

**Molecules in the Cosmos :**  
**CHEMISTRY IN INTERSTELLAR**  
**CLOUDS**

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# THE NATURE OF THE PROBLEM OF INTERSTELLAR CHEMISTRY

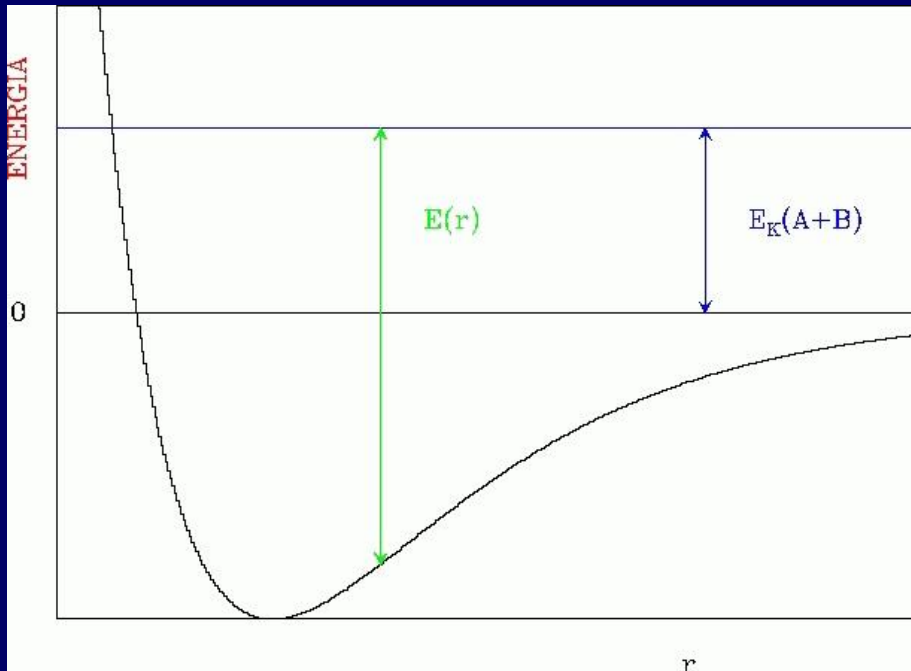
- \* **Low Temperatures**
- \* **Low Volume Density**
- \* **The Formation of H<sub>2</sub> in gas phase not possible !!!**

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 the terrestrial laboratories we can use catalizers or a third body, in the space three body collisions are very very uncommon and the only possible catalizers are dust grains.

Let us consider the reaction



It may happen that  $AB^*$  interacts with a third body (catalizer) 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  $k_3 \approx 10^{-11} \text{ s}^{-1}$ , and

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

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 large. For all other molecules we could consider the optimal case 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

$$\frac{dn(\text{BH})}{dt} \approx 10^{-36} n^3(\text{H}) \text{ cm}^{-3} \text{ s}^{-1} \quad \text{B} \in (\text{C},\text{N},\text{O})$$

# THE COMPLEXITY OF THE CHEMISTRY IN THE INTERSTELLAR MEDIUM

- The structure of molecular clouds is rather complex with strong gradients between different regions of the same cloud.



ESO PR Photo 27a-99 (30 April 1999)

The "Black Cloud" B68  
(VLT ANTU + FORS1)

© European Southern Observatory



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





**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.**

**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<sup>+</sup>. The observed clouds are badly protected against the UV galactic field.**
- \* **Between 1960 and 1970 we could consider that a new branch of Astrophysics was born : Molecular Astrophysical. Several molecular species were detected using radioastronomical techniques : OH, NH<sub>3</sub> y H<sub>2</sub>CO. These molecules were detected in dense, heavily obscured, molecular clouds.**

- \* In the 1970-1980 period several observations in the UV from space platforms had shown the presence of H<sub>2</sub>, 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<sub>3</sub>OH, SiO, CS, HCN, HNC, SiS, CN, HCO<sup>+</sup>, NNH<sup>+</sup>, ...**
- \* These 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 had been 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 was starting its scientific operation phase. 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 near 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.**

**En 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 UIBs are detected in all lines of sight and also in external galaxies.**

**Recently (2001), infrared observations with ISO have shown the presence of polyynes ( $\text{C}_n\text{H}_2$ ) and of benzene ( $\text{C}_6\text{H}_6$ ) in proto-planetary nebula.**

**How these molecules have been formed ?**

**How it is possible to have a such important chemical complexity when the formation of  $H_2$  is not obvious at all?**

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

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

**How  $H_2$  is formed ?**

## 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.



## Some early papers on the formation of H<sub>2</sub> in the 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

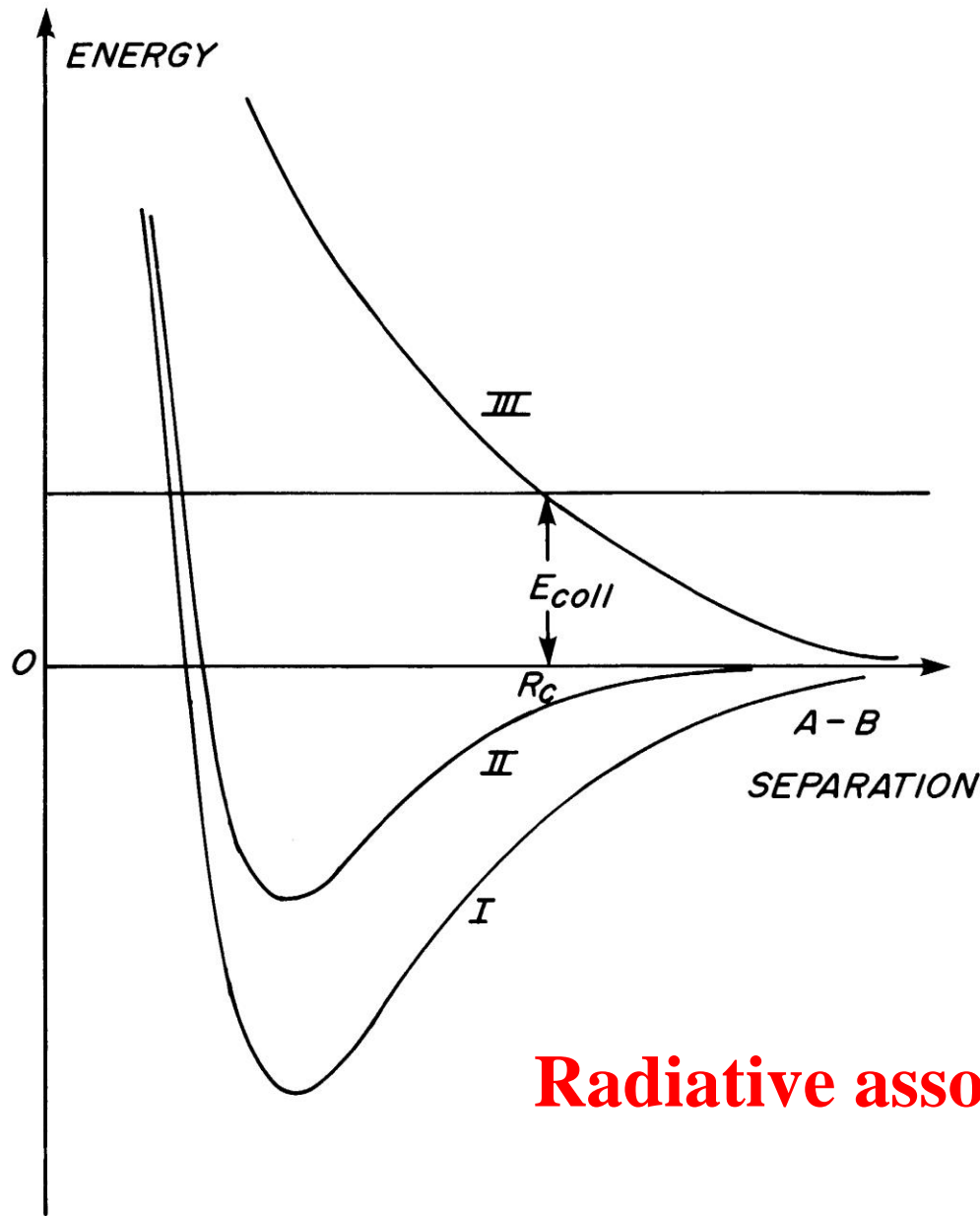
\* Takahashi et al., 1999, ApJ, 520, 724

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

**Key chemical processes leading to the formation and  
destruction of gas phase  
molecules in interstellar clouds**



Collision rate  $10^{-11} \text{ s}^{-1}$

Radiative time  $10^{-8} \text{ s}^{-1}$

Collision time  $10^{-14} \text{ s}^{-1}$

Probability  $10^{-6} \text{ s}^{-1}$

Rate = Collision rate x  
Probability =  
 $10^{-17} \text{ s}^{-1}$

**Radiative association (too 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  $E_{\text{coll}}$ .

Let us assume that  $\text{H}_2$  has been formed on the surface of the dust grains. How to form other molecular species ?



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

For example, let us consider the reaction

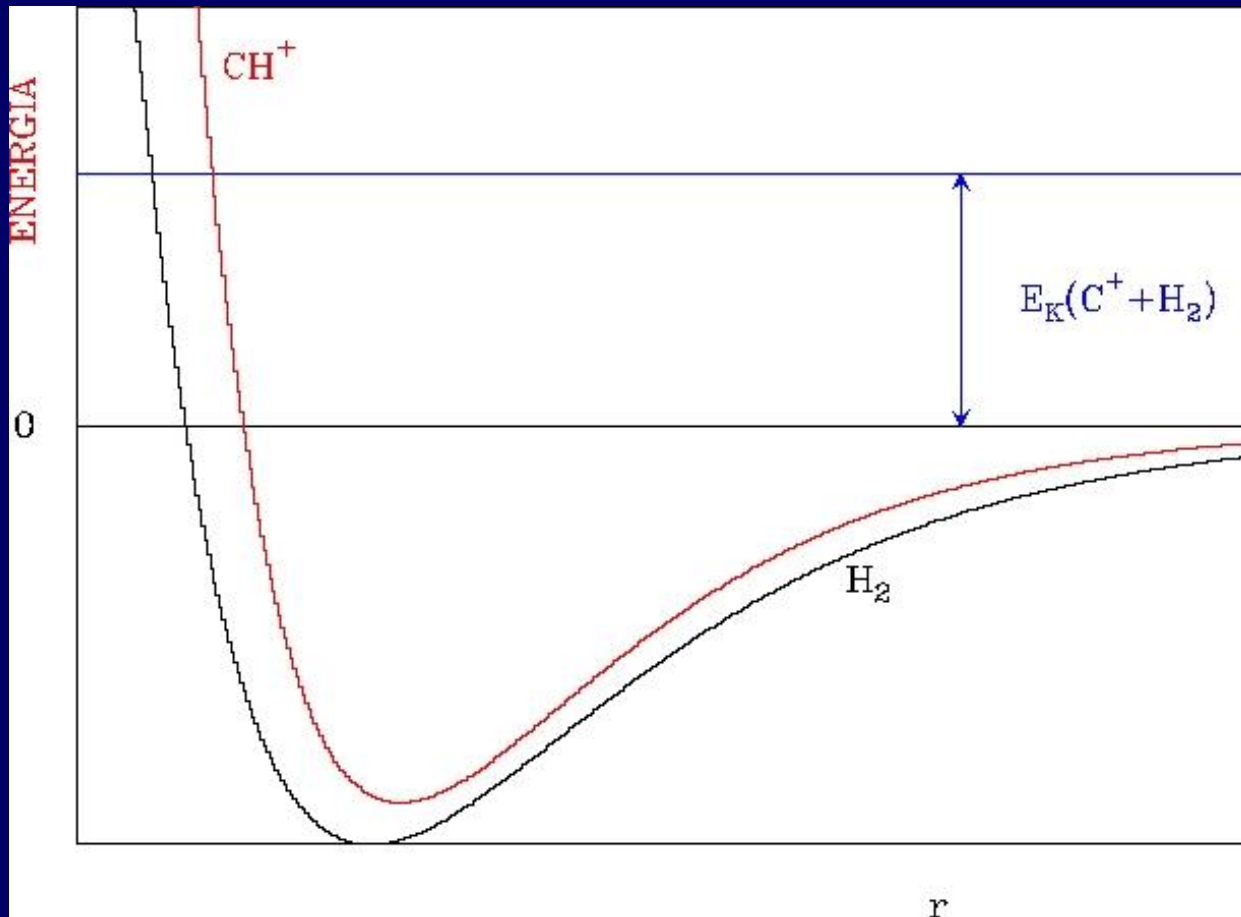


Remember all reactions in ISM have to be bimolecular !!

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



The dissociation energy of  $\text{H}_2$  is 4.48 eV and that of  $\text{CH}^+$  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  $E_K > 0.39 \text{ eV}$

# DISOCIATION ENERGIES OF A FEW MOLECULES (eV)

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



## The reaction



Has also little 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  $0.61 \text{ eV}$

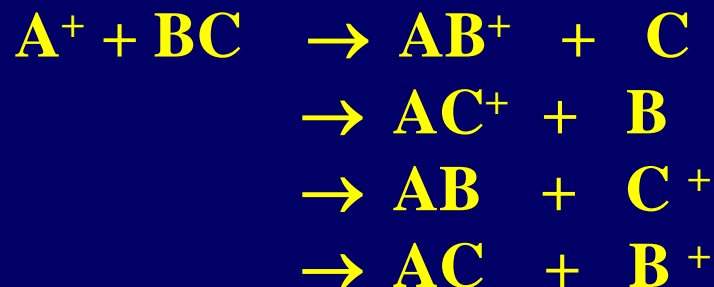
The reaction rate has been measured in the laboratory and is rather fast,  $k \approx 1.6 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . But, how we form  $\text{O}^+$  in a dark cloud protected against the UV field ?

As the ionization potentials of H and O are nearly identical, the process of charge exchange



could occur efficiently. But, how we form  $\text{H}^+$  ?

And, in any case, are fast enough all the ion-neutral reactions?



¿? ¿? ¿?

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

$$K n(A^+) n(BC)$$

**¿K? ¿depends on the temperature?**

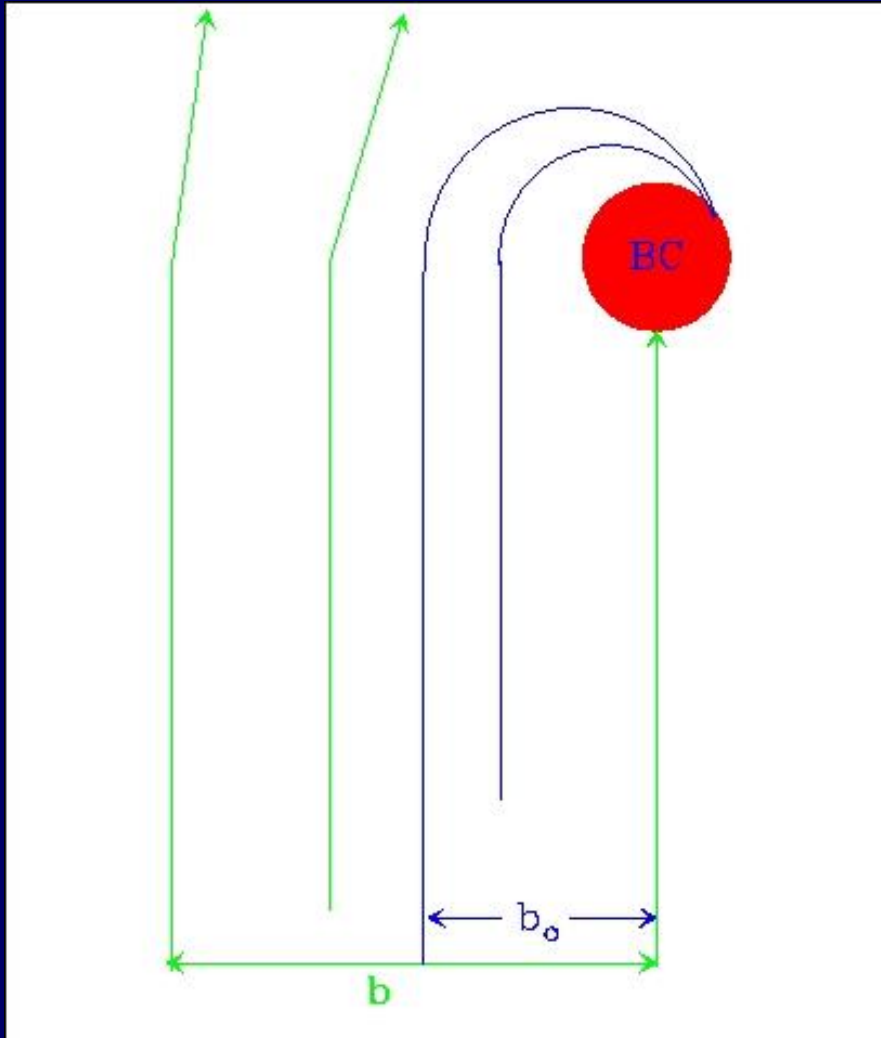
**Several ion-neutral reactions have been measured in the laboratory. For most of these reactions (exothermic of course),  $K$  does not depend on the temperature and is of the order of  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .**

**Why?**

**Let us consider the classical treatment of the problem. Let us Assume that  $BC$  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  $\alpha$  is the polarizability of the molecule BC.



For impact parameters  $>$  a critical value,  $b_0$ , 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 allow to reorder the orbitals and to remove any problem related to activation barriers. In the case of an impact parameter equal to  $b_0$  the particle A remains moving around BC.**

**The collision cross section is  $b_0^2$  and the reaction rate is given by**

$$K = \pi b_0^2 v = 2 \pi (\alpha / \mu)^{1/2}$$

**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”**

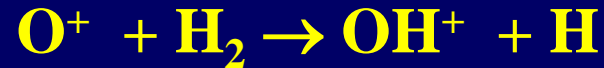
## POLARIZABILITY OF ATOMS AND MOLECULES ( $10^{-24} \text{ cm}^3$ )

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

*$\alpha$  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 path for the reaction



is slightly endothermic

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

and it is much less probable than the formation of  $\text{OH}^+$

**However, this simple theory does not work always fine  
(as it could be expected)**



**(highly exothermic)**

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

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

**Or**



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

**Experimental value**  $1.0 \cdot 10^{-13} \text{ cm}^3\text{s}^{-1}$  !!!

**Why?**

## The reactions



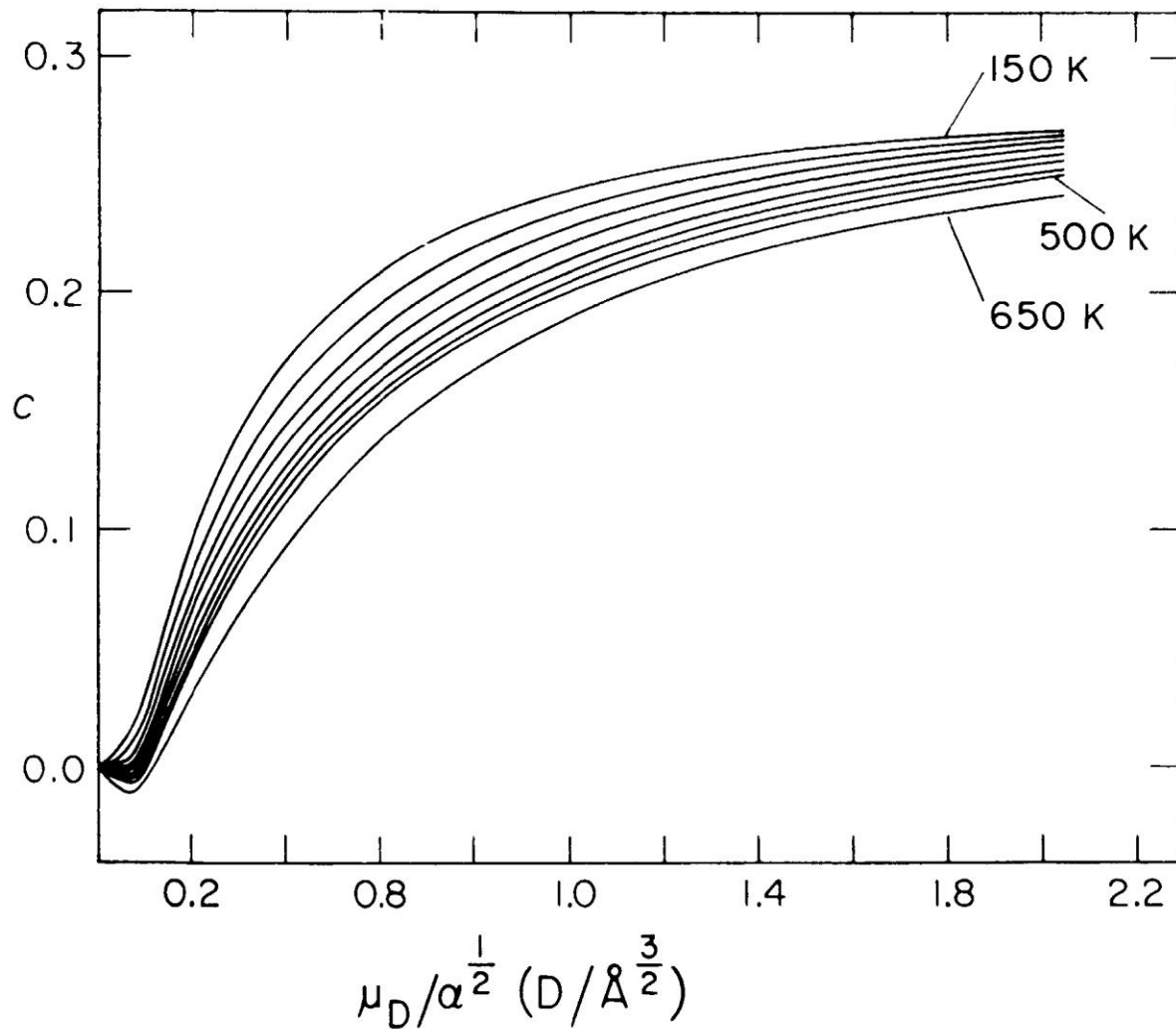
Are much faster (charge exchange)

What happens if the molecules are polar ?

A classical treatment of the problem (ADO = Averaged Dipole Orientations) of the interaction of two dipoles gives a result

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

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



**Fig. 3.2** Plot of the constant  $c$  against  $\mu_D / \alpha^2$  for temperatures of 150–500 K at intervals of 50 K, and for a temperature of 650 K. (T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 1975, **17**, 211.)

**Now  $K$  does depend on the temperature**

**The contributions of the ADO theory to the Langevin approximation are of the order of 30-50% (depending on the temperature)**

**It is possible to estimate many reaction rates. If we know which are the “key” reactions in the chemistry of ISM then we could model the chemistry and predict molecular abundances.**

**But :: A low temperatures these simple theories perhaps are very poor approximations (low velocities and hence large interaction times between the particles.)**

| 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 is the key process in the chemistry of the ISM?

**H<sub>2</sub> is formed in the dust grains**

**But, how we do to ionize atoms and molecules inside molecular clouds ?**

**With cosmic rays !!!**



**and H<sub>3</sub><sup>+</sup> is the key molecule !!!! Typical rates are 10<sup>-17</sup> s<sup>-1</sup>**

**H<sub>3</sub><sup>+</sup> does not react with H<sub>2</sub> !!!**

**He<sup>+</sup> does not react with H<sub>2</sub> !!!**

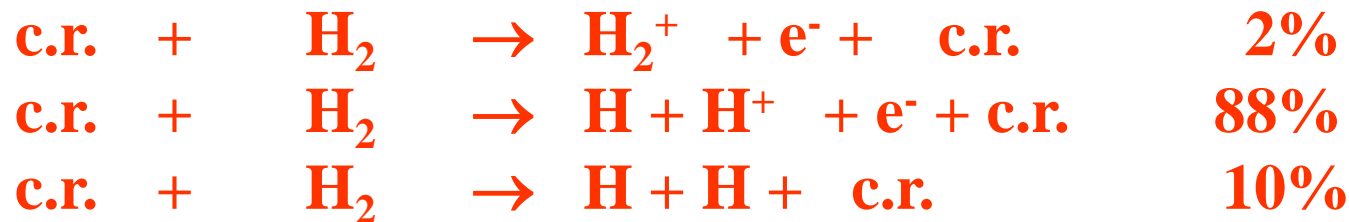
**He<sup>+</sup> ionization source for other species**

# THE FORMATION AND DEPLETION OF MOLECULES IN DENSE INTERSTELLAR CLOUDS\*

ERIC HERBST† AND WILLIAM KLEMPERER

THE ASTROPHYSICAL JOURNAL, 185:505-533, 1973 October 15

Ionization is produced in dense clouds by cosmic rays sufficiently energetic to penetrate the interior. Since  $\text{H}_2$  and He are the dominant species, the major initial ions produced are  $\text{H}_2^+$ ,  $\text{H}^+$  (Solomon and Werner 1971), and  $\text{He}^+$ . The exothermic reaction  $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$  is rapid (Bowers, Elleman, and King 1969), but the highly exothermic reaction of  $\text{He}^+$  with  $\text{H}_2$  does not occur for kinetic reasons (Fehsenfeld *et al.* 1966*b*). Thus  $\text{He}^+$ , unlike  $\text{H}_2^+$ , will exist in appreciable concentration. Having an electron affinity of 24 eV,  $\text{He}^+$  ionizes most neutral species other than  $\text{H}_2$  rapidly. The reactions of the primal ions— $\text{H}^+$ ,  $\text{H}_3^+$ ,  $\text{He}^+$ —with abundant neutral species such as CO, O, N,  $\text{O}_2$ , and  $\text{N}_2$  produce secondary ions such as  $\text{C}^+$ ,  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{N}_2^+$ ,  $\text{O}_2^+$ ,  $\text{HCO}^+$ , and  $\text{HN}_2^+$ .



*All pictures and theory from Duley and Williams, "Interstellar Chemistry"*



**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 protonic affinity of the reactants.**

**H<sub>2</sub> as a low protonic affinity and the reactions of H<sub>3</sub><sup>+</sup> with neutral species (B) will always produce BH<sup>+</sup>**



**If the reaction is exothermic the main channel for the reaction is the transfer of the proton**

# PROTONIC AFFINITIES

|                |      |                |      |
|----------------|------|----------------|------|
| H              | 2.69 | O <sub>2</sub> | 4.34 |
| H <sub>2</sub> | 4.34 | CO             | 6.20 |
| He             | 1.82 | NO             | 4.99 |
| O              | 5.03 | C <sub>2</sub> | 7.20 |
| C              | 6.46 | CN             | 4.99 |
| N              | 4.21 | N <sub>2</sub> | 5.03 |
|                |      | CS             | 7.57 |

**H<sub>3</sub><sup>+</sup> could transfer protons to all atoms (except N, H y He) and to most molecules**

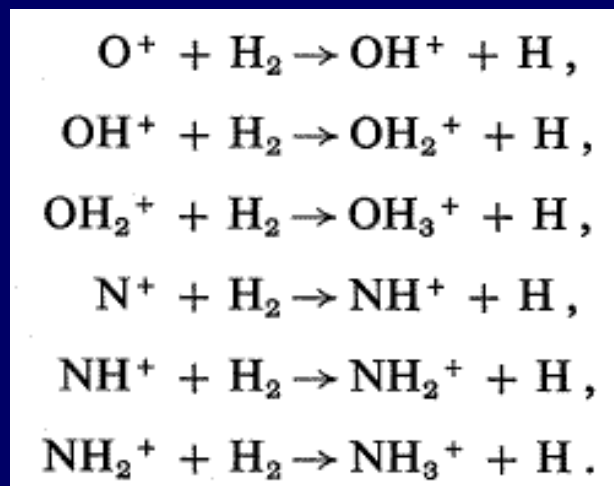
TABLE 1  
COSMIC ABUNDANCES

| Element | Relative Abundance<br>(by number)* |
|---------|------------------------------------|
| H.....  | 1                                  |
| He..... | 0.14†                              |
| C.....  | 3.75 × 10 <sup>-4</sup>            |
| N.....  | 8.7 × 10 <sup>-5</sup>             |
| O.....  | 4.4 × 10 <sup>-4</sup>             |
| Ne..... | 2.6 × 10 <sup>-5</sup>             |
| Si..... | 3.2 × 10 <sup>-5</sup>             |
| S.....  | 1.4 × 10 <sup>-5</sup>             |
| Fe..... | 3.2 × 10 <sup>-5</sup>             |

# ABSTRACTION OF THE HYDROGEN ATOM



Classic theory is not working 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



It is not very efficient although some of them could be important for the ISM chemistry



## CONDENSATION REACTIONS

**New bonds between heavy atoms are created**



**And they occur often through the removal of H or H<sub>2</sub>. They have often very efficient alternate channels**



**(proton transfer)**

# CHARGE TRANSFER REACTIONS

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



**Example**



**The reactions**



**could only be important in HII regions**

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 <b>1.2</b>                           |
| 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 <b>8.2</b>                           |
| 61. | $\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{H} \dots\dots\dots$                 | 1.0 <b>5.2</b>                           |
| 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 <b>0.85</b>                          |
| 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**



**This mechanism could 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  $10^{-12} \text{ cm}^3 \text{ s}^{-1}$**



## **Dissociative recombination**

**Molecular positive ions recombine with electrons to dissociate into neutral species**



**The reaction rates have a dependency on T as  $T^{-1/2}$**

**Typical values for the dissociative recombination rate are  $10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1}$**

**Hence, these reactions are very important in ISM.**

**Table 3.8** Some measured values of  $k_{\text{DR}}$ .

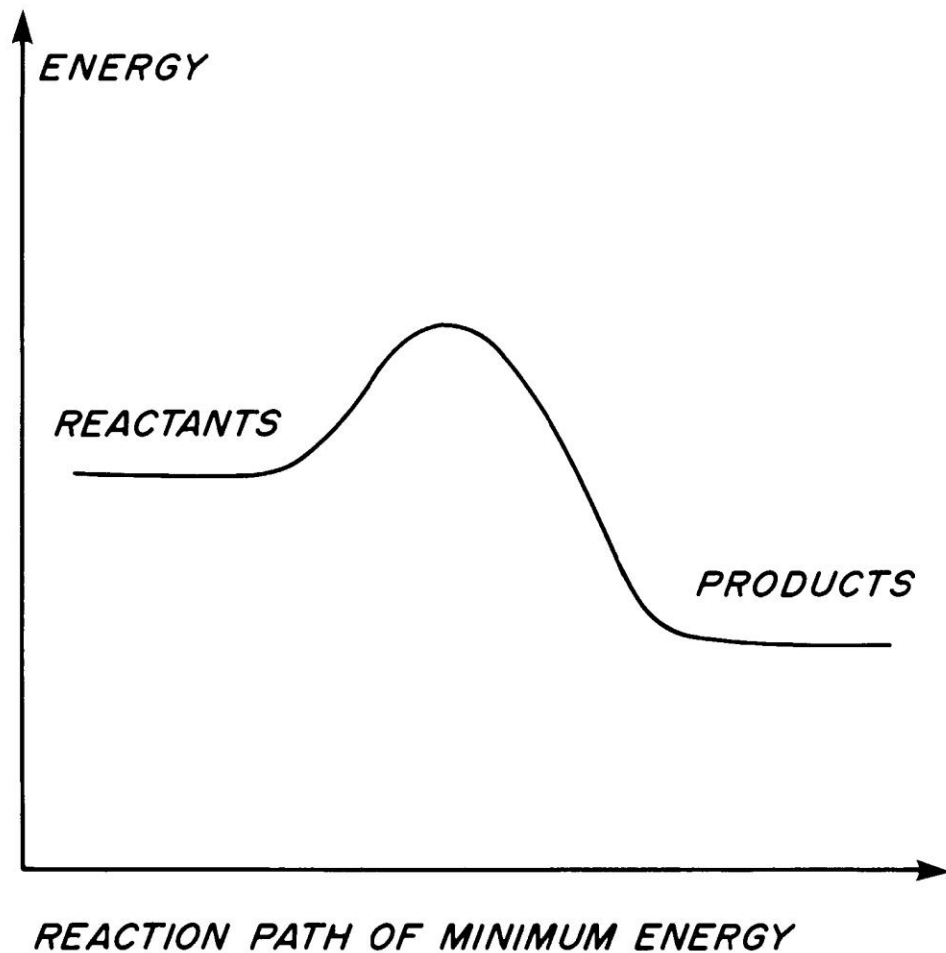
| Species          | Rate coefficient ( $\text{cm}^3 \text{s}^{-1}$ ) |                      | Species                  | Rate coefficient ( $\text{cm}^3 \text{s}^{-1}$ ) |                      |
|------------------|--|----------------------|--------------------------|--|----------------------|
|                  | 100 K  | 40 K                 |                          | 100 K  | 40 K                 |
| <i>Diatomics</i> |  |                      | <i>Polyatomics</i>       |  |                      |
| $\text{CH}^+$    | $3.3 \times 10^{-7}$                             | $5.2 \times 10^{-7}$ | $\text{H}_3^+$           | $7.2 \times 10^{-7}$                             | $1.1 \times 10^{-6}$ |
| $\text{NH}^+$    | $1.9 \times 10^{-7}$                             | $3.0 \times 10^{-7}$ | $\text{H}_2\text{O}^+$   | $1.3 \times 10^{-6}$                             | $2.1 \times 10^{-6}$ |
| $\text{OH}^+$    | $1.4 \times 10^{-7}$                             | $2.2 \times 10^{-7}$ | $\text{H}_3\text{O}^+$   | $1.1 \times 10^{-6}$                             | $1.7 \times 10^{-6}$ |
| $\text{C}_2^+$   | $1.0 \times 10^{-6}$                             | $1.6 \times 10^{-6}$ | $\text{CH}_2^+$          | $8.7 \times 10^{-7}$                             | $1.4 \times 10^{-6}$ |
| $\text{N}_2^+$   | $6.2 \times 10^{-7}$                             | $9.8 \times 10^{-7}$ | $\text{CH}_3^+$          | $1.2 \times 10^{-6}$                             | $1.9 \times 10^{-6}$ |
| $\text{O}_2^+$   | $3.3 \times 10^{-7}$                             | $5.2 \times 10^{-7}$ | $\text{CH}_4^+$          | $1.3 \times 10^{-6}$                             | $2.1 \times 10^{-6}$ |
| $\text{NO}^+$    | $4.1 \times 10^{-7}$                             | $6.5 \times 10^{-7}$ | $\text{CH}_5^+$          | $1.3 \times 10^{-6}$                             | $2.1 \times 10^{-6}$ |
|                  |  |                      | $\text{C}_2\text{H}^+$   | $1.0 \times 10^{-6}$                             | $1.6 \times 10^{-6}$ |
|                  |  |                      | $\text{C}_2\text{H}_2^+$ | $1.0 \times 10^{-6}$                             | $1.6 \times 10^{-6}$ |
|                  |  |                      | $\text{C}_2\text{H}_3^+$ | $1.6 \times 10^{-6}$                             | $2.5 \times 10^{-6}$ |
|                  |  |                      | $\text{N}_2\text{H}^+$   | $1.5 \times 10^{-6}$                             | $2.4 \times 10^{-6}$ |

## Neutral exchanges



Strong temperature dependence has been found for many of these reactions ( $K = A e^{-E/T}$ ).

|  | A(cm <sup>3</sup> s <sup>-1</sup> ) | E(K) |
|--|-------------------------------------|------|
| H + H <sub>2</sub> CO = H <sub>2</sub> + HCO | 2.7 10 <sup>-11</sup>               | 1300 |
| H + H <sub>2</sub> S = H <sub>2</sub> + SH   | 1.3 10 <sup>-11</sup>               | 860  |
| H + O <sub>2</sub> = OH + O                  | 3.7 10 <sup>-10</sup>               | 8500 |
| O + H <sub>2</sub> = OH + H                  | 1.0 10 <sup>-11</sup>               | 5700 |
| O + H <sub>2</sub> S = OH + SH               | 6.6 10 <sup>-13</sup>               | 900  |
| OH + CO = H + CO <sub>2</sub>                | 5.1 10 <sup>-13</sup>               | 300  |



**Fig. 3.6** A diagram indicating the variation in the potential energy along the path of minimum energy in an exothermic reaction. The barrier height gives the activation energy.

# Photodissociation

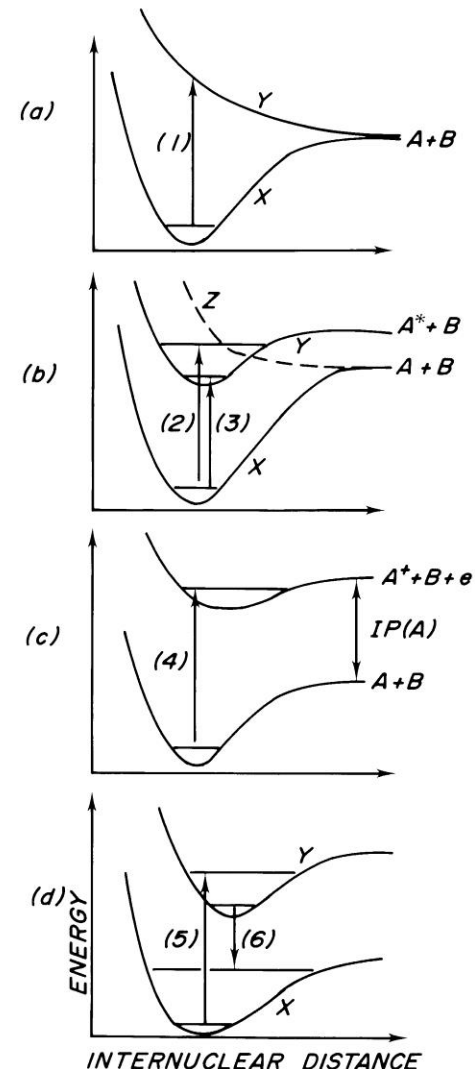
*The main path to destroy molecules in the diffuse ISM is via photodissociation*

*What we need ?*

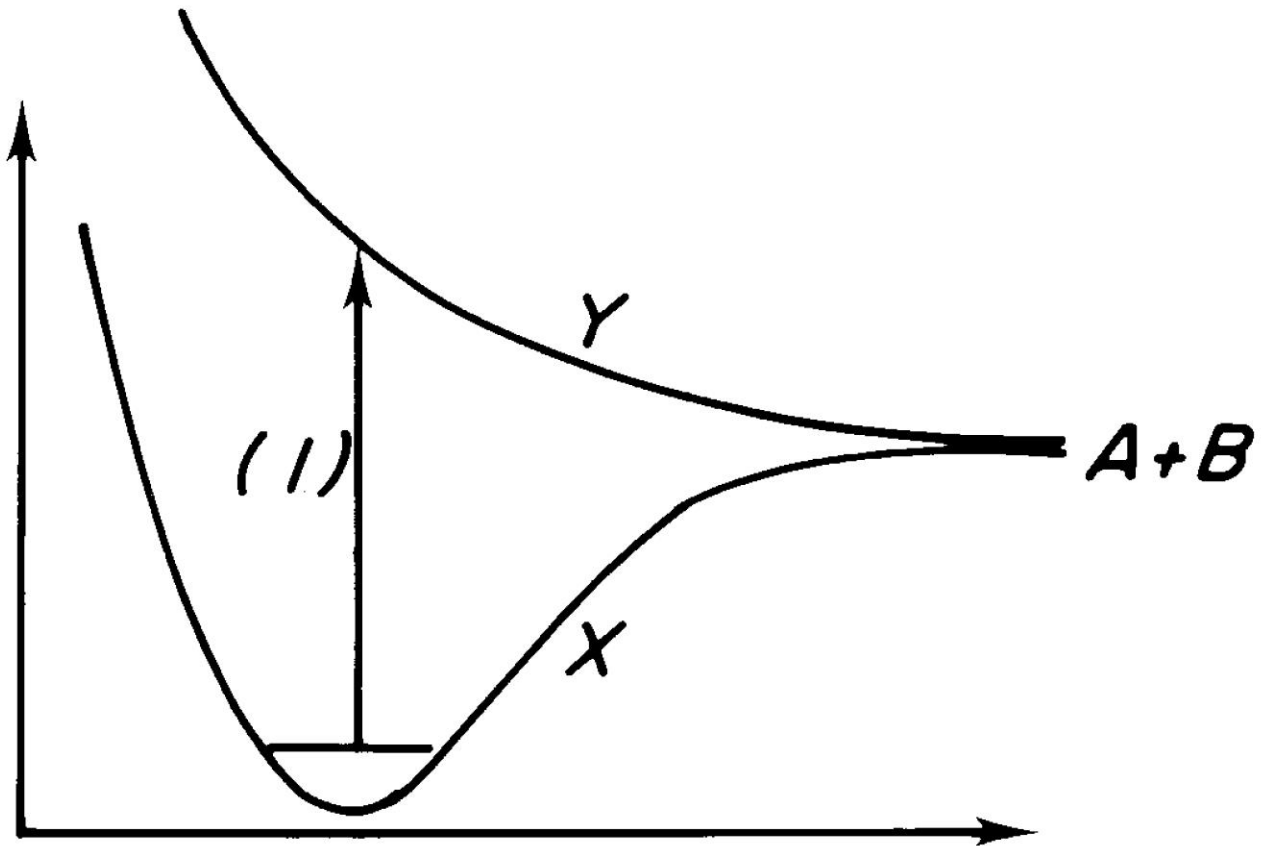
*1) The electronic, vibrational and rotational levels of the molecule*

*2) The radiation field*

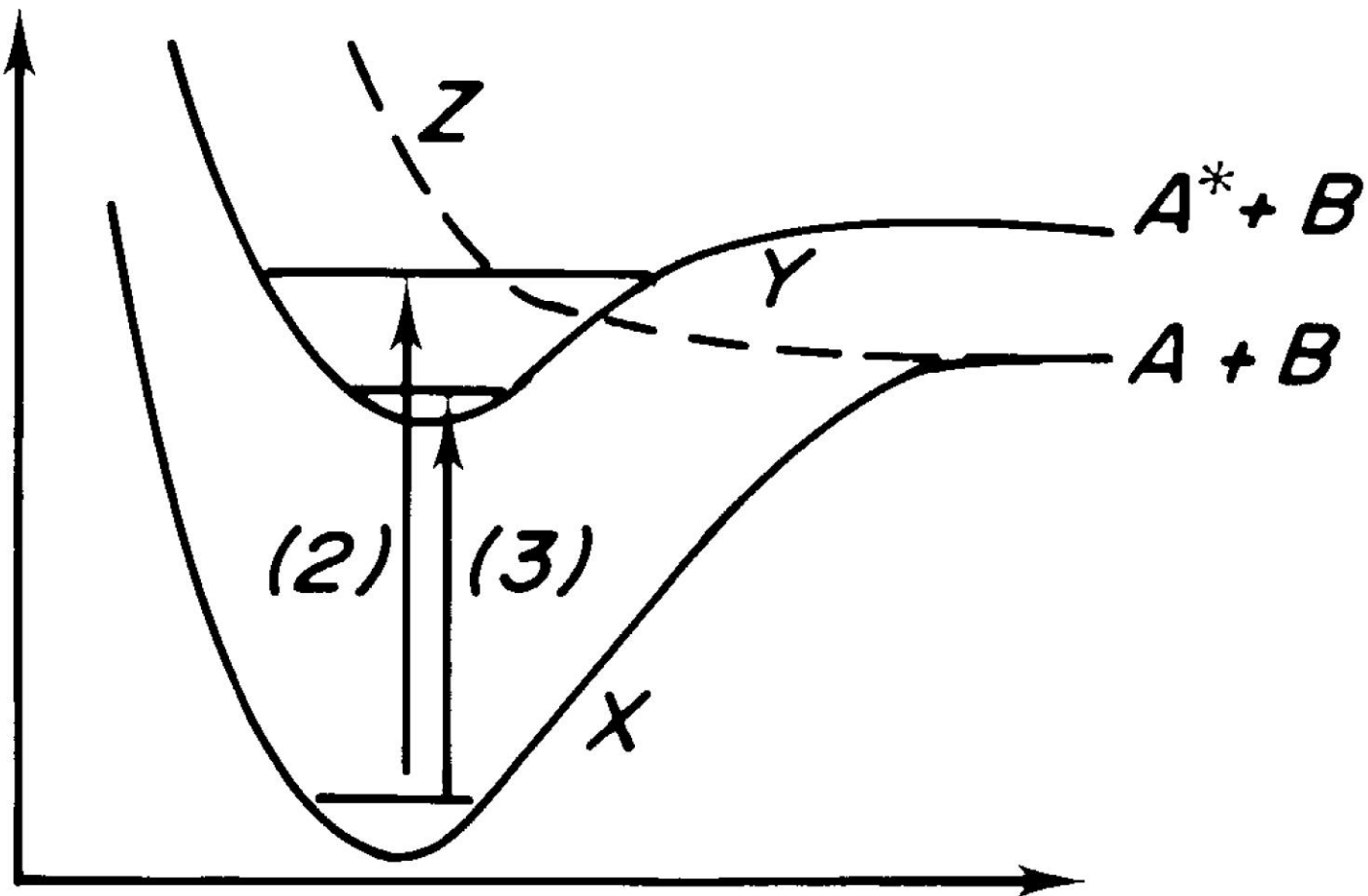
*Hence, photodissociation rates will depend on the object under study*



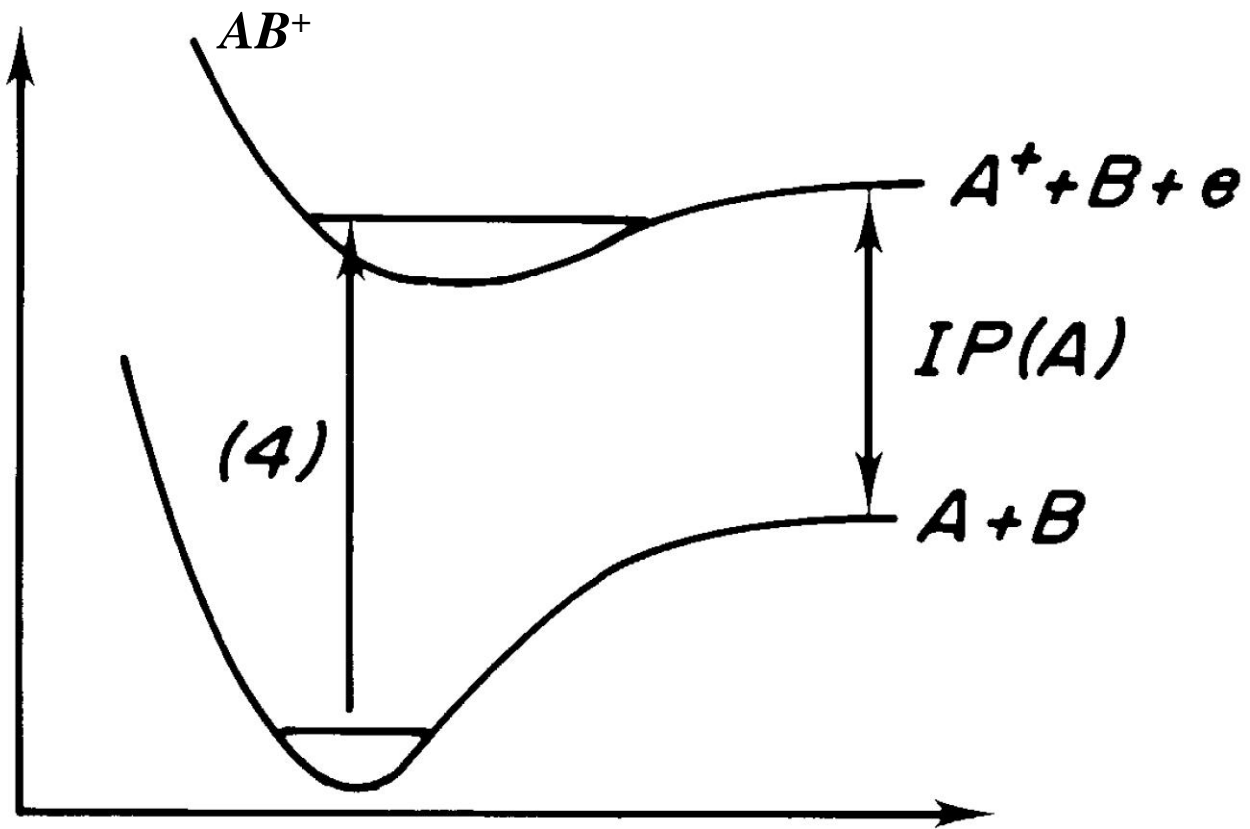
**Fig. 4.1** Potential energy curves and transitions illustrating (a) photodissociation, (b) photo-predissociation, (c) photoionization, and (d) dissociation via fluorescent emission.



**Direct Photodissociation**

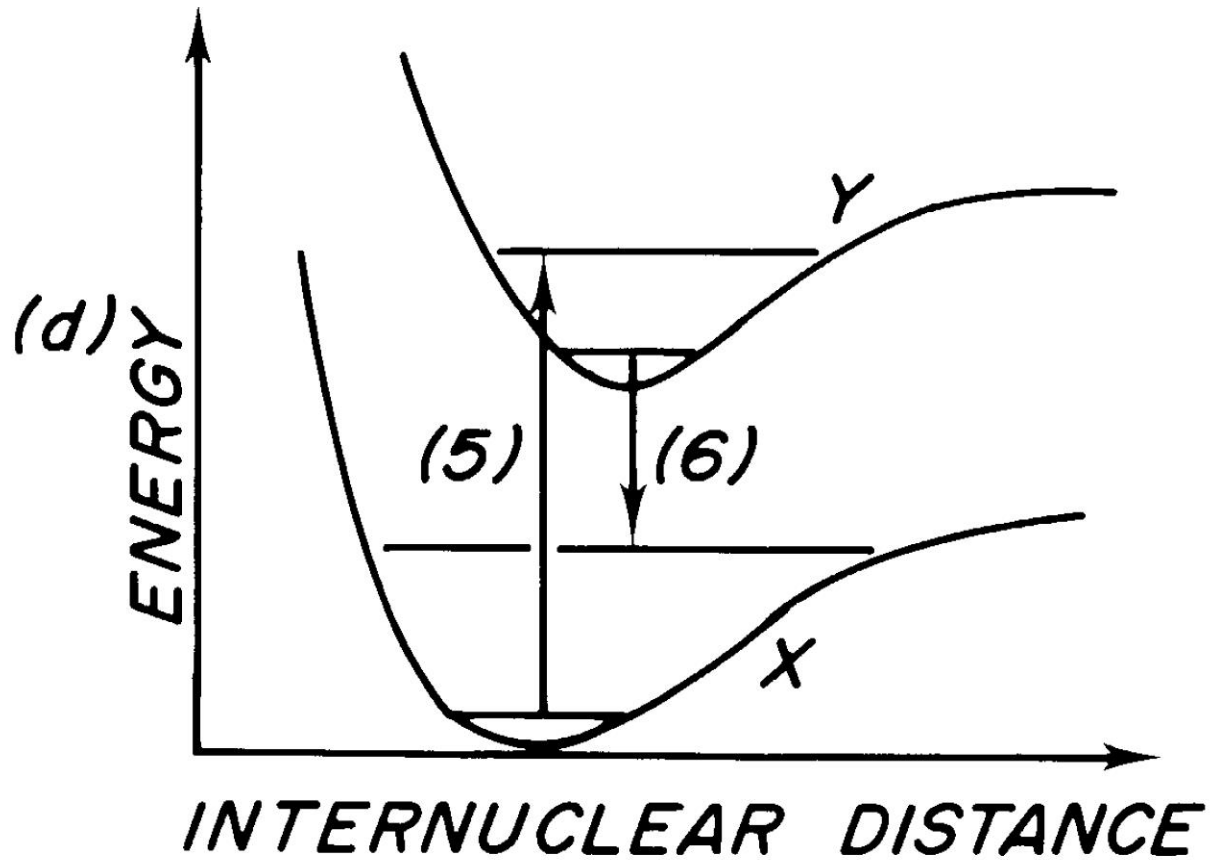


**Photo-Predissociation**

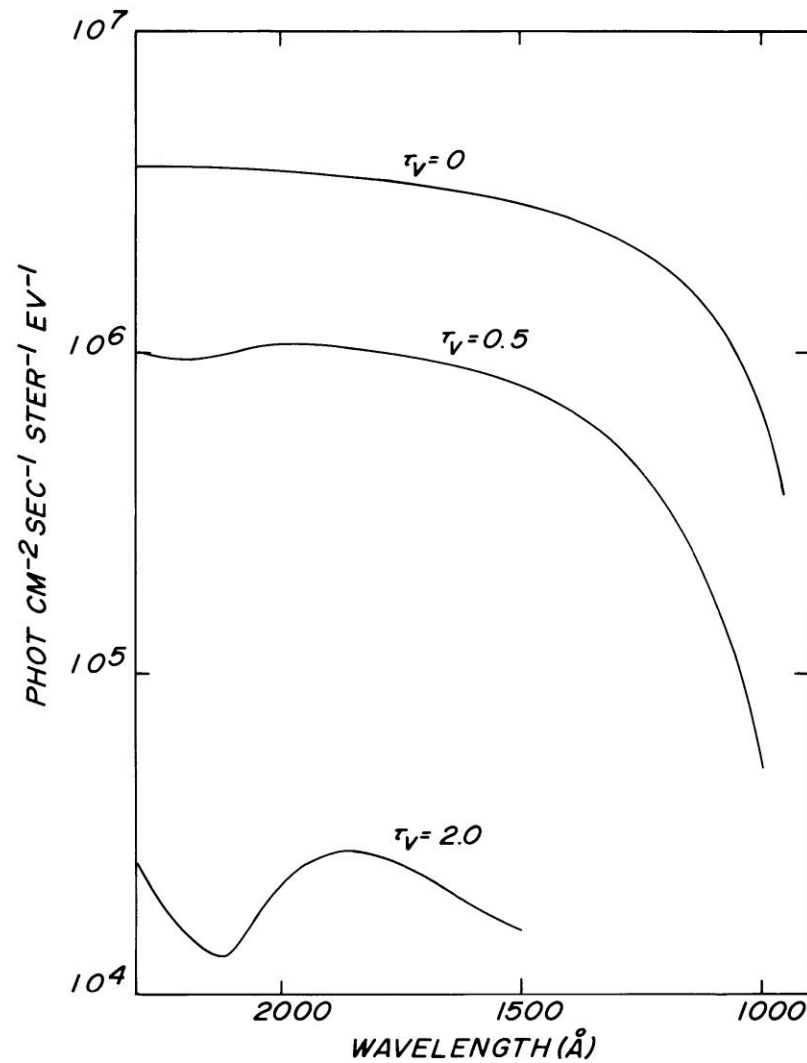


**Photoionization**





**Dissociation via fluorescent emission**



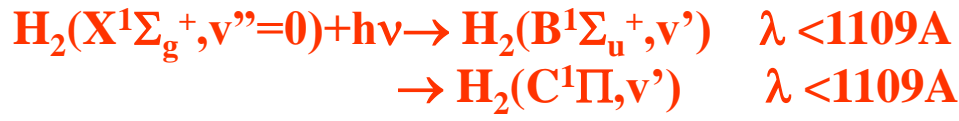
**Fig. 4.4** The interstellar radiation flux  $F(E)$  photons  $\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1} \text{ster}^{-1}$  in unobscured regions of the interstellar medium, in a typical diffuse cloud with  $\tau_V \approx 0.5$ , and in a denser cloud with  $\tau_V \approx 2$ .

### Interstellar radiation flux, $F(E)$

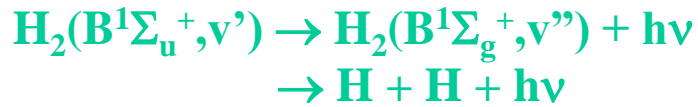
$$F(E) = 1.658 \cdot 10^6 E - 2.152 \cdot 10^5 E^2 + 6.919 \cdot 10^3 E^3 \text{ photons cm}^{-2} \text{ s}^{-1} \text{ ster}^{-1} \text{ eV}^{-1}$$

**Table 4.1** Dissociation rates,  $\beta_0$ , and  $\alpha$  [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.)

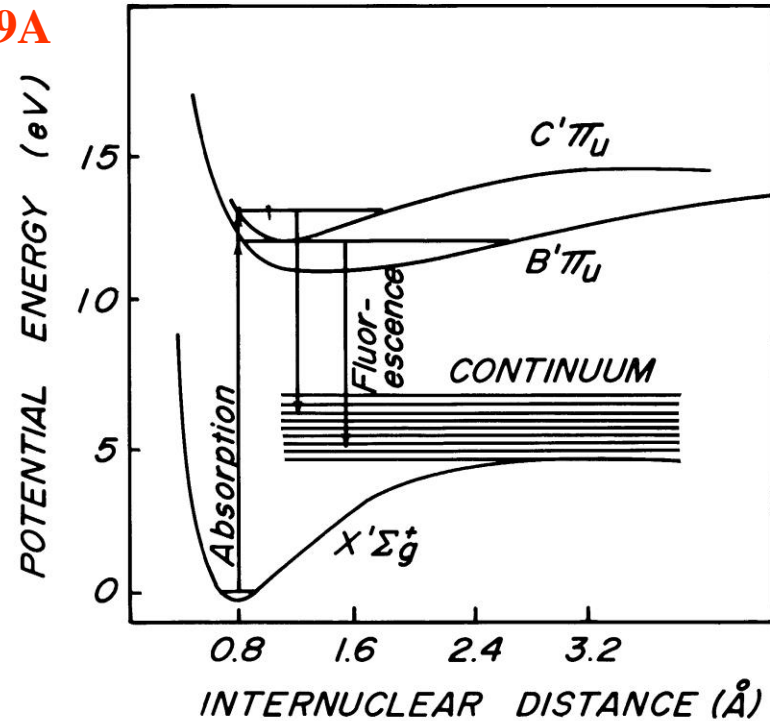
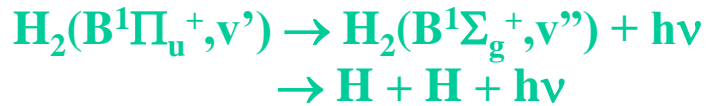
| Molecule       | $\beta_0$ (s <sup>-1</sup> ) | $\alpha$ | Molecule                     | $\beta_0$ (s <sup>-1</sup> ) | $\alpha$ |
|----------------|------------------------------|----------|------------------------------|------------------------------|----------|
| H <sub>2</sub> | $5 \times 10^{-11}$          | —        | HCN                          | $1 \times 10^{-10}$          | 1.8      |
| HD             | $5 \times 10^{-11}$          | —        | HCO                          | $8.8 \times 10^{-10}$        | 1.6      |
| CH             | $1.4 \times 10^{-10}$        | 1.5      | H <sub>2</sub> CO            | $8.8 \times 10^{-10}$        | 1.6      |
| CO             | $5 \times 10^{-12}$          | 3.0      | NH <sub>3</sub>              | $5.5 \times 10^{-10}$        | 2.0      |
| CN             | $5 \times 10^{-11}$          | 1.7      | H <sub>2</sub> O             | $3.2 \times 10^{-10}$        | 1.7      |
|                |                              |          | CH <sub>3</sub> <sup>+</sup> | $2 \times 10^{-9}$           | 1.7      |



There is not allowed electric dipole  
Transitions to repulsive electronic  
States with energies <13.6 eV !!!!



and



**Fig. 4.6** Energy levels in  $\text{H}_2$  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.)

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

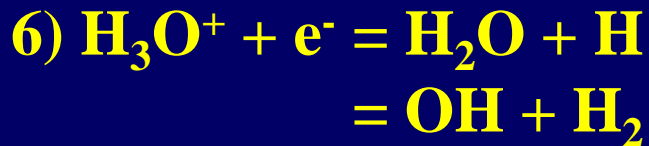
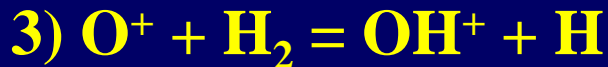
Photodissociation is produced by lines !!! => shelf-shielding of  $\text{H}_2$  in  
molecular clouds (but HD much less protected as frequencies will  
be different than for  $\text{H}_2$ )

## REPRESENTATIVE RATES FOR DIFFERENT TYPES OF REACTIONS IN THE ISM

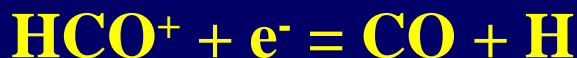
|                                 |                       |                              |
|---------------------------------|-----------------------|------------------------------|
| Cosmic ray ionization           | $10^{-17}$            | $\text{s}^{-1}$              |
| Ion-Molecule reaction           | $10^{-09}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Charge Transfer reaction        | $10^{-09}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Radiative association -diatomic | $10^{-17}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| -polyatomic                     | $10^{-09}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Neutral exchange                | $10^{-12}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Radiative recombination         | $10^{-12}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Dissociative recombination      | $10^{-06}$            | $\text{cm}^3 \text{ s}^{-1}$ |
| Photodissociation               | $10^{-09} - 10^{-12}$ | $\text{cm}^3 \text{ s}^{-1}$ |

## EXAMPLE : THE FORMATION OF WATER VAPOR

$\text{H}_2$  from reactions in the grain surfaces

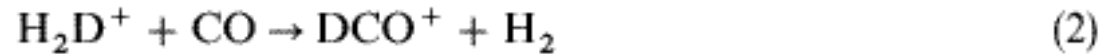


A total of six steps are needed to form  $\text{H}_2\text{O}$  or  $\text{OH}$ . But now



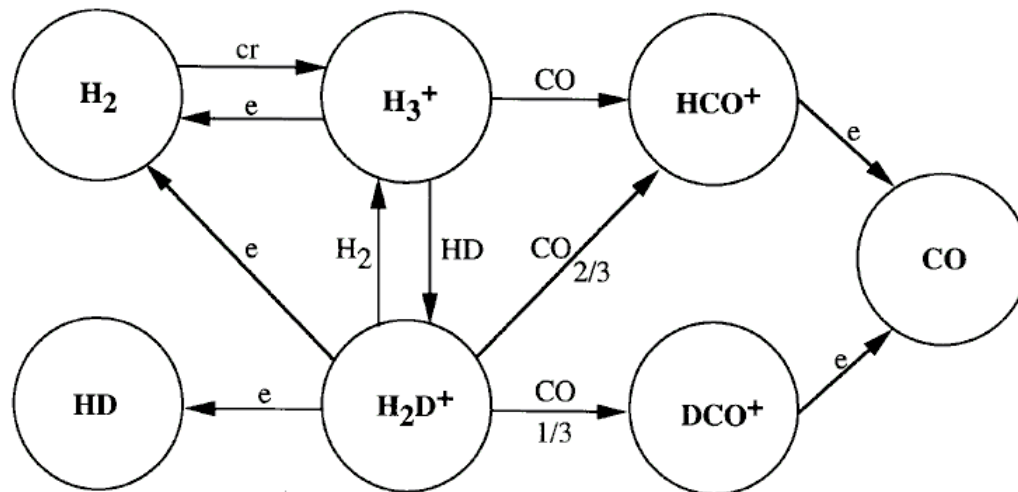


The forward reaction is exothermic by an amount  $\Delta E/k \approx 230 \text{ K}$  and, therefore, at low temperatures, the primary destruction mechanism for  $\text{H}_2\text{D}^+$  is *via* recombination with electrons. Formation of  $\text{DCO}^+$  follows through the reaction:



*R. Plume et al.*

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

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

