H_2 formation on graphitic and amorphous-carbon grains in the ISM

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Overview

Molecular Hydrogen

  Importance of H_2 in the Universe

  Observations in astrophysical objects

Model

  Understanding H_2 formation:

  - Laboratory experiments and DFT calculations
  - Rate equations and Monte carlo simulations

Comparison with observations

Conclusions

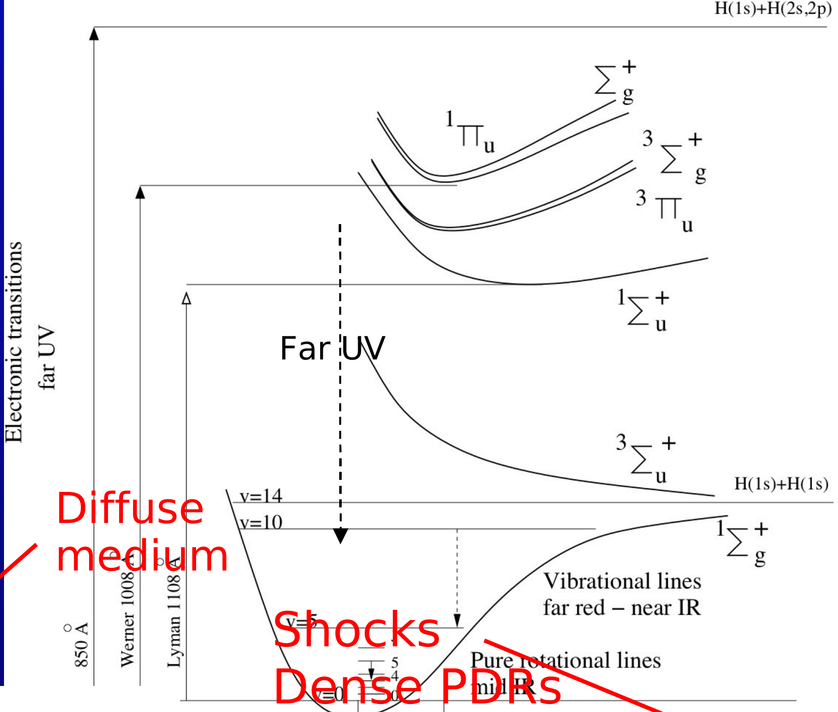
Importance of H_2

- Most abundant molecule in the universe

$M(H_2) \sim 5.10^9\ M_\odot$ in the Milky Way

- Formation of the first stars of the Universe: H_2 is the only coolant available.
- Key specie for the formation of other chemical species

How can you observe H_2



Far UV

In emission:

- red-mid IR
- far UV

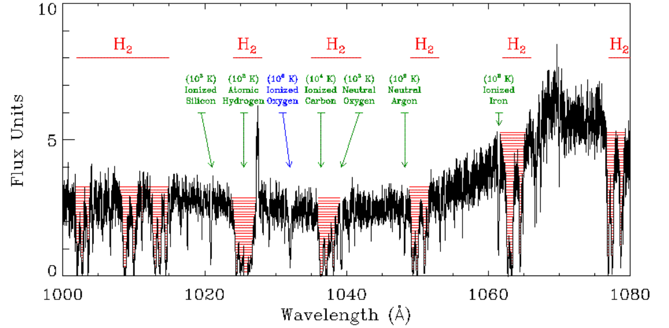
In absorption

- far UV

Mechanisms:

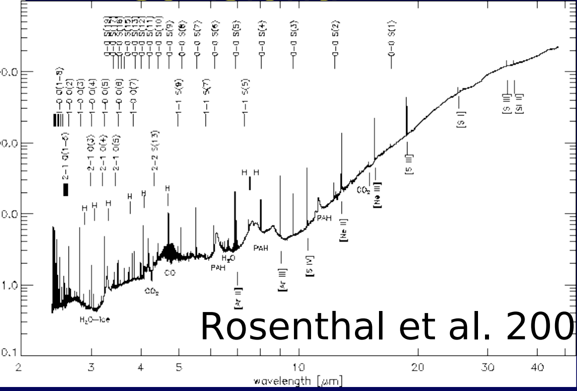
- UV pumping +Fluorescence cascade (90%)
- Collisional

Diffuse medium



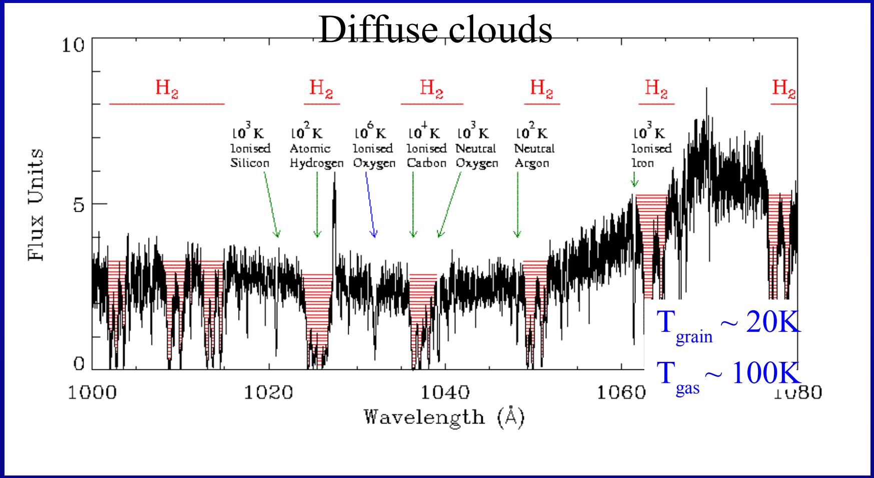
Shull &Tumlinson

Shocks
Dense PDRs



Rosenthal et al. 200

H_2 observations in astrophysical environments

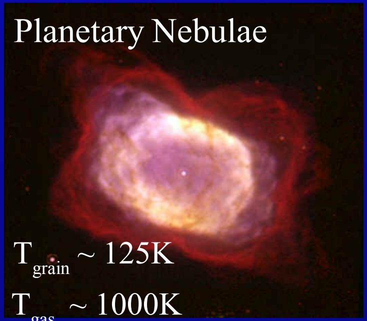


Diffuse clouds

T_{grain} ~ 20K

T_{gas} ~ 100K

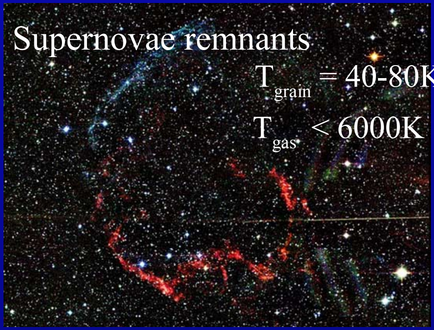
Dying stars



Planetary Nebulae

T_{grain} ~ 125K

T_{gas} ~ 1000K

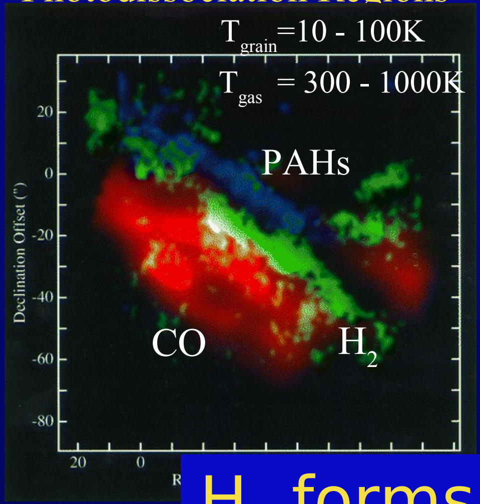


Supernovae remnants

T_{grain} = 40-80K

T_{gas} < 6000K

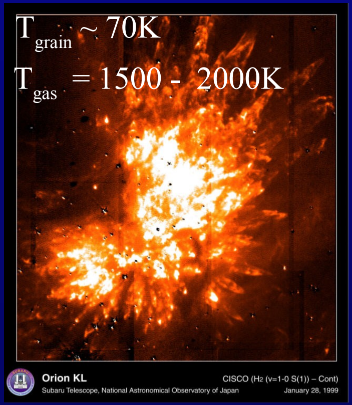
Photodissociation Regions



T_{grain} =10 - 100K

T_{gas} = 300 - 1000K

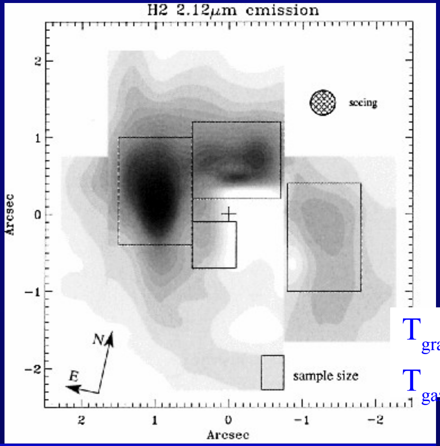
Newly born stars



T_{grain} ~ 70K

T_{gas} = 1500 - 2000K

Active galactic nuclei



T_{grain} = 15- 70K

T_{gazs} ~ 2000K

H_2 forms for a wide range of physical

H_2 formation

Gas phase reactions?

Very slow process

$H + e^{-} \rightarrow H^{-} + h\nu$

$H^{-} + H \rightarrow H_2 + e^{-}$

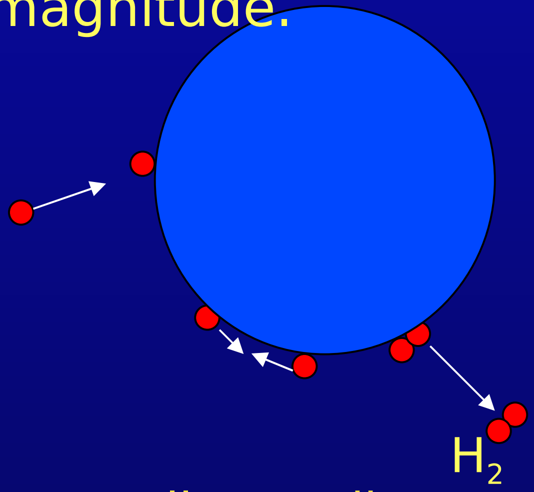
Process not efficient enough to explain the observed abundance of H_2 in the Milky Way.

For high densities $n_H > 10^8$ cm^{-3},

3 body reactions

$H + H + H \rightarrow H_2 + H$

- Grain surface chemistry: Gould & Salpeter 1963
- In the Milky Way, H_2 formation on dust grains dominates by many order of magnitude.

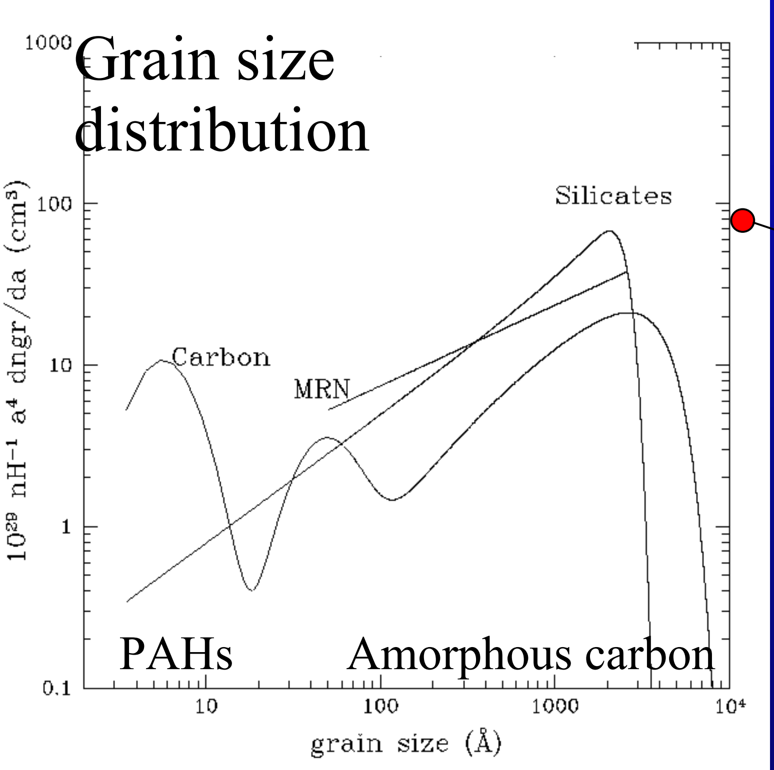


<u>Interstellar medium composition:</u>

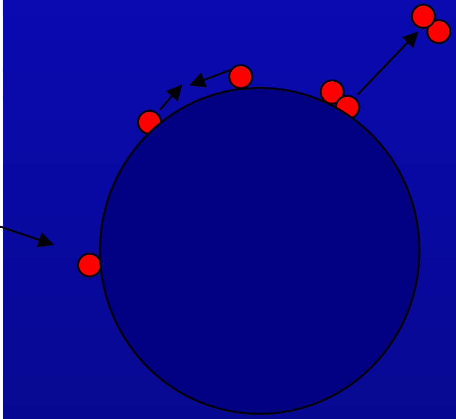
gas (99%) and dust (1%) by mass

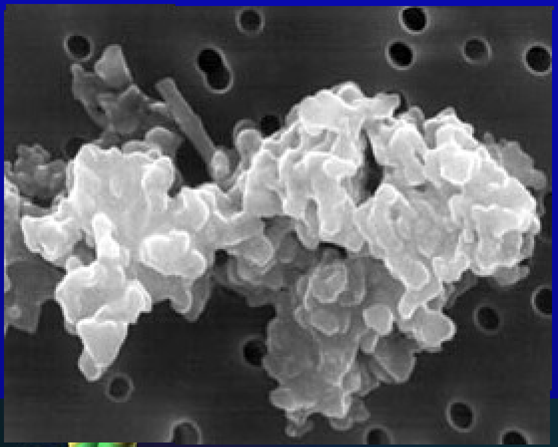
Dust composition:

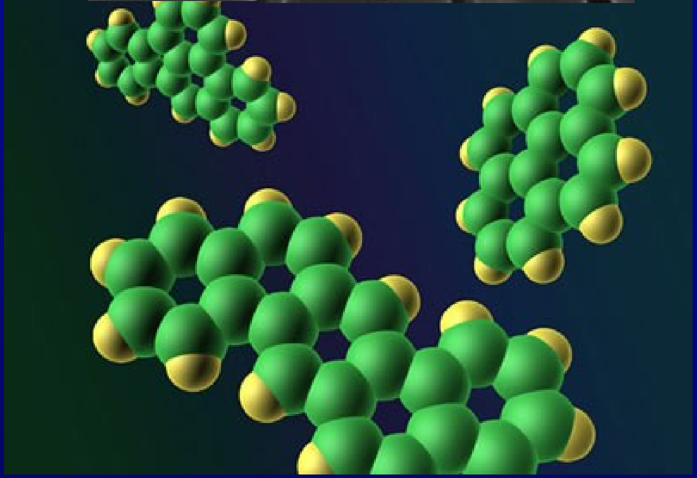
Interstellar dust grains



Weingartner & Draine 2001
Mathis, Rumpl & Nordsieck 1977







How does H_2 form on dust grains for a wide range of physical conditions?

Does the formation of H_2 changes with the size of dust grains?

H_2 formation on interstellar dust: grain surface chemistry

Process studied by several authors:

Hollenbach & Salpeter 1971, Duley 1996, Katz et al. 1999, Morisset 2004, Cuppen & Herbst 2005, Cuppen & Hornekaer 2008

Our model:

Interactions atom/surface:

- Experiments: TPD
- DFT calculations

Rate equations and Monte carlo simulations

Comparison with observations

Grain surface chemistry: laboratory experiments

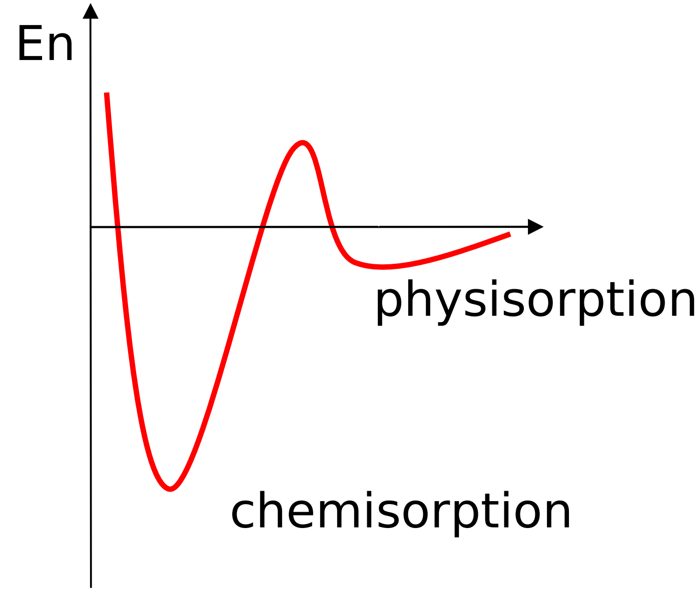
Temperature programmed desorption

Graphite at high temperatures

Amorphous carbon at low temperatures

Pirronello et al. 1999
Beam H and D at 150-200K
Surface 5-15K
Mass spectrometer to measure the amount of HD that desorbs

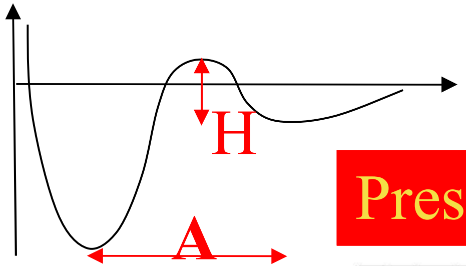
Zecho et al. 2002
beam at 1800 - 2200 K
Surface 150-1000K
Mass spectrometer H_2 and D_2



Model:
Physisorption + chemisorption
Tunnel + thermal hopping

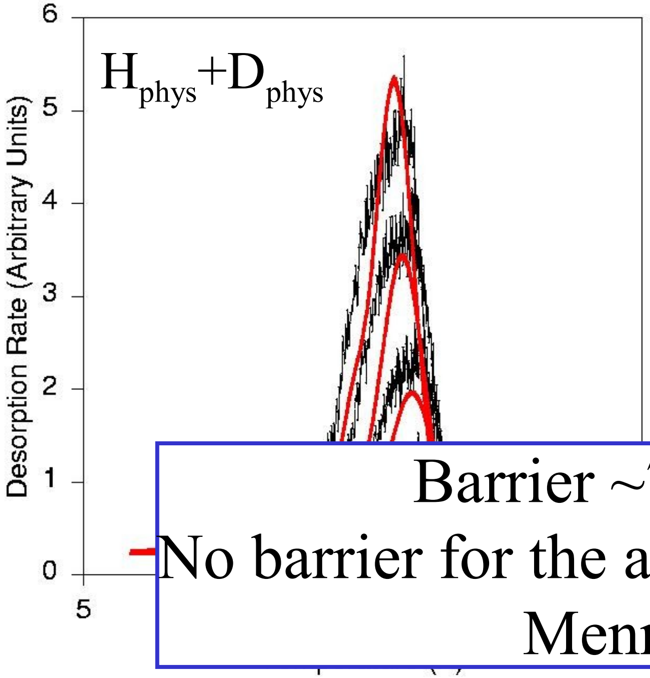
Surface characteristics: Amorphous Carbon

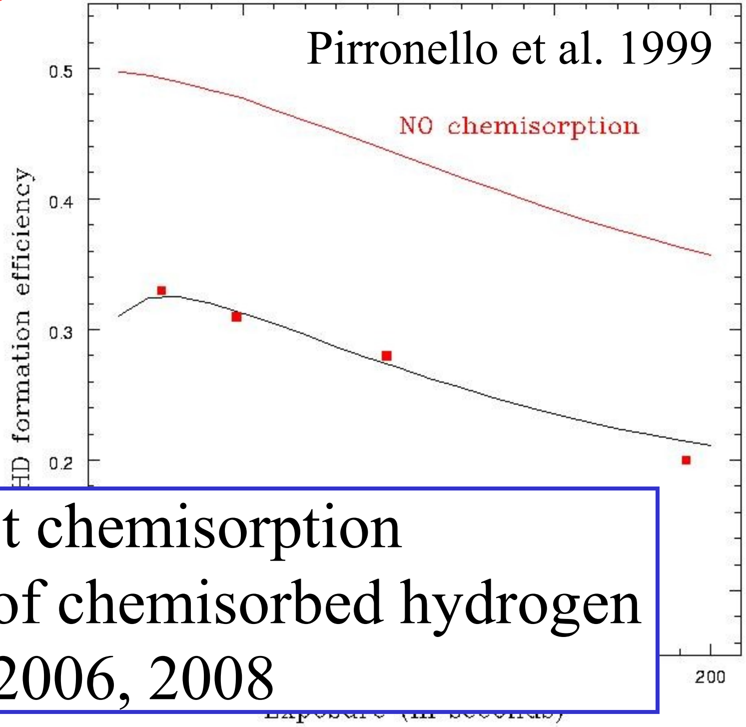
Amorphous Carbon



A√H

Presence of chemisorbed sites?




Pirronello et al. 1999

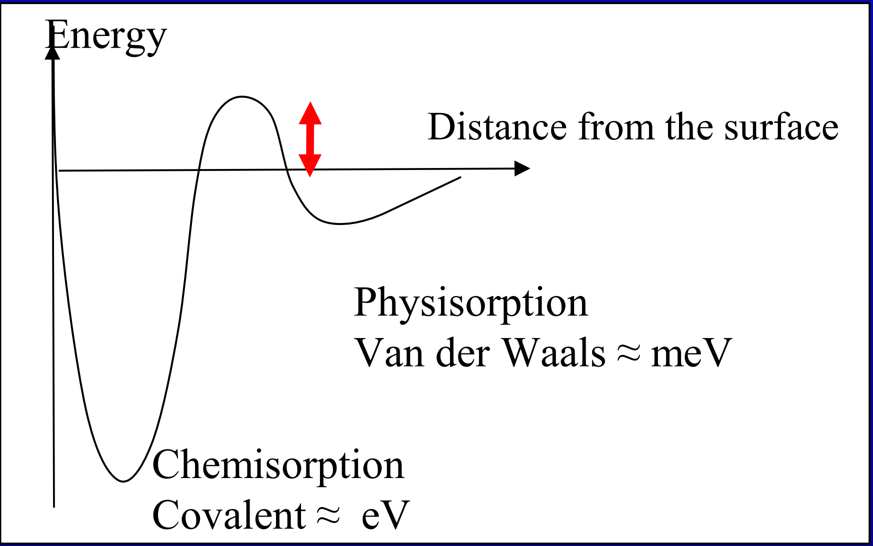
Barrier ~70K against chemisorption

No barrier for the abstraction of chemisorbed hydrogen

Mennella et al. 2006, 2008

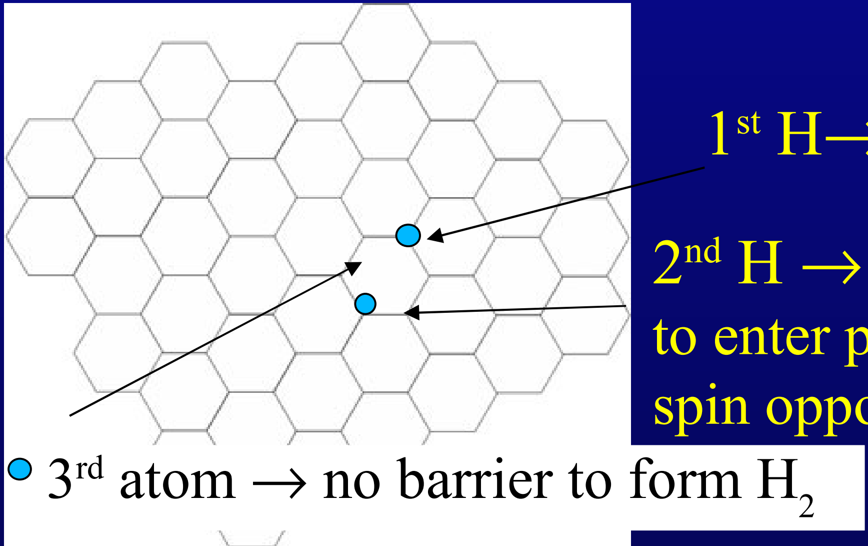
Cazaux & Tielens

Surface characteristics: Graphite



Graphite:
Chemisorption of H
C puckered out of the basal plane
associated with an activation barrier ~ 0.2 eV.
Jeloaica & Sidis 1999
Sha & Jackson 2002

Recent studies:
Hoernekær et al. 2006
Rougeau et al. 2006
Bachellerie et al. 2007



1st H→ barrier

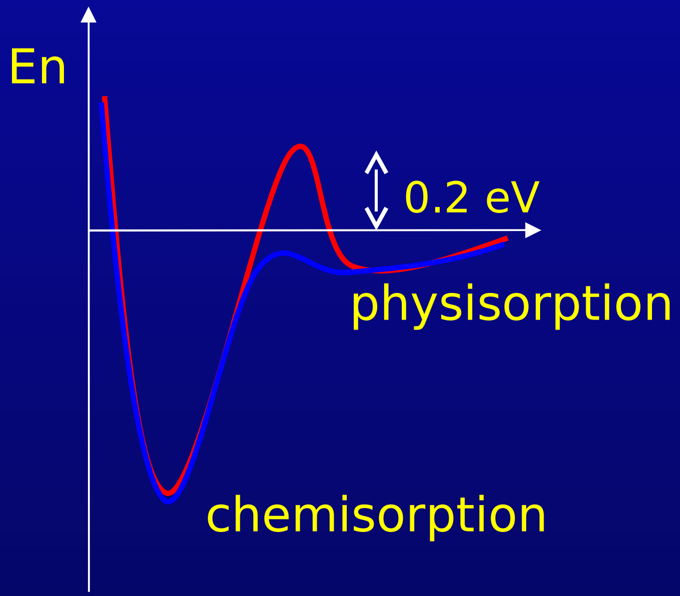
2nd H → no barrier to enter para site if spin opposite to 1st H

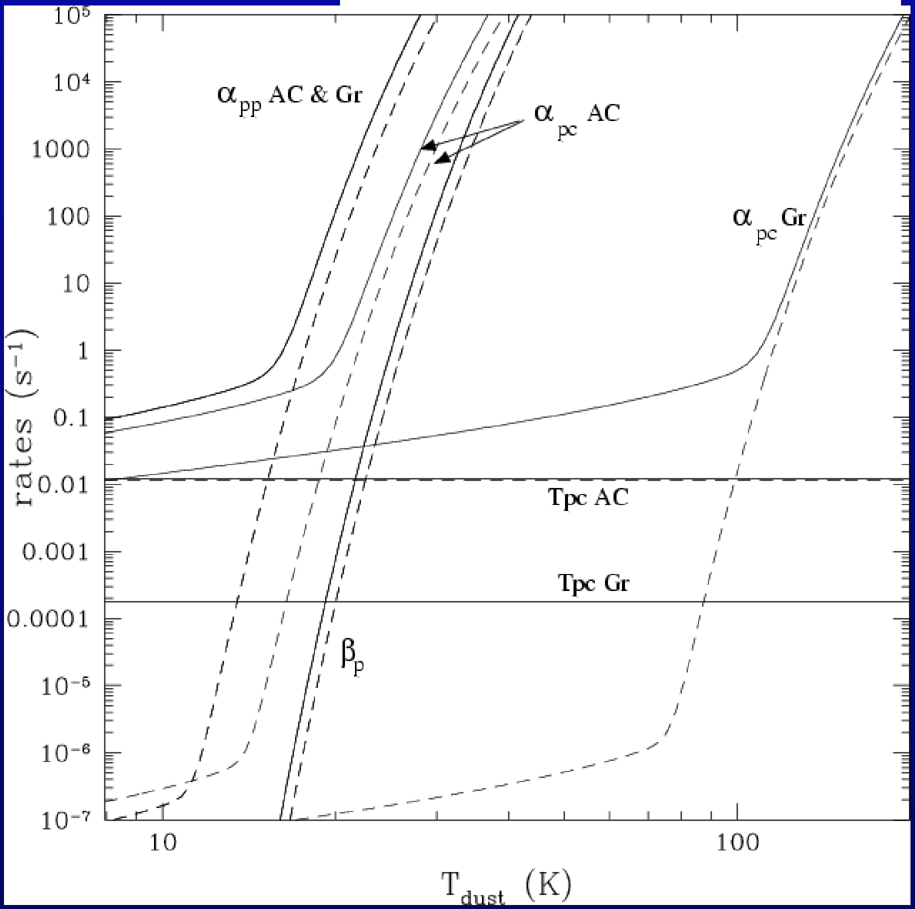
● 3rd atom → no barrier to form H_2

Grain surface chemistry: mobility

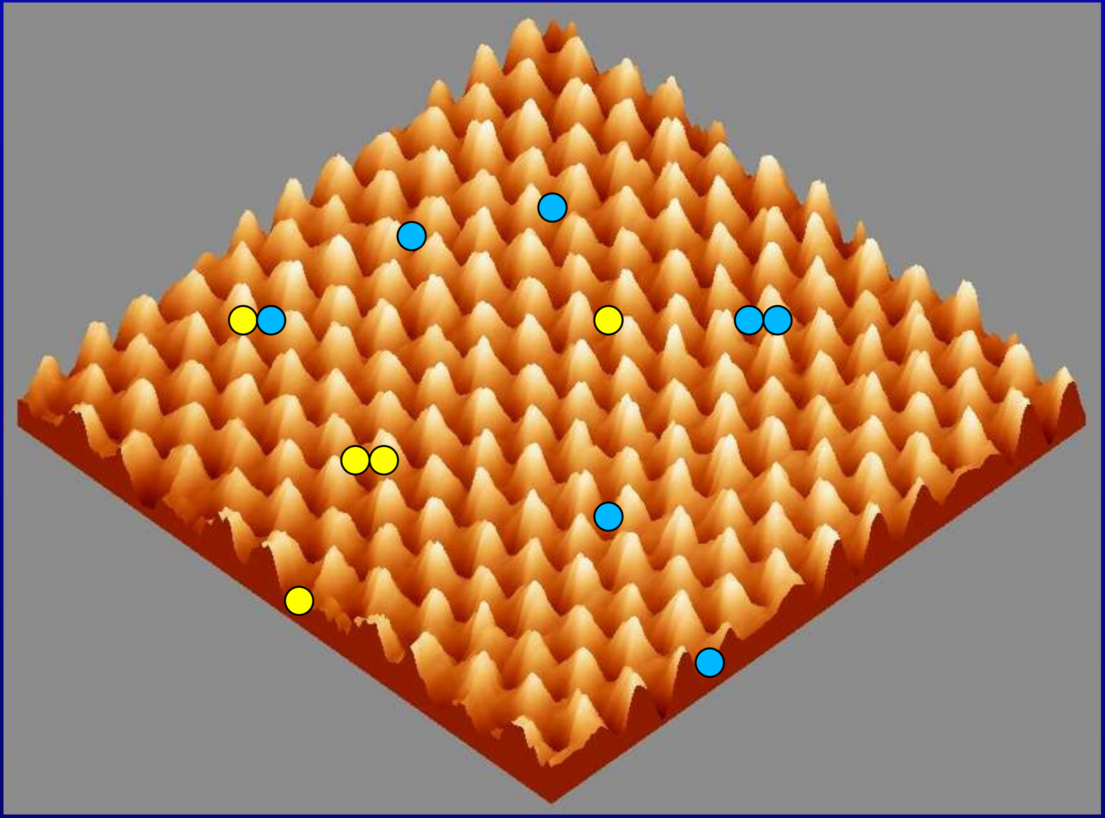
- Physisorption + chemisorption
- Atoms move on the surface by thermal hopping and tunneling effects

$$P_{ij} = \frac{1}{kT}\int_0^{B_i} \exp\left(-\frac{E}{kT}\right) T_{ij}^{(1)}\, dE + \frac{1}{kT}\int_{B_i}^{\infty} \exp\left(-\frac{E}{kT}\right) T_{ij}^{(2)}\, dE,$$





Rate equations:
Method



Rate equations:

Follow the population of the different chemical species on the surface

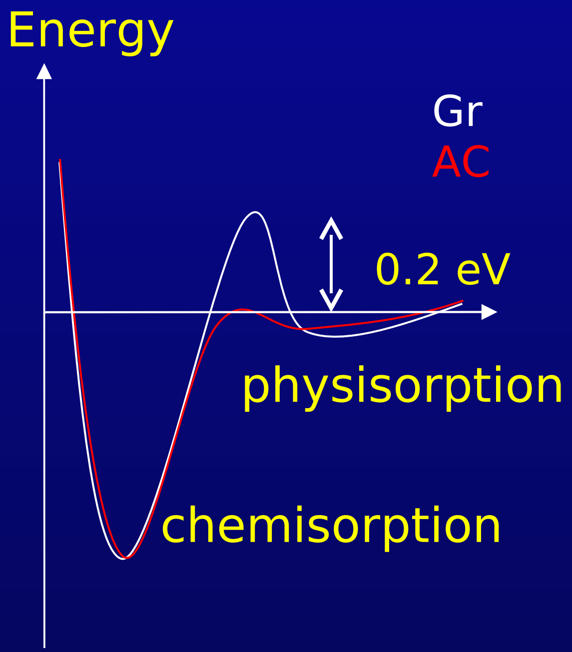
- **physisorbed H atoms**
- **physisorbed D atoms**
- **chemisorbed H atoms**
- **chemisorbed D atoms**
- **H2**
- **HD**
- **D2**

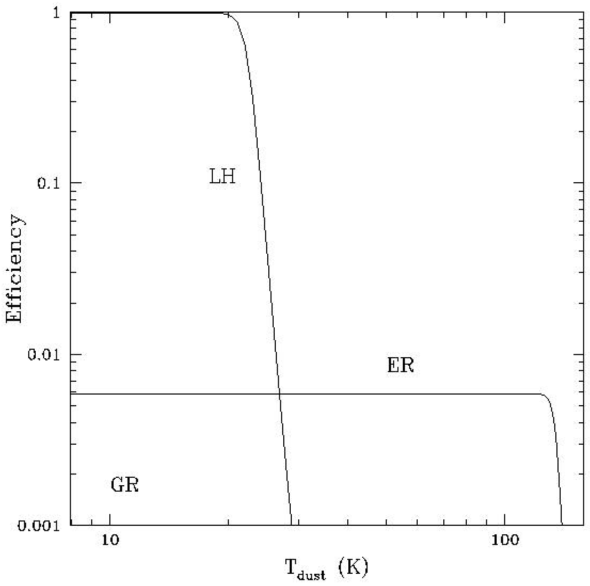
Mechanisms:

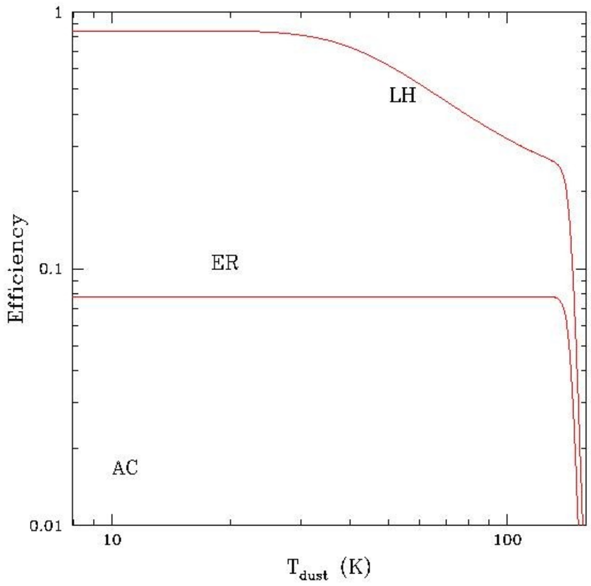
Rate equations:

Results

H_2 formation involves:
Physisorbed atoms at low temperatures
Chemisorbed atoms at high temperatures
Molecular hydrogen forms on dust grains until Tdust>100K.





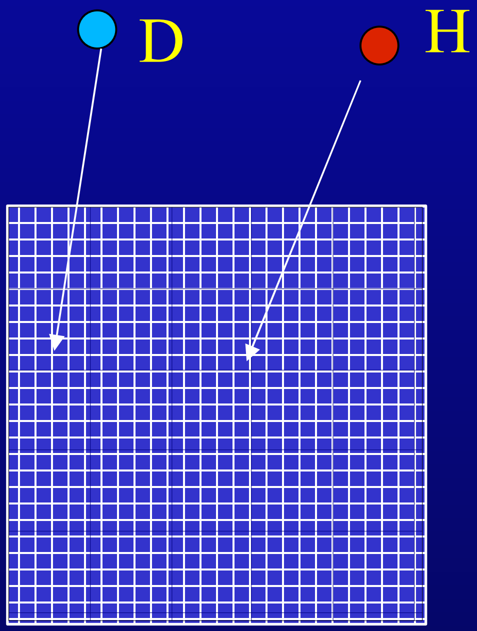


Model
Monte Carlo simulations

- chemistry on small grains
- detailed characteristics of the surface (graphite, incusion of para sites properties)

grid sizes vary from
few Å to 0.1 μm

Atoms arrive randomly on the grain and have a random walk
Each point of the grid is a site: physisorbed and chemisorbed



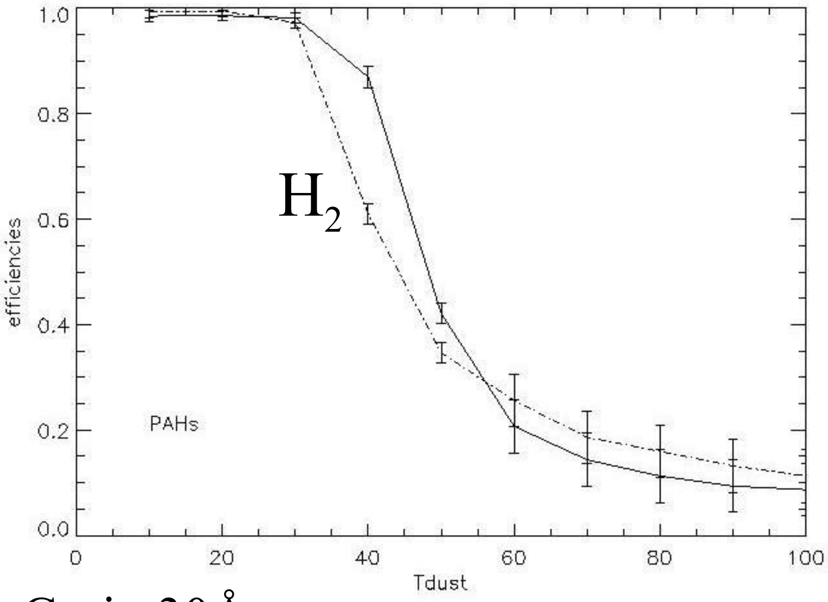
$t=-\ln(xrand)/t(evt)$

List of accretions times (random number depending on the flux of atoms)

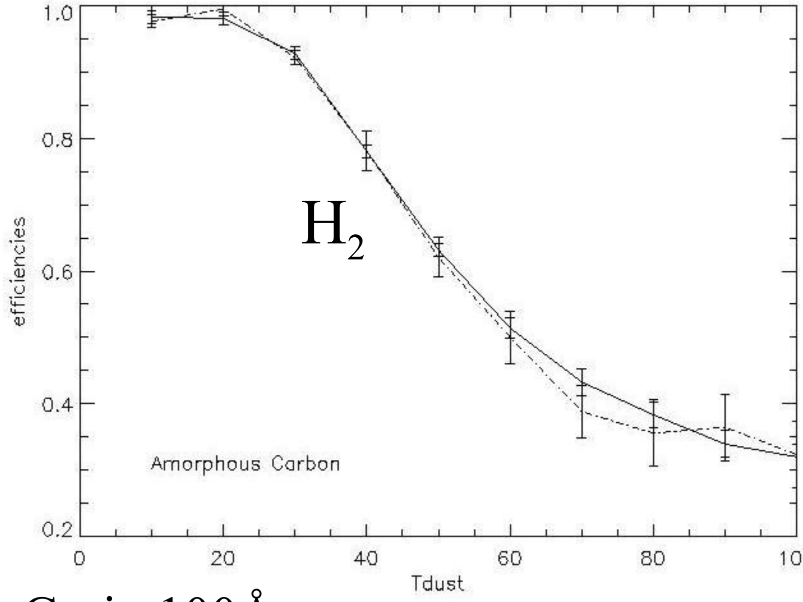
Each time an atom arrives on the grain → possible events

Determine the next event that is ordered in the list

Model
Monte Carlo simulations



Grain 30Å



Grain 100Å

Rate equations and Monte Carlo simulations give the same results for AC. For PAHs, the inclusion of the para sites properties increases the H_2 formation efficiency by more than 1 order of magnitude

H_2 formation rate in the ISM

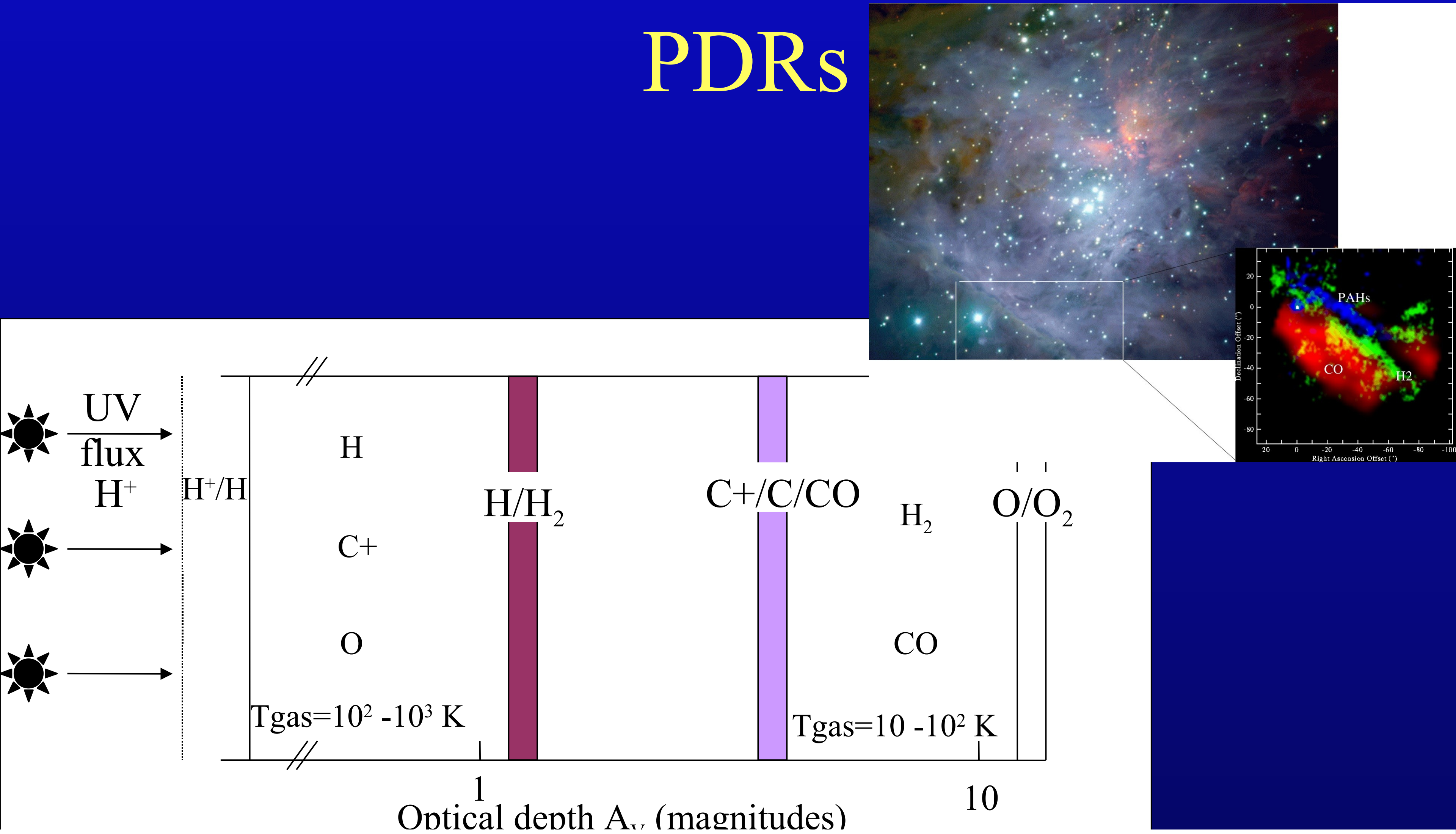
$$R_{H2}=(1/2)\ n_H\ v_H\ \sigma\ n_d\ S_H\ \varepsilon$$

- n_H number density of H atoms
- v_H speed of H atoms in the gas phase
- σ area of the grain
- n_d number density of dust grain
- S_H sticking coefficient of the H atoms on the grain
- ε H_2 recombination efficiency

Tielens & Hollenbach 1985

$$R_{H2}= 3.\ 10^{-17}\ (T_g/100)^{0.5}\ S_H\ \varepsilon\ \mathrm{cm}^{+3}\ \mathrm{s}^{-1}$$

H_2 formation rate: PDRs

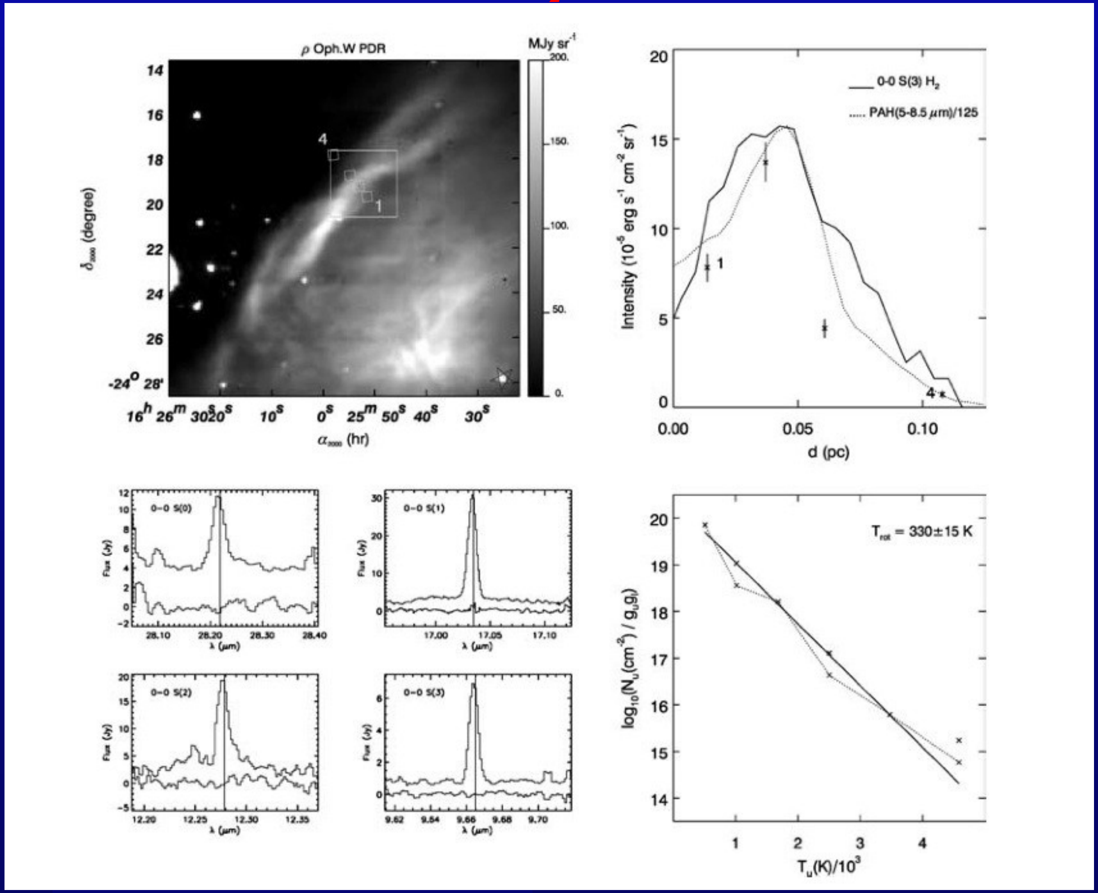


Schematic diagram of a photodissociation region. A PRD extends from the atomic surface region to the point where O_2 is not appreciably photodissociate (~ 10 visual magnitude). In PDRs, hydrogen is mainly into the H_2 form and carbon mostly into CO. From Hollenbach and Tielens 1997.

H_2 formation rate: Photodissociation Regions

ISOCAM MAP (in the LW2 filter)

Rotational transitions of H_2 and PAHs emission



Abergel et al. 1996
Habart et al. 2003

☐ ISO SWS

Rotational transitions of H_2

○ ISO LWS

☐ ISOCAM- CVF

Spectro- imaging

Rotational transitions of H_2

Gas temperature

Photodissocation of H_2

Formation rate of H_2

Grain temperature

H_2 formation rate: Photodissociation Regions

Region	Tsg	Tbg	Tgas	Rate H2
	K	K	K	cm^3s^{-1}
chamaeleon	>2.7	15	60	$4\ 10^{-17}$
Oph W	10	36	330	$1.5\ 10^{-16}$
S 140	10	36	500	$1.5\ 10^{-16}$
IC 63	12	44	620	$1.5\ 10^{-16}$
NGC 2023	25	60	330	$3\ 10^{-17}$
Orion bar	62	90	390	$3\ 10^{-17}$

Habart et al. 2004

H_2 formation rate: Photo-dissociation Regions

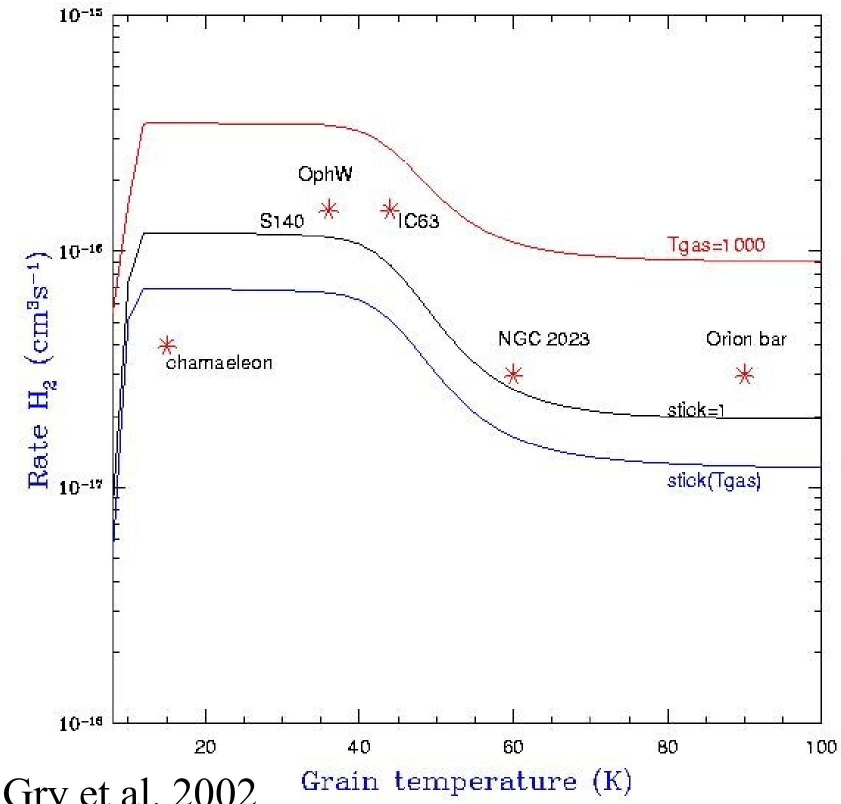
The H_2 formation rate derived in different PDRs cannot be reproduced if high barrier against chemisorption.

With the inclusion of para sites properties, H_2 formation at high dust and gas temperatures can be explained.

Nevertheless the formation rate depends on other factors

$R_{H2}=(1/2)\, n_H\, v_H\, \sigma\, n_d\, S_H\, \varepsilon$

Changes of relative abundances between PAHs and very small grains (AC)



Gry et al. 2002
Habart et al. 2004

Conclusions

H_2

- H_2 forms very efficiently in cold environments, and is observed under extreme conditions in our Universe (Shocks, high UV, low metallicity).
- To understand the formation of H_2 on cold and warm dust grains, 2 interactions atom/surface are needed: physisorption and chemisorption.
- Observations of PDRs show that the efficiency of H_2 formation on warm grains is important.
- The inclusions of the barrier-less route to form H_2 on graphite (para sites properties) is necessary to reproduce the observations of PDRs.

Conclusions: H_2 observations

H_2 has been observed in many astrophysical environments, under extreme conditions (high UV, shocks, early Universe)

The formation rates are:

In diffuse clouds, R=1-4 10^{-17} cm^3 s^{-1}

In PDRs, R=0.3-2 10^{-16} cm^3 s^{-1}

In other environments, H_2 is observed but no rate of formation has been derived.

Models

Explain observations of diffuse clouds
Concentrate on low grain temperatures
Hollenbach & Salpeter 1971
Inclusion of impurities to extend the efficiency to higher grain temperature.

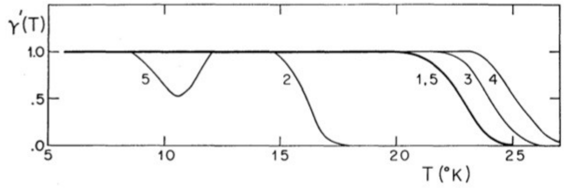


FIG. 1.—Numerical results for the recombination efficiency as a function of grain temperature. Case 1 has the following adsorption parameters: $n_2 = 500$ cm^{-3}, $n = 10$ cm^{-3}, $D = 450°$ K, $D_2 = 550°$ K, $D_m = 200°$ K, $D_{m2} = 250°$ K, $N' = 10$, $D' = 1050°$ K, and $D'_2 = 850°$ K. The other cases have these same parameters with the following exceptions: case 2 has $D' = 750°$ K and $D'_2 = 700°$ K, case 3 has $N' = 100$, case 4 has $n_2 = 5$ cm^{-3} and $n = 1000$ cm^{-3}, and case 5 has $D_m = 115°$ K.

Duley 1996
Hydrogenated Amorphous Carbon
Interstitial H atoms at low grain temperatures (bonding en. 0.05-0.2 eV, with Ea~0.1 eV)
H chemically bond to -CH, -CH2 and -CH3 at high grain temperatures (2.5-3.5 eV)
Efficiency of formation increases with the gas kinetic temperature.

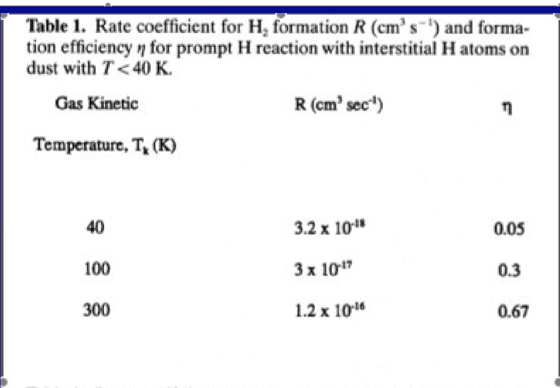


Table 1. Rate coefficient for H_2 formation R (cm^3 s^{-1}) and formation efficiency η for prompt H reaction with interstitial H atoms on dust with $T < 40$ K.

Gas Kinetic Temperature, T_k (K)	R (cm^3 sec^{-1})	η
40	3.2×10^{-18}	0.05
100	3×10^{-17}	0.3
300	1.2×10^{-16}	0.67

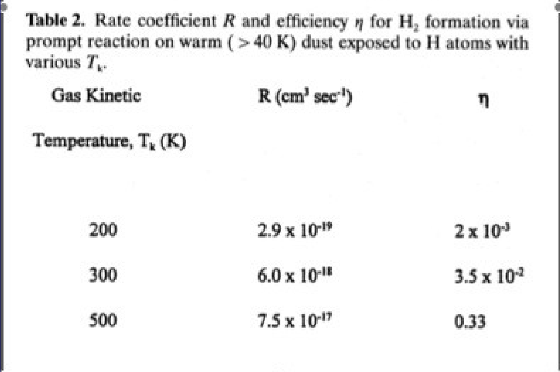


Table 2. Rate coefficient R and efficiency η for H_2 formation via prompt reaction on warm (> 40 K) dust exposed to H atoms with various T_k.

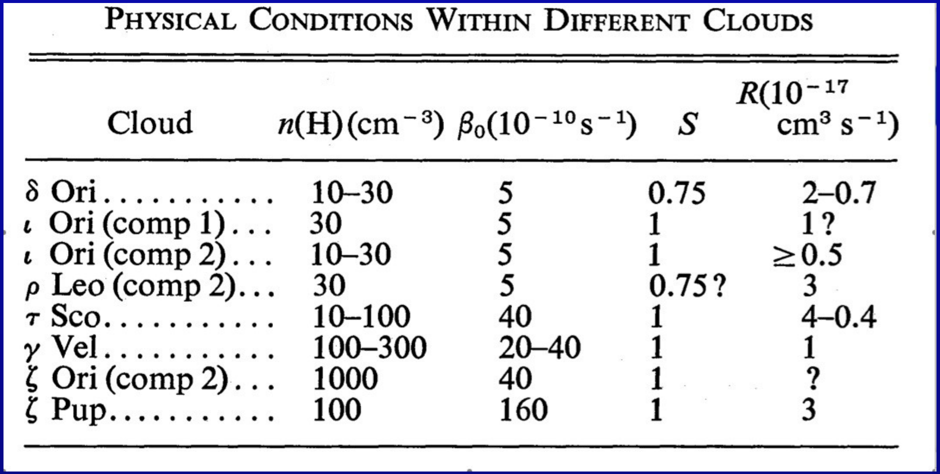
Gas Kinetic Temperature, T_k (K)	R (cm^3 sec^{-1})	η
200	2.9×10^{-19}	2×10^{-3}
300	6.0×10^{-18}	3.5×10^{-2}
500	7.5×10^{-17}	0.33

Models

Models based on TPD experiments:

- Katz et al. 1999
  Rate equations
  Langmuir-hinshelwood
  physisorption
- Cupen & Herbst 2005
  Monte carlo simulations
  Langmuir-hinshelwood + Eley-Rideal
  Physisorption + rough surface
- Cazaux & Tielens 2002
  Rate equations
  Langmuir-hinshelwood + Eley-Rideal
  Physisorption + Chemisorption

H_2 formation rate: Diffuse clouds

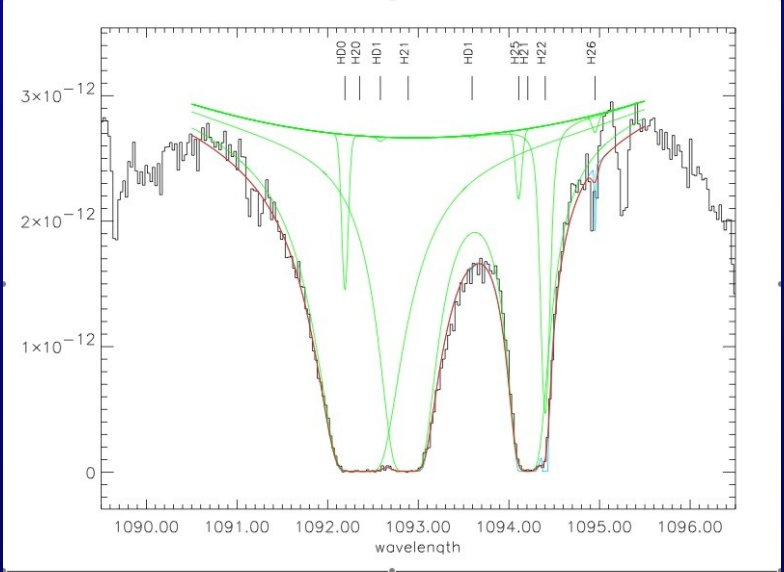


PHYSICAL CONDITIONS WITHIN DIFFERENT CLOUDS

Cloud	n(H) (cm^{-3})	β_0(10^{-10} s^{-1})	S	R(10^{-17} cm^3 s^{-1})
δ Ori.	10–30	5	0.75	2–0.7
ι Ori (comp 1). . .	30	5	1	1 ?
ι Ori (comp 2). . .	10–30	5	1	≥0.5
ρ Leo (comp 2). . .	30	5	0.75 ?	3
τ Sco.	10–100	40	1	4–0.4
γ Vel.	100–300	20–40	1	1
ζ Ori (comp 2). . .	1000	40	1	?
ζ Pup.	100	160	1	3

Jura et al. 1975
Copernicus observations
Photo-absorption in the Lyman and Werner bands leads for 90 % of excited molecules in the ground electronic state.

Gry et al. 2002
Far-UV absorption spectra with FUSE
R=4 10 $^{-17}$ cm^3 s^{-1}



In diffuse clouds, H_2 formation rate is 1-4 10 $^{-17}$ cm^3 s^{-1}