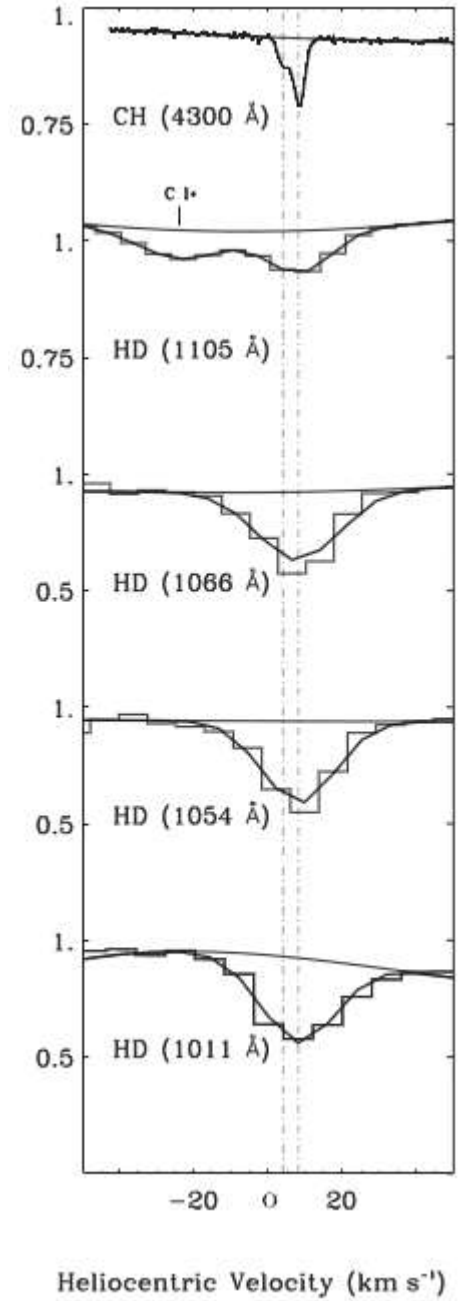
→ **H_2 is favored, low HD/H2 ratio**

- D atoms have a lower mobility on grains, formation mechanism may be much slower
- HD has a gas-phase formation channel

$H_2 + D^+ \longrightarrow HD + H^+$ (exothermic)

(depends on ionization rate)

Too complicated to infer reliable Information on D/H.



Summary H_2 / HD

H_2

- Observed in the diffuse ISM through UV satellite observations,
- Formed exclusively on dust grains,
- Ortho/para ratio reflects the cloud kinetic temperature (50-100 K),
- Destroyed through radiative dissociation via Werner and Lyman bands,
- Non-thermal rotational populations in the outer layers (optical pumping),
- Increasing self-shielding with cloud depth.

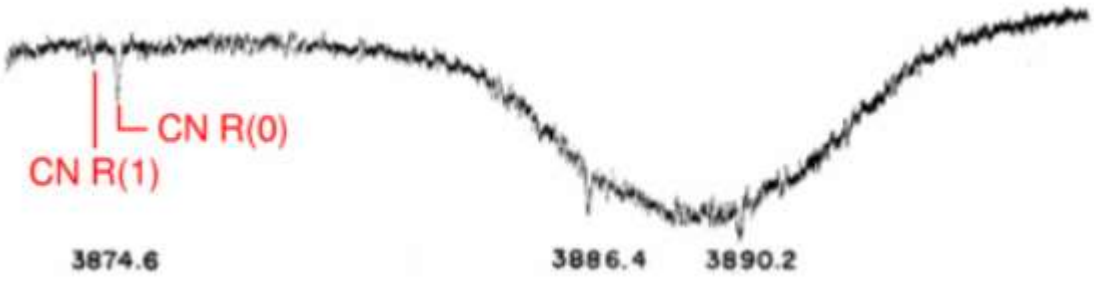
HD

- Can also be observed in the diffuse ISM through UV satellite observations,
- Has a gas-phase formation rate,
- reduced self-shielding pushes $N(HD)/(2\ N(H_2))$ below cosmic D/H.

PAUSE

Other interesting molecules: CN and the CMB

- One of the first interstellar molecules that were discovered (McKellar PASP 1940)
  (actually Interstellar molecule no 2, after CH in 1937)
- Large dipole moment -> **in low-collision environment, state population reflects radiation field**
- Rotational temperature of (2.3 ± 0.5) K derived by McKellar in 1940
  pre-discovery of the CMB
- Origin of this temperature was not understood until 1965



Anecdote:

Gerhard Herzberg, in his textbook on Diatomic Molecules 1950 noted that the 2.3 K rotational temperature of the cyanogen molecule (CN) in interstellar space is interesting, but stated that it had "only a very restricted meaning." **Missed Nobel Prize in Physics?**

The mysterious abundance of CH^+

NOTES

CH^+ IN INTERSTELLAR SPACE AND IN THE LABORATORY

At a recent conference on interstellar molecules at the Yerkes Observatory, P. Swings called attention to three sharp interstellar lines—λλ 4232.58, 3957.72, and 3745.33—for which no identification was available. He suggested that the three lines belong to a light-ionized molecule such as CH^+, CN^+, CO^+, NH^+, or NO^+. The molecule should have a small energy of dissociation in the excited state. E. Teller and G. Herzberg suggested the CH^+ molecule as most likely, by analogy to BH. However, at the time no laboratory data were available. Since then we have investigated the spectrum of a discharge through helium to which a trace of C_2H_6 vapor was added. This spectrum shows three bands with heads at λλ 4225.3, 3954.0, and 3743.4 A. They have a very widely spaced fine structure which can be readily analyzed. Each band consists of three singlet branches—P, Q, and R—corresponding to a $^1\Pi - {}^1\Sigma$ transition. The numbering of the lines is found by inspection. The R(0) lines of the three bands have the wave lengths λλ 4232.57, 3957.71, and 3745.30 A, which agree with those of the three interstellar lines given above. Since it is known that in interstellar absorption practically only the lines coming from the lowest rotational level of the lower state occur and since just these lines [R(0)] of the new bands agree with the interstellar lines, we consider it as proved that *the three interstellar lines belong to the three new bands* observed by us in the laboratory and are therefore *due to the same molecule*.

A $^1\Pi - {}^1\Sigma$ system with a 0–0 band at about 4300 A is to be expected for the CH^+ molecule, since the isoelectronic BH molecule has such a system in this region. CH^+ is also strongly suggested by the conditions of excitation. The rotational constant B_v'' in the lower state of the new bands was found to be 14.0 cm.$^{-1}$, which is close to that of CH ($B_v = 14.189$), as one would expect if CH^+ is the emitter. At any rate the value of B_v'' shows that the emitter must be a hydride molecule belonging to the second period of the periodic system ($Li - F$). The observation of the band system in interstellar space shows that the lower state is the electronic ground state of the molecule. Now the ground states of all neutral and singly ionized diatomic hydrides of the second period are known with the exception of LiH^+, CH^+, NH^+, and FH^+. Since the observed B_v'' value does not agree with that of any of the known hydrides and since of the four unknown ionized hydrides, only CH^+ can have singlet bands, we conclude that *the new bands and the interstellar lines are due to the CH^+ molecule.*

The presence of CH^+ in interstellar space, thus established, appears very plausible in view of the known presence of CH as well as of comparatively large amounts of H^+.

A more complete report on this work including a full discussion of the structure of the CH^+ molecule will be submitted later.

A. E. Douglas
G. Herzberg

Department of Physics
University of Saskatchewan
Saskatoon, Saskatchewan

- Discovered in 1941 (Herzberg)
- First interstellar molecular ion
- Thought to be created by

$$C^+ + H_2 \rightarrow CH^+ + H \quad \text{(endothermic by 4600K)}$$

Where does the energy come from to overcome the reaction barrier?

Candidates:
Shocks? Magnetohydrodynamic waves?
Alv'en waves? Turbulence?

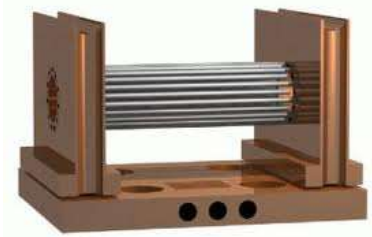
Why do these mechanisms not enrich other endothermic species?

Presently no answer.

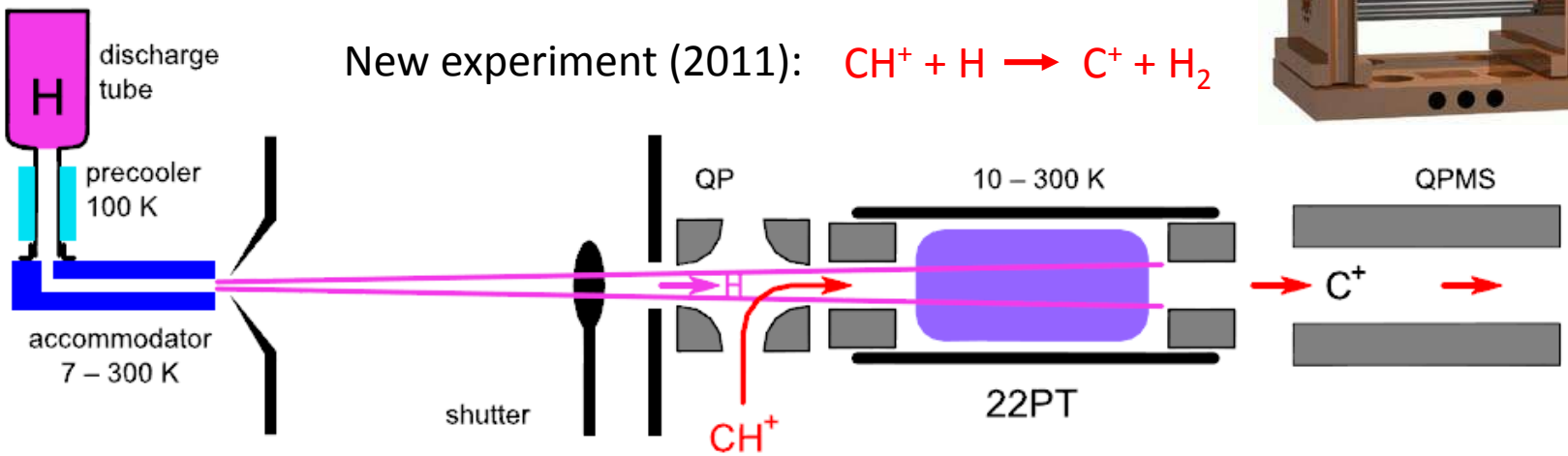
The mysterious abundance of CH^+

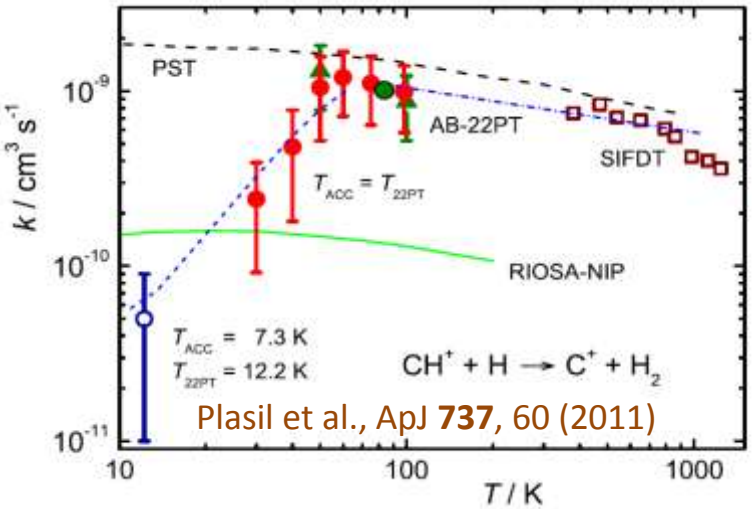
In equilibrium the formation and destruction processes will determine the abundance of CH^+

22 pole ion trap



New experiment (2011): $CH^+ + H \rightarrow C^+ + H_2$





Plasil et al., ApJ **737**, 60 (2011)

The rate coefficient for the reaction

$$CH^+ + H \rightarrow C^+ + H_2$$

is a **factor of 50 smaller** than the classical Langevin value at low energy

H_3^+: the Engine of Interstellar Chemistry

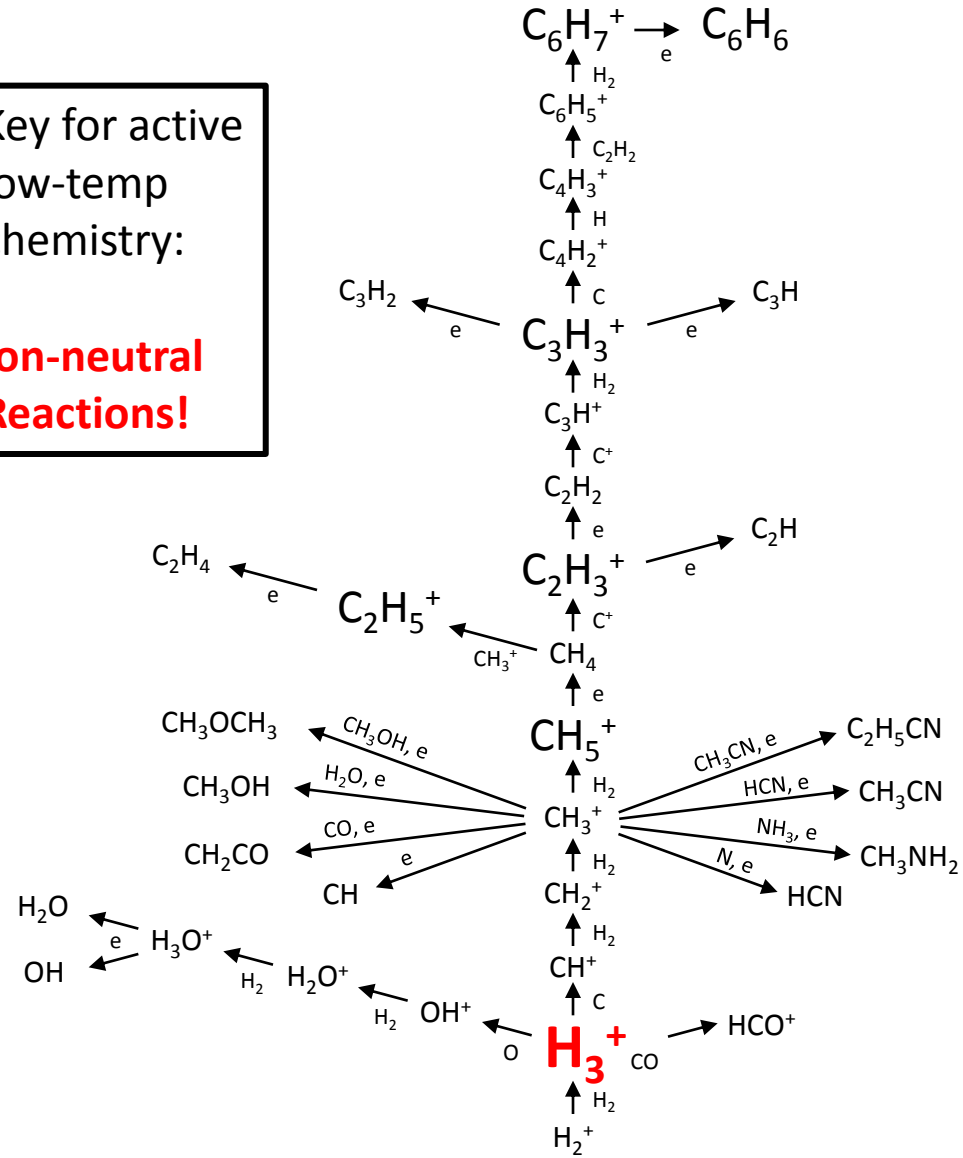
Molecular clouds:
It's cold and (relatively empty)

temperatures: **10-100 K**
density: **10^2 - 10^4 cm^{-3}**

Key for active low-temp chemistry:

Ion-neutral Reactions!

- No endothermic reactions
- No 3-body collisions
- No reactions with barriers



McCall, PhD thesis, Chicago 2001

First quantitative cloud model

(Herbst & Klemperer 1973)

THE ASTROPHYSICAL JOURNAL, **185**: 505–533, 1973 October 15

THE FORMATION AND DEPLETION OF MOLECULES IN DENSE INTERSTELLAR CLOUDS*

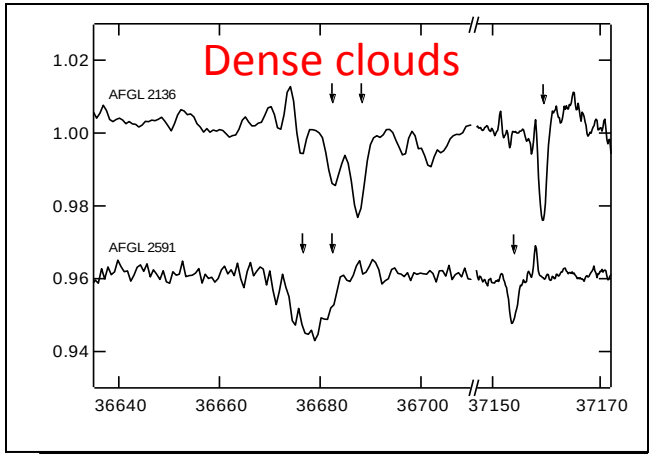
ERIC HERBST† AND WILLIAM KLEMPERER
Department of Chemistry, Harvard University
Received 1973 April 9; revised 1973 May 24

Ionization

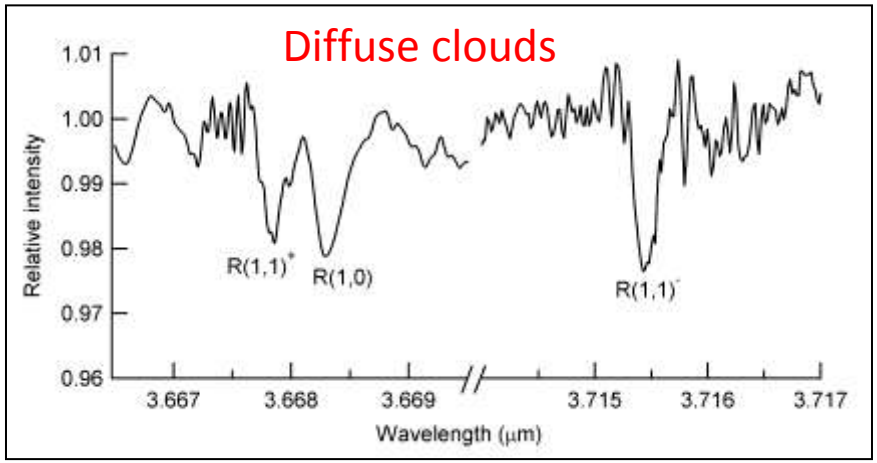
1. H_2 + cosmic-ray proton → $H_2^+ + e$ + C.R.P.′ ($k_1 = 0.95\zeta_{H_2}\ s^{-1}$)
2. H_2 + cosmic-ray proton → $H + H^+ + e$ + C.R.P.′ ($k_2 = 0.05\zeta_{H_2}$)
3. He + cosmic-ray proton → $He^+ + e$ + C.R.P.′ ($k_3 \sim \zeta_{H_2}\ s^{-1}$)

	Reaction	$k(10^{-9}\ cm^3\ s^{-1})$	Reference/Remarks
4.	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1	Bowers *et al.* 1969
5.	$CO^+ + H_2 \rightarrow HCO^+ + H$	2.0	Fehsenfeld *et al.* 1967
6.	$N_2^+ + H_2 \rightarrow HN_2^+ + H$	1.7	Fehsenfeld *et al.* 1967
7.	$He^+ + H_2 \rightarrow$ products	$< 10^{-4}$	Fehsenfeld *et al.* 1966*b*
8.	$O^+ + H_2 \rightarrow OH^+ + H$	2.0	Fehsenfeld *et al.* 1967
9.	$N^+ + H_2 \rightarrow NH^+ + H$	0.7	Fehsenfeld *et al.* 1967
10.	$OH^+ + H_2 \rightarrow OH_2^+ + H$	1.5	Fehsenfeld *et al.* 1967
11.	$NH^+ + H_2 \rightarrow NH_2^+ + H$	0.6	Ferguson 1973
12.	$OH_2^+ + H_2 \rightarrow OH_3^+ + H$	1.4	Fehsenfeld *et al.* 1967
13.	$NH_2^+ + H_2 \rightarrow NH_3^+ + H$	0.23	Ferguson 1973
14.	$NH_3^+ + H_2 \rightarrow NH_4^+ + H$	$< 5 \times 10^{-4}$	Ferguson 1973
15.	$CH^+ + H_2 \rightarrow CH_2^+ + H$	10^{-2}	
16.	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	10^{-2}	
17.	$HCN^+ + H_2 \rightarrow H_2CN^+ + H$	2.0	
18.	$He^+ + CO \rightarrow C^+ + O + He$	2.0	Laudenschlager *et al.* 1973
19.	$He^+ + N_2 \rightarrow N^+ + N + He$	0.72	Farragher 1970
20.	$\rightarrow N_2^+ + He$	0.48	Farragher 1970
21.	$He^+ + O_2 \rightarrow O^+ + O + He$	0.62	Farragher 1970
22.	$\rightarrow O_2^+ + He$	0.38	Farragher 1970
23.	$He^+ + CN \rightarrow C^+ + N + He$	2.0	
24.	$H_3^+ + O \rightarrow OH^+ + H_2$	2.0	
25.	$H_3^+ + C \rightarrow CH^+ + H_2$	2.0	
26.	$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.4	Burt *et al.* 1970
27.	$H_3^+ + N_2 \rightarrow HN_2^+ + H_2$	1.5	Burt *et al.* 1970
28.	$H_3^+ + OH \rightarrow H_2O^+ + H_2$	2.0	
29.	$H_3^+ + CN \rightarrow HCN^+ + H_2$	2.0	
30.	$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	3.0	Burt *et al.* 1970
31.	$H_3^+ + CO_2 \rightarrow HCO_2^+ + H_2$	1.9	Burt *et al.* 1970
32.	$H_3^+ + NH_3 \rightarrow NH_4^+ + H_2$	3.6	Burt *et al.* 1970
33.	$H_3^+ + HCN \rightarrow H_2CN^+ + H_2$	2.0	
34.	$H_3^+ + H_2CO \rightarrow H_3CO^+ + H_2$	2.0	
35.	$HCO^+ + OH \rightarrow HCO_2^+ + H$	1.0	Only exothermic channel
36.	$HCO^+ + H_2O \rightarrow H_3O^+ + CO$	0.5	See analogous HN_2^+ reaction in Burt *et al.* 1970
37.	$HCO^+ + NH \rightarrow NH_2^+ + CO$	1.0	
38.	$HCO^+ + NH_2 \rightarrow NH_3^+ + CO$	1.0	
39.	$HCO^+ + NH_3 \rightarrow NH_4^+ + CO$	1.0	
40.	$HCO^+ + H_2CO \rightarrow H_3CO^+ + CO$	1.0	
41.	$C^+ + O_2 \rightarrow CO^+ + O$	1.1	Fehsenfeld *et al.* 1966*a*
42.	$C^+ + OH \rightarrow CO + H^+$	2.0	
43.	$C^+ + NH \rightarrow CN + H^+$	2.0	
44.	$C^+ + CH \rightarrow C_2^+ + H$	2.0	
45.	$C^+ + H_2O \rightarrow HCO^+ + H$	2.0	Bolden and Twiddy 1972
46.	$C^+ + NH_2 \rightarrow HCN + H^+$	2.0	
47.	$C^+ + CH_2 \rightarrow C_2H^+ + H$	2.0	
48.	$C^+ + HCN \rightarrow C_2N^+ + H$	2.0	
49.	$C^+ + CO_2 \rightarrow CO^+ + CO$	1.9	Fehsenfeld *et al.* 1966*b*
50.	$C^+ + NH_3 \rightarrow H_2CN^+ + H$	2.0	
51.	$C^+ + H_2CO \rightarrow HC_2O^+ + H$	2.0	
52.	$H^+ + CO_2 \rightarrow HCO^+ + O$	3.0	Fehsenfeld *et al.* 1971
53.	$O_2^+ + N \rightarrow NO^+ + O$	0.18	Goldan *et al.* 1966
54.	$HN_2^+ + CO \rightarrow HCO^+ + N_2$	1.0	See analogous CO_2 reaction in Burt *et al.* 1970
55.	$H_3O^+ + C \rightarrow HCO^+ + H_2$	2.0	
56.	$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	2.0	

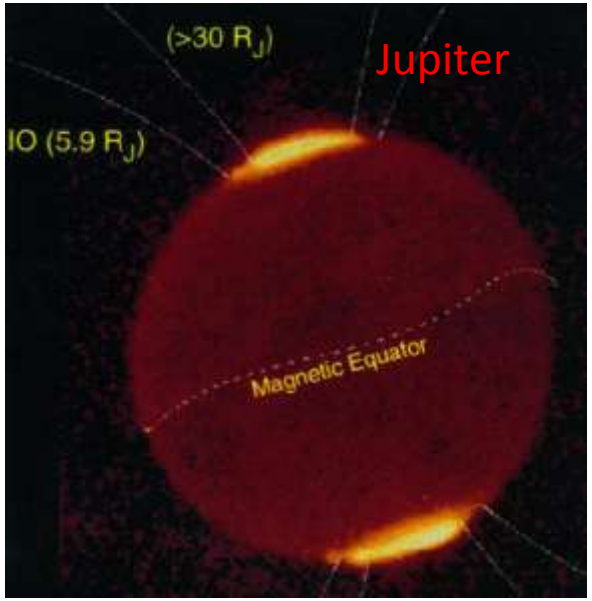
Extraterrestrial $H_3^{\pm}$



Geballe & Oka, Nature 384, 334 (1996)



McCall et al., Science 279, 1910 (1998)



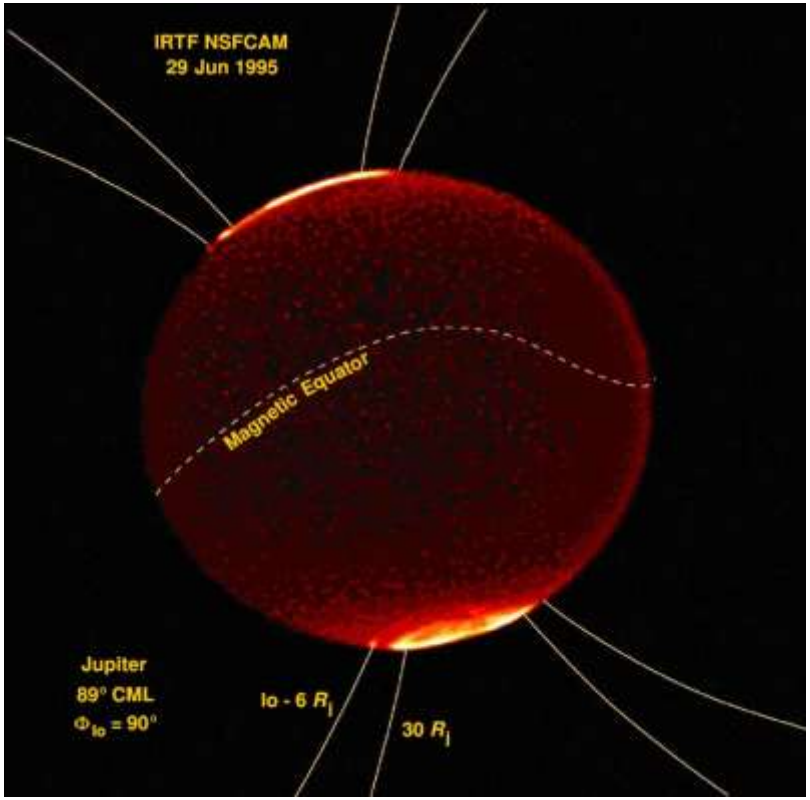
Connerney et al., Science 262 , 1035 (1993)

Plus:

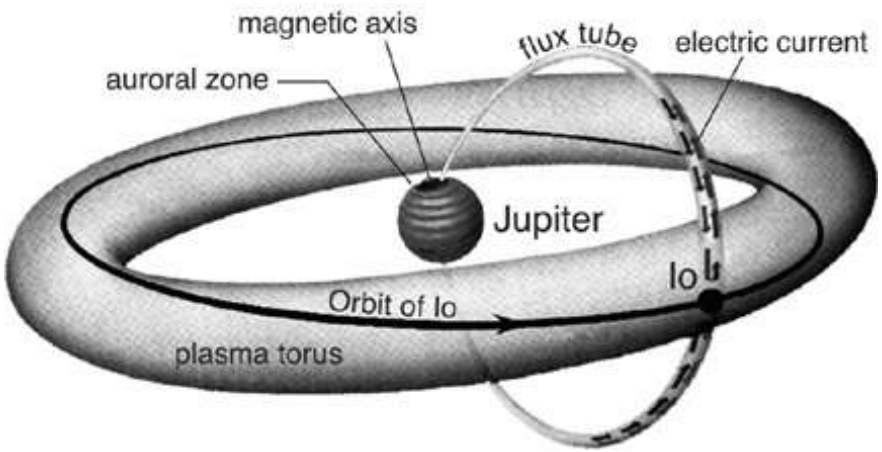
- detection in the atmosphere of Uranus
- detection in Saturn's atmosphere
- high abundance towards the galactic center
- extragalactic detection in IRAS 08572+3915NW

Extraterrestrial $H_3^{\pm}$

H_3^+ auroral emission
from the Jovian atmosphere



Connery and Satoh, Phil. Trans. R. Soc. Lond. A, 358, 2471 (2000)



Jupiter: The Planet, Satellites and Magnetosphere, Ed. F. Bagenal, T. Dowling and W. McKinnon Cambridge University Press (2004)

Plus:

- detection in the atmosphere of Uranus,
- detection in Saturn's atmosphere,
- high abundance towards the galactic center.

The enigma related to interstellar H_3^+

Dense clouds: formation

$$H_2 + c.r. \longrightarrow H_2^+$$
$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$

destruction

$$H_3^+ + CO \longrightarrow HCO^+ + H_2$$

observed column density: 6×10^{14} cm^{-2}

Diffuse clouds: formation

$$H_2 + c.r. \longrightarrow H_2^+$$
$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$

destruction

$$H_3^+ + e^- \longrightarrow H_2 + H \;\; / \;\; H + H + H$$

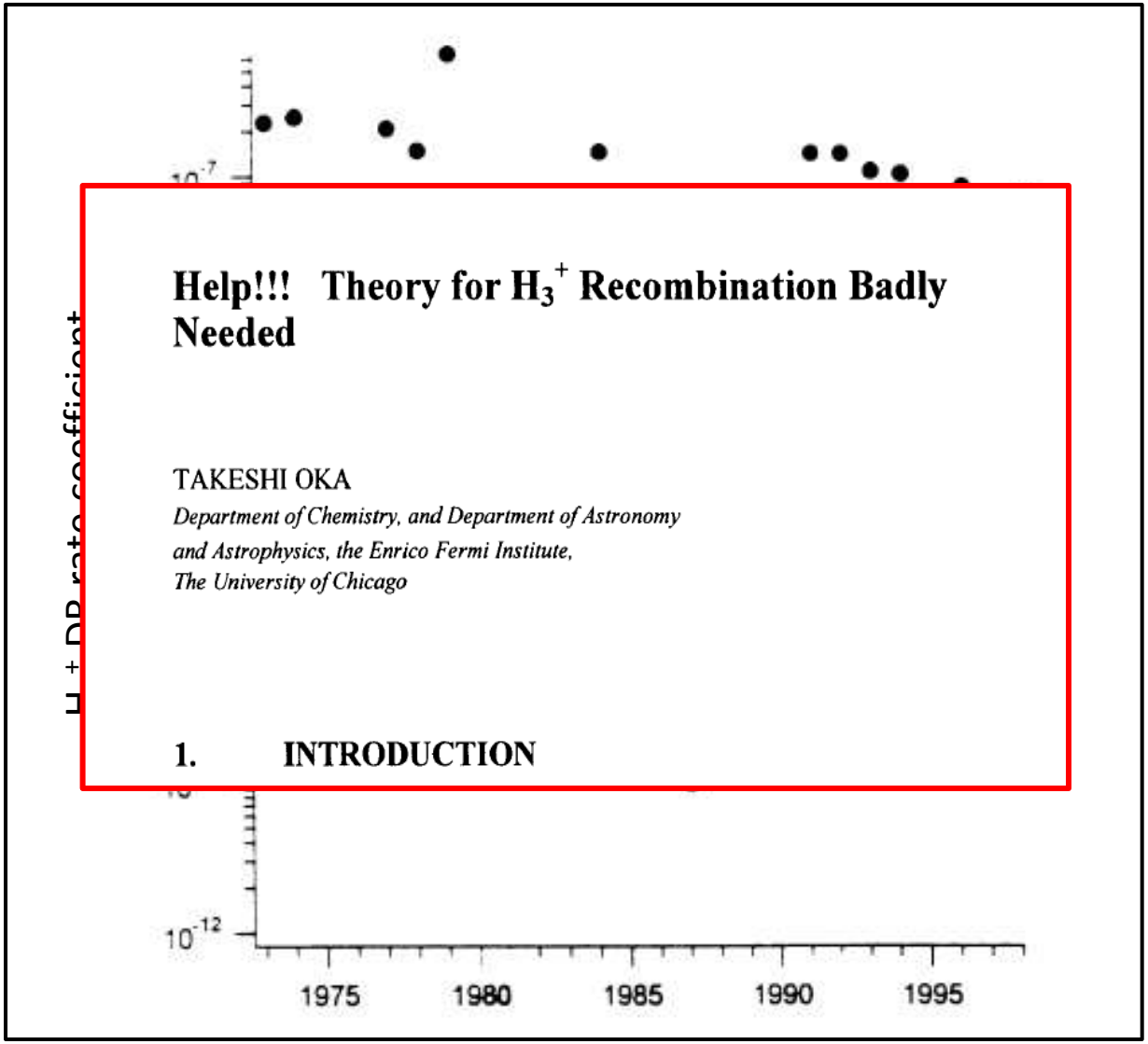
observed column density: 4×10^{14} cm^{-2}

Dissociative Recombination DR

2-3 orders of magnitude too much H_3^+ in diffuse clouds !

The Problem with H_3^+ Electron Recombination

$$H_3^+ \xrightarrow{e^-} \begin{matrix} H_2 + H \\ H + H + H \end{matrix}$$



Help!!! Theory for H_3^+ Recombination Badly Needed

TAKESHI OKA
Department of Chemistry, and Department of Astronomy and Astrophysics, the Enrico Fermi Institute, The University of Chicago

1. INTRODUCTION

The Enigma of H_3^+ in Diffuse Clouds

Cosmic ray ionization rate
(10^{-17} s^{-1})

Steady State:

$$[H_3^+] = \frac{\zeta}{k_e} \frac{[H_2]}{[e^-]}$$

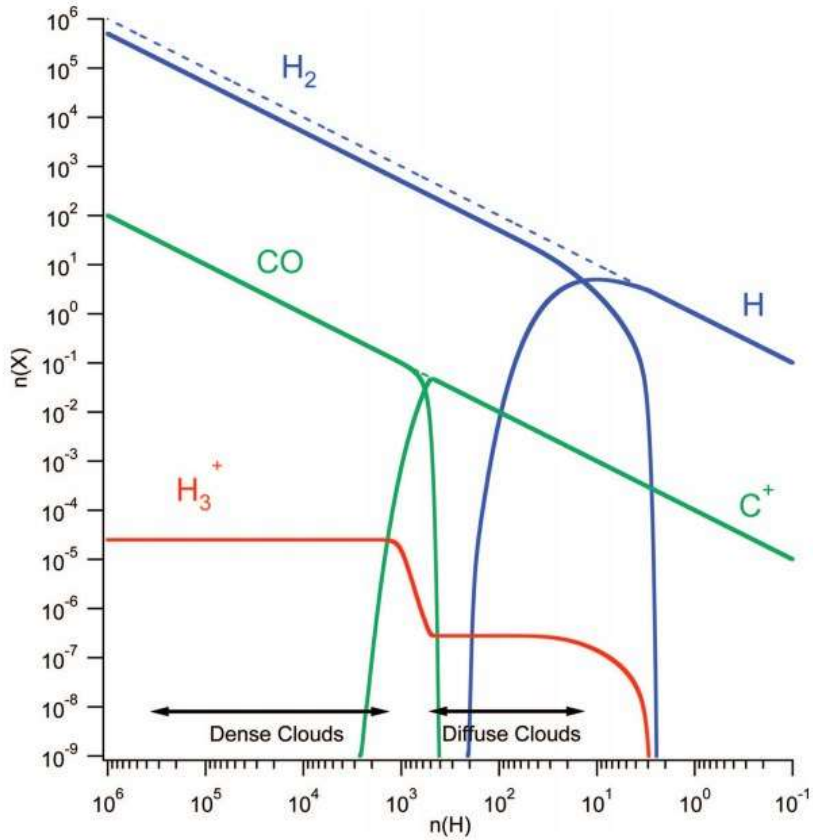
Fast DR rate coefficient
(10^{-7} cm^3 s^{-1})

Inverse ionization fraction
($1/10^{-4}$)

→ $N(H_3^+) = 10^{-6}$ cm^{-3}

With the canonical value for the Cosmic Ray Ionization Rate
Of $\zeta \approx 10^{-17}$ s^{-1} and a fast DR process,
H_3^+ should not be observable in the diffuse ISM!

Why H_3^+ observations are so useful



- H_3^+ density $n(H_3^+)$ is constant with two phases in diffuse and dense sightlines
- By measuring the column density, the length of the cloud L along the line of sight can be calculated:

$$L = N(H_3^+)/n(H_3^+)$$

Storage Ring Recombination Measurements

Advantages

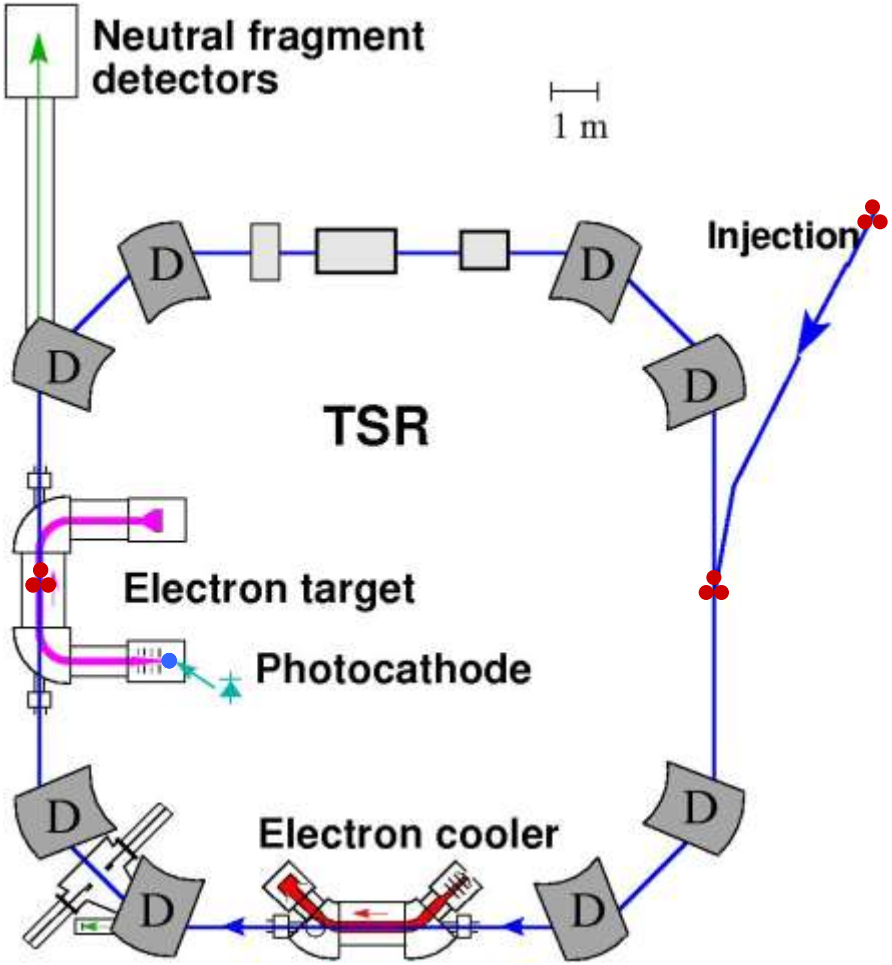
- radiative relaxation (rotations, vibrations)

- direct measurement
- 100% detection efficiency
- high resolution

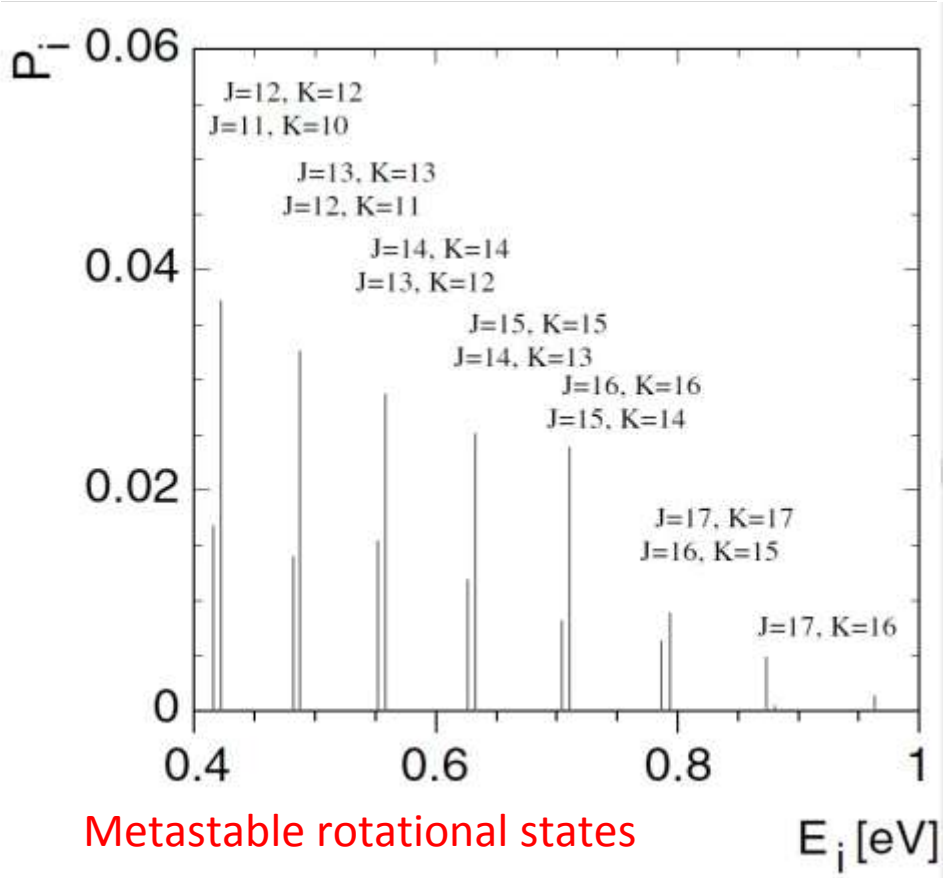
Problem

H_3^+

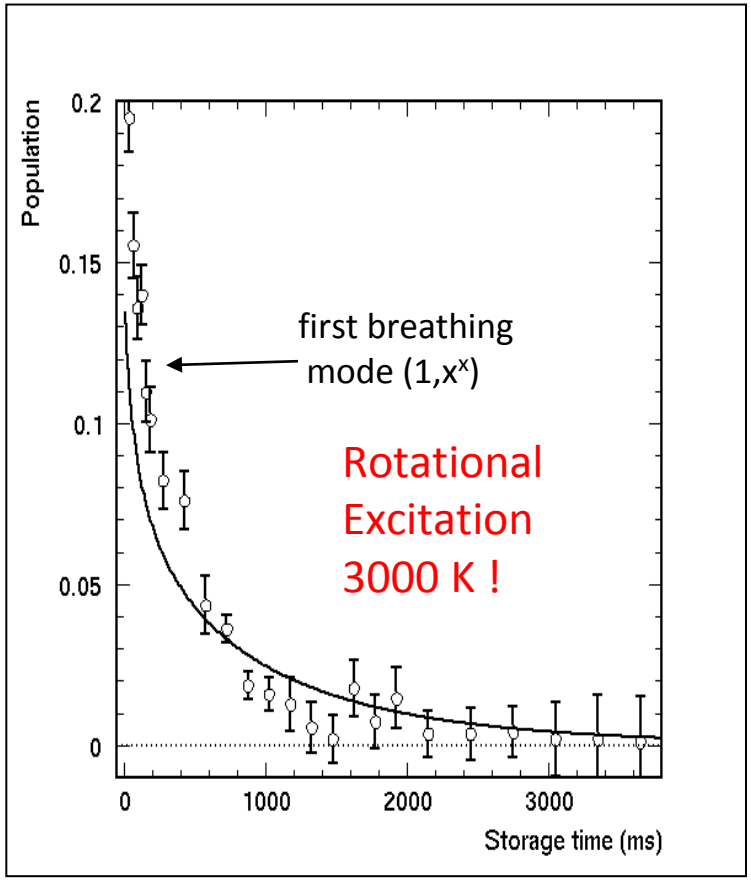
vibrational excitation?



H_3^+ Vibrational Cooling



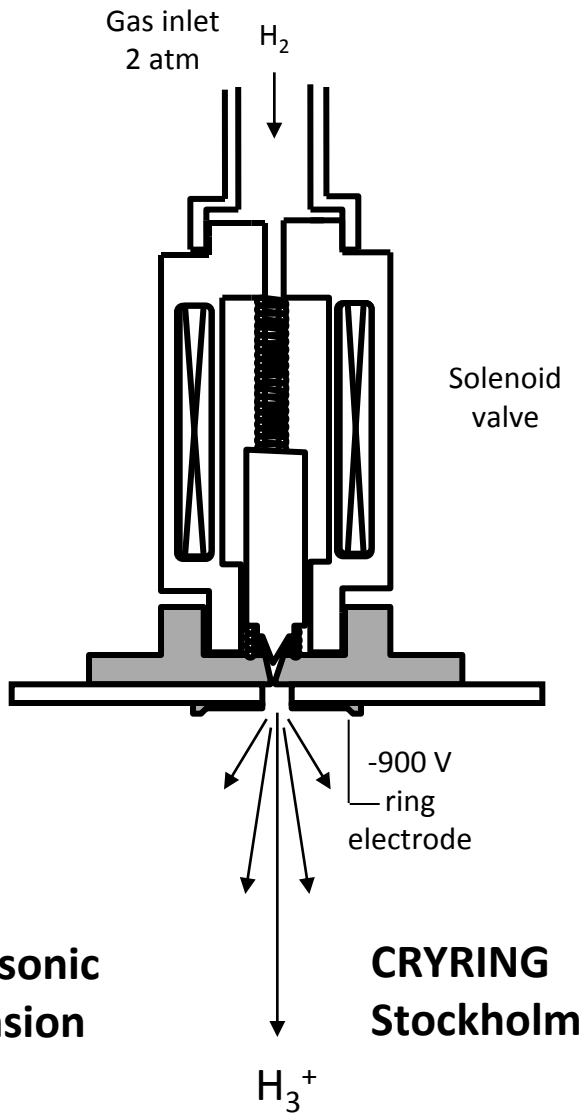
Metastable rotational states



Kreckel et al., New J. Phys. 6, 151 (2004)

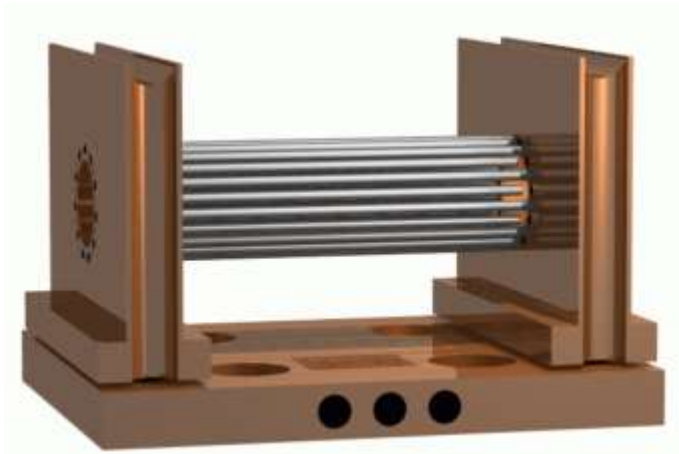
Kreckel et al., PRA 66, 052509 (2002)

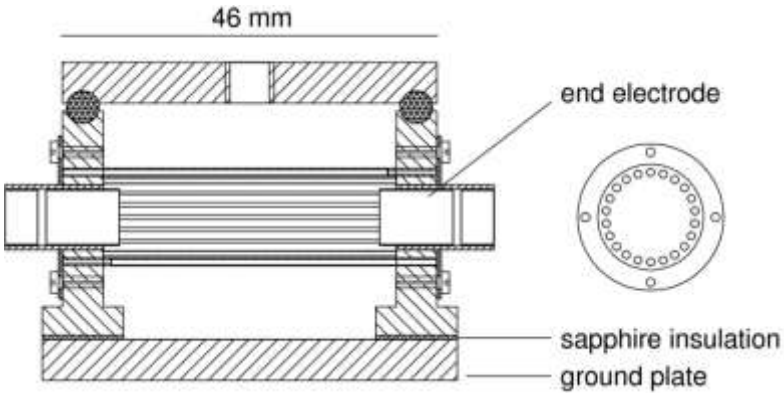
Rotationally "cold" Ion Sources



Supersonic expansion

CRYRING Stockholm





Cryogenic 22-pole ion trap

TSR Heidelberg

Gerlich, Physica Scripta, T59, 256, (1995)

H_3^+ DR Spectrum High Resolution

MOLECULAR PHYSICS

Recombination cool and fast

theoretically only recently[3,4], and, starting in 1973, many experimental measurements have

Chemical Physics Letters 462 (2008) 145–151

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

FRONTIERS ARTICLE

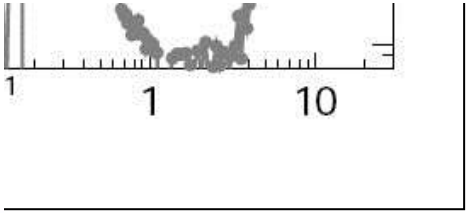
The dissociative recombination of H_3^+ – a saga coming to an end?

M. Larsson [a,*], B.J. McCall [b], A.E. Orel [c]

[a] Department of Physics, AlbaNova University Centre, Stockholm University, SE-106 91 Stockholm, Sweden
[b] Department of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[c] Department of Applied Science, University of California Davis, Davis, CA 95616, USA

energy can be lost only by emitting a photon, a slow process that seldom happens during the short time a collision takes. In most such collisions, the ion and electron fly away from each other again. If X^+ is a molecular ion, however, there is a much more efficient option: the molecule can break apart following recombination with the electron, and the resulting neutral fragments can carry away kinetic energy. This is the

Figure 1 | Cosmic mystery. When an electron and a positively charged H_3^+ ion meet, three separate neutral hydrogen atoms are formed in a process known as dissociative recombination. The image is overlaid on a wide-field image of the Perseus region: the bright stars at bottom left are the Pleiades, or Seven Sisters, and the red region to the right is the California nebula. The bright star at the arrow's head is ζ Persei, where H_3^+ has been observed in unexpectedly high abundance[2]. The results of Kreckel *et al.*[1]



Nature (News and Views) 440, 157 (2006)

H_3^+ Laboratory Astrophysics Research leads to a revised Cosmic ray ionization rate in the Diffuse ISM

High Cosmic ray ionization rate

High observed H_3^+ column densities

Steady State: $$[H_3^+] = \frac{\zeta}{k_e} \frac{[H_2]}{[e^-]}$$

Fast DR rate coefficient

THE ASTROPHYSICAL JOURNAL, 671:1736-

H_3^+ IN DIFFUSE INTE

NICK

-RAY IONIZATION RATE

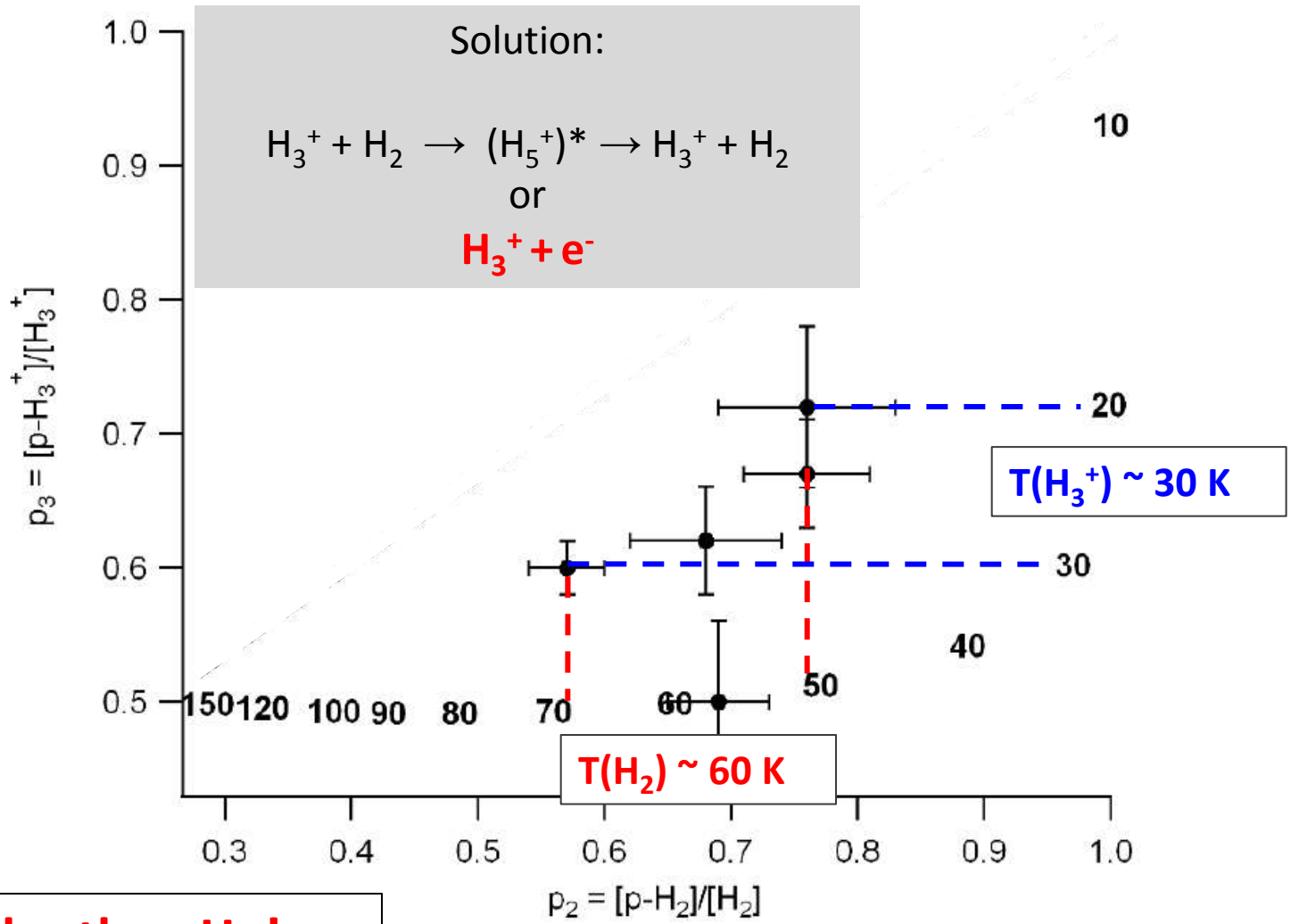
. MCCALL[1]

letters to nature

An enhanced cosmic-ray flux towards ζ Persei inferred from a laboratory study of the H_3^+–e^- recombination rate

B. J. McCall*†, A. J. Huneycutt*, R. J. Saykally*, T. R. Geballe‡, N. Djuric§, G. H. Dunn§, J. Semaniak||, O. Novotny||¶, A. Al-Khalili#, A. Ehlerding#, F. Hellberg#, S. Kalhori#, A. Neau#, R. Thomas#, F. Österdahl☆ & M. Larsson#

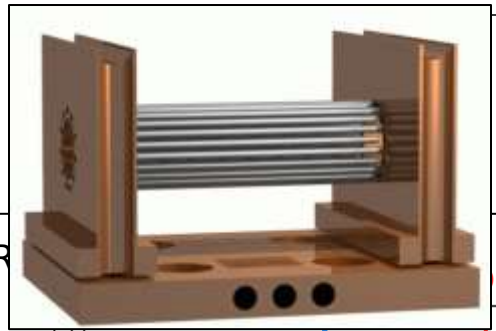
Nuclear Spin equilibrium in the diffuse ISM



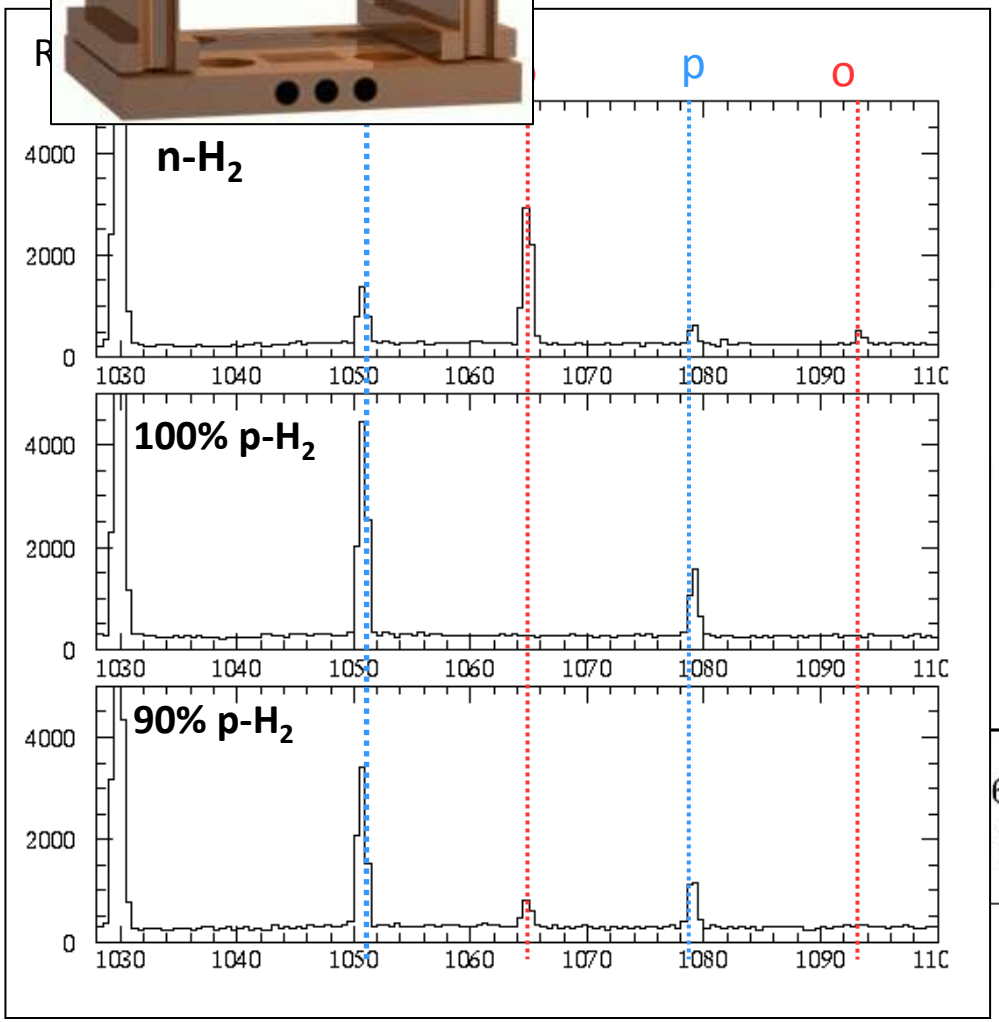
H_3^+ colder than H_2 !
Too much para-H_3^+

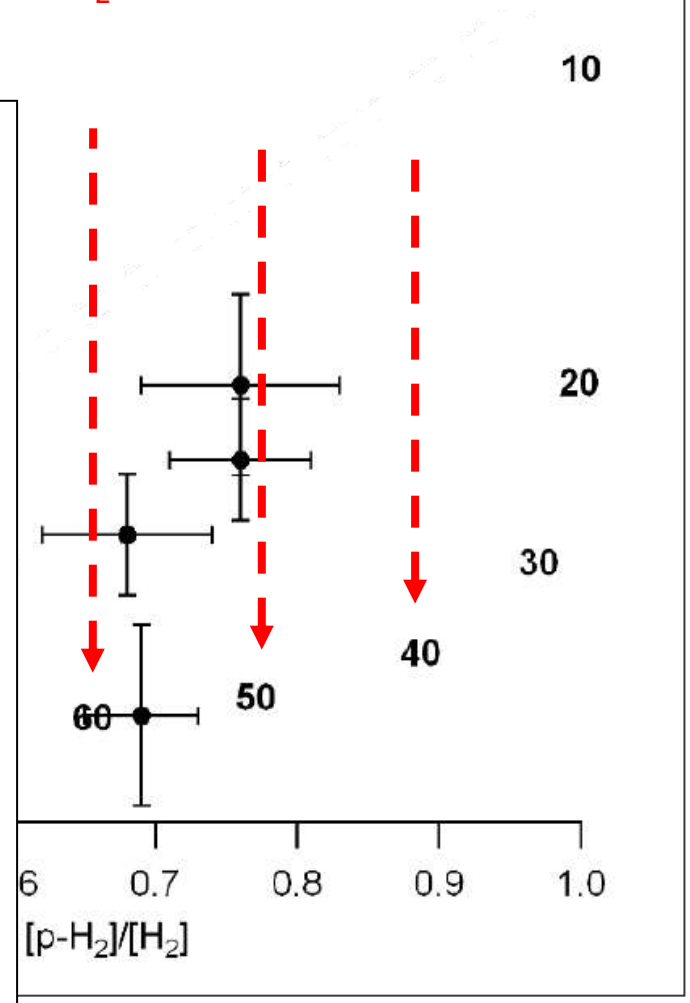
Crabtree et al., ApJ 729, 15(2011)

Understanding the H_3^+ - H_2 collision system



Measure with thermal p-H_2 samples in 10k steps





Detected Molecules

Table 2 Molecules detected in diffuse molecular clouds

Weight	Species	Method	Target	$N(X)/N_H$	Reference
2	H_2	UV	ζ Oph	0.56	1
3	HD	UV	ζ Oph	4.5 (−7)	2
3	H_3^+	IR	ζ Per	5.1 (−8)	3
13	CH	Optical	ζ Oph	1.5 (−9)	4
13	CH^+	Optical	ζ Oph	2.4 (−8)	5
14	$^{13}CH^+$	Optical	ζ Oph	3.5 (−10)	6
15	NH	Optical	ζ Oph	6.2 (−10)	7
17	OH	UV	ζ Oph	3.3 (−8)	8
24	C_2	Optical	ζ Oph	1.3 (−8)	9
25	C_2H	mm abs.	BL Lac	1.8 (−8)	10
26	CN	Optical	ζ Oph	1.9 (−9)	11
27	HCN	mm abs.	BL Lac	2.6 (−9)	12
27	HNC	mm abs.	BL Lac	4.4 (−10)	12
28	N_2	UV	HD 124314	3.1 (−8)	13
28	CO	UV	X Per	6.4 (−6)	14
29	HCO^+	mm abs.	BL Lac	1.5 (−9)	15
29	HOC^+	mm abs.	BL Lac	2.2 (−11)	15
29	^{13}CO	UV	X Per	8.9 (−8)	16
29	$C^{17}O$	UV	X Per	7.4 (−10):	16
30	$C^{18}O$	UV	X Per	2.1 (−9):	16
30	H_2CO	mm abs.	BL Lac	3.7 (−9)	17
36	C_3	Optical	ζ Oph	1.1 (−9)	18
36	HCl	UV	ζ Oph	1.9 (−10)	19
38	C_3H_2	mm abs.	BL Lac	6.4 (−10)	10
44	CS	mm abs.	BL Lac	1.6 (−9)	20
64	SO_2	mm abs.	BL Lac	≤8.2 (−10)	20

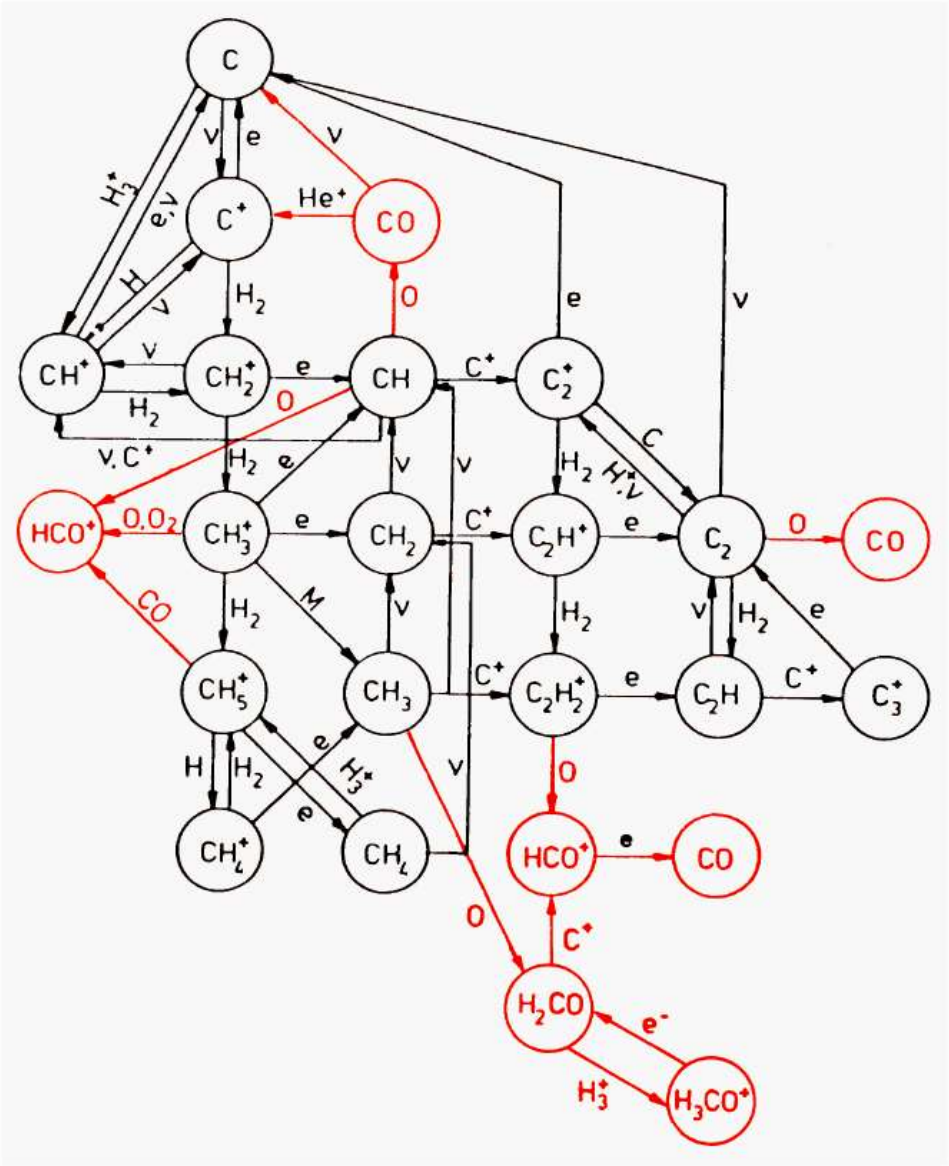
Processes in Diffuse Clouds

	k (cm^3 s^{-1})
▪ Formation of bonds	
▪ Radiative association:	$\sim 10^{-17} - 10^{-14}$
▪ Grain surface:	$\sim 10^{-17}$
▪ Destruction of bonds	
▪ Photo-dissociation:	$\sim 10^{-10} - 10^{-8}$ s^{-1}
▪ Dissociative recombination:	$\sim 10^{-7} - 10^{-6}$
▪ Rearrangement of bonds	
▪ Ion-molecule reactions:	$\sim 10^{-9} - 10^{-8}$
▪ Neutral-neutral reactions:	$\sim 10^{-10} - 10^{-9}$

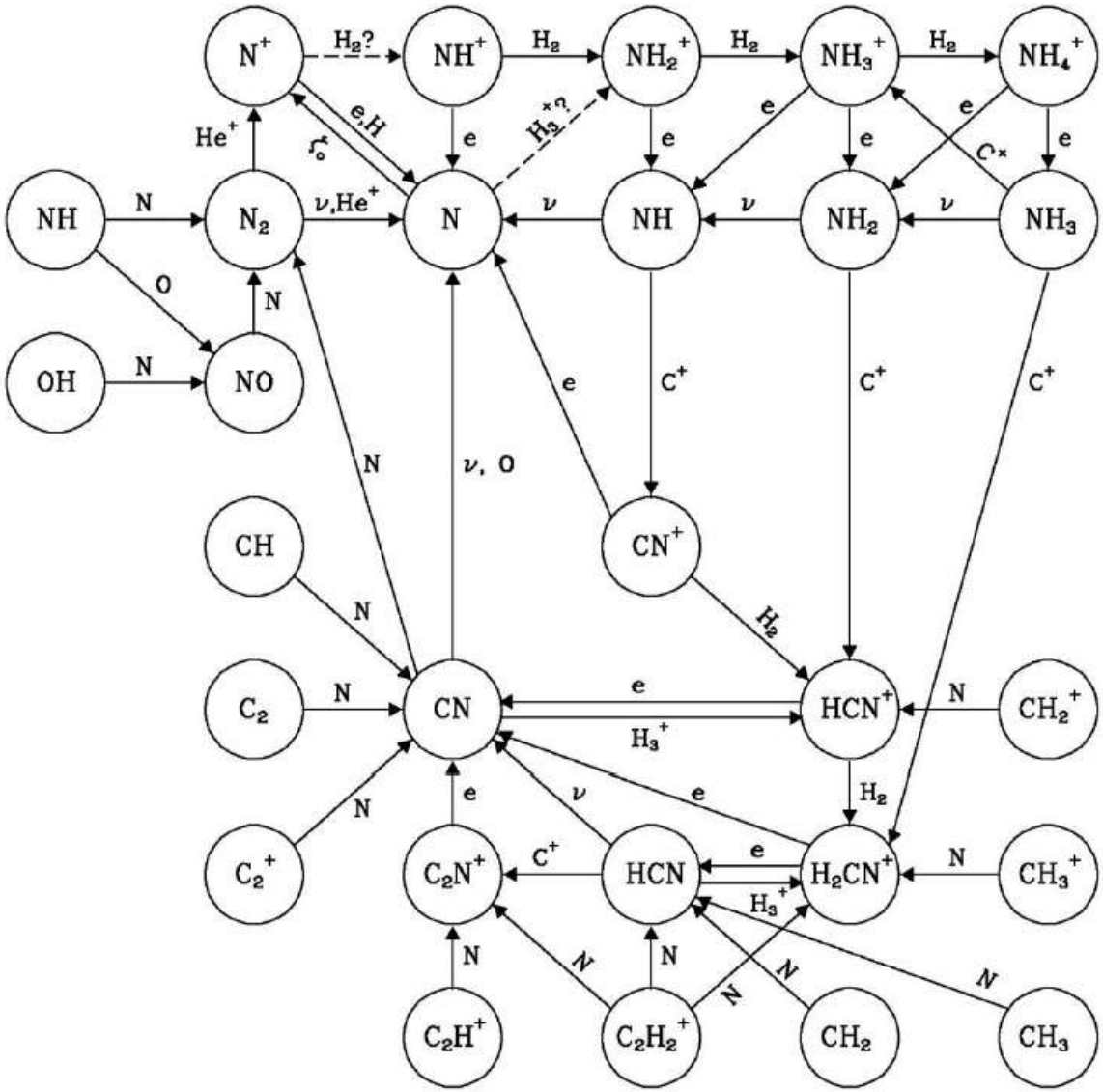
Hydrogen is dominant element $\Rightarrow$ if species can react with H or H_2, it will be the dominant route

Ewine van Dishoeck, lecture notes

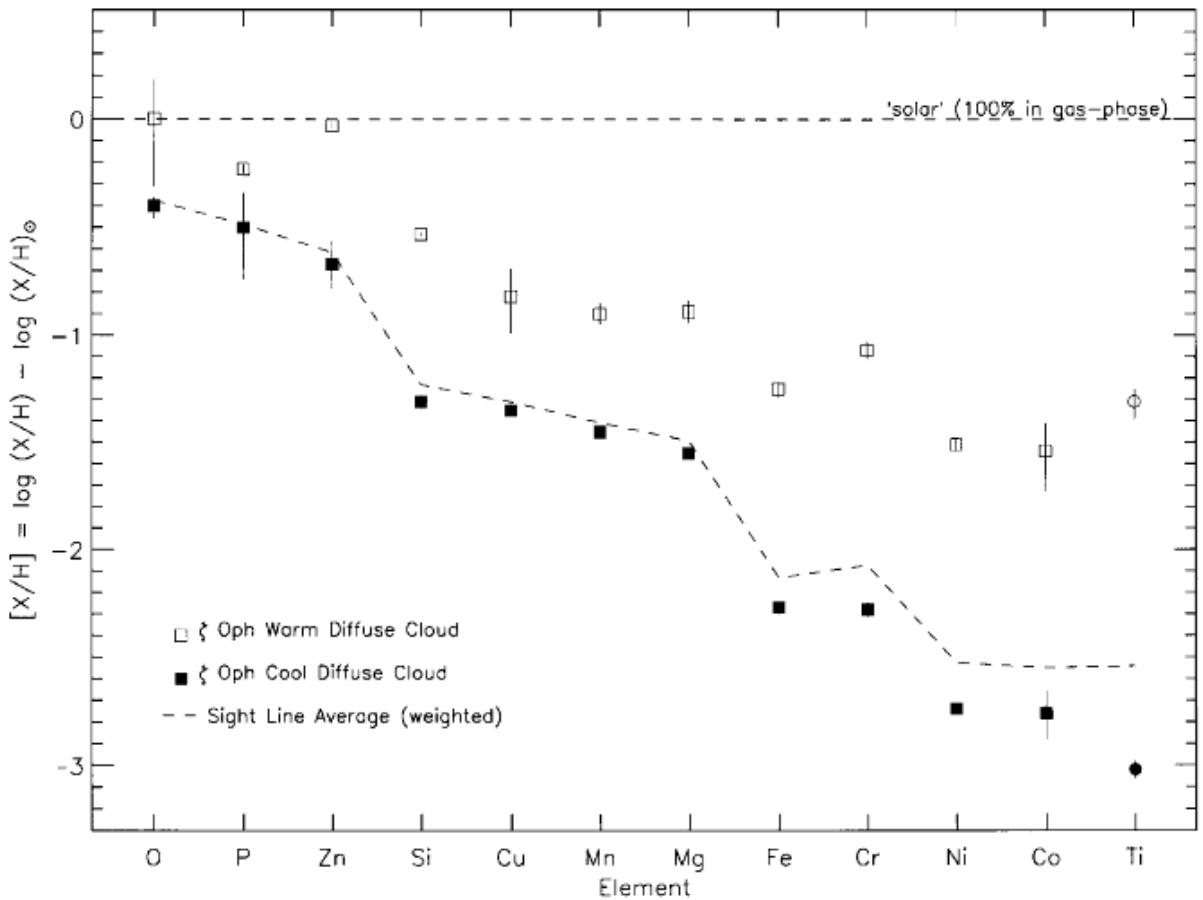
Carbon / Oxygen Network



Carbon / Nitrogen Network



Depletion on Dust Grains: also in the diffuse medium



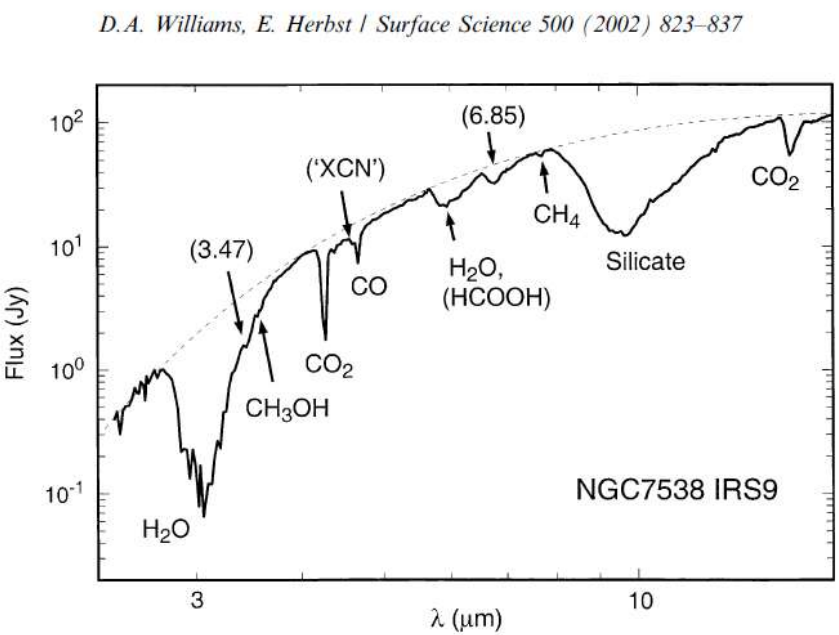
More depletion in cool clouds, more freeze-out on dust grains

Figure 5 A comparison of the gas-phase abundances, $[X/H] = \log(X/H) - \log(X/H)_{\odot}$, in the cool and warm diffuse clouds toward ζ Oph at heliocentric velocities of -15 km s^{-1} and -27 km s^{-1}, respectively. The elements are arranged in order of decreasing gas-phase abundance (which is approximately one of increasing condensation temperature). The dashed line indicates the column density-weighted sight-line average abundances. There is a general progression in abundance differences as a function of elemental depletion (see text). The data used to construct this plot are listed in Table 5.

Savage & Sembach, Annu. Rev. Astron. Astrophys. 1996. 34:279-329

Elemental Depletion

$$D_x = \log\left[\frac{N(x)}{N(H)}\right] - \log\left[\frac{N(x)}{N(H)}\right]_\odot$$



Timescale for depletion:

$$\tau_d = \frac{1}{\varepsilon\, f(X) v(X)\, n}$$

ε	Grain surface per H atom cm^{-3}
$f(X)$	Sticking probability for species X
$v(X)$	velocity of species X
n	cloud density

	Diffuse cloud ($n = 10^2\,cm^{-3}$; $T = 100\,K$)	Dark cloud ($n = 2 \times 10^4\,cm^{-3}$; $T = 30\,K$)
$M =$ 10 a.m.u.	$\tau_d = 1.0 \times 10^{14}$ s	$\tau_d = 9.4 \times 10^{11}$ s
50	2.3×10^{14}	2.1×10^{12}
100	3.3×10^{14}	3.0×10^{12}

Typical cloud lifetime: 3×10^{14} s

Non-detections

Table 3 (*Continued*)

Weight	Species	Method	Target	N(X)/N_H	Reference
145	$C_{12}H$	Optical	HD 207198	<5 (−10)	8
158	$HC_{13}H$	Optical	—[a]	<5 (−9)	12
720	C_{60}	Optical	Cyg OB2 8A	<4.8 (−11)	13

Table 3 Molecules not detected in diffuse molecular clouds

Weight	Species	Method	Target	N(X)/N_H	Reference
14	CH_2	UV	ζ Oph	≤2.4 (−8)	1
15	NH^+	UV	ζ Oph	<8.7 (−10) f^{-1}	2
18	H_2O	UV	HD 154368	<2 (−9)	3
24	NaH	UV	ζ Oph	<1.2 (−9)	2
25	MgH	UV	ζ Oph	<3.0 (−8)	2
25	MgH^+	UV	ξ Per	<1.0 (−10) f^{-1}	2
26	CN^+	UV	ξ Per	<5.3 (−10)	2
28	CO^+	UV	ζ Oph	<4.1 (−9)	2
28	AlH	UV	ζ Oph	<1.3 (−10) f^{-1}	2
29	SiH	UV	ζ Oph	<1.0 (−9)	2
29	N_2H^+	mm abs.	various	—[b]	4
30	NO	UV	ξ Per	<1.2 (−6)	2
30	NO^+	UV	ζ Oph	<5.9 (−8)	5
32	O_2	UV	o Per	<1.8 (−10) f^{-1}	2
33	SH	UV	o Per	<7.6 (−11) f^{-1}	2
37	C_3H	mm abs.	various	—[b]	6
41	CaH	UV	ζ Oph	<4.9 (−11) f^{-1}	2
41	CH_3CN	mm abs.	various	—[b]	4
44	CO_2	UV	ζ Oph	<1.5 (−9) f^{-1}	2
44	SiO	UV	ζ Oph	<1.7 (−10) f^{-1}	2
48	C_4	Optical	ζ Oph	<2.6 (−10)	7
49	C_4H	mm abs.	various	—[b]	6
50	HC_4H^+	Optical	HD 207198	<1.4 (−9)	8
52	$C_4H_4^+$	Optical	—[a]	<2 (−10)	9
60	C_5	Optical	ζ Oph	<5.3 (−11)	7
61	C_5H	Optical	—[a]	<1 (−10)	10
73	C_6H	Optical	HD 207198	<3 (−10)	8
74	HC_6H^+	Optical	HD 210839	<1.3 (−10)	8
75	HC_5N^+	Optical	HD 207198	<1.7 (−10)	8
76	$C_6H_4^+$	Optical	—[a]	<5 (−11)	11
76	NC_4N^+	Optical	HD 210839	<1 (−10)	8
85	C_7H	Optical	—[a]	<1 (−10)	10
86	HC_7H	Optical	—[a]	<1 (−9)	12
97	C_8H	Optical	HD 207198	<3 (−10)	8
98	HC_8H^+	Optical	HD 207198	<3 (−10)	8
100	$C_8H_4^+$	Optical	—[a]	<6 (−11)	9
109	C_9H	Optical	—[a]	<1 (−10)	10
110	HC_9H	Optical	—[a]	<1 (−9)	12
121	$C_{10}H$	Optical	HD 207198	<5 (−10)	8
134	$HC_{11}H$	Optical	—[a]	<5 (−9)	12

(*Continued*)

Some notable reaction chains

H_3^+ formation and destruction

$$H_2 \xrightarrow{\text{cosmic ray}} H_2^+ \xrightarrow{H_2} H_3^+ \xrightarrow{e^-} \begin{matrix} H_2 + H \\ H + H + H \end{matrix}$$

Water formation

$$O \xrightarrow{H_3^+} OH^+ \xrightarrow{H_2} OH_2^+ \xrightarrow{H_2} OH_3^+ \xrightarrow{e^-} \begin{matrix} OH + H_2 \\ H_2O + H \end{matrix}$$

Carbon chemistry

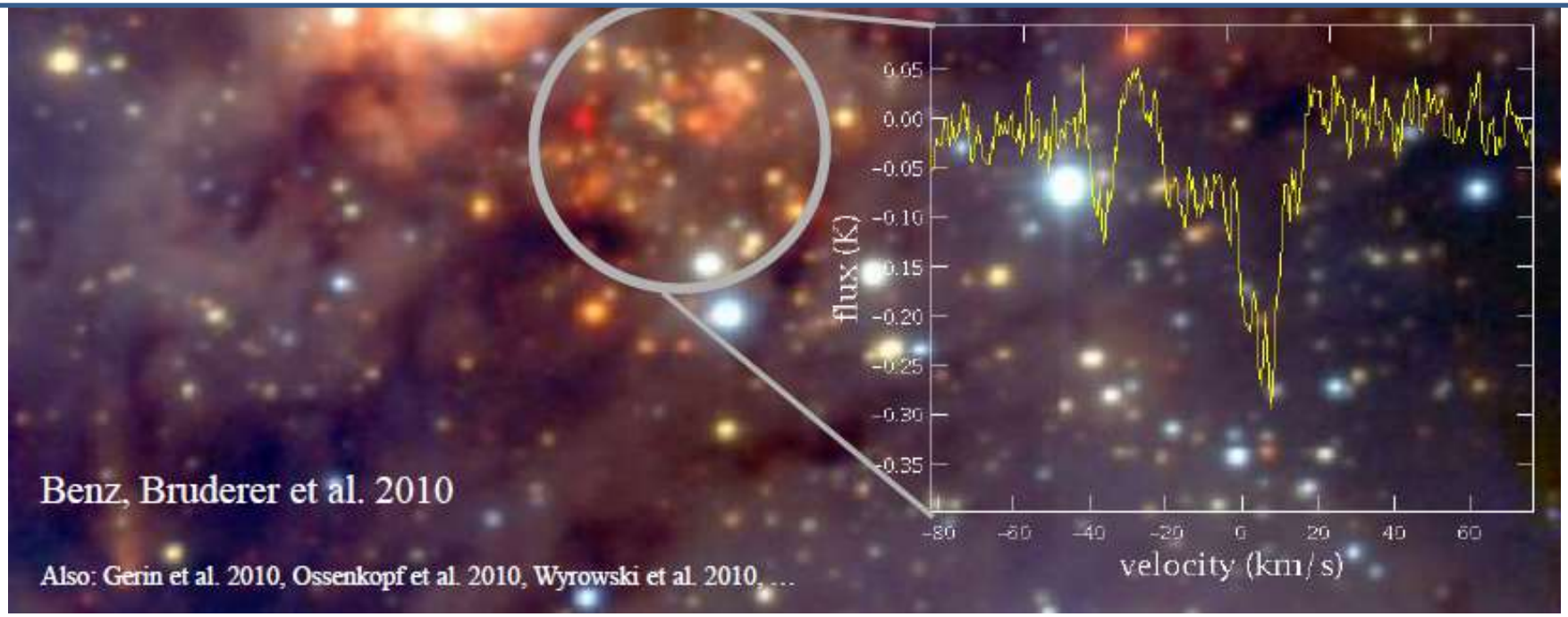
$$C^+ \xrightarrow{OH} CO^+ \xrightarrow{H_2} HCO^+ \xrightarrow{e^-} H + CO$$

Herschel surprisingly finds a lot of H_2O^+

Regions with low H_2 density?

Water formation

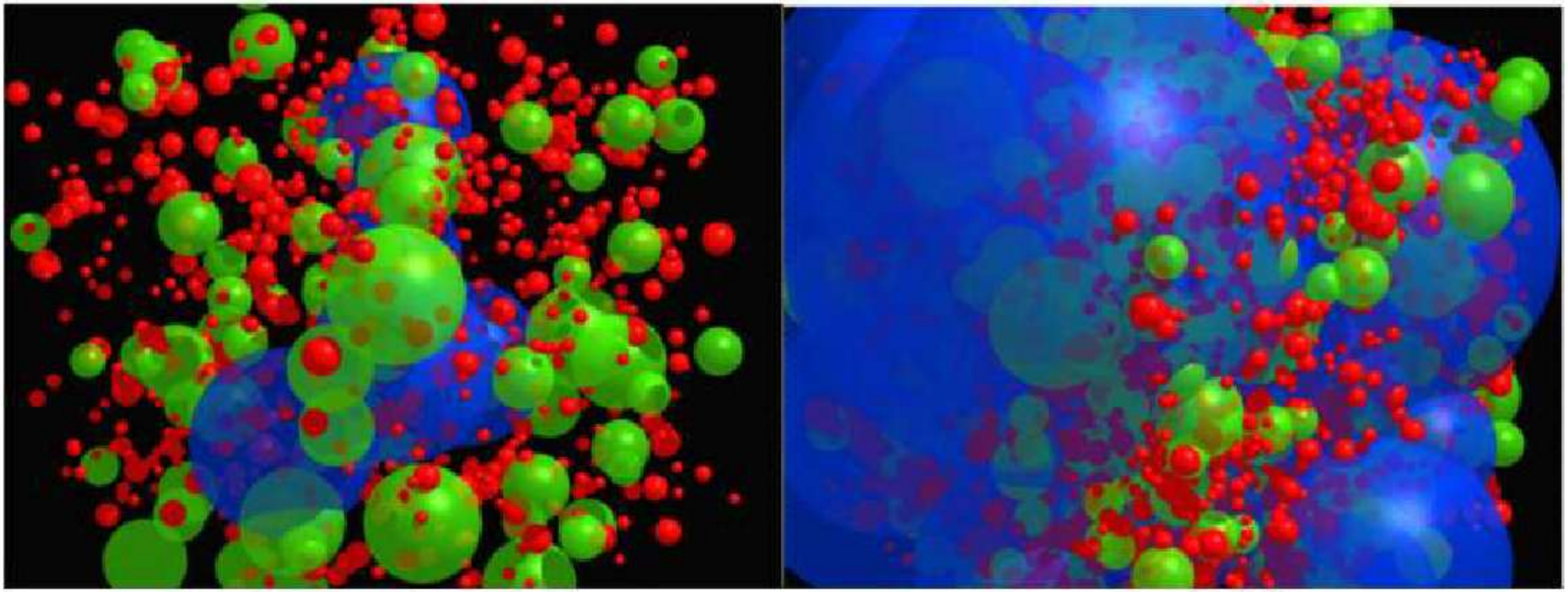
$$O \xrightarrow{H_3^+} OH^+ \xrightarrow{H_2} OH_2^+ \xrightarrow{H_2} OH_3^+ \xrightarrow{e^-} \begin{matrix} OH + H_2 \\ H_2O + H \end{matrix}$$



Benz, Bruderer et al. 2010

Also: Gerin et al. 2010, Ossenkopf et al. 2010, Wyrowski et al. 2010, ...

Or: maybe it's more complicated



J. Stutzki, "On the Complex Structure of Interstellar Clouds", 2009

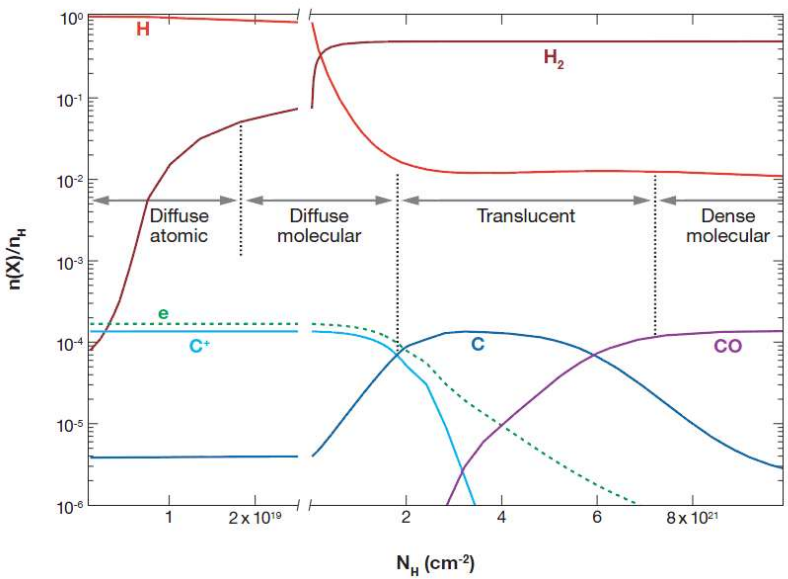
Summary

- The diffuse interstellar medium can be classified into 3 phases:
  1. diffuse atomic clouds (hydrogen atomic H)
  2. diffuse molecular clouds (hydrogen molecular H_2, carbon ionized C^+)
  3. translucent clouds (hydrogen molecular H_2, carbon neutral C)

- Active Ion-neutral collisions build up larger molecules,
- High electron fraction -> Electron recombination important,
- H_2 becomes self-shielding,
- H_2 ortho/para excitation temp. reflects the temperature of the cloud (10-100 K),
- HD can be observed easily, exact abundance difficult to predict,

Mysteries Remain:

- Formation of CH^+
- H_3^+ column densities imply higher cosmic ray ionization rate, enigma solved?
- Why so much H_2O^+?
- Why is H_3^+ colder than H_2?



Literature

Snow & McCall,
“Diffuse Atomic and Molecular Clouds”
Annu. Rev. Astron. Astrophys. 2006. 44:367-414

Tielens, A.G.G.M.
“The physics and chemistry of the interstellar medium”
Cambridge University Press