

Molecular Astrophysics: CHEMISTRY OF THE INTERSTELLAR MEDIUM Lecture III Reactions in Astrochemistry

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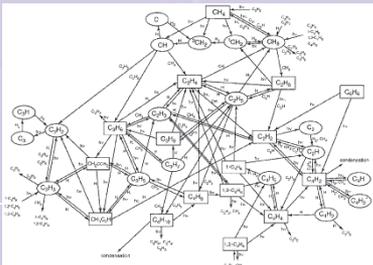


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Técnica Aeroespacial



The molecular Universe

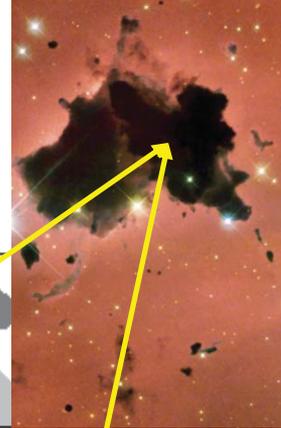
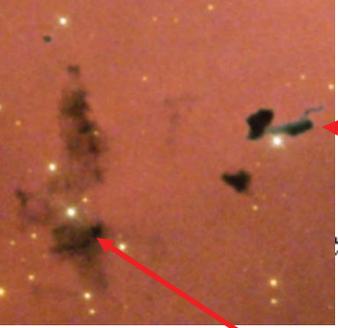
- *ISM molecular clouds are **dusty, icy** and **chemically rich**.*
- *More than **~160 (gas-phase) molecular species** have been detected.*
- *The number of **C, N, O, S ...** atoms represents **< 0.1%** of **H** atoms.*
- ***Molecules** are probes of **the physical conditions**: $T, n, \Delta v, (B, \text{age}, e \dots)$*

Diffuse Clouds

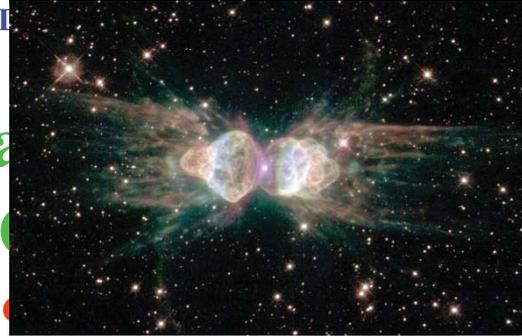
Dense Clouds
CO
CS

Gravitational Collapse

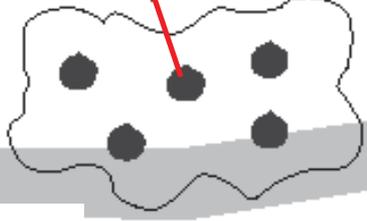
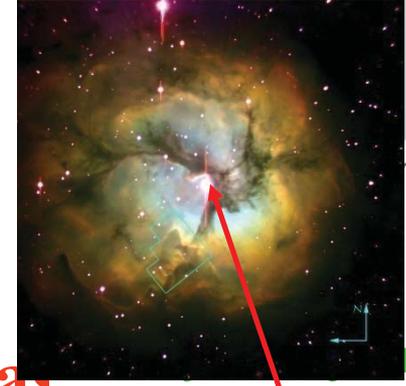
CH, CH⁺
CN



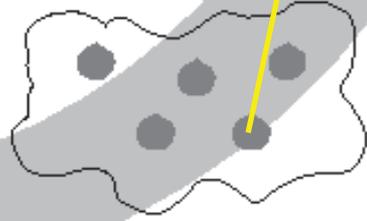
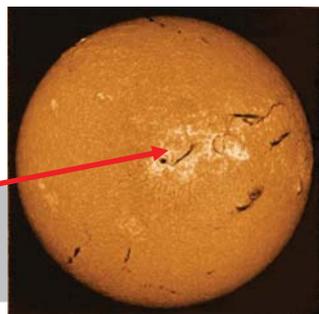
Dust grains go to



Mass Stars



Complex Organic Molecules



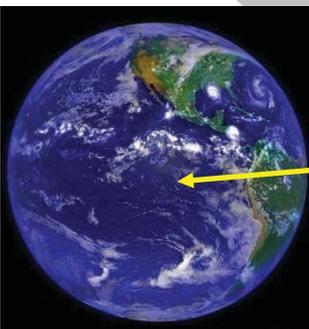
Cold cores : Carbon chains HC₅N, HC₇N, C₈H

Envelope

Aging
Red Giant

Life?

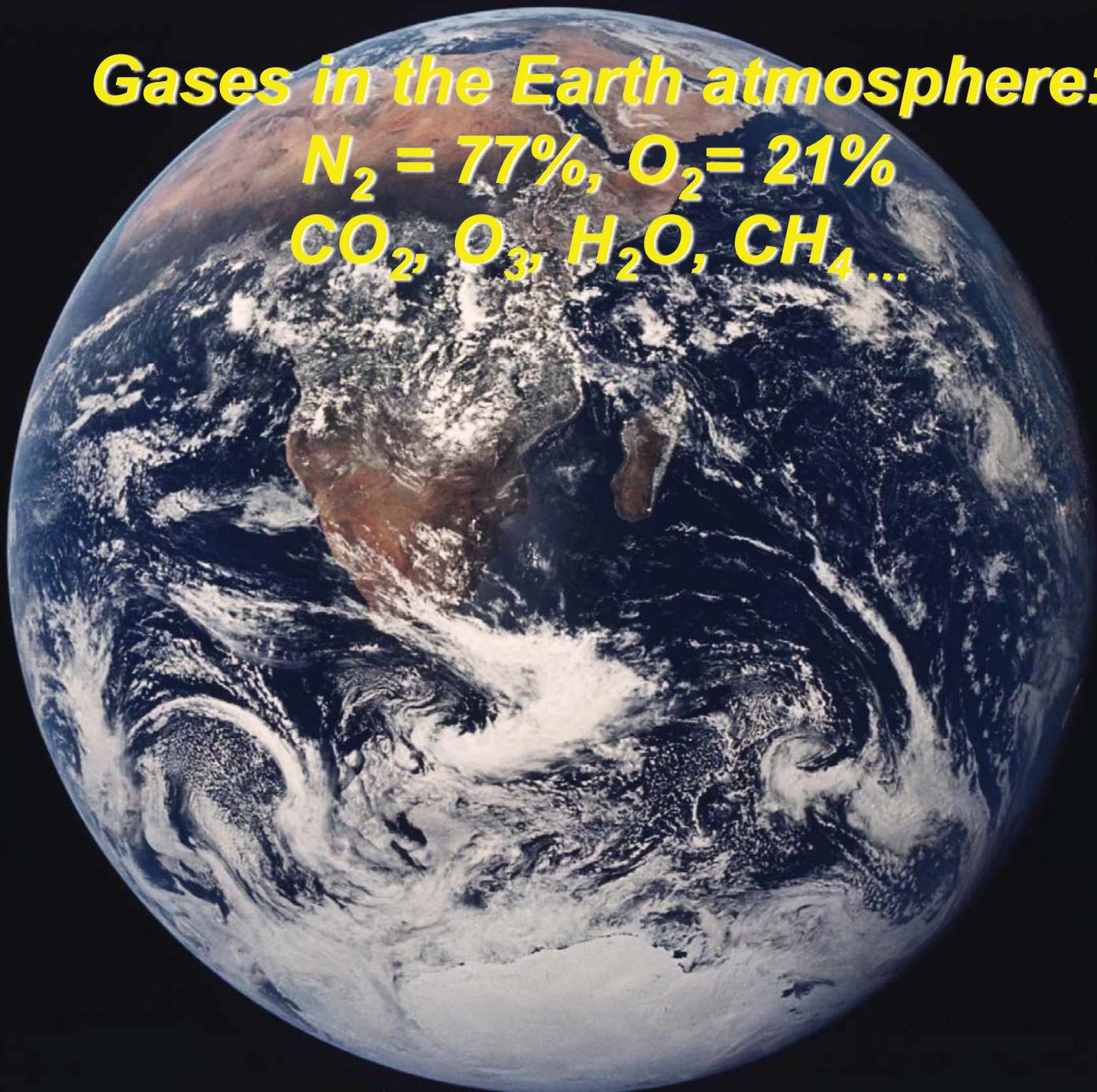
Solar type stars



Gases in the Earth atmosphere:

$N_2 = 77\%$, $O_2 = 21\%$

CO_2 , O_3 , H_2O , CH_4 ...



Los seres humanos inhalan cerca de ciento cincuenta mil trillones de moléculas cada 5-6 segundos

150,000.000,000.000,000.000,000=150,000e18!

**De las cuales 21% son moléculas de oxígeno
77% son moléculas de nitrógeno
2% (vapor de agua y otras)**



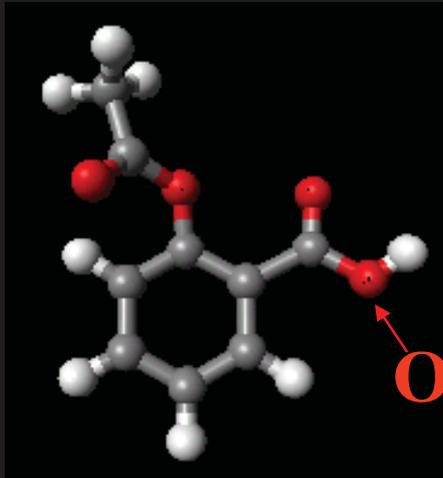
La sangre distribuye el oxígeno a las células donde se realizan procesos de combustión del tipo :



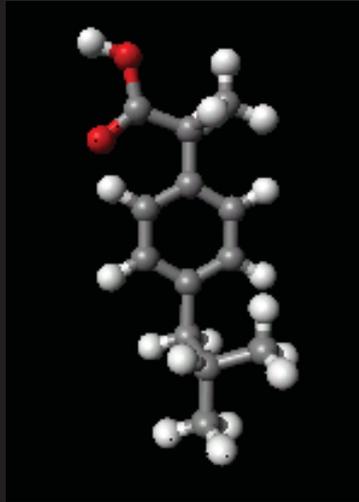
Un motor de explosión realiza un proceso similar :



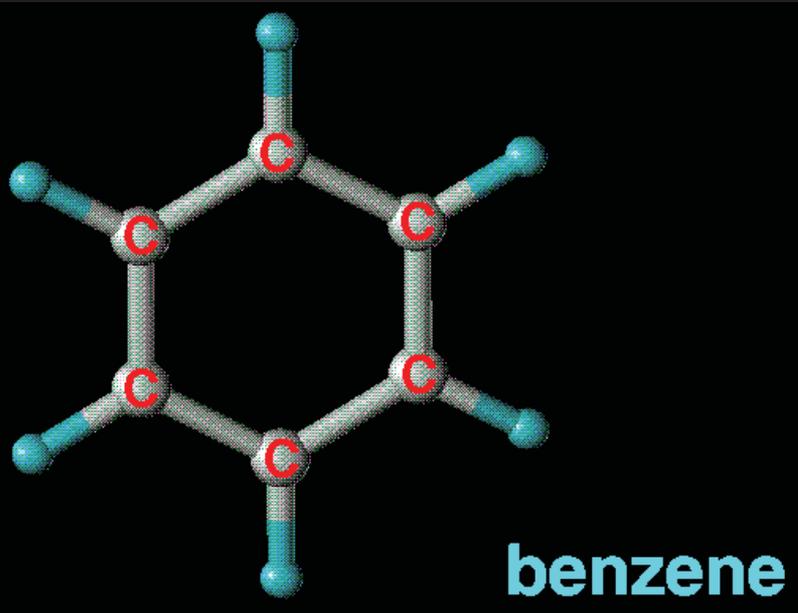
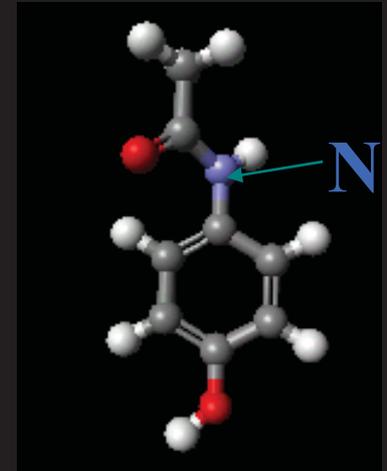
Aspirina



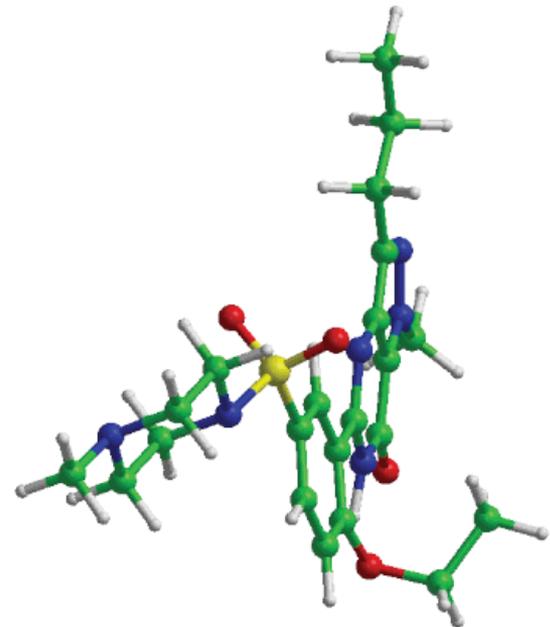
Ibuprofeno



Paracetamol



Viagra



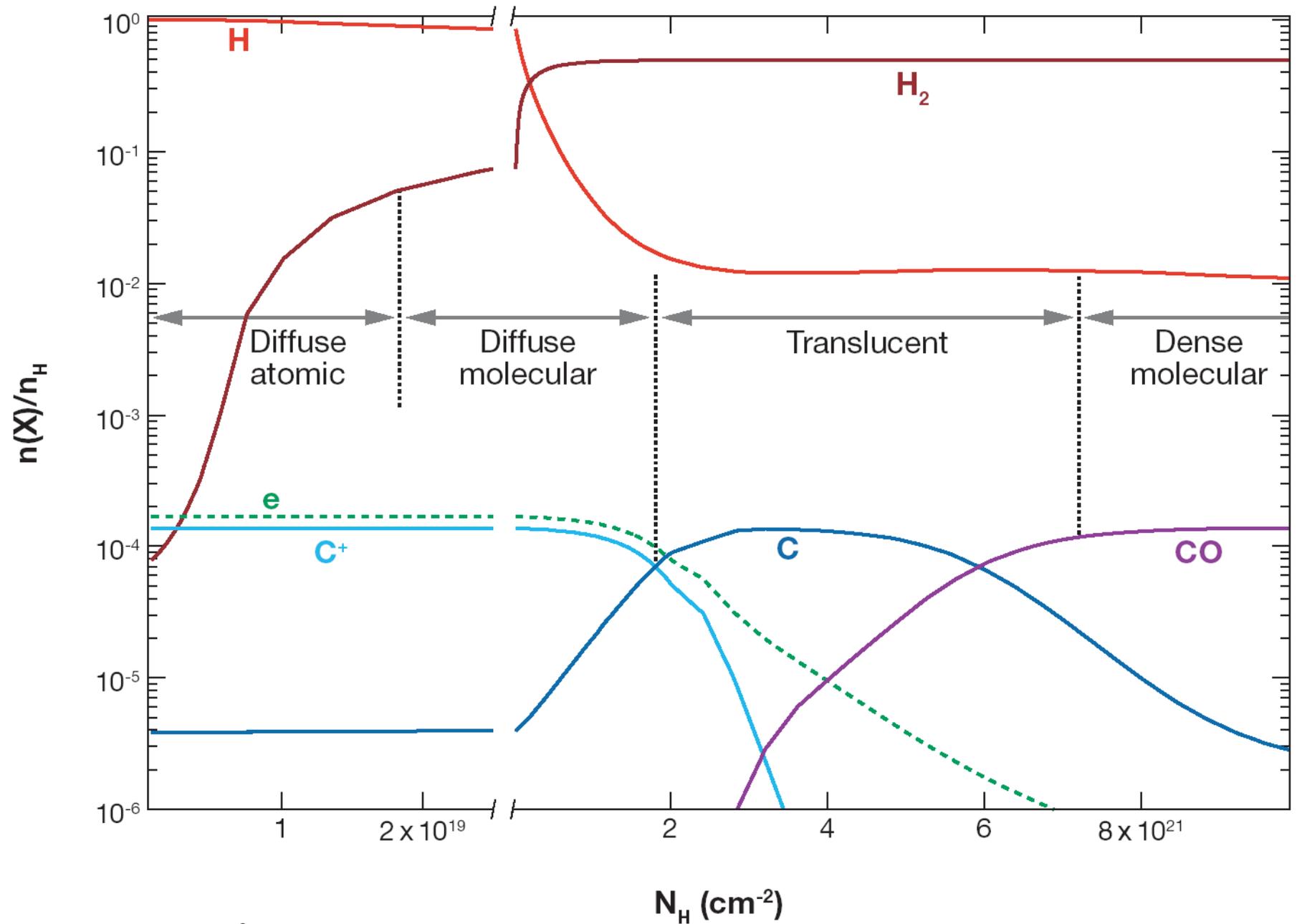
CHEMICAL COMPLEXITY IN THE INTERSTELLAR MEDIUM

- The structure of molecular clouds is quite complex with strong gradients (T, n...) between different regions of the same cloud.



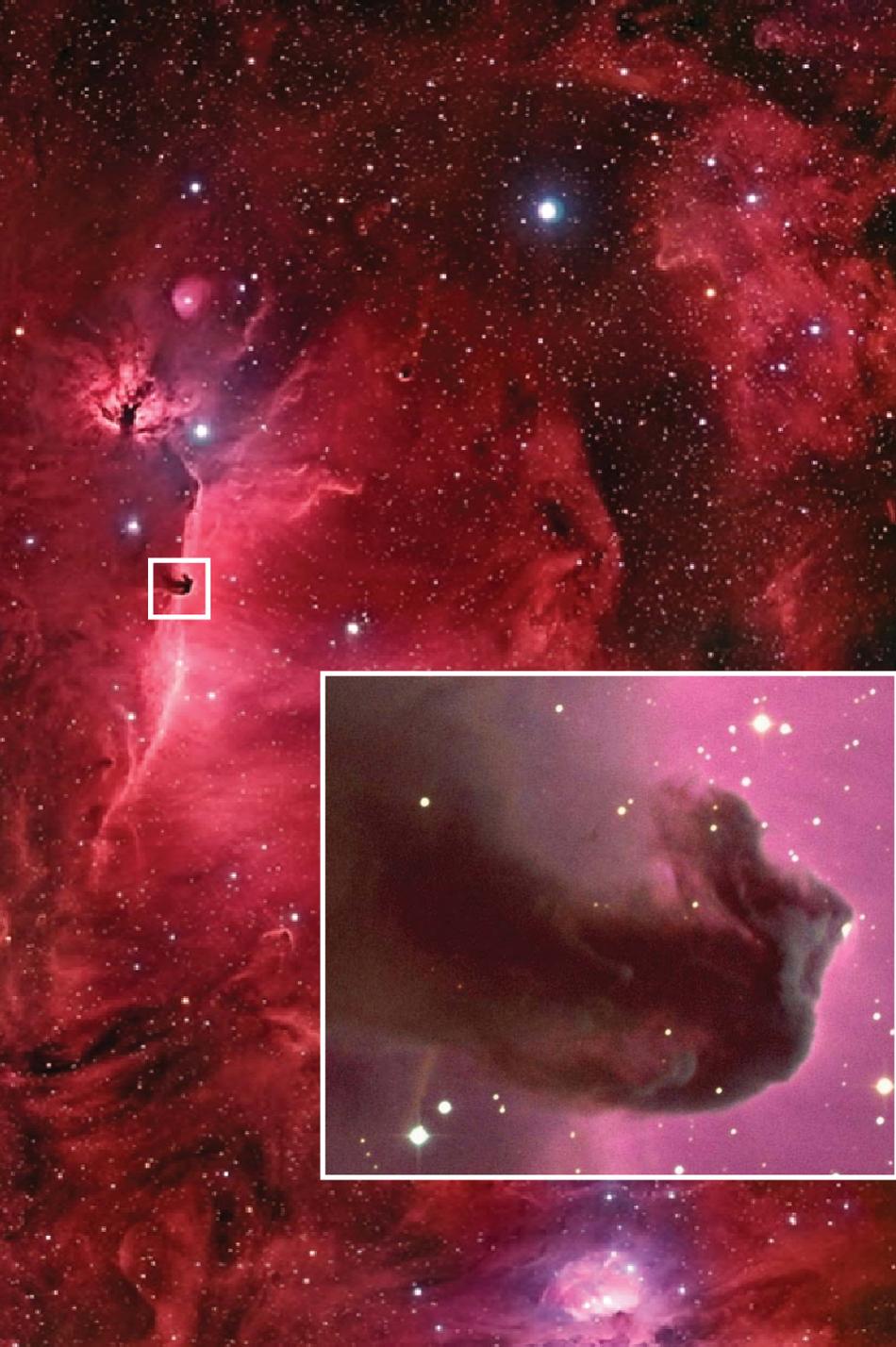
In the external layers the visual absorption increases quickly and protects the inner regions against the UV interstellar field.





$n_H = 100 \text{ cm}^{-3}$ $G_0 = 1$

from Neufeld et al. (2005)



There are not precise laws given the density and the temperature as a function of the radius.

The clouds are very inhomogeneous and the physical conditions could change strongly.

Understanding and modelling the physical and chemical properties of molecular clouds is difficult...

CHEMISTRY OF THE INTERSTELLAR MEDIUM

HISTORY

- * 1926 - Eddington proposed that molecules could be formed in dark clouds (only atomic species had been observed).
- * In 1930-1940 three molecules were observed through optical observations of slightly reddened stars : CN, CH and CH⁺. The observed clouds are not protected against the UV galactic field ($T_{\text{ex}} \sim 3$ K).
- Between 1960 and 1970 a new branch of Astrophysics was born : Astrochemistry. Several molecular species were detected using radioastronomical techniques : OH, NH₃ and H₂CO. These molecules were detected in dense, heavily obscured, molecular clouds.

- * In the 1970-1980 period several observations in the UV from space telescopes showed the presence of H_2 , HD, OH and CO in regions of low visual absorption.
- * In the same period a large number of molecular species were detected through radioastronomical observations : CH_3OH , SiO, CS, HCN, HNC, SiS, CN, HCO^+ , N_2H^+ , ...
- * Those observations were carried out with the Kitt Peak, Bell Labs and Onsala radiotelescopes. Although the number of detected species was large and several line surveys were performed, it appeared that the chemical complexity had reached its maximum. During near 10 years the number of detected species was rather stable compared with the large number of molecules initially discovered.

*** In 1985 the 30-m telescope (Pico Veleta, Spain) started scientific operations. Nobeyama radiotelescope was also in operation at the same time.**

*** In a few years the complexity of the interstellar medium was increasing after the detection of almost 30 new molecular species with these instruments.**

*** Species like C_5H , C_6H , C_7H , C_8H , C_5N , CCS, CCCS, SiC, SiC_3 , SiC_4 , SiCN, metals (NaCl, KCl, AlCl, AlF, MgNC,) CH_3NC , HCCN, CP, H_2C_3 , H_2C_4 , c- C_3H , H_2CCN ,...) and a huge variety of isotopic species have been detected using radioastronomical techniques in the last 15 years**

(≈ 50 species detected for the first time in space by our group)

* In 1984 Puget and Léger (among others) proposed the presence of PAHs to explain the UIBs and the IRAS emission at $12\ \mu\text{m}$ in the ISM.

* ISO has shown that PAHs are detected in almost all lines of sight and also in external galaxies.

* Infrared observations with ISO have shown the presence of polyynes (C_nH_2) and of benzene (C_6H_6) in proto-planetary nebula.

* >2006: Detection of molecular anions: C_6H^- , C_8H^- , C_3N^- , CN^-

* May 2009: *Herschel* is launched (FIR & smm)

New molecules detected in 2010: H_2O^+ , OH^+ , H_2Cl^+ , HCl^+ ...

* ~2012 *ALMA* (the largest radio observatory ever built)

How are these molecules formed ?

H₂ is the most abundant molecule but H₂ gas-phase formation is extremely improbable.

How it is possible to have a such important chemical complexity when the formation of H₂ is not obvious at all?

Can we be sure that our chemical models are correct when most reactions rates are unknown ?

What can we say about the large molecules, e.g., PAHs, that are present across the galaxy under all physical conditions?

Some notation...

BIMOLECULAR REACTIONS (ISM)



A,B = neutrals, ions (atoms, molecules, e)

M = molecule

N = molecule, atom or photon



Which is the abundance (or density) of molecule “M”?

n(A) = density of “A” molecules *[n(A)] = (molecules) cm⁻³*

k = “rate coefficient” *[k] = cm⁺³ s⁻¹ ~ σ (cm²) · v (cm s⁻¹)*

β = “photodissociation rate” *[β] = (molecules) s⁻¹*

*typical β ≈ 10⁻¹⁰ s⁻¹ → molecule lifetime
in diffuse ISM = 1/β ≈ 300 yr!*

BIMOLECULAR REACTIONS (ISM)



A,B = neutrals, ions,(atoms, molecules , e)

M = molecule

N = molecule, atom or photon



Formation rate of M = $k n(A) n(B)$ [$\text{cm}^{-3} \text{s}^{-1}$]

Destruction rate of M = $\beta n(M)$ [$\text{cm}^{-3} \text{s}^{-1}$]

Which is the abundance (or density) of M molecule?

$$d/dt n(M) = \text{Formation} - \text{Destruction} = k n(A) n(B) - \beta n(M)$$



$$d/dt \ n(M) = \textit{Formation} - \textit{Destruction} = k \ n(A) \ n(B) - \beta \ n(M)$$

$$\textit{Steady state} \rightarrow d/dt \ n(M) = 0 \rightarrow n(M) = k \ n(A)n(B) / \beta$$

$$k = k(T) ?? \quad \beta ??$$

- *k* and β can be determined from quantum calculations
and / or through sophisticated laboratory measurements

$$k(T) = A(T) \exp(-E_a / kT) \quad \textit{“Arrhenius law”}$$

General bibliography on chemical processes in the ISM (Books)

- * “The Physics and Chemistry of the ISM”

A.G.G. Tielens, *Cambridge University Press*, 2005.

- * “Interstellar Chemistry”

These Lectures



W.W. Duley and D.A. Williams, *Academic Press*, 1984.

- * “Physical Processes in the Interstellar Medium”

L. Spitzer, Jr., *New York: Wiley*, 1978.

THE NATURE OF THE PROBLEM OF INTERSTELLAR CHEMISTRY

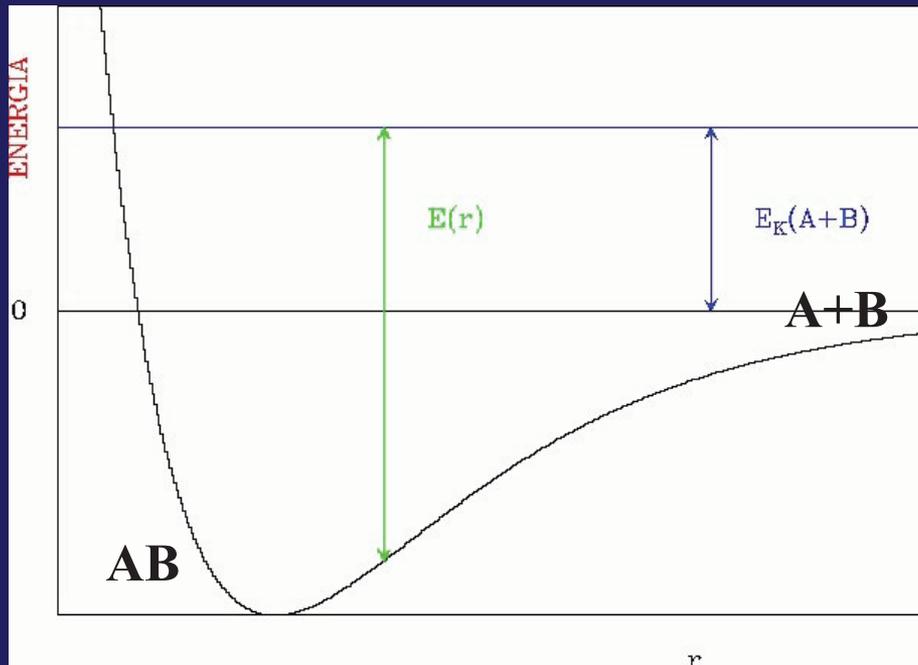
- 1) Low Temperatures
- 2) Low Volume Density
- 3) The Formation of H_2 in gas phase not possible !!!

In all chemical processes the interaction between two species (atoms or molecules) produces an **activated complex** that has to loss energy in a very short time period, often similar to the vibration time of the nuclei that form the molecule. There are many ways for the activated complex to loss energy. But, while in terrestrial laboratories we can use catalysers or a third body, **in space three body collisions are very uncommon** and the only possible catalysers are dust grain surfaces.

Let us consider the reaction



It may happen that AB^* interacts with a third body (catalyser) to remove the energy excess produced in the formation of the activated complex. However, also AB^* could dissociate into the initial particles A and B



The formation rate of the molecule AB, assuming that the activated complex reaches an equilibrium between formation and destruction is given by

$$\frac{dn(AB)}{dt} = n(AB^*) \times n(M) k_2$$

$$\frac{dn(AB^*)}{dt} = n(A) \times n(B) \times k_1 - n(AB^*) \times n(M) \times k_2 - n(AB^*) \times k_3$$

$$\frac{dn(AB^*)}{dt} = 0$$

$$n(AB^*) = \frac{n(A) n(B) k_1}{(k_3 + k_2 n(M))}$$

and

$$\frac{dn(AB)}{dt} = \frac{k_1 k_2 n(A) n(B) n(M)}{k_3 + k_2 n(M)}$$

If A, B y M are neutral species then $k_1 \approx 10^{-11} \text{ cm}^3\text{s}^{-1}$
and $k_2 \approx 10^{-10} \text{ cm}^3\text{s}^{-1}$, but $k_3 10^{+11} \text{ s}^{-1} !!$, and

$$dn(\text{AB})/dt \approx 10^{-32} n(\text{A}) n(\text{B}) n(\text{M}) \text{ cm}^{-3}\text{s}^{-1}$$

The best case in the ISM occurs for $\text{A}=\text{B}=\text{M}=\text{H}$



and we will see that formation times are very long...

NOTE: For other molecules the optimal case is when:

$\text{A}=\text{H}$, $\text{M}=\text{H}$ and $\text{B} \in (\text{C},\text{N},\text{O})$, i.e., $n(\text{B}) \approx 10^{-4} n(\text{H})$ and

$dn(\text{BH})/dt \approx 10^{-36} n^2(\text{H}) n(\text{B}) \text{ cm}^{-3} \text{ s}^{-1}$ $\text{B} \in (\text{C},\text{N},\text{O})$ (even worse...)

EXAMPLE: The simplest trimolecular reaction

Let us consider an atomic cloud without dust grains and without radiation field. For $t=0$ the density of atomic hydrogen is n and that of molecular hydrogen is 0. The formation of H_2 occurs through the reaction



with a k rate of $10^{-32} \text{ cm}^6 \text{ s}^{-1}$

The formation rate of H_2 is given by (“molecular fraction”)

$$\frac{dn(H_2)}{dt} = k n^3_H(t); \quad f(t) = \frac{2 n_{H_2}(t)}{n_H(t) + 2 n_{H_2}(t)} = \frac{2 n_{H_2}(t)}{n}$$

$$\frac{df(t)}{dt} = k n^2 (1-f(t))^3$$

Time to reach $f=0.5$??

EXAMPLE

(Earth at sea level density $\sim 10^{19} \text{ cm}^{-3}$)

(ultra-high vacuum chamber density $\sim 10^5 \text{ cm}^{-3}$)

$$f(t_0)=0.5$$

$n(\text{cm}^{-3})$...	10^5	10^{10}	10^{12}	10^{15}	10^{16}	10^{18}
t_0 (years)	...	$6 \cdot 10^{14}$	$6 \cdot 10^4$	6	$6 \cdot 10^{-6}$	$6 \cdot 10^{-8}$	$6 \cdot 10^{-10}$
				(600 s)	(6s)	(0.0006s)	

3-body reactions are only efficient for densities larger than 10^{10} cm^{-3} .
Even in this case, the density is not enough taken into account the dynamical time scale of evolution of the object.



**BUT MOLECULES HAVE BEEN DETECTED, in particular H_2 ,
THUS, WE HAVE TO FIND OTHER MECHANISMS
TO FORM MOLECULES IN THE SPACE**

MOLECULE FORMATION ON INTERSTELLAR GRAINS

W. D. WATSON AND E. E. SALPETER

THE ASTROPHYSICAL JOURNAL, 174:321-340, 1972 June 1

Adsorption binding energies D depend greatly on the particular adsorbed particle, and on the chemical nature and surface condition of the dust grain. For saturated molecules on an inert surface only physical adsorption (van der Waals interaction) occurs. The corresponding adsorption energy D for nonpolar molecules depends on the polarizability of the molecule but seems to be similar for likely nonmetallic grain materials, such as ice, graphite, and silicates (cf. Williams 1968; Dormant and Adamson 1968; Augason 1970; HS1). Based on this available data and extrapolation according to the polarizability, the lowest possible values (disregarding the special case of H_2) are expected to be D/k ($k =$ Boltzmann constant) $\sim (800^\circ-1200^\circ \text{ K})$. These values are appropriate for particles of modest polarizability such as CH_4 (as well as for radicals such as C, N, O, CO, etc., if these are not bound by chemical forces). For small polar molecules (e.g., H_2O , NH_3 , H_2CO) on a regular inert surface D/k may be $\sim 1000^\circ-2000^\circ \text{ K}$.

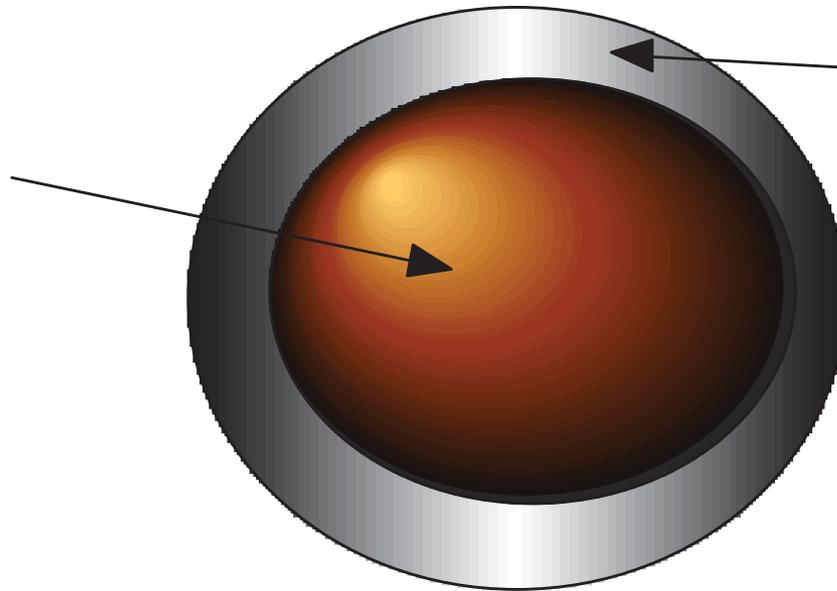
Binding energies in pure molecular crystals are slightly larger than the adsorption energies quoted above (methane $\sim 1100^\circ \text{ K}$, ammonia $\sim 3300^\circ \text{ K}$, water $\sim 6200^\circ \text{ K}$). If a molecule like H_2O , CH_4 , etc., is adsorbed on a pure molecular crystal of the same material, it could migrate to a "growth edge" on the surface and become a part of the crystal. Similarly, a carbon atom adsorbed on a graphite grain could in principle find a growth edge and become chemically bound into the crystal. We disregard these possibilities for most of this paper but return to them in § IVe.

AN INTERSTELLAR GRAIN

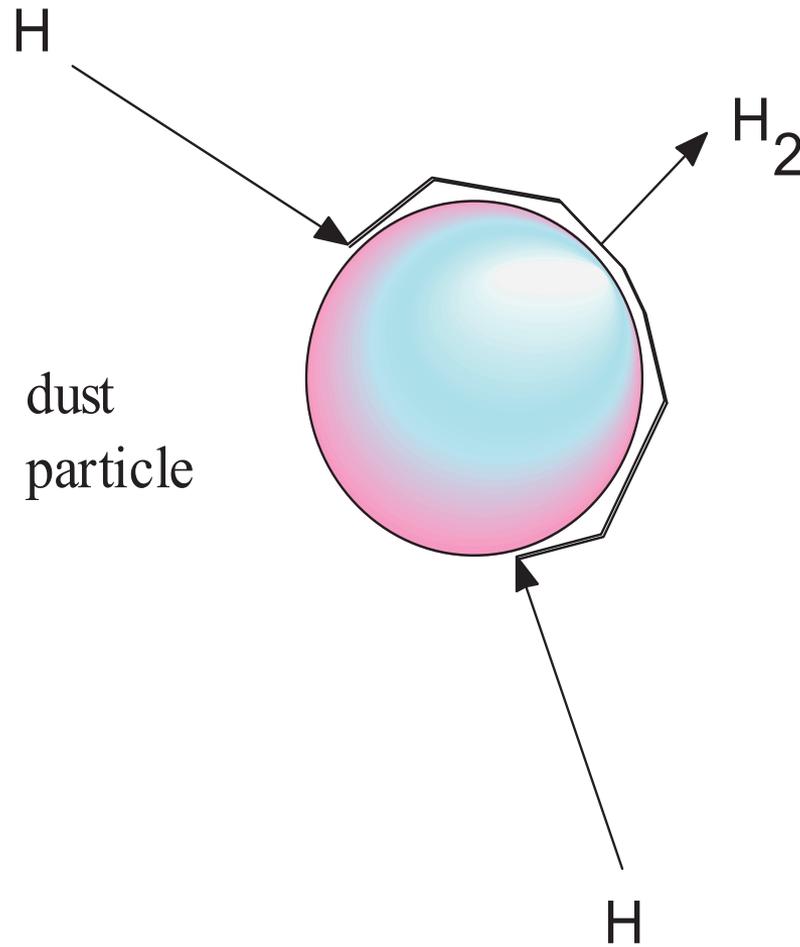
0.1 μ

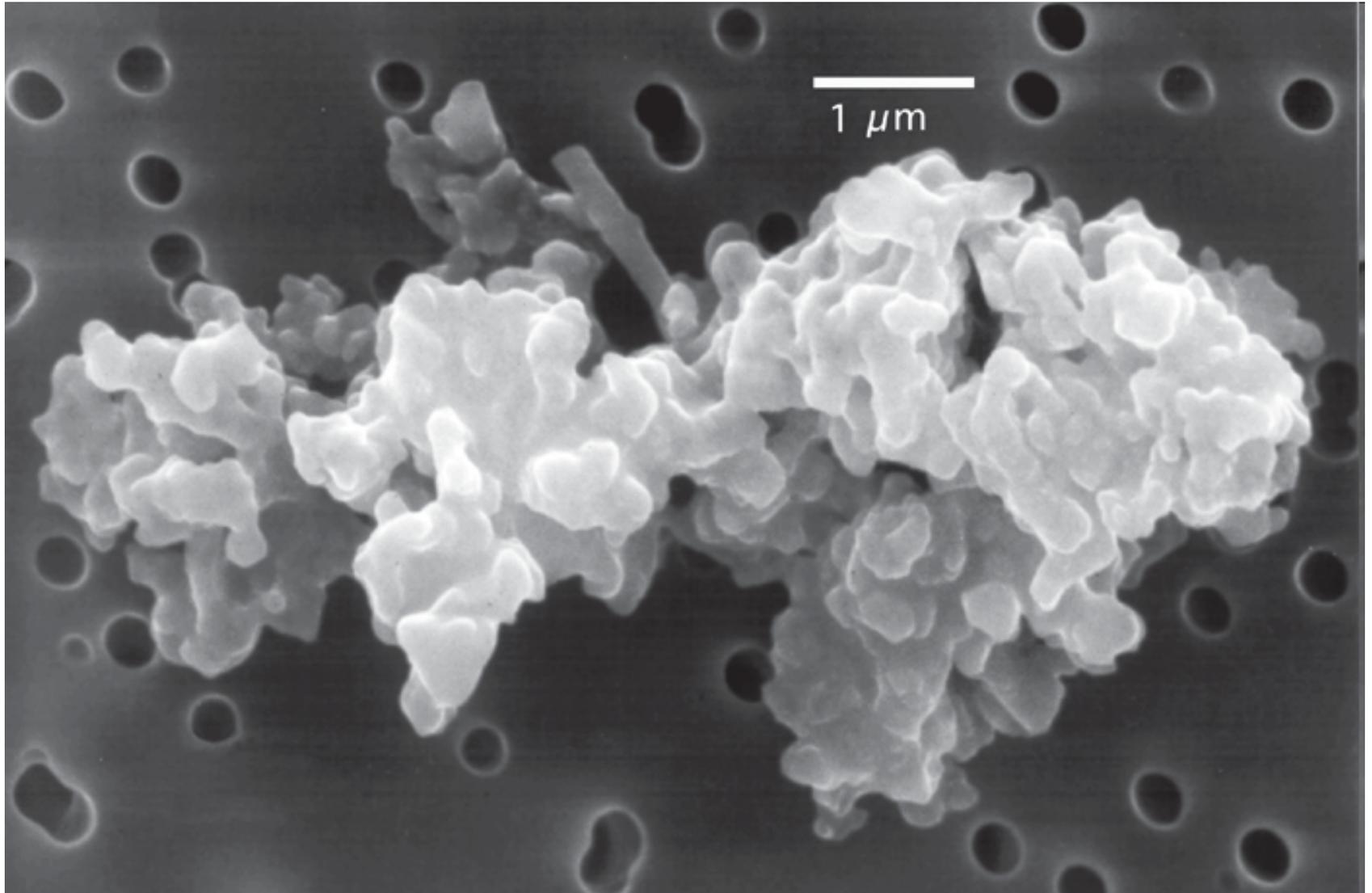
silicates &
carbonaceous
material

ices



H₂ formation in the ISM





Porous chondrite interplanetary dust particle

FORMATION OF MOLECULAR HYDROGEN ON AMORPHOUS WATER ICE: INFLUENCE OF MORPHOLOGY AND ULTRAVIOLET EXPOSURE

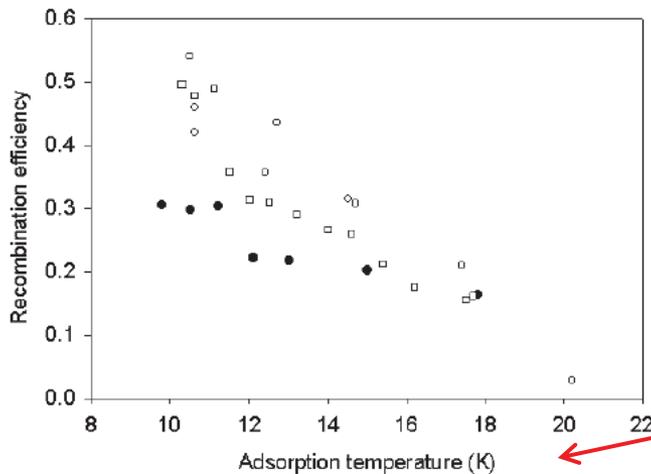
J. E. ROSER,¹ G. MANICÒ,^{1,2} V. PIRRONELLO,² AND G. VIDALI¹

Received 2002 April 26; accepted 2002 August 14

ABSTRACT

In this paper, we report on the formation of molecular hydrogen on different types of amorphous water ice. We show that mass spectra of desorbing molecules upon formation are sensitive to the way in which ice is deposited on a cold substrate, to its thermal history, and to the action of UV photons. Implications that these results bear on H₂ formation in dense quiescent clouds are presented and discussed.

Subject headings: astrochemistry — dust, extinction — ISM: molecules — methods: laboratory — molecular processes



**H atoms are adsorbed
in ice-surfaces and H₂ forms**

T typical of ISM !

FIG. 3.—Recombination efficiency of molecular hydrogen vs. sample temperature of H atoms. Filled circles are for high-density amorphous ice (Manicò et al. 2001), open circles are for low-density amorphous ice prepared by heating high-density amorphous ice, and open squares are for water vapor-deposited low-density amorphous ice. The error bars are comparable to the size of the symbols. The scatter in the data points reflects the variability in the ice preparation methods.

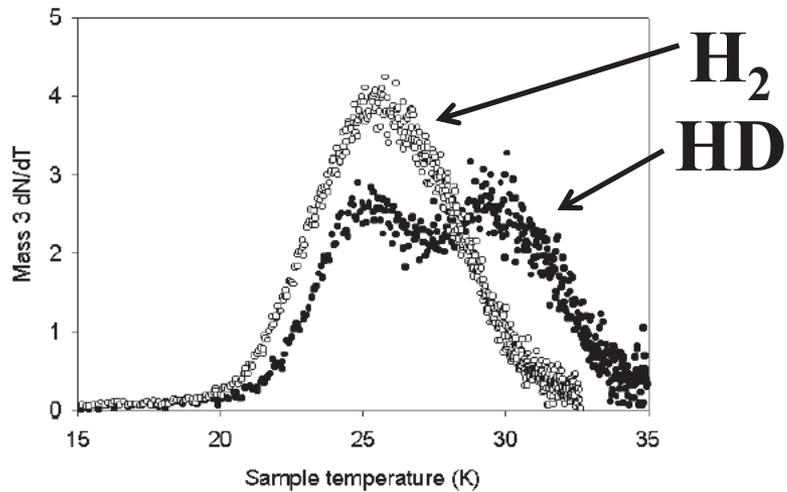


FIG. 4.—Desorption rate (dN_{HD}/dT) vs. ramp temperature after adsorption of H and D for 4 minutes on high-density amorphous water ice at ~ 10 K before (filled circles) and after (open circles) UV exposure for 15 minutes. Traces have been scaled to yield the same area.

H₂ in grain evaporates and leaves the surface

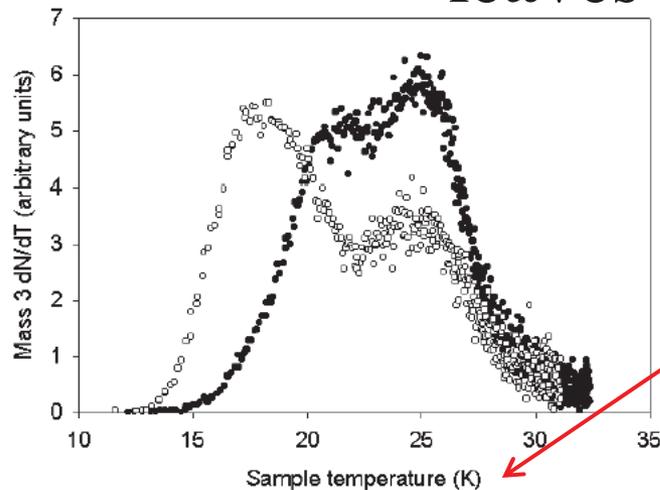


FIG. 5.—Same as in Fig. 4, except for low-density amorphous ice

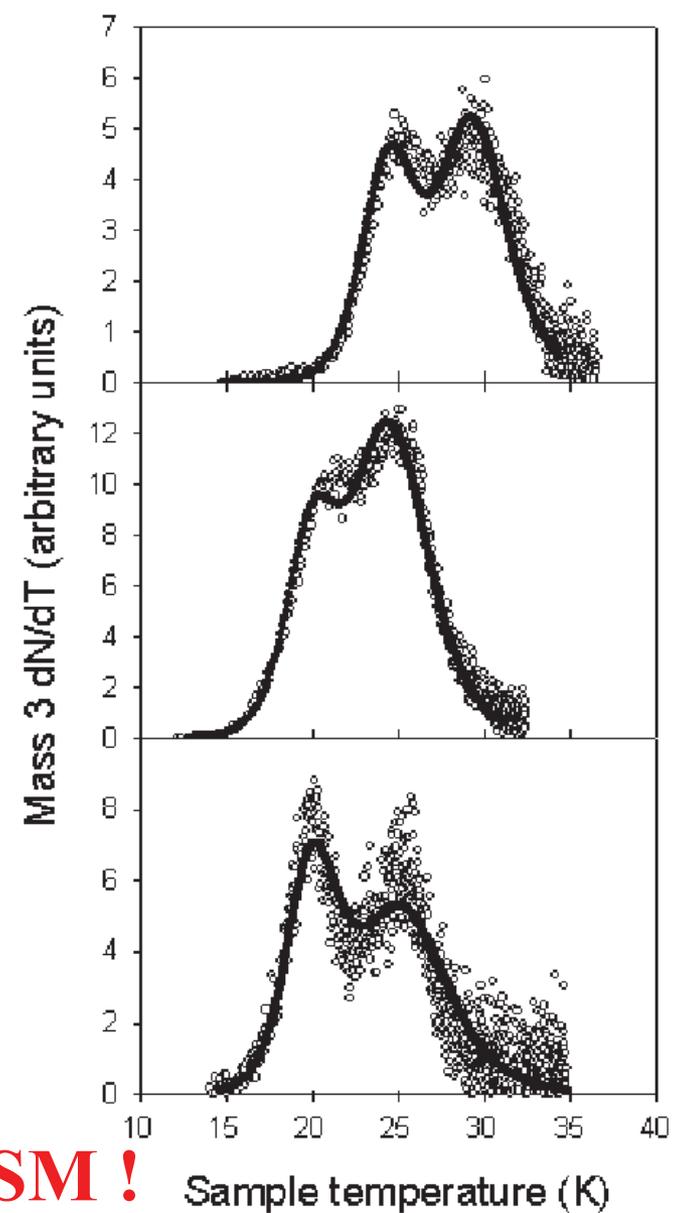


FIG. 6.—Desorption rate (dN_{HD}/dT) vs. ramp temperature after adsorption of H and D for 4 minutes with a sample temperature of ~ 10 K. Graphs from top to bottom are for desorptions from high-density amorphous ice, low-density amorphous ice prepared by heating a high-density amorphous ice, and water vapor-deposited low-density amorphous ice. The solid line is a fit using the method and parameters described in the text.

Some old “pionering” papers on the formation of H₂ on dust grains

* Katz et al., 1999, ApJ, 522, 305

Molecular Hydrogen Formation on Astrophysically Relevant Surfaces

* Pirronello et al., 1999, A&A, 344, 681

Measurements of molecular hydrogen formation on carbonaceous grains

* Takahashi et al., 1999, ApJ, 520, 724

Product Energy Distribution of Molecular Hydrogen Formed on Icy Mantles of Interstellar Dust

* Takahashi et al., 1999, MNRAS, 306, 22

The formation mechanism of molecular hydrogen on icy mantles of interstellar dust

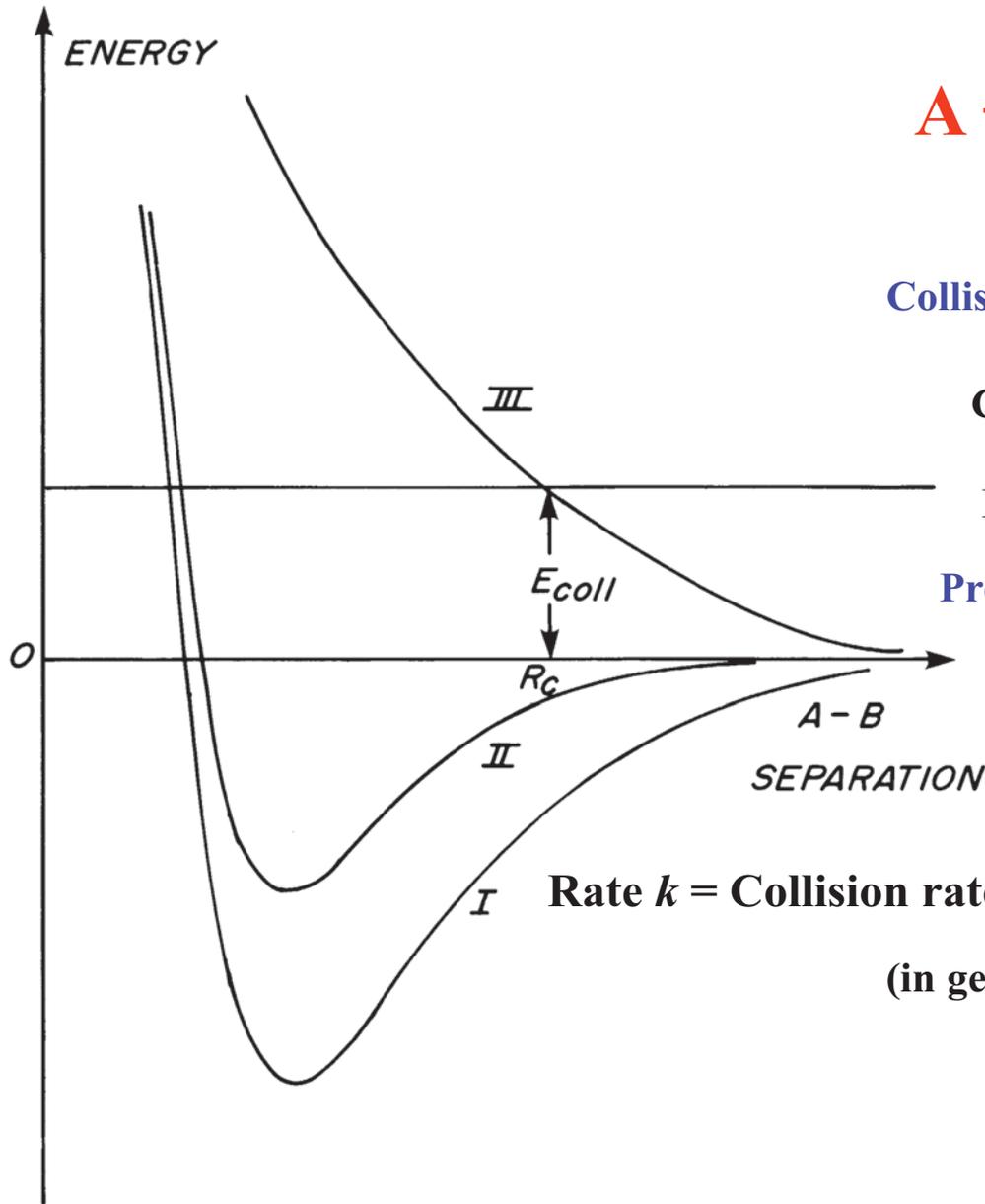
Let assume that H_2 has been formed on the surface of the dust grains. How do we form other molecular species ?



let us consider the following reaction;



is it possible? is it fast enough to be efficient in the ISM?



Collision rate coef. $= \sigma v = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

C=Collision duration 10^{-14} s

R= Radiative time $10^{-8} \text{ s} (1/A_{ij})$

Probability: $C/R=10^{-6}$ per collision

Rate $k = \text{Collision rate} \times \text{Probability} = 10^{-17} \text{ cm}^3 \text{ s}^{-1}$

(in general slow...)

Fig. 3.4 A diagram showing possible types of potential energy curves belonging to the diatomic molecule AB. The colliding partners have relative kinetic energy E_{coll} .



The reaction will occur if the change of energy in the reaction is positive in order to account for the low temperatures of the interstellar medium (reactions must be exothermic)

For example, let us consider the reaction



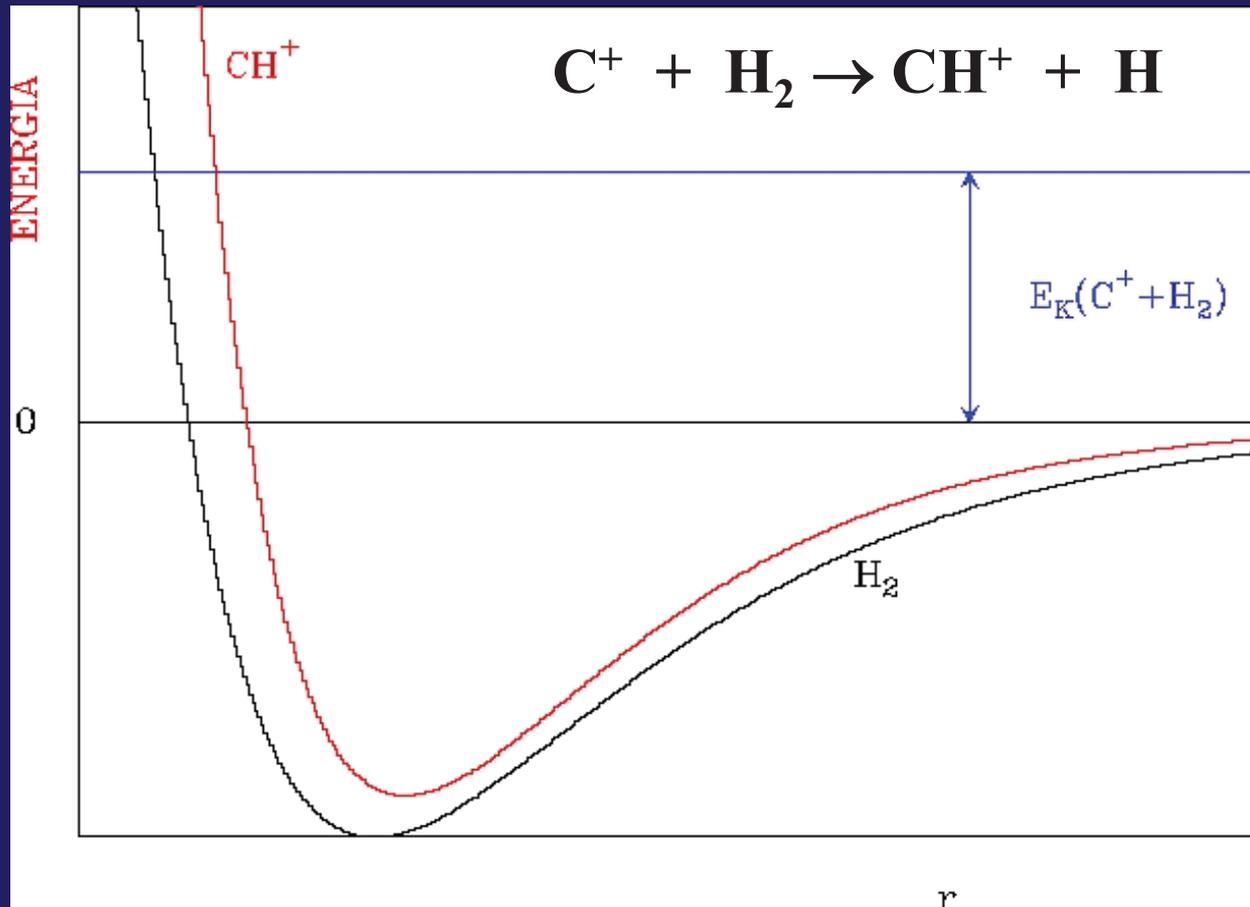
Remember all reactions in ISM have to be bimolecular !!

Association reactions $\text{A} + \text{B} = \text{AB} + h\nu$ are very slow !!

$\text{A} + \text{B} + \text{M} = \text{AB} + \text{M}$ only good for the Earth and AGBs

$D(\text{products}) - D(\text{reactants}) > 0 \rightarrow \text{exothermic}$
 $< 0 \rightarrow \text{endothermic}$

The dissociation energy of H_2 is 4.48 eV and that of CH^+ is 4.09 eV



The reaction will be produced if we add 0.39 eV to the system (about 4000 K).

This reaction is endothermic and has little probability to occur in the ISM as we need

$T_{\text{gas}} = E/k > 4000 \text{ K}$

Herschel/HIFI: first science highlights

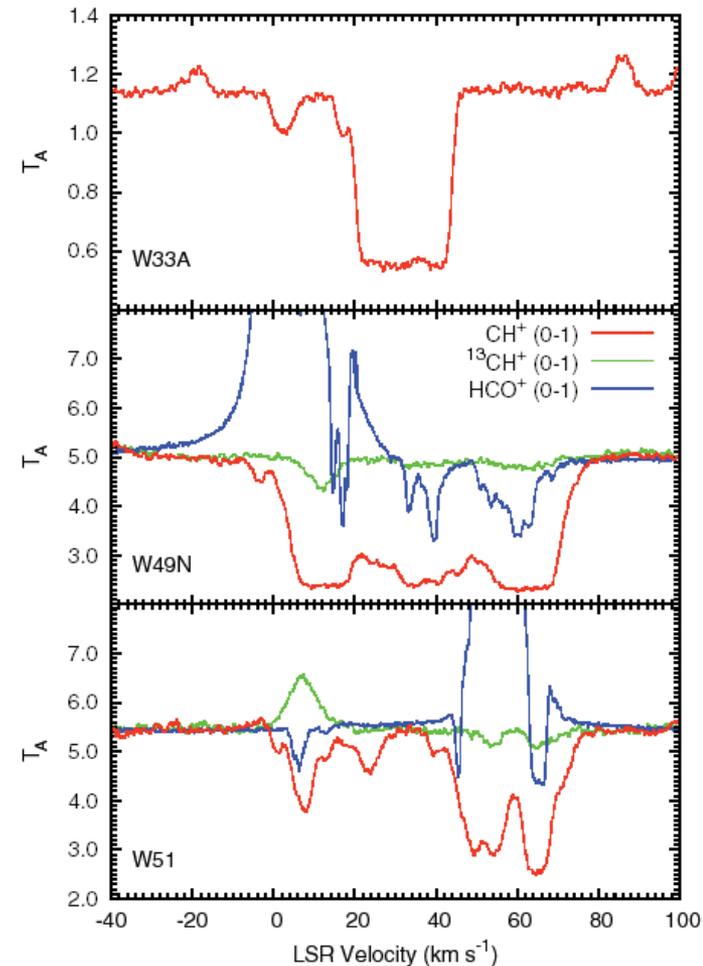
LETTER TO THE EDITOR

CH⁺(1–0) and ¹³CH⁺(1–0) absorption lines in the direction of massive star-forming regions^{★,★★}

E. Falgarone¹, B. Godard^{8,1}, J. Cernicharo³, M. De Luca¹, M. Gerin¹, T. G. Phillips⁷, J. H. Black⁷, T. A. Bell⁷, F. Boulanger⁸, A. Coutens^{12,13}, E. Dartois⁸, P. Encrenaz¹, T. Giesen⁹, J. R. Goicoechea³, H. Gupta⁶, C. Gry¹⁰, P. Hennebelle¹, E. Herbst⁴, P. Hily-Blant¹¹, C. Joblin^{12,13}, M. Kaźmierczak¹, J. Krełowski¹⁵, J. Martin-Pintado³, R. Monje⁷, B. Mookerjee¹⁶, D. A. Neufeld⁵, M. Perault¹, J. C. P. Persson², R. Plume¹⁷, M. Salez¹, M. Schmidt¹⁵, P. Sonnentrucker⁵, J. Stutzki⁹, D. Teyssier¹⁸, C. V. K. Menten¹⁹, T. R. Geballe²⁰, S. Schlemmer⁹, R. Shipman²¹, A. G. G. M. Tielens²², S. Philipp²³, J. Zmuidzinas⁷, L. A. Samoska⁶, K. Klein²⁴, A. Lorenzani²⁵, R. Szczerba¹⁸, I. Péron^{26,1}, P. Cais², A. Cros^{12,13}, L. Ravera^{12,13}, P. Morris²⁸, S. Lord²⁸, and P. Planesas^{29,30}

(Affiliations are available on page 5 of the online edition)

Received 31 May 2010 / Accepted 19 July 2010



The reaction



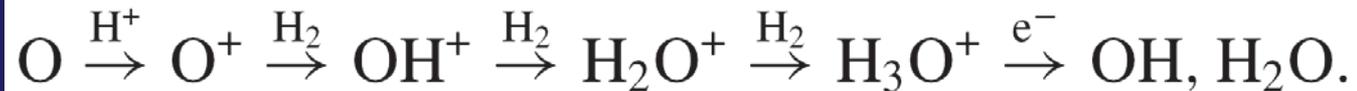
Has also **few chances to occur in the ISM**

$D(\text{H}_2)=4.49 \text{ eV}$ and $D(\text{SH}^+)=3.5 \text{ eV}$

However, the reaction



could occur as $D(\text{H}_2)=4.49 \text{ eV}$, $D(\text{OH}^+)=5.1 \text{ eV}$ and it is exothermic by 0.61 eV !



DISOCIATION ENERGIES OF A FEW MOLECULES (eV)

H ₂	4.48	Si ₂	3.21	O ₂ ⁺	6.66	MgO	(3.5)
CH	3.47	Mg ₂	0.05	S ₂ ⁺	5.37	SiS	6.4
NH	<3.47	H ₂ ⁺	2.65	CN	7.80	MgS	<2.4
OH	4.39	CH ⁺	4.09	CO	11.09	CN ⁺	4.85
SH	3.60	NH ⁺	3.39	CS	7.36	CO ⁺	8.34
SiH	<3.06	OH ⁺	5.1	SiC	4.60	CS ⁺	6.38
MgH	1.34	SH ⁺	3.5	NO	6.50	NO ⁺	10.85
C ₂	6.21	SiH ⁺	3.17	NS	4.80	NS ⁺	6.30
N ₂	9.76	MgH ⁺	2.08	SO	5.36	SO ⁺	5.43
O ₂	5.12	C ₂ ⁺	5.32	SiO	8.26	SiO ⁺	5.0
S ₂	4.37	N ₂ ⁺	8.71				



The reaction rate has been measured in the laboratory and is rather fast, $k \approx 1.6 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. But, how do we form O^+ in molecular clouds protected against the UV field ?

As the ionization potentials of H and O are nearly identical, (“*accidental resonance*”) the process of



could occur efficiently. (H^+ formation a few slides ahead)

Are all ion-neutral reactions fast enough?



!?! ? !?! ? !?!

We start studying:



The formation rate of the product AB^+ is given by



$$\text{formation} = k n(A^+) n(BC)$$

¿ k [$\text{cm}^3 \text{s}^{-1}$]? ¿depends on the gas temperature?

Several ion-neutral reactions have been measured in the laboratory. For most of these reactions (exothermic and BC non-polar):

k does not depend on the temperature
and is of the order of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (high!)

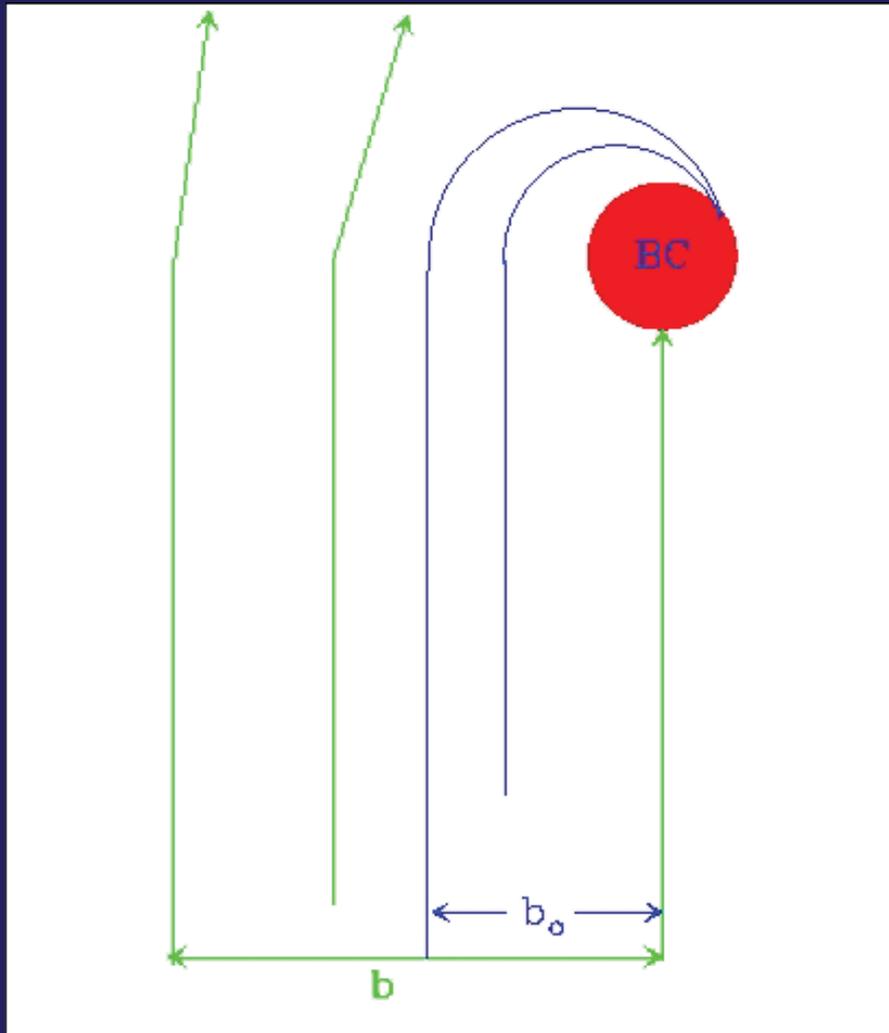
Why?

Let us consider the classical treatment of the collision problem.

Let BC is a non polar molecule.

A^+ induces a dipole moment in BC during the collision process.

The interaction energy is $-2\alpha e^2/r^4$, where α is the polarizability of the molecule BC.



For impact parameters $> b_0$, although the particles interact, the particle A is only deviated from its trajectory but it is not captured by BC.

For impact parameters $< b_0$, A is captured by BC. b_0 is given by

$$b_0 = (4\alpha e^2 / \mu v^2)^{1/4}$$

where $\mu = (M_A M_{BC} / M_A + M_{BC})$ and v is the relative velocity



The energy produced in the collision could reorder the orbitals and overcome any possible activation barrier. (In the case of an impact parameter equal to b_0 the particle A remains moving around BC.)

The collisional cross section σ is πb_0^2 (area) and the reaction rate is given by

$$k = \sigma \cdot v = \pi b_0^2 v = \dots = 2 \pi e (\alpha / \mu)^{1/2} \quad [\text{cm}^3 \text{s}^{-1}]$$

and does not depend on T, only on the polarizability and on the reduced mass of the system !!!

This reaction rate is known as “The Langevin rate”

POLARIZABILITY OF ATOMS AND MOLECULES (10^{-24} cm^3)

H	0.67	H ₂	0.79	H ₂ O	1.40	C ₂ H ₂	3.33
He	0.20	N ₂	1.76	CO ₂	2.65	NH ₃	2.26
N	1.13	O ₂	1.58	SO ₂	4.27	CH ₄	2.60
O	0.77	CO	1.95	OCS	5.20	C ₂ H ₆	4.47
Na	24.75	CN	2.59	HNC	2.46		
K	42.40			HCN	2.59		

α varies very little and the reaction rate could be very similar for all the reactions !!

Example:



Langevin value $1.6 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

Experimental value $1-2 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

The other reaction “channel” :



is slightly endothermic

$D(\text{H}_2)=4.48 \text{ eV}$ y $D(\text{OH})=4.39 \text{ eV}$

and thus less probable than the OH^+ formation

However, this simple theory does not always work
(as expected ...)



(highly exothermic)

Langevin value (approx) $0.9 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

Experimental value (real) $0.06 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

Or



Langevin value (approx) $1.8 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

Experimental value (real) $1.0 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad !!!$

Why?

The following reactions



Are much faster (charge exchanges) !



What happens in ion-neutral reactions if the BC molecule is polar ?

A classical treatment of the problem (ADO = Averaged Dipole Orientations) of the dipole interaction

$$k_{\text{ADO}} = 2 \pi e (\alpha^{1/2} + c \mu_{\text{D}} (2 / \pi kT)^{1/2})$$

Where μ_{D} is the dipole moment of the molecule, T is the gas temperature and c is a function of $\mu_{\text{D}} / \alpha^{1/2}$

Some typical ion-neutral reactions

Reaction	$k(10^{-9} \text{ cm}^3 \text{ s}^{-1})$
4. $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$	2.1
5. $\text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}$	2.0
6. $\text{N}_2^+ + \text{H}_2 \rightarrow \text{HN}_2^+ + \text{H}$	1.7
7. $\text{He}^+ + \text{H}_2 \rightarrow \text{products}$	$< 10^{-4}$
8. $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$	2.0
9. $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$	0.7
10. $\text{OH}^+ + \text{H}_2 \rightarrow \text{OH}_2^+ + \text{H}$	1.5
11. $\text{NH}^+ + \text{H}_2 \rightarrow \text{NH}_2^+ + \text{H}$	0.6
12. $\text{OH}_2^+ + \text{H}_2 \rightarrow \text{OH}_3^+ + \text{H}$	1.4
13. $\text{NH}_2^+ + \text{H}_2 \rightarrow \text{NH}_3^+ + \text{H}$	0.23
14. $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$	$< 5 \times 10^{-4}$
15. $\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$	10^{-2}
16. $\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H}$	10^{-2}
17. $\text{HCN}^+ + \text{H}_2 \rightarrow \text{H}_2\text{CN}^+ + \text{H}$	2.0
18. $\text{He}^+ + \text{CO} \rightarrow \text{C}^+ + \text{O} + \text{He}$	2.0
19. $\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{N} + \text{He}$	0.72
20. $\quad \quad \quad \rightarrow \text{N}_2^+ + \text{He}$	0.48
21. $\text{He}^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + \text{He}$	0.62
22. $\quad \quad \quad \rightarrow \text{O}_2^+ + \text{He}$	0.38
23. $\text{He}^+ + \text{CN} \rightarrow \text{C}^+ + \text{N} + \text{He}$	2.0
24. $\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$	2.0
25. $\text{H}_3^+ + \text{C} \rightarrow \text{CH}^+ + \text{H}_2$	2.0
26. $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$	1.4
27. $\text{H}_3^+ + \text{N}_2 \rightarrow \text{HN}_2^+ + \text{H}_2$	1.5
28. $\text{H}_3^+ + \text{OH} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2$	2.0
29. $\text{H}_3^+ + \text{CN} \rightarrow \text{HCN}^+ + \text{H}_2$	2.0
30. $\text{H}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2$	3.0
31. $\text{H}_3^+ + \text{CO}_2 \rightarrow \text{HCO}_2^+ + \text{H}_2$	1.9
32. $\text{H}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_2$	3.6
33. $\text{H}_3^+ + \text{HCN} \rightarrow \text{H}_2\text{CN}^+ + \text{H}_2$	2.0
34. $\text{H}_3^+ + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{CO}^+ + \text{H}_2$	2.0
35. $\text{HCO}^+ + \text{OH} \rightarrow \text{HCO}_2^+ + \text{H}$	1.0
36. $\text{HCO}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CO}$	0.5

Which are the key processes in ISM chemistry?

- 1) H_2 is formed in dust grain surfaces
- 2) We need atomic or molecular ions (ok for diffuse ISM)

But, how are molecules ionized inside molecular clouds ?

With cosmic rays !!! (e.g. high speed p^+ , He nuc... with $E \sim 1000$ MeV)



and H_3^+ a key molecule !!!! Formation rate = $\zeta_{\text{CR}} n(\text{H}_2)$
with $\zeta_{\text{CR}} \approx 10^{-16} - 10^{-17} \text{ s}^{-1}$ “CR ionization rate”

H_3^+ does not react with H_2

He^+ does not react with H_2 , ionization source for other species

OBSERVATIONS OF H_3^+ IN THE DIFFUSE INTERSTELLAR MEDIUM

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ABSTRACT

Surprisingly large column densities of H_3^+ have been detected using infrared absorption spectroscopy in seven diffuse cloud sight lines (Cygnus OB2 12, Cygnus OB2 5, HD 183143, HD 20041, WR 104, WR 118, and WR 121), demonstrating that H_3^+ is ubiquitous in the diffuse interstellar medium. Using the standard model of diffuse cloud chemistry, our H_3^+ column densities imply unreasonably long path lengths (~ 1 kpc) and low densities (~ 3 cm^{-3}). Complimentary millimeter-wave, infrared, and visible observations of related species suggest that the chemical model is incorrect and that the number density of H_3^+ must be increased by 1–2 orders of magnitude. Possible solutions include a reduced electron fraction, an enhanced rate of H_2 ionization, and/or a smaller value of the H_3^+ dissociative recombination rate constant than implied by laboratory experiments.

Subject headings: cosmic rays — infrared: ISM: lines and bands — ISM: clouds — ISM: molecules — molecular processes

520

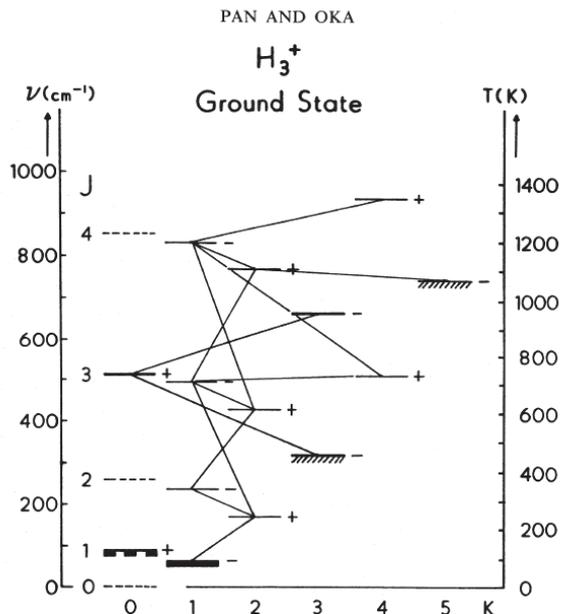


FIG. 1.—Rotational energy levels of H_3^+ in the ground vibrational state. Three types of "stable" levels are indicated: the lowest ($J=1, K=1$) level by a bold line, the ($J=1, K=0$) level which is metastable both collisionally and radiatively by a broken bold line, and the ($J=5, K=5$) and ($J=3, K=3$) levels which are metastable for radiative transitions by shadowed lines. The forbidden rotational transitions are shown by lines connecting levels.

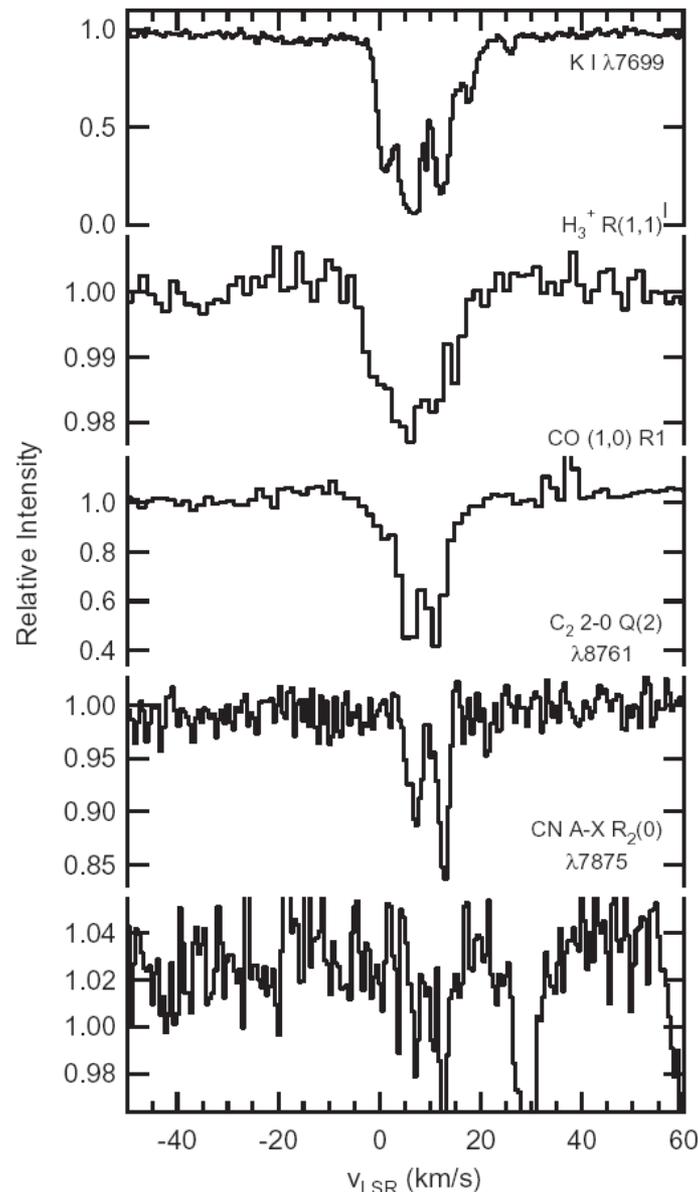


FIG. 13.—Summary of spectra of Cygnus OB2 12, in velocity space. The structure near 30 and 60 km s^{-1} in the lower trace is due to atmospheric lines.

FAR-INFRARED DETECTION OF H_2D^+ TOWARD SGR B2¹

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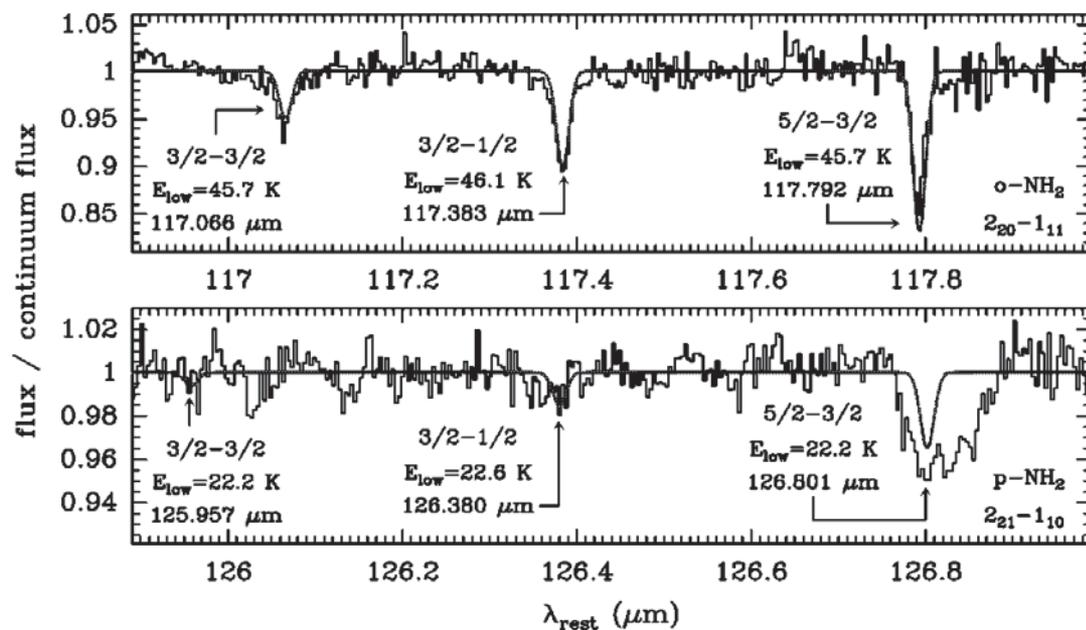


FIG. 2.—Rest *ISO* LWS/FP spectrum of Sgr B2 around 117 and 126 μm , corrected by the averaged velocity of far-IR lines toward the source (62.7 km s^{-1}). Lines due to o-NH₂ (*top panel*) and p-NH₂ plus o-H₂D⁺ (*bottom panel*) are shown. The expected absorption for the NH₂ lines is shown by solid lines in both panels (see text). An NH₂ ortho/para ratio of 3 has been assumed. Note that the NH₂ lines show absorption only at the velocity of Sgr B2. [See the electronic edition of the *Journal* for a color version of this figure.]

What kind of ion-neutral could occur in the ISM ?

PROTON TRANSFER



The reaction is efficient if it is exothermic and it will depend on the proton affinity of the reactants.

H_2 has a low proton affinity and the reactions of H_3^+ with neutral species (B) will always produce BH^+



If the reaction is exothermic the main channel for the reaction is the proton transfer.

PROTON AFFINITIES

H	2.69	O ₂	4.34
H ₂	4.34	CO	6.20
He	1.82	NO	4.99
O	5.03	C ₂	7.20
C	6.46	CN	4.99
N	4.21	N ₂	5.03
		CS	7.57

H₃⁺ will transfer protons to all atoms (except N, H y He) and to most molecules

$$n(\text{H}_3^+)_{\text{dense}} \approx (\zeta/k_{\text{CO}})[n(\text{H}_2)/n(\text{CO})]$$

and

$$n(\text{H}_3^+)_{\text{diffuse}} \approx (\zeta/k_e)[n(\text{H}_2)/n(e^-)].$$

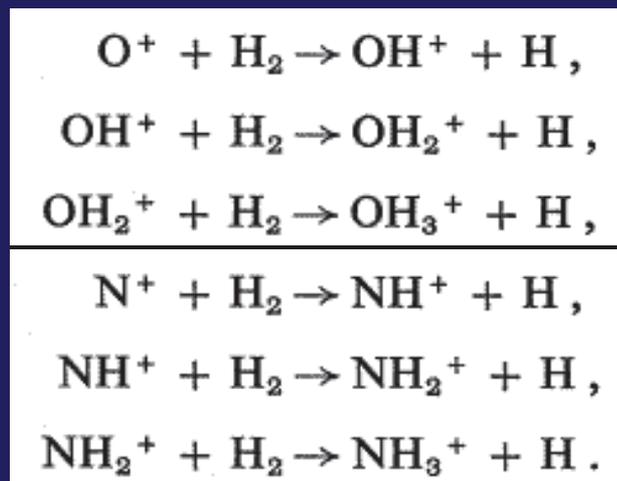
TABLE 1
COSMIC ABUNDANCES

Element	Relative Abundance (by number)*
H.....	1
He.....	0.14†
C.....	3.75×10^{-4}
N.....	8.7×10^{-5}
O.....	4.4×10^{-4}
Ne.....	2.6×10^{-5}
Si.....	3.2×10^{-5}
S.....	1.4×10^{-5}
Fe.....	3.2×10^{-5}

ABSTRACTION OF THE HYDROGEN ATOM



Classic theory does not work well in this case and the reaction rates are poorly determined. In addition, these reactions have often activation energy barriers. Some of them have been studied in the Lab and could be important paths to formation of ionized molecular species



$O^+ + H_2 \rightarrow OH^+ + H$	2.0
$N^+ + H_2 \rightarrow NH^+ + H$	0.7
$OH^+ + H_2 \rightarrow OH_2^+ + H$	1.5
$NH^+ + H_2 \rightarrow NH_2^+ + H$	0.6
$OH_2^+ + H_2 \rightarrow OH_3^+ + H$	1.4
$NH_2^+ + H_2 \rightarrow NH_3^+ + H$	0.23
$NH_3^+ + H_2 \rightarrow NH_4^+ + H$	$< 5 \times 10^{-4}$

PROTON ELIMINATION



Not very efficient although some of them could be important in the ISM:



CONDENSATION REACTIONS

New bonds between heavy atoms are created



And they occur often through the removal of H or H₂. They often have very efficient alternative channels



(proton transfer)

CHARGE TRANSFER REACTIONS

They are the **KEY** reactions for the chemistry of the ISM



Example



The reactions



could be important in HII regions with high ionization fractions but not in molecular clouds.

TABLE 4
CHARGE-TRANSFER REACTIONS

	Reaction	$k(10^{-9} \text{ cm}^3 \text{ s}^{-1})$
57.	$\text{H}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{H} \dots\dots\dots$	1.9
58.	$\text{H}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H} \dots\dots\dots$	1.0 1.2
59.	$\text{H}^+ + \text{OH} \rightarrow \text{OH}^+ + \text{H} \dots\dots\dots$	1.0
60.	$\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H} \dots\dots\dots$	1.0 8.2
61.	$\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{H} \dots\dots\dots$	1.0 5.2
62.	$\text{H}^+ + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{CO}^+ + \text{H} \dots\dots\dots$	1.0
63.	$\text{C}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{C} \dots\dots\dots$	1.0 0.85
64.	$\text{C} + \text{O}_2^+ \rightarrow \text{C}^+ + \text{O}_2 \dots\dots\dots$	1.0

Values in red have been measured
in the laboratory

RADIATIVE RECOMBINATION



These mechanisms produce neutral species from a chemistry based on ion-neutral reactions.

In this reaction the energy excess of the system is released as radiation.



Typical reaction rates are slow $k_{RR} \approx 10^{-12} \text{ cm}^3 \text{ s}^{-1}$

Molecular ions recombine much faster through other mechanism...

DISSOCIATIVE RECOMBINATION

Molecular positive ions recombine with electrons to dissociate into neutral species (not by radiating a photon)



Besides, the reaction rates have a T dependency as $T^{-1/2}$!

Typical values for the dissociative recombination rate are

$$k_{DR} \approx 10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ (fast)}$$



Hence, these reactions are very important in ISM.

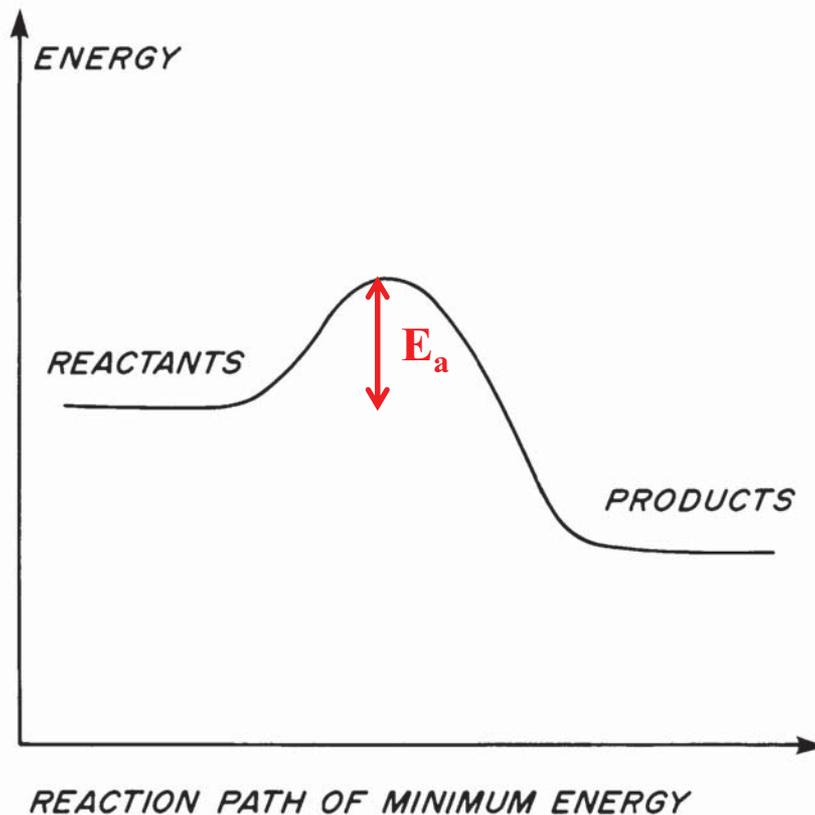
Table 3.8 Some measured values of k_{DR} .

Species	Rate coefficient ($\text{cm}^3 \text{s}^{-1}$)		Species	Rate coefficient ($\text{cm}^3 \text{s}^{-1}$)	
	100 K	40 K		100 K	40 K
<i>Diatomics</i>			<i>Polyatomics</i>		
CH^+	3.3×10^{-7}	5.2×10^{-7}	H_3^+	7.2×10^{-7}	1.1×10^{-6}
NH^+	1.9×10^{-7}	3.0×10^{-7}	H_2O^+	1.3×10^{-6}	2.1×10^{-6}
OH^+	1.4×10^{-7}	2.2×10^{-7}	H_3O^+	1.1×10^{-6}	1.7×10^{-6}
C_2^+	1.0×10^{-6}	1.6×10^{-6}	CH_2^+	8.7×10^{-7}	1.4×10^{-6}
N_2^+	6.2×10^{-7}	9.8×10^{-7}	CH_3^+	1.2×10^{-6}	1.9×10^{-6}
O_2^+	3.3×10^{-7}	5.2×10^{-7}	CH_4^+	1.3×10^{-6}	2.1×10^{-6}
NO^+	4.1×10^{-7}	6.5×10^{-7}	CH_5^+	1.3×10^{-6}	2.1×10^{-6}
			C_2H^+	1.0×10^{-6}	1.6×10^{-6}
			C_2H_2^+	1.0×10^{-6}	1.6×10^{-6}
			C_2H_3^+	1.6×10^{-6}	2.5×10^{-6}
			N_2H^+	1.5×10^{-6}	2.4×10^{-6}

NEUTRAL-NEUTRAL REACTIONS



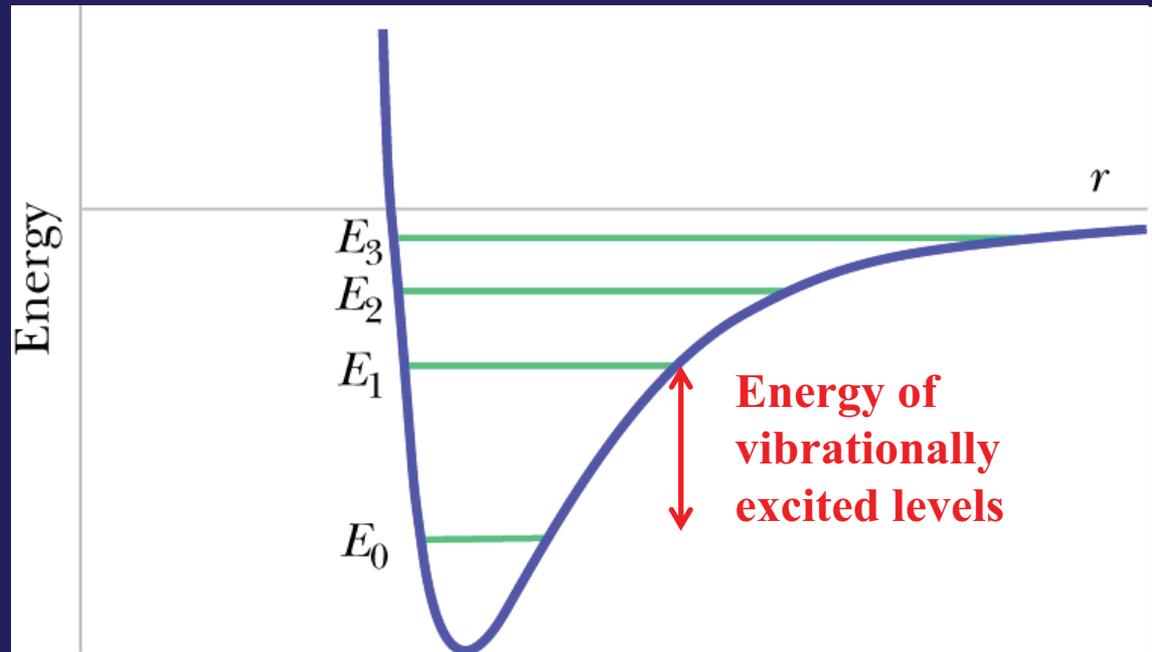
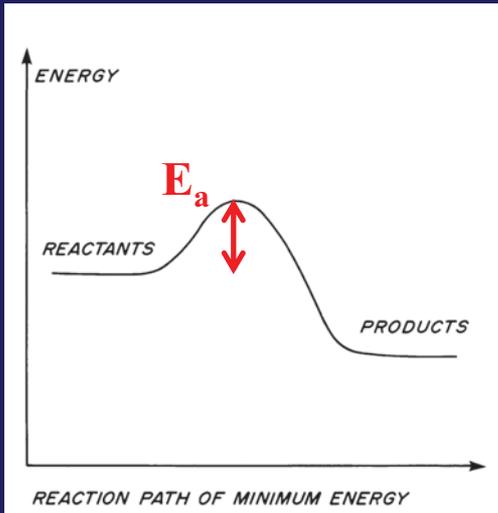
Strong temperature dependence has been found for many of these reactions + activation energy barriers E_a



$$k(T) = A(T) \exp(-E_a / kT)$$

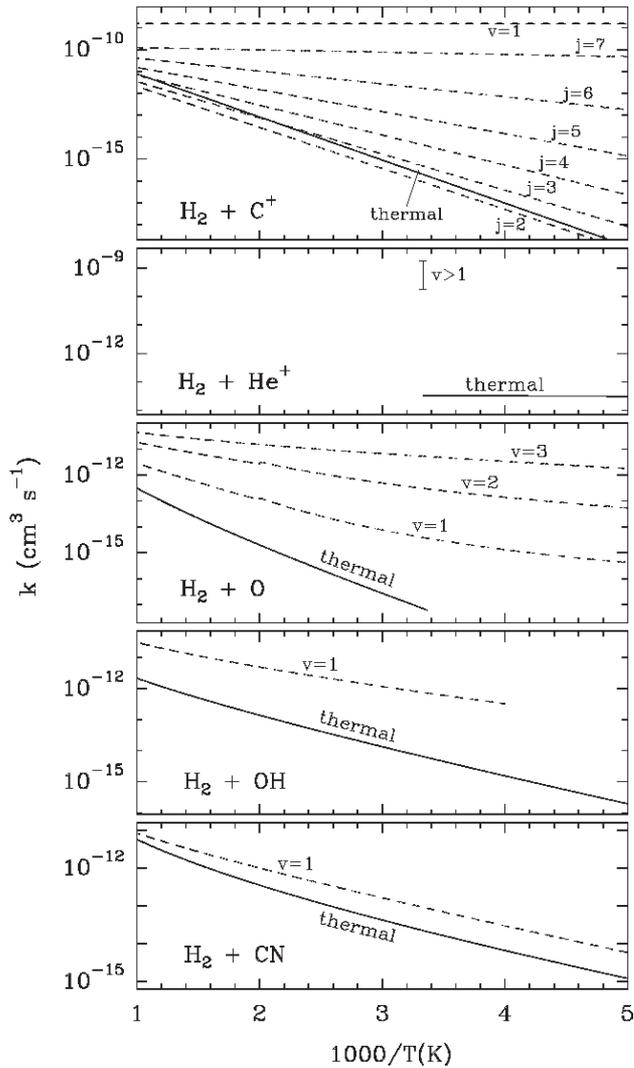
	$A(\text{cm}^3\text{s}^{-1})$	$E_a(\text{K})$
$\text{H} + \text{H}_2\text{CO} = \text{H}_2 + \text{HCO}$	$2.7 \cdot 10^{-11}$	1300
$\text{H} + \text{H}_2\text{S} = \text{H}_2 + \text{SH}$	$1.3 \cdot 10^{-11}$	860
$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	$3.7 \cdot 10^{-10}$	8500
$\text{O} + \text{H}_2 = \text{OH} + \text{H}$	$1.0 \cdot 10^{-11}$	5700
$\text{O} + \text{H}_2\text{S} = \text{OH} + \text{SH}$	$6.6 \cdot 10^{-13}$	900
$\text{OH} + \text{CO} = \text{H} + \text{CO}_2$	$5.1 \cdot 10^{-13}$	300

Non-thermal reactions may overcome endothermicities or activation energy barriers E_a

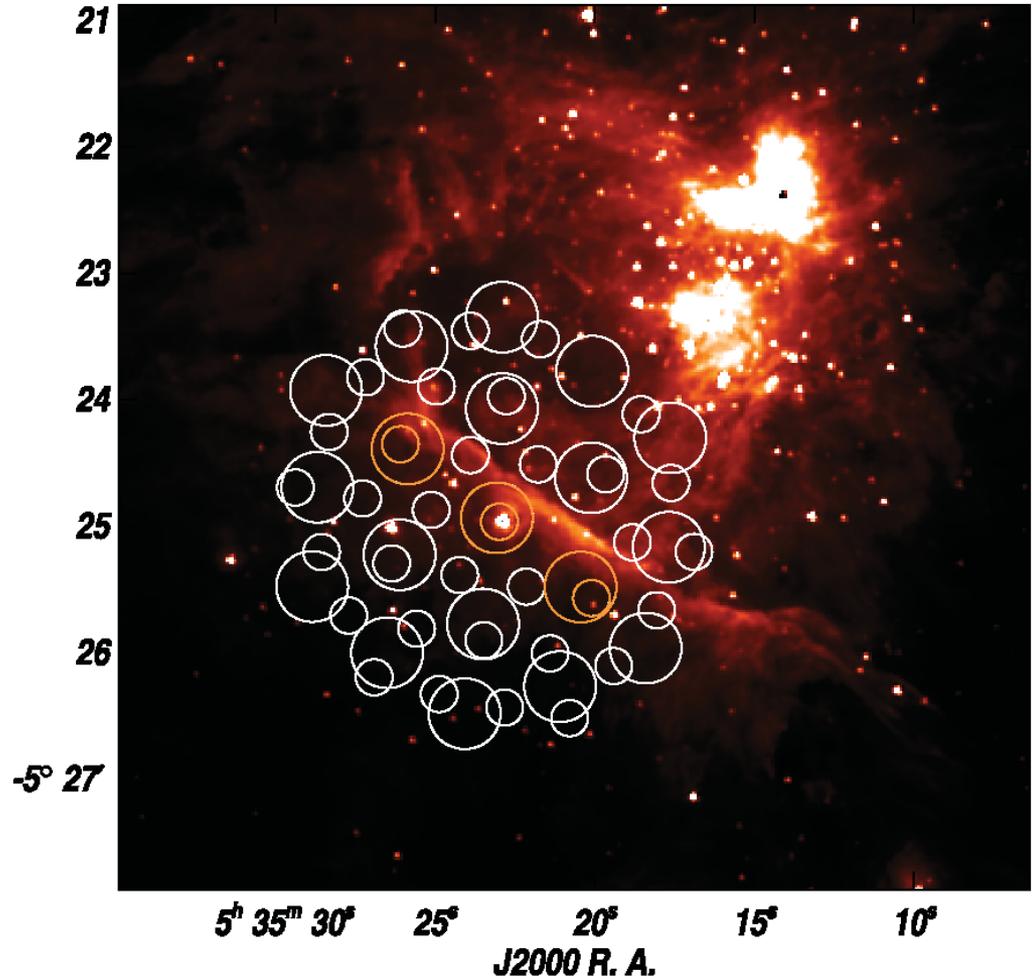


The H_2 ($v=1$) level has an energy of ~ 0.5 eV (~ 5800 K)
- In some particular cases the H_2^* levels can be significantly populated
e.g. by absorption of UV photons in Photodissociation Regions.

Non-thermal reactions may overcome endothermicities or activation energy barriers E_a



J2000 Dec.



Non-thermal reactions may overcome endothermicities or activation energy barriers E_a

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THE CHEMISTRY OF VIBRATIONALLY EXCITED H_2 IN THE INTERSTELLAR MEDIUM

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Table 1
Thermal and State-specific Rate Constants for Chemical Reactions of H_2 Relevant for Astrophysics

No.	Reaction	k ($\text{cm}^3 \text{s}^{-1}$)	ΔT (K) ^a	$\Delta H_r^0(0K)$ (K)	Reference
1	$H_2 + C^+ \rightarrow CH^+ + H$	$7.4 \times 10^{-10} \exp(-4537/T)$	400–1300	+4280	(1)
2	$H_2(j = 0, 7) + C^+ \rightarrow CH^+ + H$	$1.58 \times 10^{-10} \exp(-[4827 - E_j/k]/T)$ ^b	200–1000	(+4280, –310)	(2)
3	$H_2(v = 1) + C^+ \rightarrow CH^+ + H$	1.6×10^{-9}	800–1300	–1710	(1)
4	$H_2 + He^+ \rightarrow He + H + H^+$	$3.7 \times 10^{-14} \exp(-35/T)$	10–300	–75560	(3)
5	$H_2(v > 1) + He^+ \rightarrow He + H + H^+$	$0.18\text{--}1.8 \times 10^{-9}$	300	–87190	(4)
11	$H_2 + O \rightarrow OH + H$	$3.52 \times 10^{-13} (T/300)^{2.60} \exp(-3241/T)$	297–3532	+920	(5)
6	$H_2(v = 1) + O \rightarrow OH + H$	$1.68 \times 10^{-16} (T/300)^{9.34} \exp(943/T)$	100–500 ^c	–5070	(6)
7	$H_2(v = 2) + O \rightarrow OH + H$	$1.52 \times 10^{-13} (T/300)^{5.13} \exp(209/T)$	100–500 ^c	–10720	(6)
8	$H_2(v = 3) + O \rightarrow OH + H$	$2.07 \times 10^{-11} (T/300)^{0.98} \exp(-412/T)$	100–4000	–16040	(6)
9	$H_2 + OH \rightarrow H_2O + H$	$2.22 \times 10^{-12} (T/300)^{1.43} \exp(-1751/T)$	200–3000	–7370	(5)
10	$H_2(v = 1) + OH \rightarrow H_2O + H$	$1.52 \times 10^{-11} (T/300)^{1.33} \exp(-902/T)$	250–2000	–13360	(7)
11	$H_2 + CN \rightarrow HCN + H$	$1.17 \times 10^{-12} (T/300)^{2.31} \exp(-1188/T)$	200–3500	–10250	(5)
12	$H_2(v = 1) + CN \rightarrow HCN + H$	$9.65 \times 10^{-12} (T/300)^{1.04} \exp(-1397/T)$	200–1000	–16240	(8)

(UV) Photodissociation and photoionization

The main path to destroy molecules in UV illuminated gas is photodissociation and photoionization

What do we need to know ?

- 1) The electronic, vibrational and rotational levels of each molecule
- 2) The far-UV radiation field ($>911 \text{ \AA}$)

Hence, photo rates (β) will be different in each source (SFRs, planetary disks...)

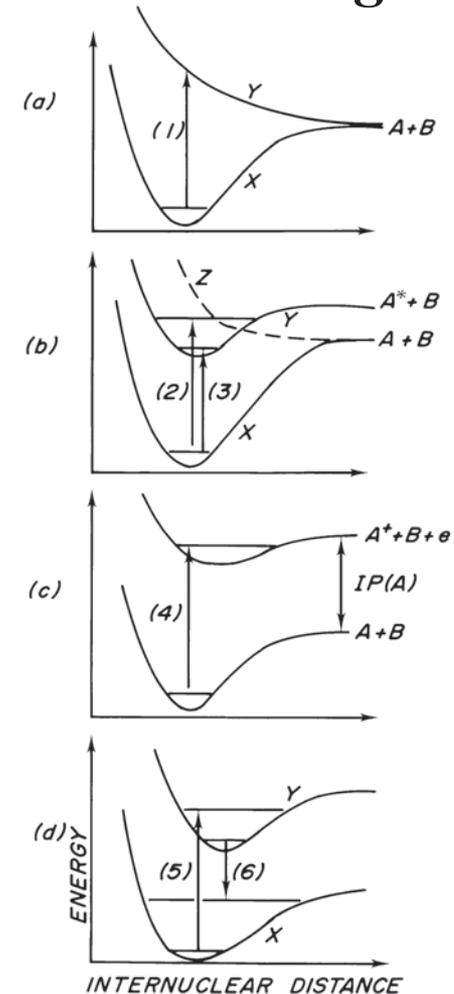
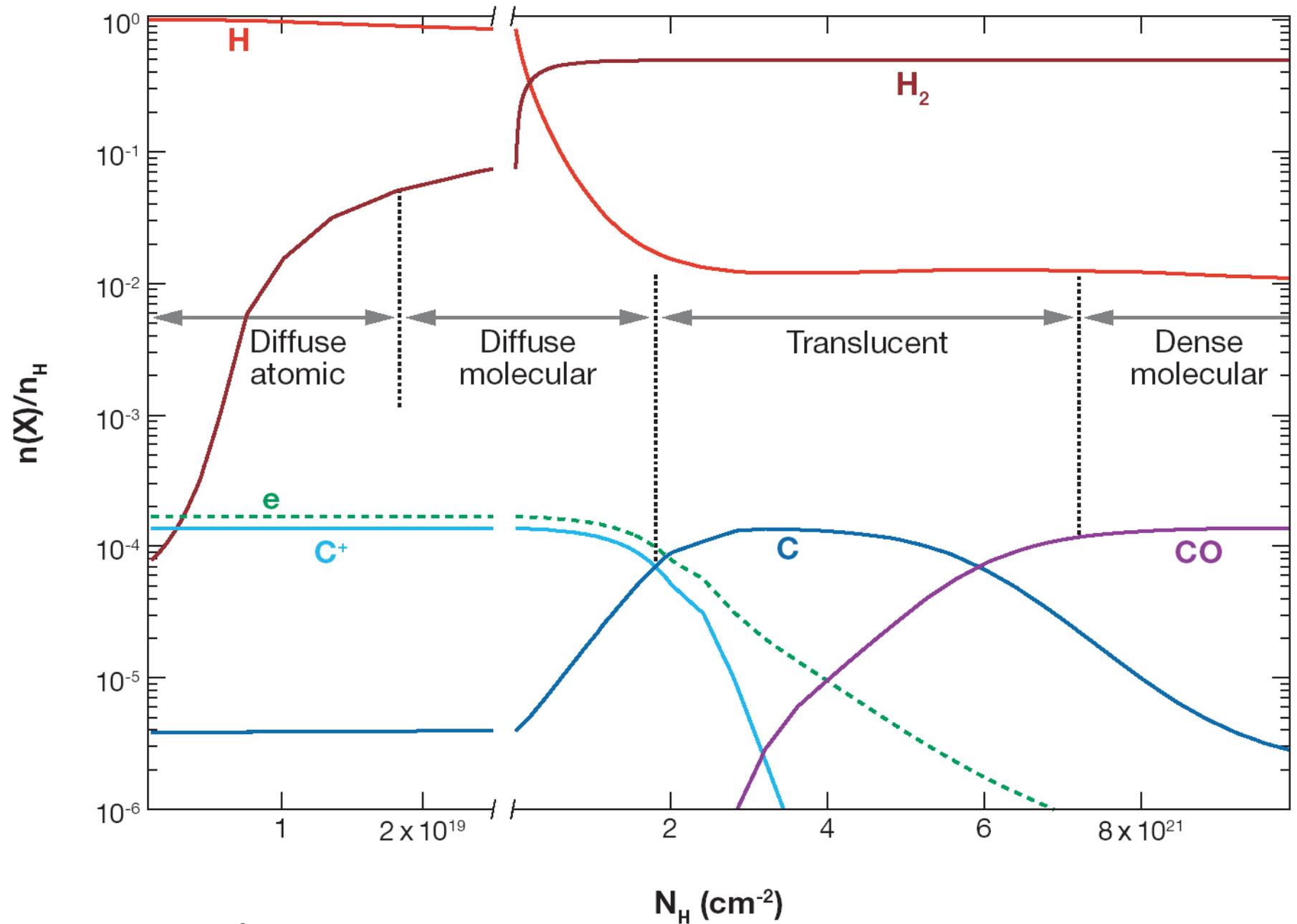
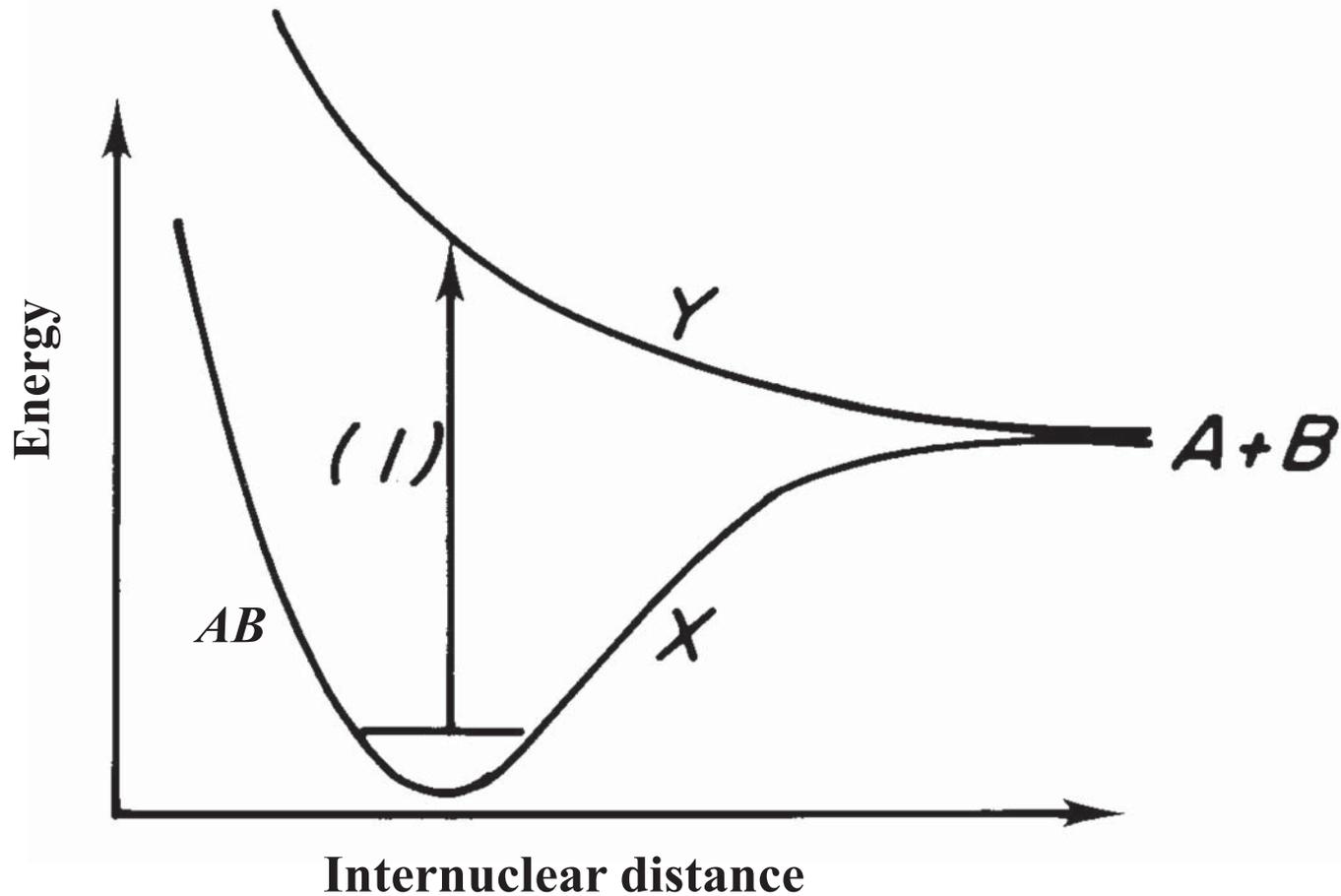


Fig. 4.1 Potential energy curves and transitions illustrating (a) photodissociation, (b) photo-predissociation, (c) photoionization, and (d) dissociation via fluorescent emission.



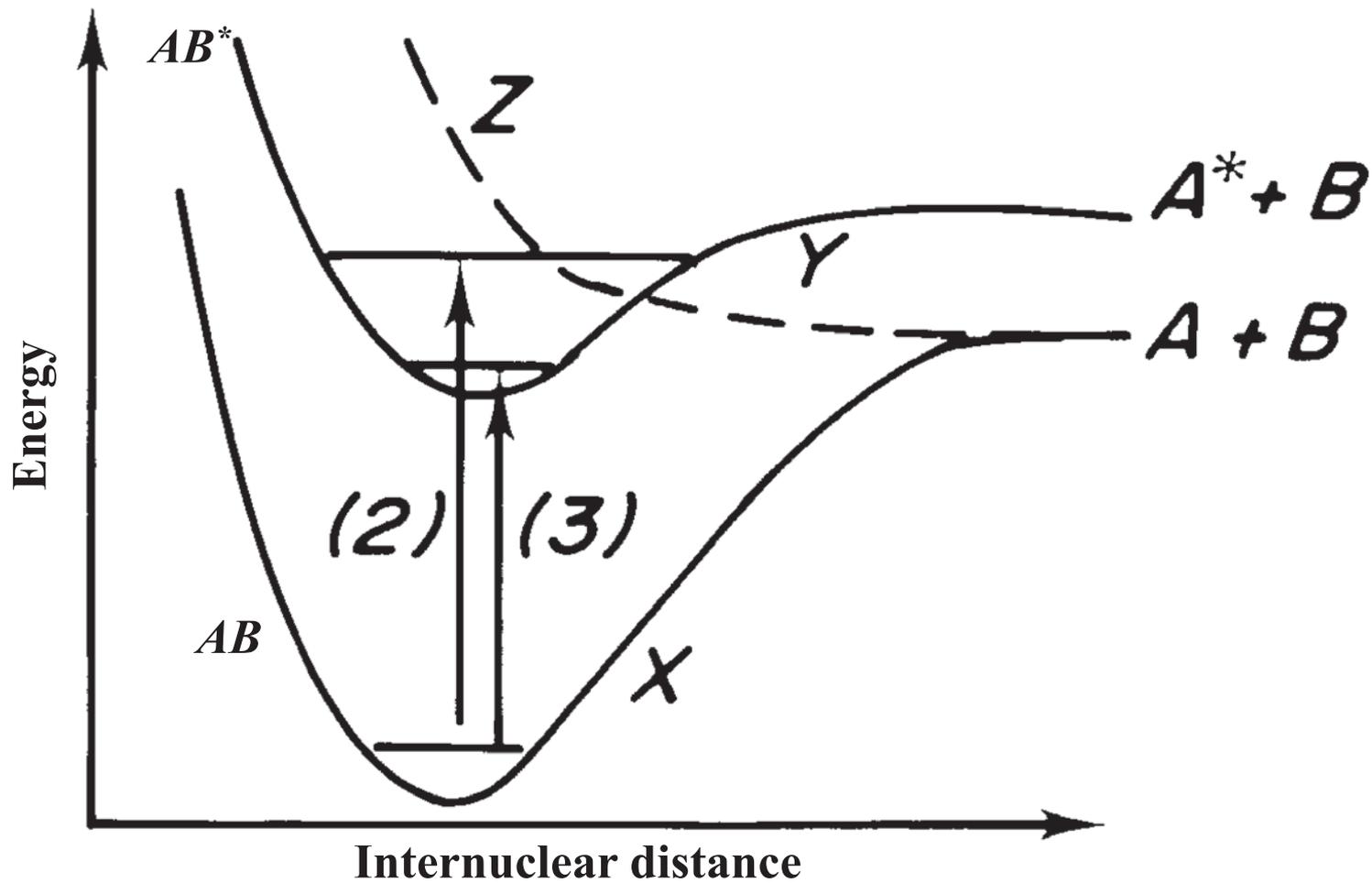
$n_H = 100 \text{ cm}^{-3}$ $G_0 = 1$

from Neufeld et al. (2005)



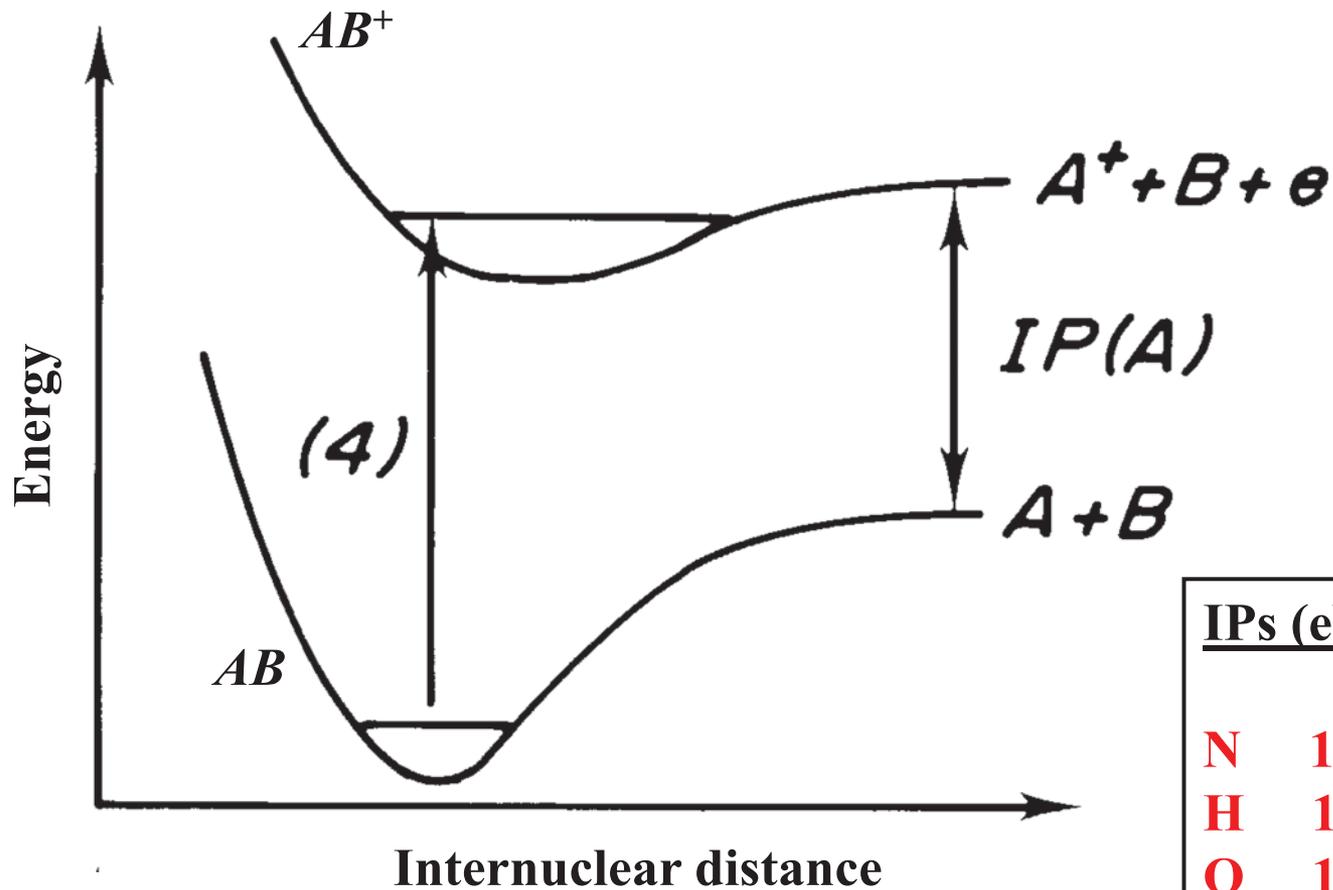
“Direct Photodissociation”





“Photo-Predissociation”





IPs (eV)

N 14.6

H 13.6

O 13.6

C 11.3

S 10.4

Mg 7.7

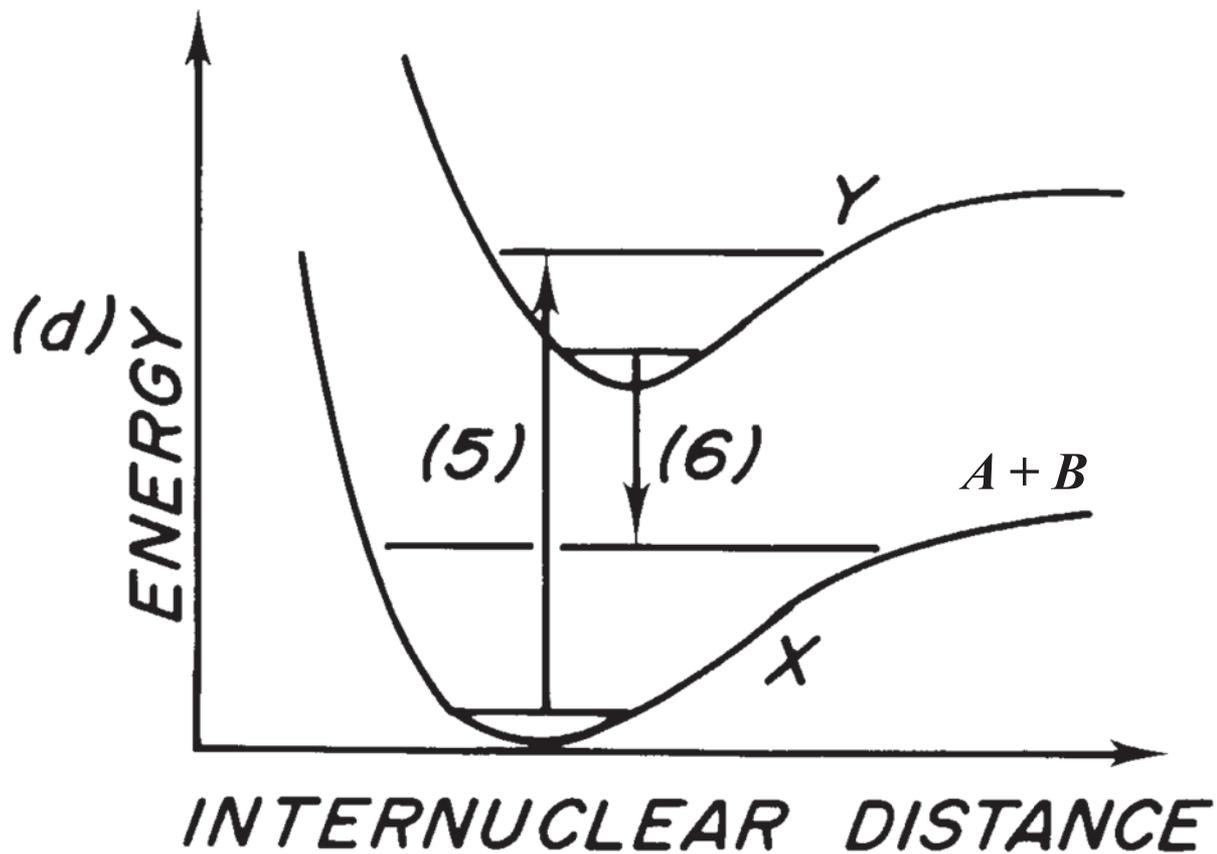
H₂ 15.4

CO 14.0

H₂O 12.6

“Photoionization”

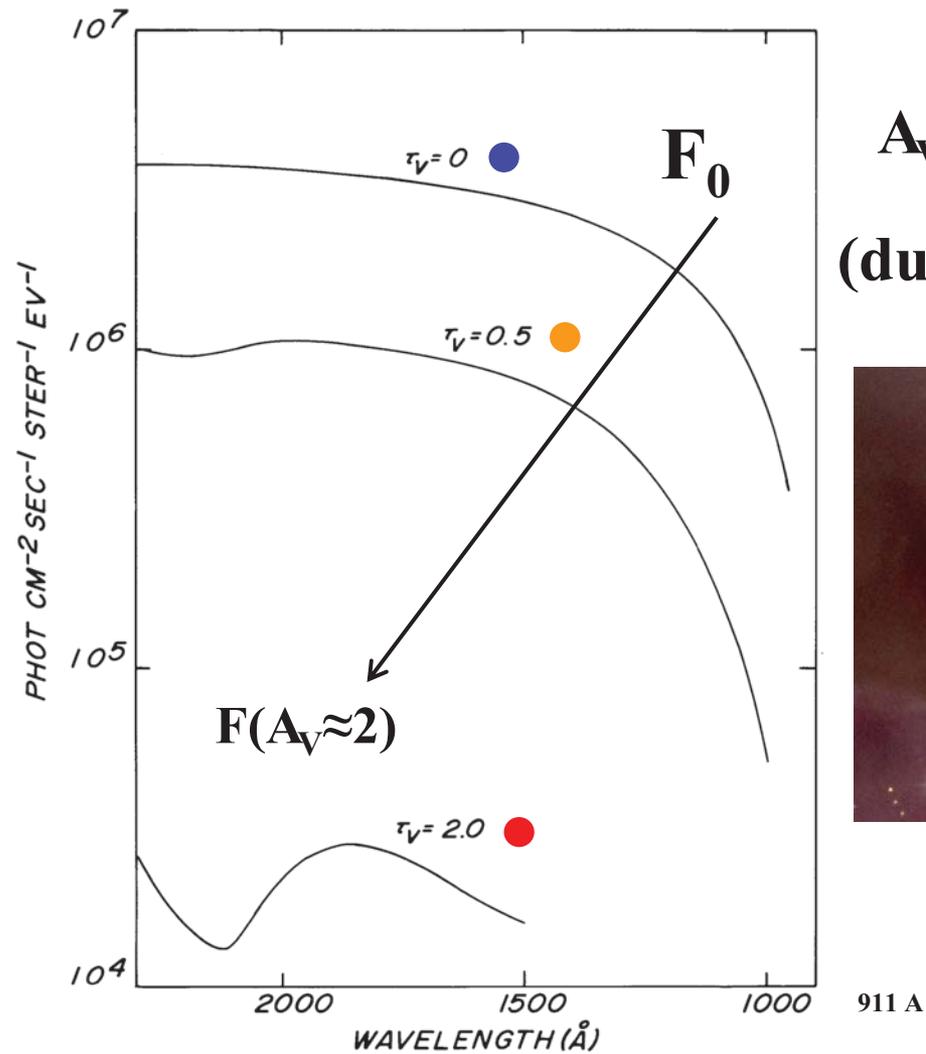




“Dissociation via fluorescent emission”



Interstellar
radiation
far-UV field
 $F = F(\lambda)$
or
 $F = F(E)$



$$A_V = 1.086 \cdot \tau_V$$

(dust attenuation)

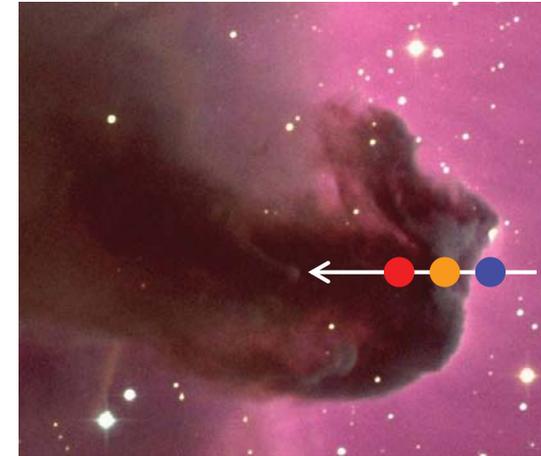


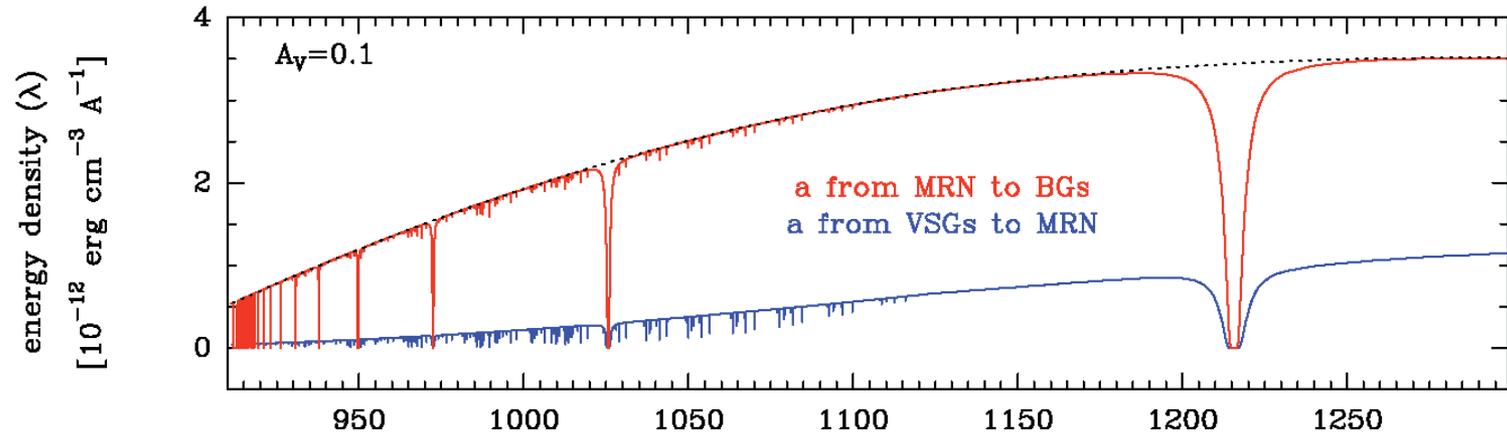
Fig. 4.4 The interstellar radiation flux $F(E)$ photons $\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1} \text{ster}^{-1}$ in unobscured regions of the interstellar medium, in a typical diffuse cloud with $\tau_V \approx 0.5$, and in a denser cloud with $\tau_V \approx 2$.

Mean interstellar radiation field flux, $F(E)$

$$F_0(E) = 1.658 \cdot 10^6 E - 2.152 \cdot 10^5 E^2 + 6.919 \cdot 10^3 E^3 \text{ photons cm}^{-2} \text{ s}^{-1} \text{ ster}^{-1} \text{ eV}^{-1}$$

β photodissociation rate (complex calculation)

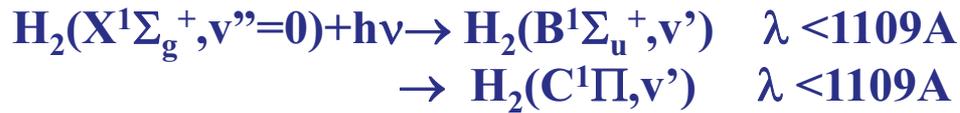
$$\beta(A_V) = 4\pi \int_0^{13.6eV} F(E, A_V) \sigma_{PD}(E) dE$$



$$\beta = \beta_0 \exp(-\alpha A_V)$$

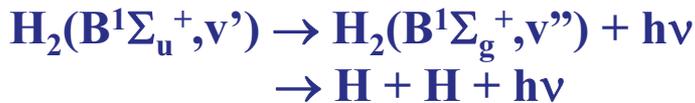
Table 4.1 Dissociation rates, β_0 , and α [equation (4.14)] for simple molecules exposed to the unshielded interstellar radiation field. (S. S. Prasad and W. T. Huntress, Jr, *Astrophysical Journal Supplement Series*, 1980, **43**, 1.)

Molecule	β_0 (s ⁻¹)	α	Molecule	β_0 (s ⁻¹)	α
H ₂	5 × 10 ⁻¹¹	—	HCN	1 × 10 ⁻¹⁰	1.8
HD	5 × 10 ⁻¹¹	—	HCO	8.8 × 10 ⁻¹⁰	1.6
CH	1.4 × 10 ⁻¹⁰	1.5	H ₂ CO	8.8 × 10 ⁻¹⁰	1.6
CO	5 × 10 ⁻¹²	3.0	NH ₃	5.5 × 10 ⁻¹⁰	2.0
CN	5 × 10 ⁻¹¹	1.7	H ₂ O	3.2 × 10 ⁻¹⁰	1.7
			CH ₃ ⁺	2 × 10 ⁻⁹	1.7

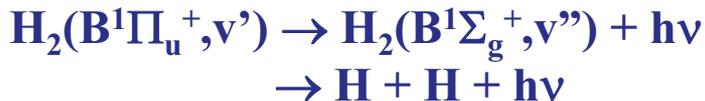


“Lyman and Werner bands”

There are not allowed electric dipole transitions from $\text{X}^1\Sigma_g^+$ to repulsive Electronic states with energies $< 13.6 \text{ eV}$!!



and



23% of the X-B transitions produce photodissociation
1% of the X-C transitions produce photodissociation

Photodissociation is produced by lines !!! => shelf-shielding of H_2 (and CO) in clouds...

H_2 photodissociation

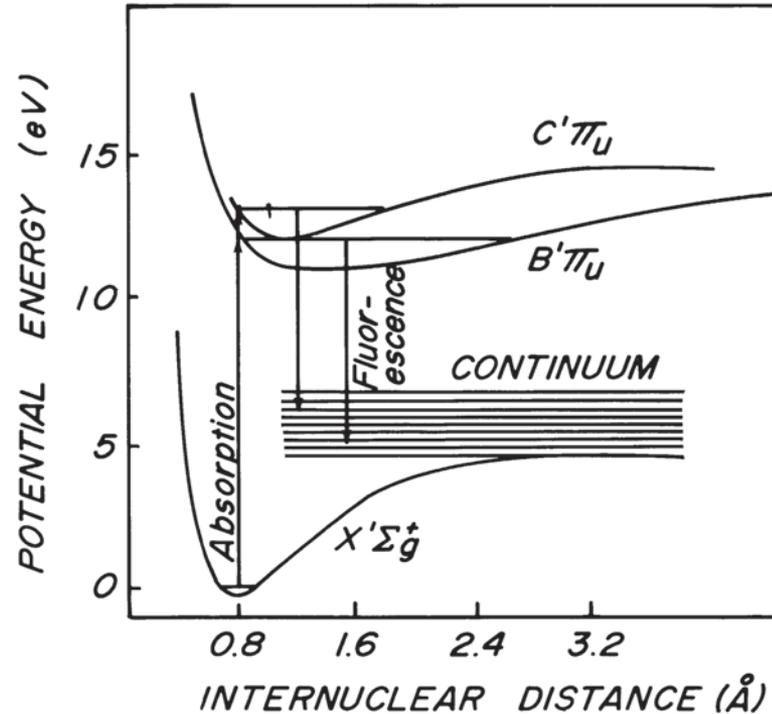


Fig. 4.6 Energy levels in H_2 molecule participating in absorption and dissociation via fluorescent emission. (The designation of molecular states follows G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, Princeton, NJ, 1950.)

PDR Chemical Models

Model Name	Authors
Cloudy	G. J. Ferland, P. van Hoof, N. P. Abel, G. Shaw (Ferland et al. 1998; Abel et al. 2005; Shaw et al. 2005)
COSTAR	I. Kamp, F. Bertoldi, G.-J. van Zadelhoff (Kamp & Bertoldi 2000; Kamp & van Zadelhoff 2001)
HTBKW	D. Hollenbach, A. G. G. M. Tielens, M. G. Burton, M. J. Kaufman, M. G. Wolfire (Tielens & Hollenbach 1985; Kaufman et al. 1999; Wolfire et al. 2003)
KOSMA- τ	H. Störzer, J. Stutzki, A. Sternberg (Störzer et al. 1996), B. Köster, M. Zielinsky, U. Leuenhagen Bensch et al. (2003), Röllig et al. (2006)
Lee96mod	H.-H. Lee, E. Herbst, G. Pineau des Forêts, E. Roueff, J. Le Bourlot, O. Morata (Lee et al. 1996)
Leiden	J. Black, E. van Dishoeck, D. Jansen and B. Jonkheid (Black & van Dishoeck 1987; van Dishoeck & Black 1988; Jansen et al. 1995)
Meijerink	R. Meijerink, M. Spaans (Meijerink & Spaans 2005)
Meudon	J. Le Bourlot, E. Roueff, F. Le Petit (Le Petit et al. 2005, 2002; Le Bourlot et al. 1993)
Sternberg	A. Sternberg, A. Dalgarno (Sternberg & Dalgarno 1989, 1995; Boger & Sternberg 2005)
UCL_PDR	S. Viti, W.-F. Thi, T. Bell (Taylor et al. 1993; Papadopoulos et al. 2002; Bell et al. 2005)

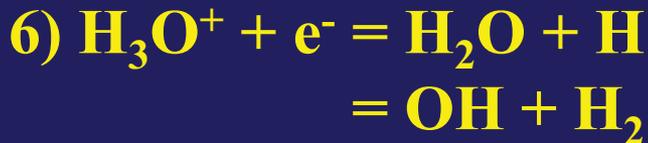
Summary

REPRESENTATIVE RATES FOR DIFFERENT TYPES OF GAS REACTIONS IN THE ISM

Cosmic ray ionization	ζ_{CR}	10^{-17}	s^{-1}
Ion-Molecule reaction	k	10^{-09}	$\text{cm}^3 \text{ s}^{-1}$
Charge Transfer reaction	k	10^{-09}	$\text{cm}^3 \text{ s}^{-1}$
Radiative association -diatomic		10^{-17}	$\text{cm}^3 \text{ s}^{-1}$
-polyatomic		10^{-09}	$\text{cm}^3 \text{ s}^{-1}$
Neutral exchange	k, E_a	10^{-12}	$\text{cm}^3 \text{ s}^{-1}$
Radiative recombination	k_{RR}	10^{-12}	$\text{cm}^3 \text{ s}^{-1}$
Dissociative recombination	k_{DR}	10^{-06}	$\text{cm}^3 \text{ s}^{-1}$
Photodissociation	β_0	$10^{-09}-10^{-12}$	$\text{cm}^3 \text{ s}^{-1}$

EXAMPLE : THE FORMATION OF WATER VAPOR

H_2 from reactions in the grain surfaces



A total of six steps are needed to form H_2O or OH . But now



LETTER TO THE EDITOR

Herschel/HIFI observations of interstellar OH⁺ and H₂O⁺ towards W49N^{*}: a probe of diffuse clouds with a small molecular fraction

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(Affiliations can be found after the references)

Received 28 May 2010 / Accepted 28 June 2010

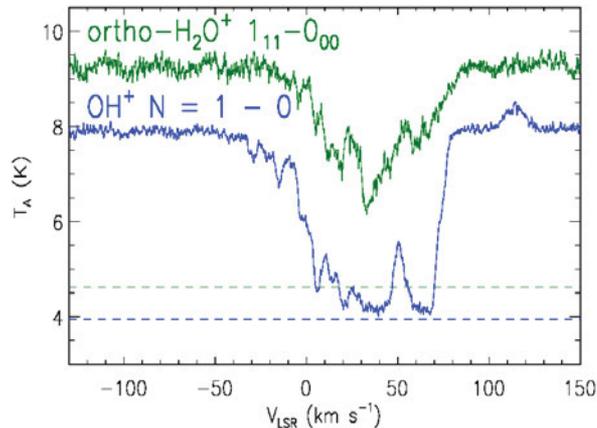
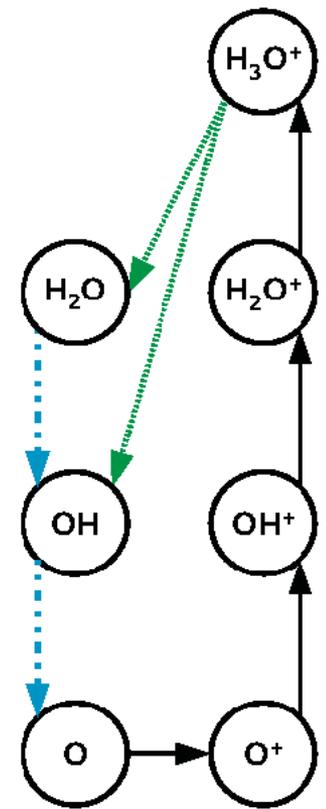
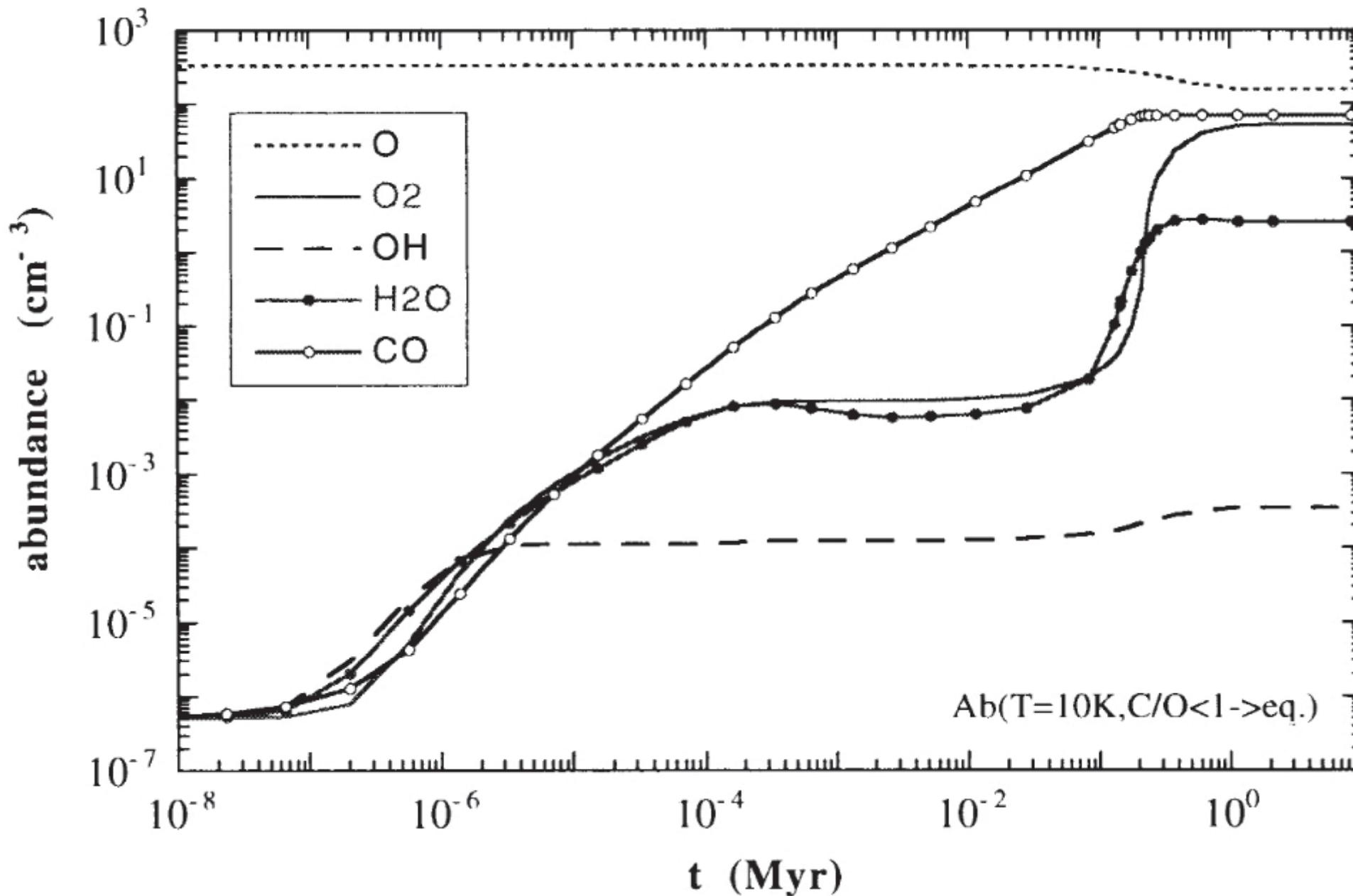


Fig. 1. Spectra of H₂O⁺ 1₁₁-0₀₀ (green) and OH⁺ N = 1-0 (blue) transitions obtained toward W49N. The velocity scale applies to the strongest hyperfine component, with assumed frequencies of 971 803.8 MHz for OH⁺ and 1 115 204 MHz for H₂O⁺. Note that because HIFI employs double sideband receivers, the complete absorption of radiation at a single frequency will reduce the measured antenna temperature to one-half the apparent continuum level.



$n_H = 5 \cdot 10^5 \text{ cm}^{-3}$; $T = 10\text{K}$; $C/O < 1$: equilibrium



Stationary Chemical Models (Sternberg & Dalgarno 1995)

SELECTED MOLECULAR DIAGNOSTICS^a

Density Ratio	Hot H I H/H ₂ <i>A_V</i> = 0.6	C II <i>A_V</i> = 1.5	S II <i>A_V</i> = 3	Si II <i>A_V</i> = 5	S I <i>A_V</i> = 7	Dark Core <i>A_V</i> > 10
OH/H ₂ O	4.5 (1) ^b	2.3 (1)	9.3	9.2 (-2)	4.4 (-3)	3.4 (-4)
OH ⁺ /H ₃ O ⁺	1.8	1.3	7.5 (-2)	9.6 (-3)	1.3 (-3)	1.4 (-5)
CO ⁺ /HCO ⁺	5.1 (-2)	3.5 (-2)	1.5 (-4)	1.7 (-6)	2.9 (-7)	2.0 (-7)
SO ⁺ /SO	1.7	2.3 (-1)	2.8 (-3)	6.4 (-4)	1.2 (-4)	5.7 (-4)
SiO ⁺ /SiO	1.6 (-1)	5.7 (-3)	3.0 (-5)	1.2 (-7)	1.8 (-9)	1.7 (-10)
NH/NH ₃	7.8 (4)	2.2 (5)	9.2 (3)	9.3 (-1)	1.7 (-2)	4.9 (-4)
CN/HCN	4.7	1.1 (1)	8.4	3.3 (-1)	1.3 (-3)	1.8 (-4)

^a Selected molecular density ratios at specific locations in the different chemical zones present in a photon-dominated region with a total hydrogen particle density $n_T = 10^6 \text{ cm}^{-3}$, which is exposed to a FUV radiation field with $\chi = 2 \times 10^5$, and a cosmic-ray ionization rate of $\zeta = 5 \times 10^{-17} \text{ s}^{-1}$. The total elemental abundances are listed in Table 1.

^b Numbers in parentheses are exponents. For example, $4.5 (1) = 4 \times 10^1$.

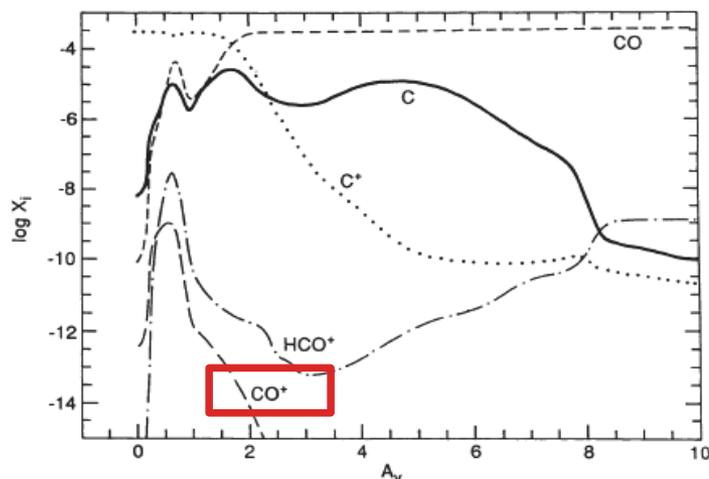


FIG. 11a

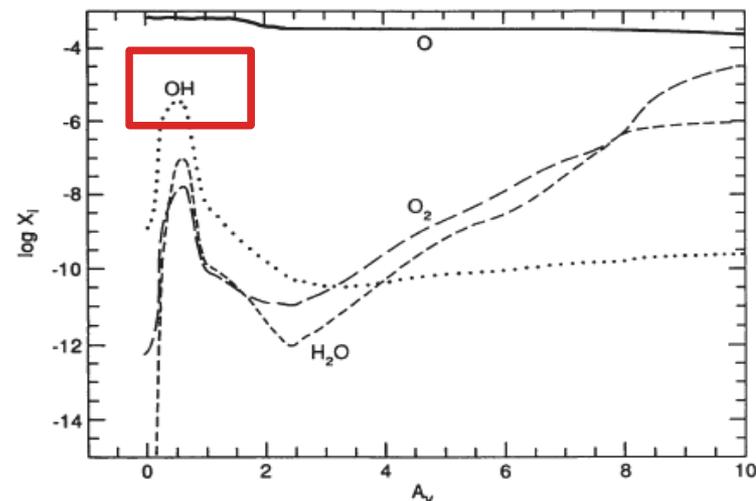


FIG. 9a

Stationary Chemical Models

(Sternberg & Dalgarno 1995, ApJ SS 99, 565)

TABLE 2
ATOMIC AND MOLECULAR SPECIES IN DENSE PDRS^a

Family	Hot H I H/H ₂ <i>A_V</i> = 0 → 0.7	C II 0.7 → 1.7	S II 1.7 → 3.7	Si II 3.7 → 6	S I 3.7 → 7.6	Dark Core <i>A_V</i> > 10
Hydrogen	H H ⁺ H ₂ ⁺ H ₂ ⁺ H ₃ ⁺	H ₂ H ₂ [*]	H ₂	H ₂	H ₂	H ₂ H ₃ ⁺
Oxygen	O O ⁺ OH H ₂ O OH ⁺ H ₂ O ⁺ H ₃ O ⁺ O ₂ O ₂ ⁺	O OH	O	O	O	O H ₂ O H ₃ O ⁺ O ₂ O ₂ ⁺
Carbon	C C ⁺ CH CH ₂ CH ₃ CH ⁺ CH ₂ ⁺ CH ₃ ⁺ CH ₄ ⁺ CH ₅ ⁺	C C ⁺ CH CH ₂ CH ₃ CH ⁺ CH ₂ ⁺ CH ₃ ⁺ CH ₄ ⁺ CH ₅ ⁺	CH ₄ CH ₅ ⁺
Sulfur	S ⁺ SH ⁺	S ⁺	S ⁺ SH H ₂ S ⁺	S	S H ₂ S H ₂ S ⁺	...
Nitrogen	N NH NH ₂ NH ⁺ NH ₂ ⁺ NH ₃ ⁺	N	N	N	N N ⁺ N ₂	N N ⁺ NH ₂ NH ₃ NH ₄ ⁺ N ₂ N ₂ H ⁺
Silicon	Si ⁺	Si ⁺	Si ⁺	Si Si ⁺ SiH SiH ₂ ⁺	Si Si ⁺	...
Oxygen intermediates	CO CO ⁺ HCO ⁺ SO ⁺ No NO ⁺ SiO ⁺ SiOH ⁺	CO ⁺ HCO ⁺	CO	CO	CO SO	CO HCO ⁺ SO SO ₂ SO ⁺ NO NO ⁺ SiOH ⁺ SiO SiO ₂
Carbon intermediates	CS ⁺ HCS ⁺ CN HCN CN ⁺ HCN ⁺ H ₂ CN ⁺	CS ⁺ HCS ⁺ CN HCN CN ⁺ HCN ⁺	CS HCS HCS ⁺ HCN OCS	HCS ⁺ HCN OCS

^a This table lists the atomic and molecular species that are preferentially produced in the different chemical zones present in a photon-dominated region with a total hydrogen particle density $n_T = 10^6 \text{ cm}^{-3}$, which is exposed to a FUV radiation field with $\chi = 2 \times 10^5$, and a cosmic-ray ionization rate of $\zeta = 5 \times 10^{-17} \text{ s}^{-1}$. The total elemental abundances are listed in Table 1.



The forward reaction is exothermic by an amount $\Delta E/k \approx 230 \text{ K}$ and, therefore, at low temperatures, the primary destruction mechanism for H_2D^+ is *via* recombination with electrons. Formation of DCO^+ follows through the reaction:



R. Plume et al.

49

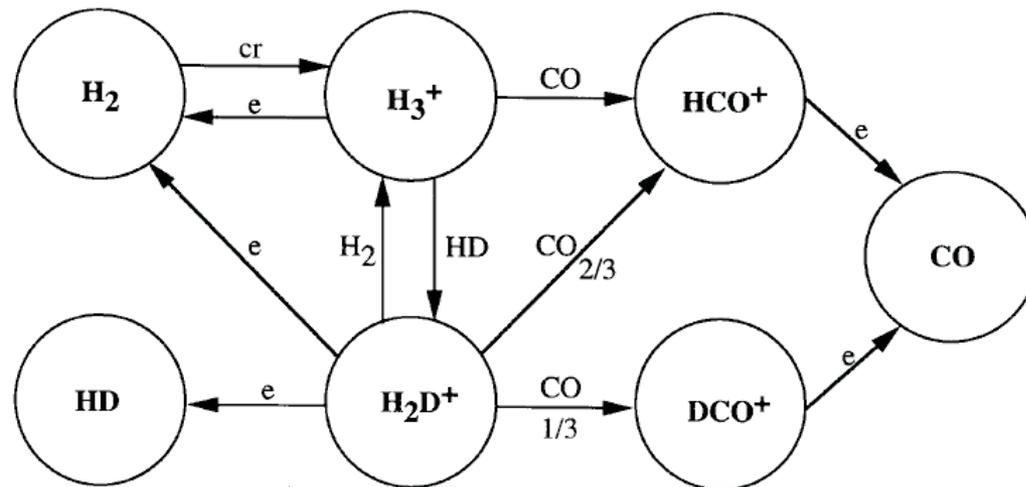
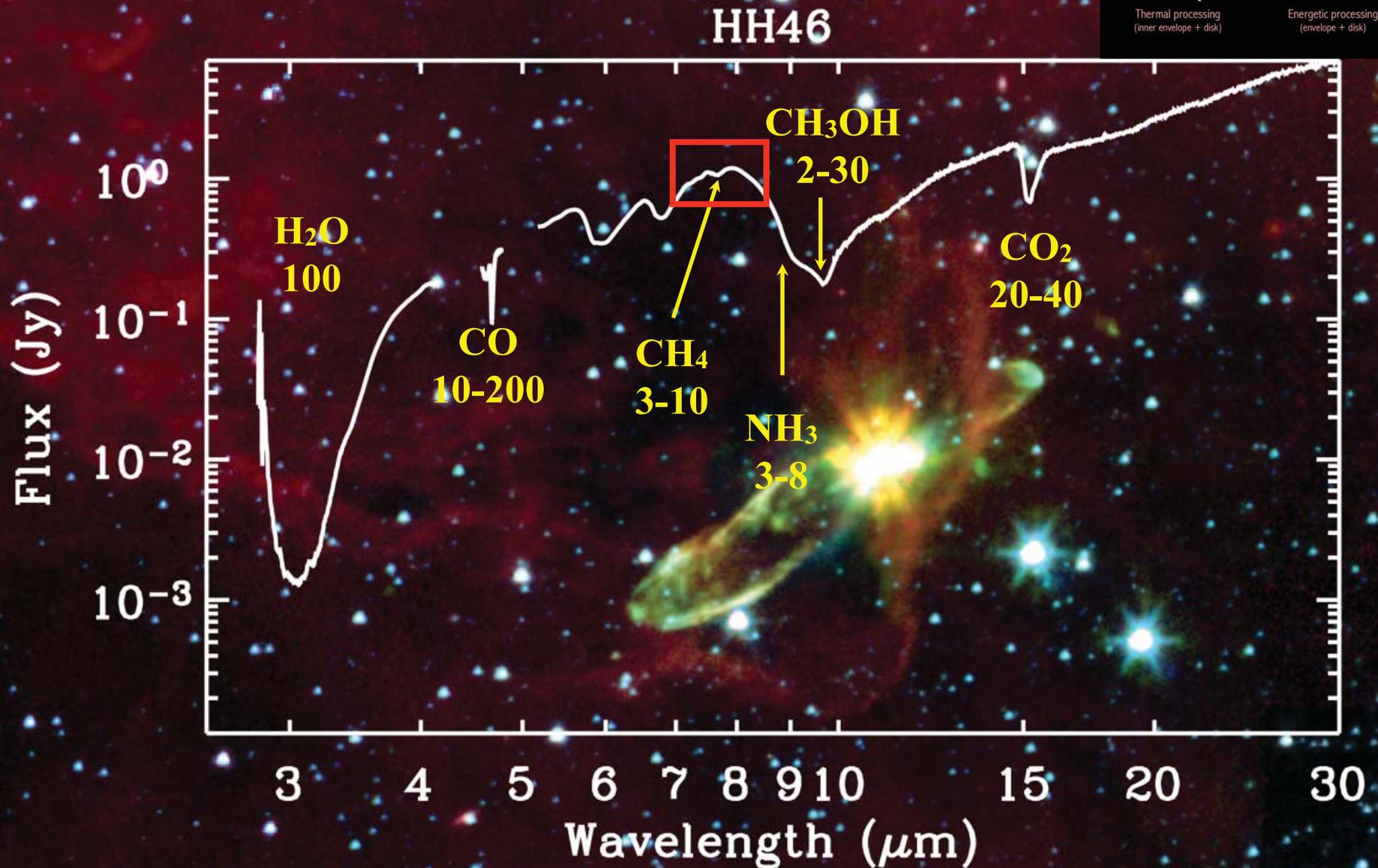


Fig. 1 Schematic diagram representing the chemical network responsible for the creation and destruction of DCO^+ and HCO^+ , reproduced from ref. 19 with kind permission

Similar effects for $^{12}\text{CO} + ^{13}\text{C}^+ \Rightarrow ^{13}\text{CO} + \text{C}^+ + \Delta E$ (35K)

Ices are abundant and common!

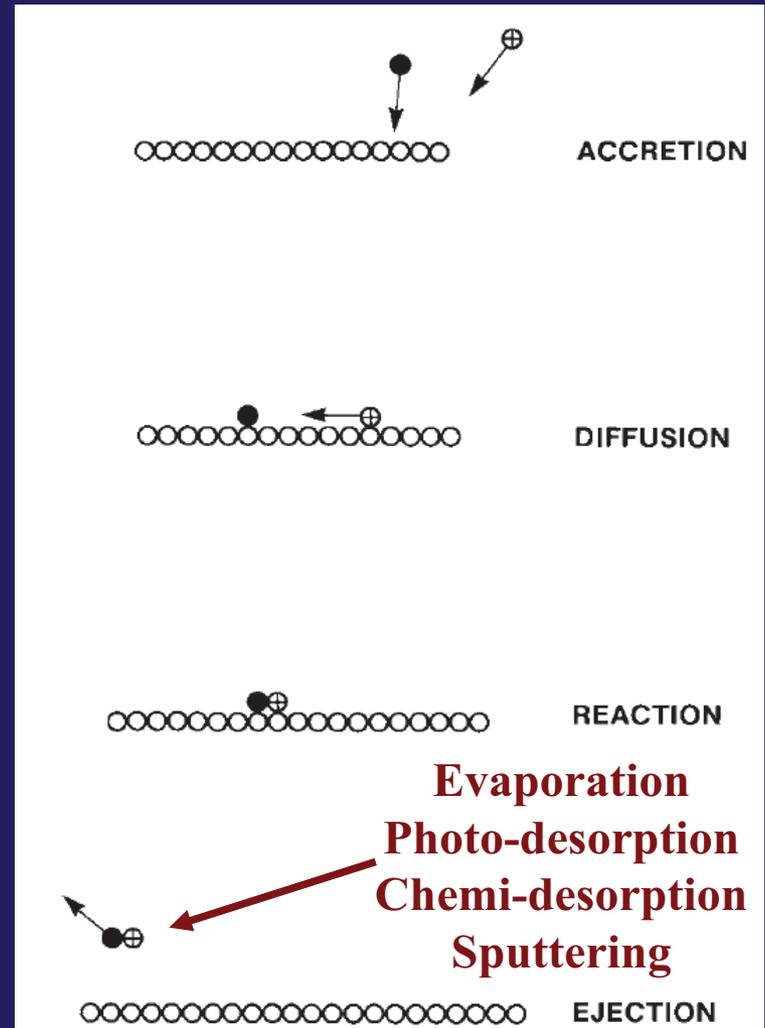
Freeze-out and atomic processing
clouds and prestellar cores



Basic concepts on grain surface chemistry

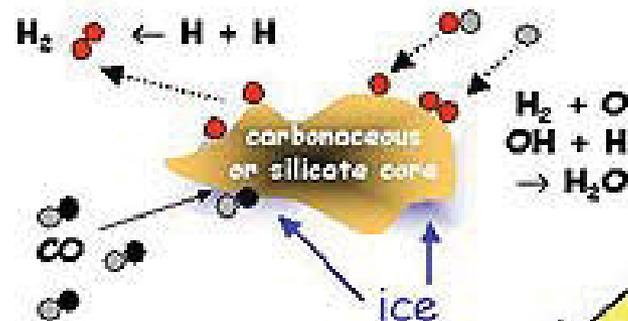
The most abundant molecule in space, H_2 , cannot be formed in gas phase. Must be formed on grain surfaces.

Grain-surface reactions are also key to explain the abundances of other molecules such as CH_3OH , H_2CO , NH_3 or H_2O .





The "Black Cloud" B99 (VLT ANTU + FORS)



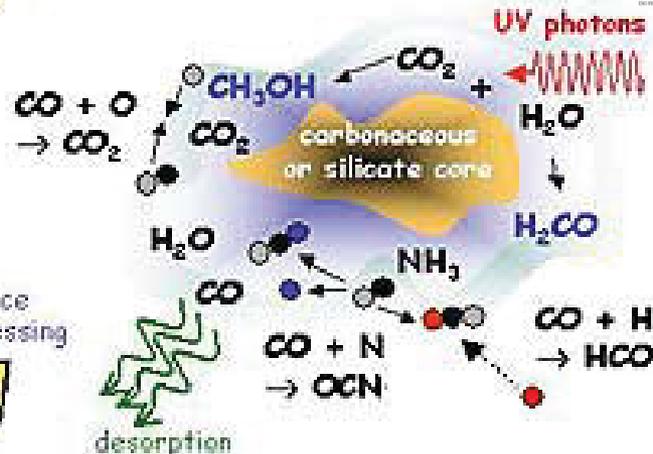
Forming interstellar ice:

Atoms and molecules stick onto the cold dust, reacting to form H_2 and H_2O or freezing to form "solids".

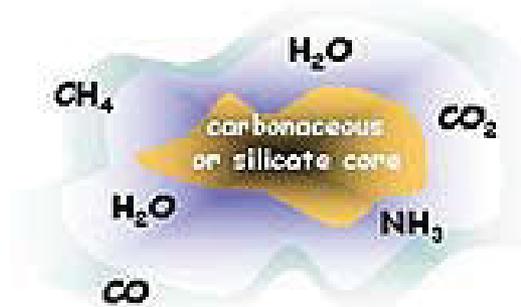
An ICY GRAIN of INTERSTELLAR DUST:

A 'crust' of ice entirely covers the dust. Dominated by H_2O , the ice contains many different chemicals - the least volatile molecules in the top layers.

...after some time



...ice processing



Processing interstellar ice:

Atoms and molecules react at the ice surface to form new, more complex molecules. UV photons and electrons from cosmic rays also "kick start" chemical reactions in the ice. When the ice is heated, many molecules are desorbed.

A schematic representation of the life cycle of an interstellar dust grain in star forming regions. (from Fraser et al. Rev. Sci. Inst., 73, 2161 (2002)).

The accretion rate of a molecule into a dust grain is

$$k_{\text{ac}} = n_{\text{d}} \sigma_{\text{d}} v S(T, T_{\text{d}}) \simeq 10^{-17} \left(\frac{T}{10 \text{ K}} \right)^{1/2} n \text{ s}^{-1}$$

$$S(T, T_{\text{d}}) = \left[1 + 4 \times 10^{-2} (T + T_{\text{d}})^{1/2} + 2 \times 10^{-3} T + 8 \times 10^{-6} T^2 \right]^{-1},$$

The depletion time for a cold core is $(4 \times 10^9)/n$, i.e., less than 10^5 yr in a dense core. We can also express this lifetime as the time required for a species to arrive at a grain. In a gas with kinetic temperature of 10 K, for CO

$$\tau_{\text{ar}} = (n_i \sigma_{\text{d}} v)^{-1} \simeq 3 \left[\frac{10^4 \text{ cm}^{-3}}{n} \right] \left[\frac{1000 \text{ \AA}}{a} \right]^2 \text{ days,}$$

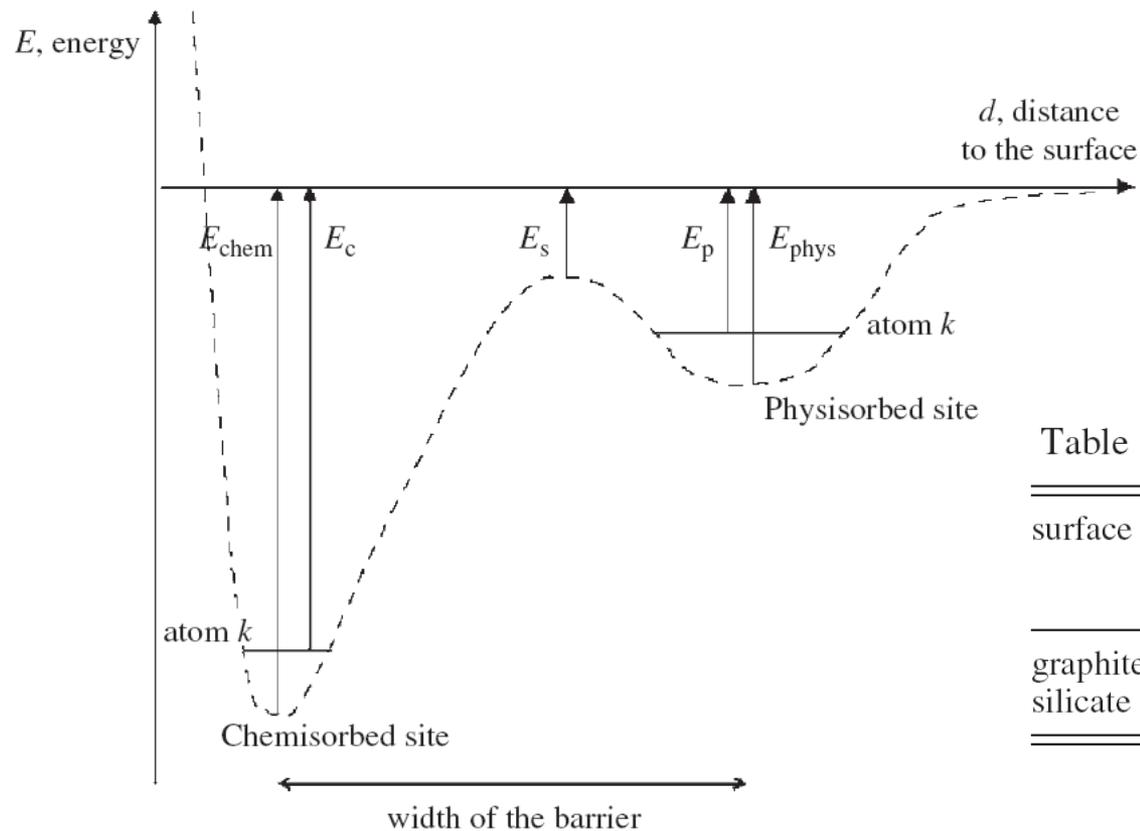


Table 4.12 H -surface interaction energies

surface	Energy(eV)	
	physisorbed	chemisorbed
graphite	0.06	~ 2.5
silicate	0.05	~ 2.5

Figure 4.2 The interaction between an adsorbate and a surface as a function of the distance to the surface. Two types of sites can be recognized: physisorbed sites due to van der Waals interaction (binding energy, E_{phys}) and chemisorbed sites involving shared electrons (binding energy, E_{chem}). The actual binding energies of a species, E_p and E_c , take the zero-point energy into account. The two types of sites are separated by a saddle point with energy, E_s .

The evaporation time is

$$\tau_{\text{ev}} = \nu_0^{-1} \exp(E_b/kT_d) \quad \mathbf{E_b = binding energy}$$

The evaporation time is very sensitive to the dust temperature T_d .

In PDRs, the main mechanism to release molecules from the grain mantles is photo-desorption. Assuming the mean interstellar UV field, the grains will remain clean of ices for

$$A_v < 4.1 + \ln \left[G_0 \left(\frac{Y_{\text{pd}}}{10^{-2}} \right) \left(\frac{10^4 \text{ cm}^{-3}}{n} \right) \right]$$

Table 4.14

Radical-radical surface reactions

reactants		products
H + O	→	OH
H + OH	→	H ₂ O
H + C	→	CH
H + CH	→	CH ₂
H + CH ₂	→	CH ₃
H + CH ₃	→	CH ₄
H + N	→	NH
H + NH	→	NH ₂
H + NH ₂	→	NH ₃
H + O ₂ H	→	H ₂ O ₂
H + NO	→	HNO
H + CN	→	HCN
H + CNO	→	HCNO
H + HCO	→	H ₂ CO
H + HCOO	→	HCOOH
H + CH ₃ O	→	CH ₃ OH
H + NCHO	→	NHCHO
H + NHCHO	→	NH ₂ CHO
H + CCHO	→	CHCHO
H + CHCHO	→	CH ₂ CHO
H + CH ₂ CHO	→	CH ₃ CHO
H + N ₂ H	→	N ₂ H ₂
O + O	→	O ₂
O + N	→	NO
O + C	→	CO
O + CN	→	OCN
O + HCO	→	HCOO
C + N	→	CN
C + HCO	→	CCHO
N + N	→	N ₂
N + NH	→	N ₂ H
N + HCO	→	NCHO

Other important concept is migration time. Migration time is the time to move from one position to another on the grain surface. When the migration time is lower than the evaporation time, surface reactions occur

Table 4.15 *Hydrogen reactions with activation barriers*

reactants		products	E_a (K)
H + CO	→	HCO	1000
H + H ₂ CO	→	CH ₃ O ^a	1000
H + O ₂	→	HO ₂	1200
H + H ₂ O ₂	→	H ₂ O + OH	1400
H + O ₃	→	O ₂ + OH	450
H + C ₂ H ₂	→	C ₂ H ₃	1250
H + C ₂ H ₄	→	C ₂ H ₅	1100
H + H ₂ S	→	SH + H ₂	860
H + N ₂ H ₂	→	N ₂ H + H ₂	650
H + N ₂ H ₄	→	N ₂ H ₃ + H ₂	650

^a Product species could also be CH₂OH.

Table 4.13 *The interaction of atoms and molecules with an H₂O surface*

species	E_b^a (K)	10 K		30 K	
		τ_{ev}^b (s)	τ_m^c (s)	τ_{ev}^b (s)	τ_m^c (s)
H	350	1.6 (3)	1 (-12)	1 (-7)	1 (-12)
H ₂	450	3 (7)	4 (-12)	3 (-6)	4 (-12)
C	800		1 (-2)	4 (-1)	2 (-9)
N	800		1 (-2)	4 (-1)	2 (-9)
O	800		1 (-2)	4 (-1)	2 (-9)
S	1100		1 (2)	8 (13)	4 (-8)
CO	1900		6 (12)		2 (-4)
N ₂	1700		1 (10)		2 (-5)
O ₂	1600		7 (8)		9 (-6)
CH ₄	2600				2 (-1)
H ₂ O	4000				2 (5)

^a Estimated binding energy on an H₂O surface.

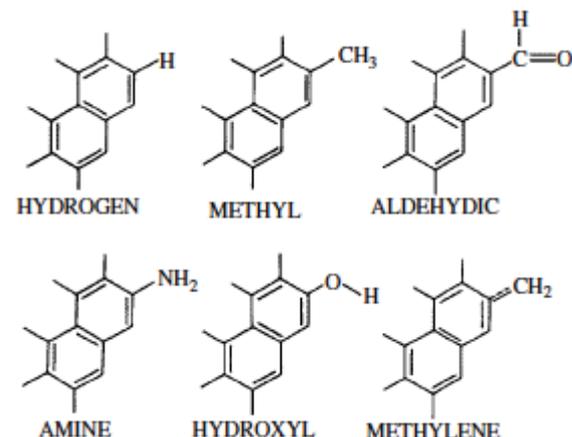
^b Evaporation time scale from an H₂O surface. No value given when it exceeds the molecular cloud lifetime.

^c Migration time scale on an H₂O surface. No value given when it exceeds the molecular cloud lifetime.

PAHs

Table 6.3 *Unimolecular dissociation*

Sidegroup ^a	Bond ^b	E_b (eV)	p_d^c
Hydrogen	PAH – H	4.47	10^{-10}
Methyl	PAHCH ₂ – H	3.69	10^{-2}
	PAH – CH ₃	4.0	10^{-4}
Ethyl	PAHCH ₂ – CH ₃	3.1	0.9
Hydroxyl	PAHO – H	3.69	10^{-2}
	PAH – OH	4.5	10^{-10}
Amine	PAHNH – H	3.47	10^{-1}
	PAH – NH ₂	4.0	10^{-4}
Acetylene	PAH' – C ₂ H ₂ ^d	8.0	negligible



^a Structural formulae of these sidegroups are illustrated in Fig. 6.11.

^b Bond denoted by –.

^c Estimated photodissociation probability for a 50 carbon atom PAH, assuming $E = 10$ eV and $k_{\text{IR}} = 1 \text{ s}^{-1}$ (cf. Eq. 6.82).

^d Loss of acetylene group from PAH skeleton.

Incorporation of stochastic chemistry on dust grains in the Meudon PDR code using moment equations

I. Application to the formation of H₂ and HD

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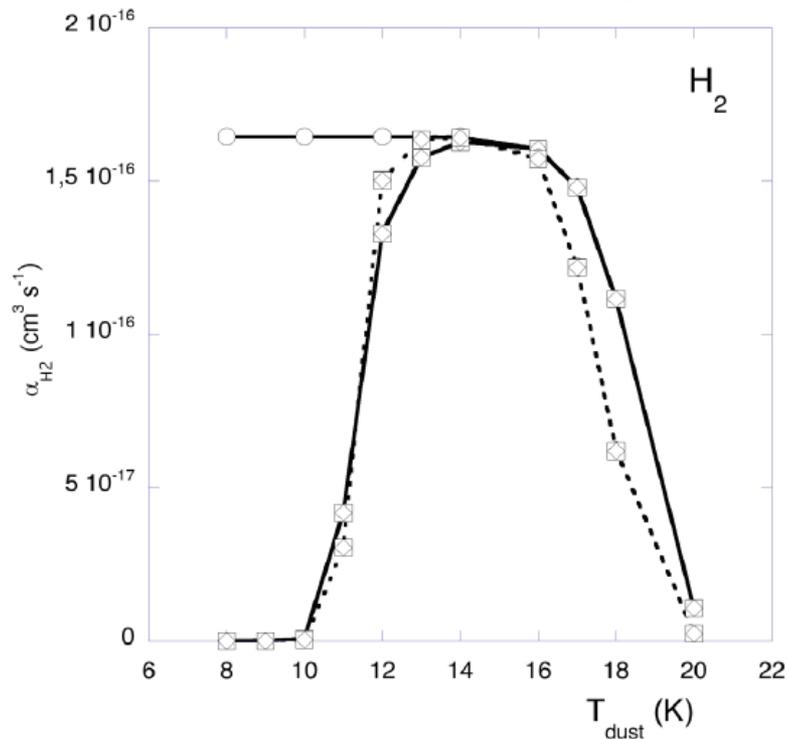


Fig. 1. The formation rate $\alpha(\text{H}_2)$ (cm³s⁻¹) of H₂ molecules on grains, obtained from the rate equations (solid line) and from the moment equations (dashed lines), where the grain sizes follow the MRN size distribution. Results obtained from the three models of Table 3 are presented: Model A which includes no rejection (open circles), model B which includes rejection only due to adsorbed H atoms (open squares), and model C that includes rejection caused by both adsorbed H and adsorbed D (open diamonds).

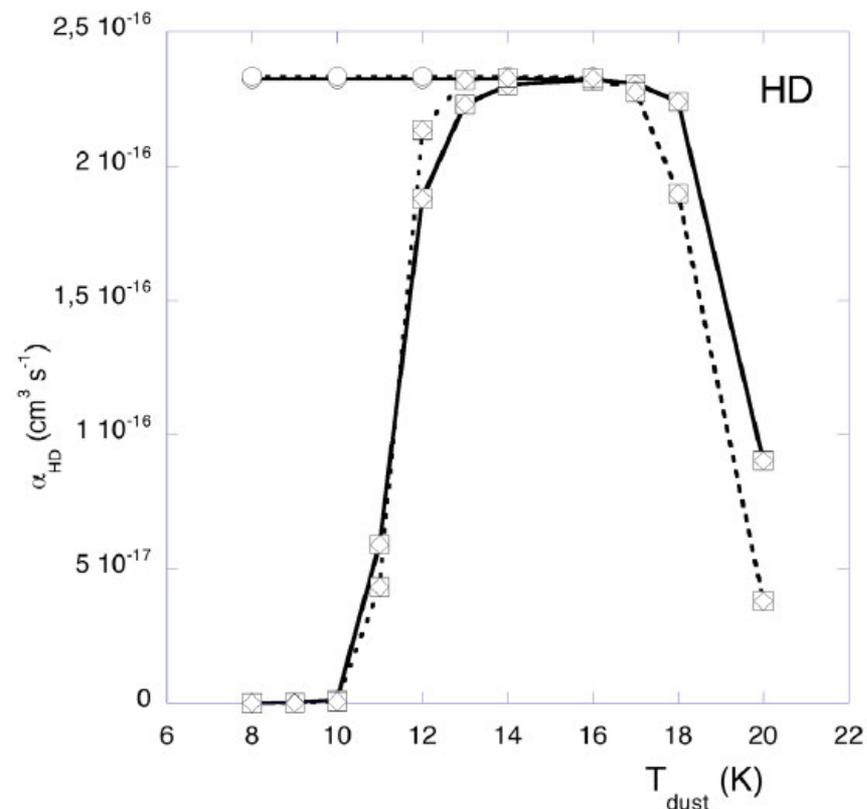


Fig. 2. The formation rate $\alpha(\text{HD})$ (cm³s⁻¹) of HD molecules on grains, obtained from the rate equations and the moment equations, where the grain sizes follow the MRN size distribution. Same conventions as in Fig. 1.