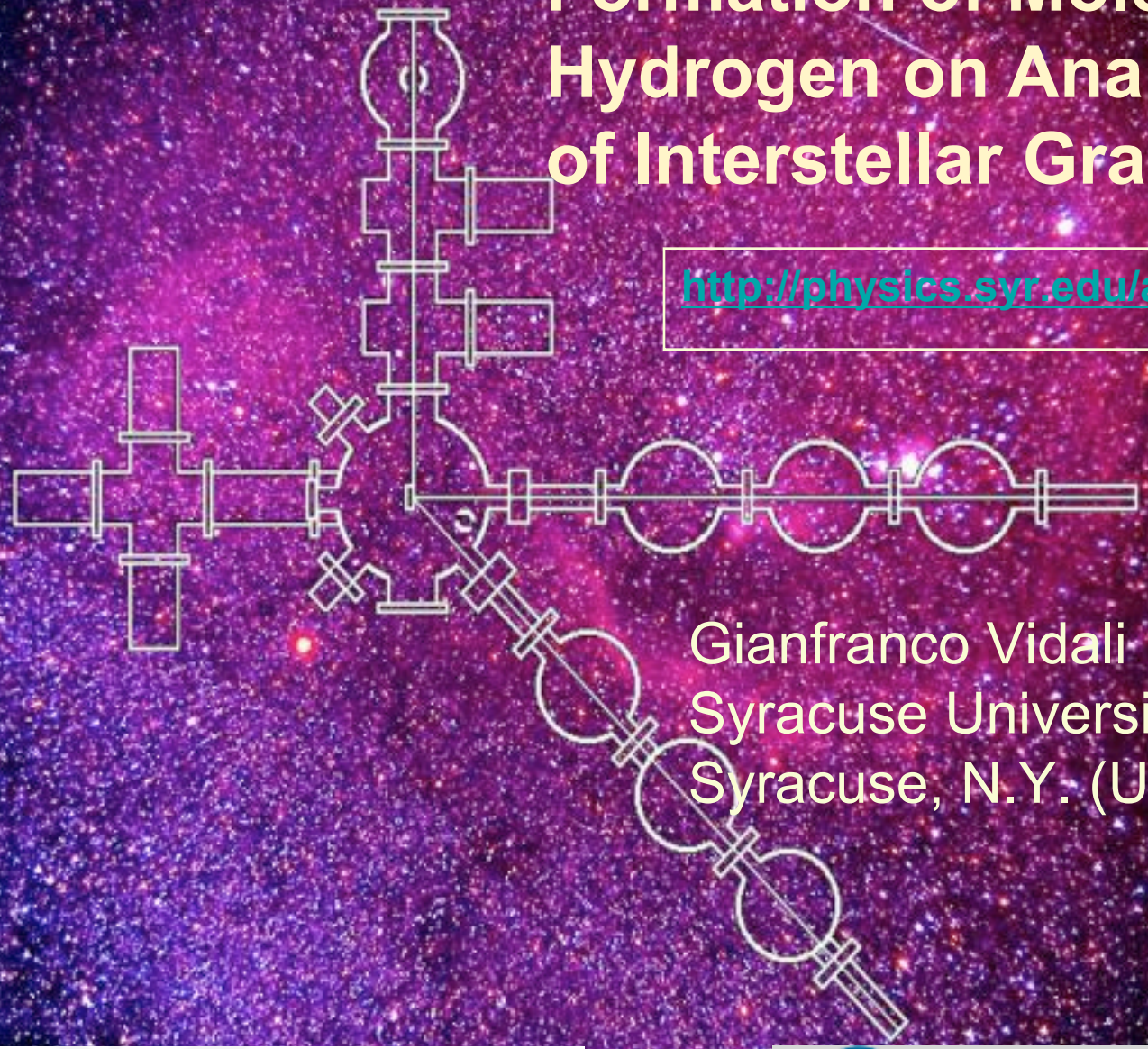
# Formation of Molecular Hydrogen on Analogues of Interstellar Grains

http://physics.syr.edu/astro



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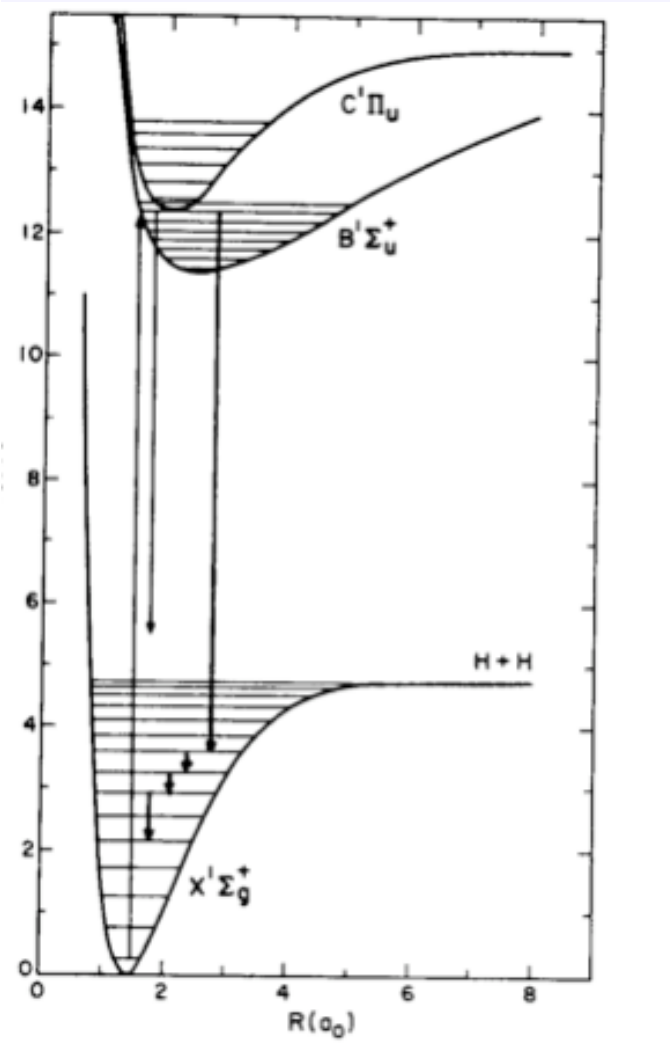
National Science Foundation
WHERE DISCOVERIES BEGIN

National Aeronautics
and Space Administration

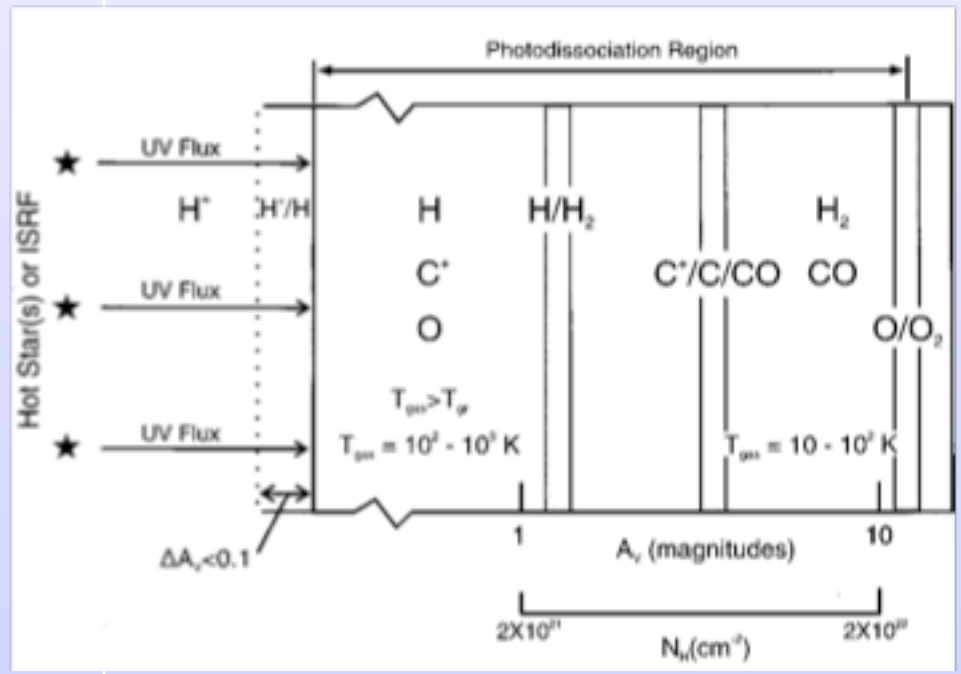
# Outline

1. Use laboratory techniques to:
   1. ***Measure the efficiency of $H_2$ formation on dust grain analogues***
   2. Obtain information on kinetics, energetics of elementary steps of atom/molecule interaction with surfaces
   3. Determine of the mechanism(s) of reaction
   4. Characterize surfaces
2. Apply the above to model processes in actual ISM conditions

# Molecular Hydrogen in the Universe



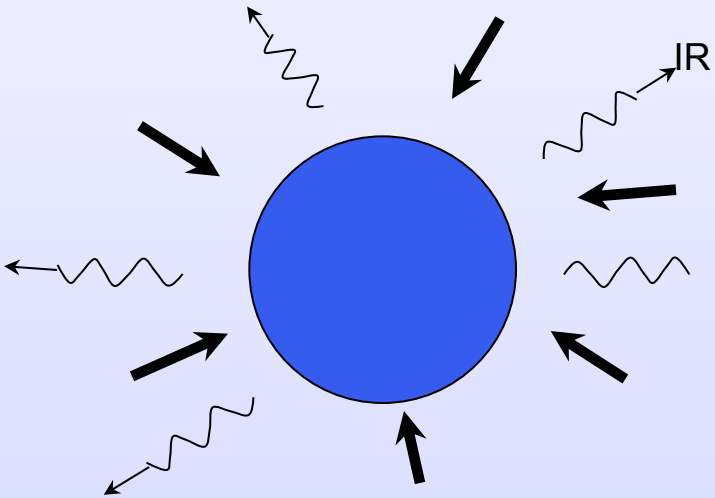

- Most abundant molecule Carruther (1970)
- Tracer of warm gas
  - collisional excitation
  - FUV excitation




Hollenbach and Tielens (1999)

# Molecular Hydrogen in the Universe

- Role in star formation




Molecular hydrogen contributes to the cooling of the cloud by radiating in the IR, thus allowing further gravitational contraction

- Promotes interstellar chemistry

$H_2 + cr \rightarrow H_2^+ + e$

$H_2^+ + H_2 \rightarrow H_3^+ + H$

oxygen chemistry:

$H_3^+ + O \rightarrow OH^+ + H_2$

hydrocarbon chemistry:

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

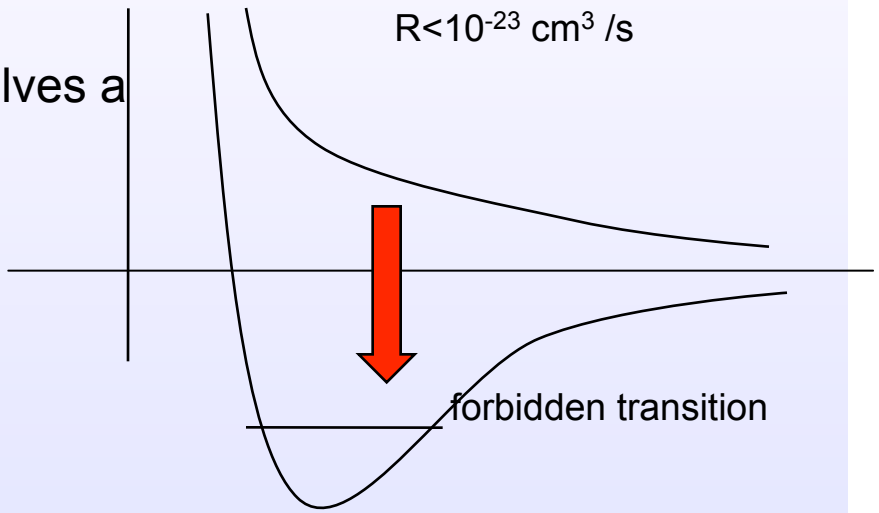
# Formation of $H_2$ in the ISM

$H+H \rightarrow H_2$ not in the gas phase because it involves a forbidden transition

$$d\, n(H_2) / dt = R\, n\, n(H) - \beta\, n(H_2)$$

$R = 3\ 10^{-17}\ cm^3\ s^{-1}$ $\beta = 5\ 10^{-11}\ s^{-1}$

(Jura '75, Habart et al. 2004)




Other routes:

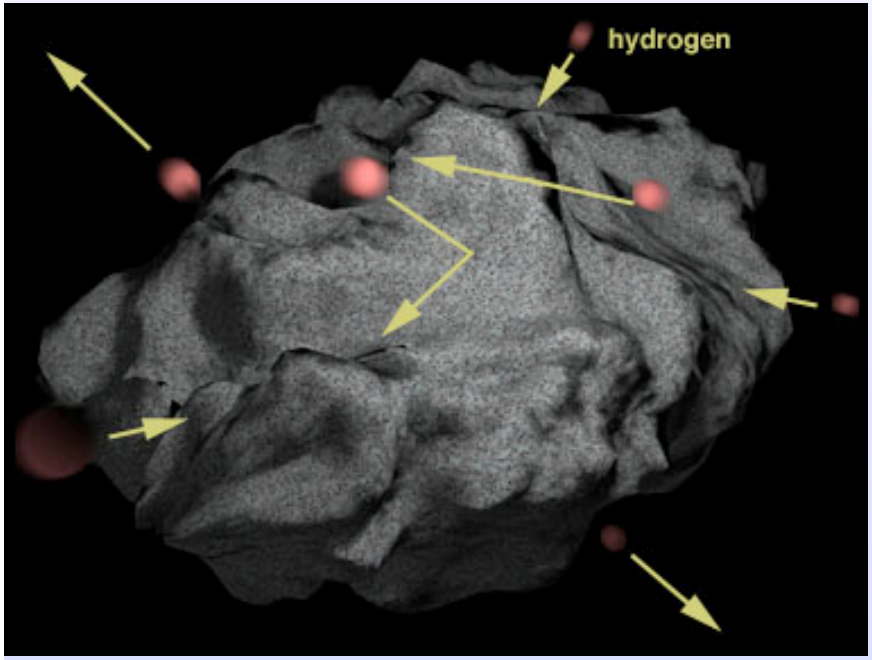
$H + e \longrightarrow H^- + h\nu$

$H^- + H \longrightarrow H_2 + e$ but they require an ionized medium

$H + H^+ \longrightarrow H_2^+ + h\nu$

$H_2^+ + H \longrightarrow H_2 + H^+$

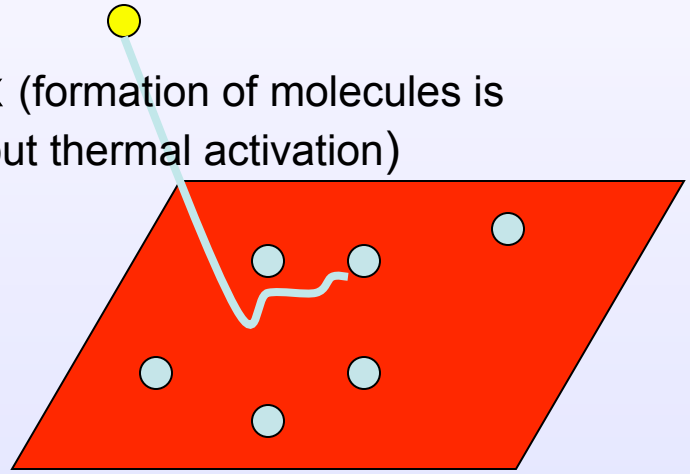
# Formation of $H_2$ in the ISM




- $H+H \rightarrow H_2$ on dust grains (polycrystalline ice) Theory of Salpeter & Hollenbach ~1970
- Model: $R_{H_2} = 1/2\ (n_H\ v_H\ \sigma\ \xi)\ n_g$ ($cm^{-3}\ s^{-1}$) fast mobility because of tunneling
- $H+H \rightarrow H_2$ on amorphous ice - Smoluchowski, 1979 → rates too low because H atoms are trapped at defects
- Early experiments: Scoles' group

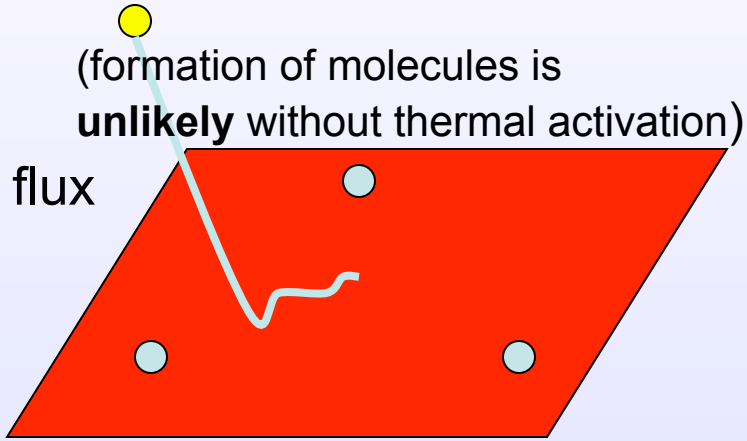
# Effect of flux on the lab measurements

High flux (formation of molecules is likely without thermal activation)



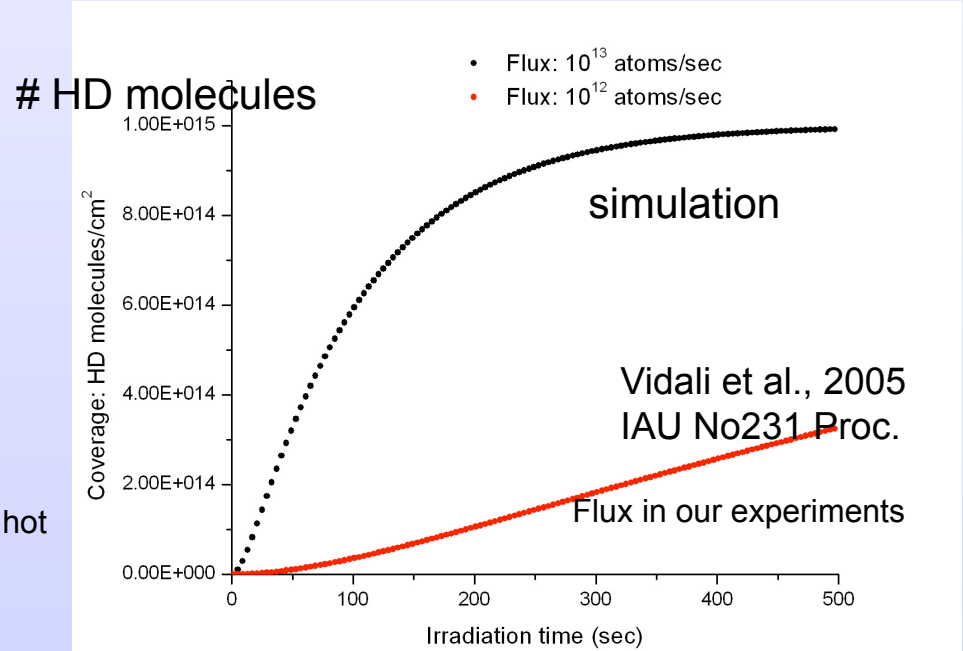
Low flux

(formation of molecules is **unlikely** without thermal activation)



Hot-atom mechanism : atoms lands on surface and travel tens of Angstrom before coming to rest (as per MD simulations of H on ice – Buch & Zhang Ap.J. '91; Takahashi & Uehara, Ap.J. 2001; Al-Halabi et al, MNRAS 2007)

The hot atom mechanism can be responsible for molecule formation if the flux is high; we use a flux low enough so the hot atom mechanism is not the main mechanism of molecule formation. This condition is closer to actual ISM conditions.




Typical irradiation time: ~ a few minutes

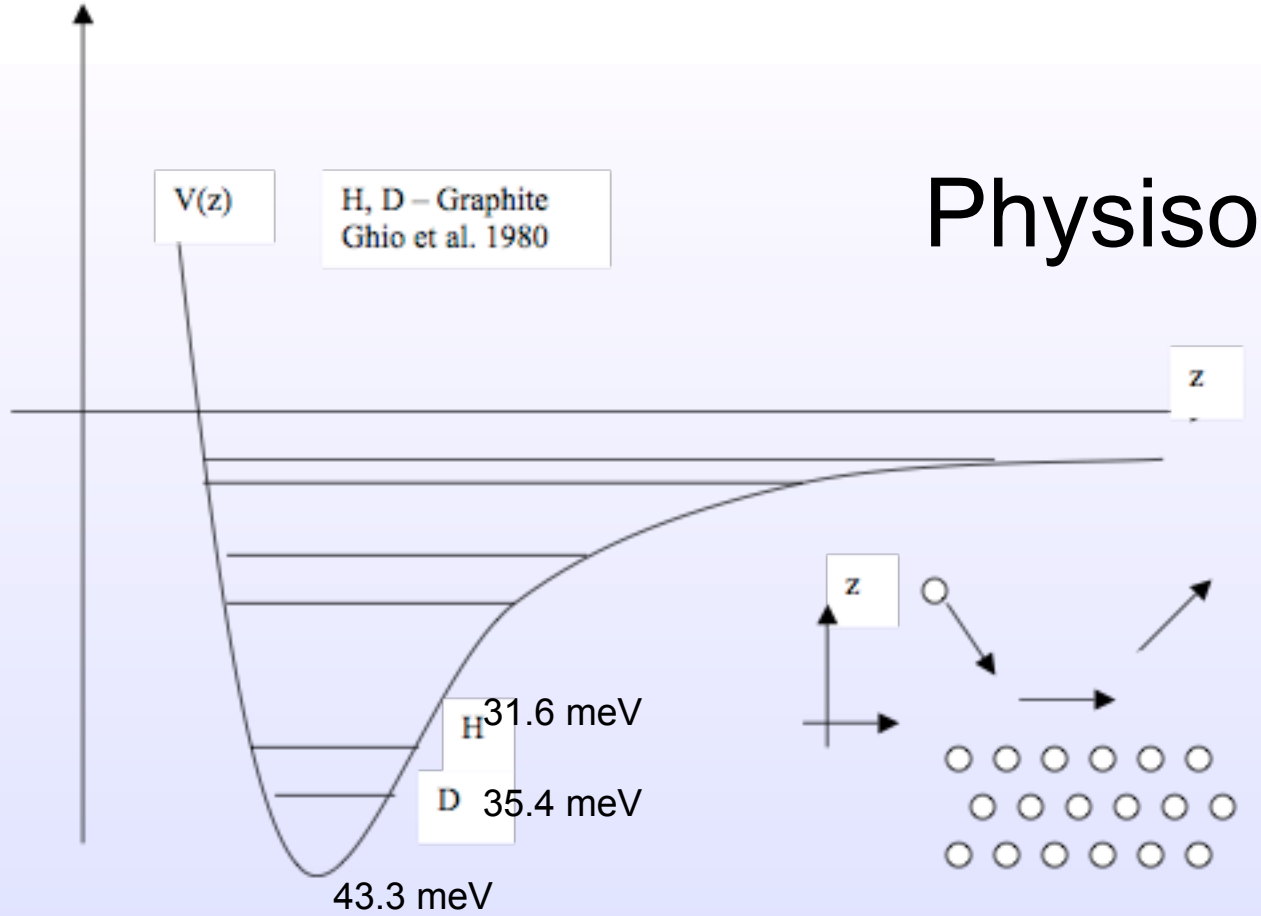
- Questions:

  * How does $H_2$ form on grains?
  * Under what conditions (temperature, grain morphology, etc.)?
  * With what rates?
  - What happens to the energy released in the reaction?

- We initiated a research program at Syracuse University in 1996 to answer these questions

- **Efficiency & Mechanism** of formation of $H_2$ in diffuse clouds - grains are bare (T~15-25 K) (Syracuse University, 1997 –now: Vidali, Pirronello et al.)
- **Efficiency & Mechanism** of formation of $H_2$ in dense clouds - grains are coated with ices (mostly $H_20$) (T ~ 10-20 K) (Syracuse University - 2001-2003, Denmark – 2003: Hornekaer; Cergy-Pontoise: Lemaire et al, 2006)
- **Mechanism** of formation of $H_2$ in PDRs- (T >50K) (Zecho, 2002; Hornekaer, 2006; Mennella, 2008)
- **Partition of energy** released in the $H_2$ bond formation (Syracuse University – 2003, Hornekaer, 2003; UCL: Price 2003, Lemaire 2008)
- Other studies: $H_2$ interaction with ices (Scoles, Lemaire); theoretical studies (Salpeter, Brechignac, Sidis, Clary, Martinazzo, Jackson, etc.); applications to ISM: Herbst, Williams, Tielens, Biham, etc.)

# Physisorption




Results of Gio et al. obtained using scattering of a beam of thermal H atoms from a single crystal graphite surface

Atom-surface interaction

Physical adsorption
(physisorption) ~1-300 meV

Chemical adsorption
(chemisorption) ~ eV

van der Waals (two atoms)

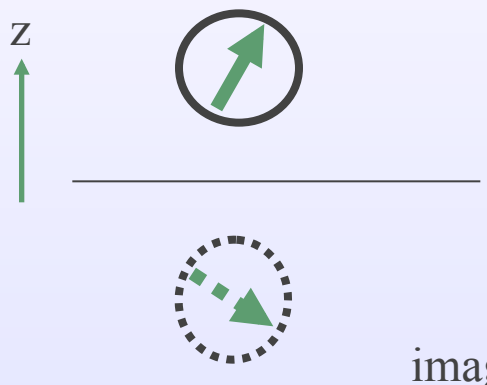
Dipolar field ~ $p_A/r^3$

Induced dipole on atom B ~ $\alpha_B\, p_A/r^3$

Dipolar field on atom A ~ $\alpha_B\, p_B\, p_A/r^6$

$\Rightarrow$ $\mathbf{V(r) \sim - C_6 / r^6}$

Long-range attractive interaction




$$p_{im} = p_a\,[\varepsilon(i\omega) - 1] / [\,\varepsilon(i\omega)+1]$$

image dipole

$$V(z) \sim -\,C_3 / z^3$$

$$C_3 = \int h/4\pi\,[\varepsilon(i\omega) - 1] / [\,\varepsilon(i\omega)+1]\;\;\alpha(i\omega)\,d\omega$$

$$\langle p^2 \rangle = h\;\;\alpha(i\omega)\,d\omega$$

$$\varepsilon(i\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$$

$$[\varepsilon(i\omega) - 1] / [\varepsilon(i\omega) + 1] = g_0 (1 + \omega^2/\omega_s^2)$$

$$\alpha(i\omega) = \alpha_0 / [1 + \omega^2/\omega_a^2]$$

$$C_3 / \alpha_0 \sim 0.5 \text{ eV}$$

$$C_3 = g_0 \alpha_0 h \omega / 16$$

$$2/\omega = 1/\omega_a + 1/\omega_s$$

$h\omega \sim 10$ eV $\qquad g_0 \sim 0.5 - 0.9$

$C_3 / \alpha_0 \sim 0.5$ eV

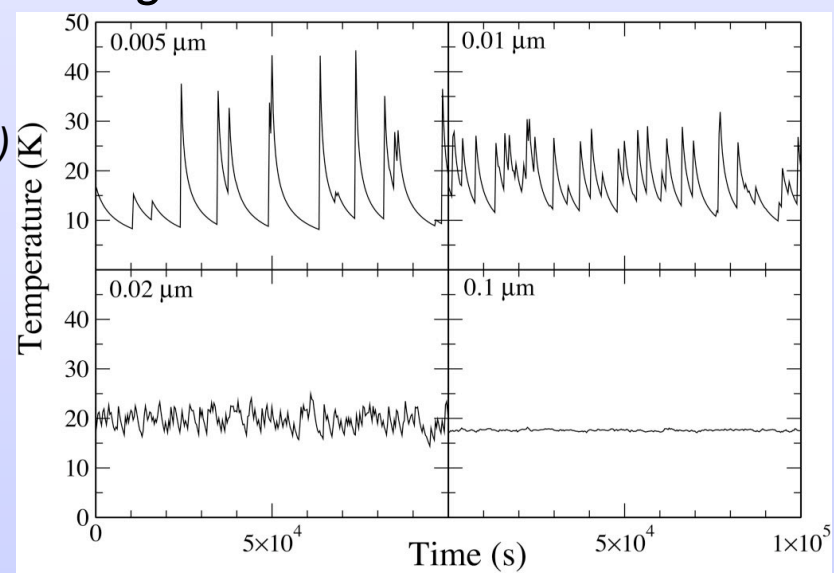
if $\alpha_0 \sim 1$ A$^3$; $z \sim 2$ A
strength $\sim 50$ meV

Vidali & Cole, Surf. Sci. 110, 10 (1981)
Vidali et al., Surf. Sci. Rep. 12, 133 (1991)

# Formation of $H_2$ on grains in the ISM

- Arrival rate: $n_H v_H \sigma$
- Residence time: $t_H = \nu^{-1} \exp(E^{des}_H / k_B T)$
- *For:* $n_H \sim 10^2$ *H/cm*$^3$, $v_H \sim 10^5$ *cm/sec*, $\nu \sim 10^{12} - 10^{13}$ */sec*, $A \sim 10^{-9}$ *cm*$^2$, $E_H^{des} \sim 500$ *K*
- $t_H \sim 10^8$ *sec at 10 K but 300 sec at 15 K*
- $t_{photon} = (\sigma Q \Phi)^{-1}$ $\quad 2.6\ 10^{-3}$ *(erg cm*$^{-2}$ *sec*$^{-1}$*)*
- *Large grains: t~10s sec, T~15-20 K; small grains t~100s T~10-20 K*
- *Need* $\zeta\, dN/dt > 1/t_{photon}$ *(2 atoms on grain)*

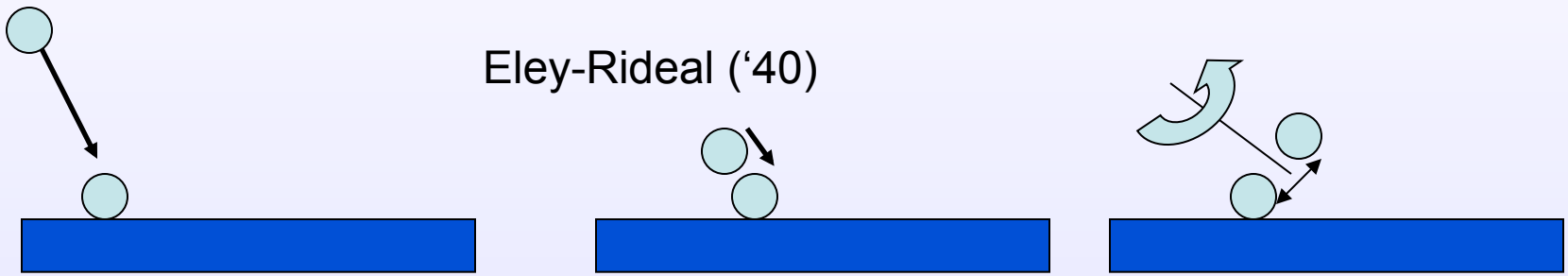
These conditions are too restrictive; therefore there must be a range of energies



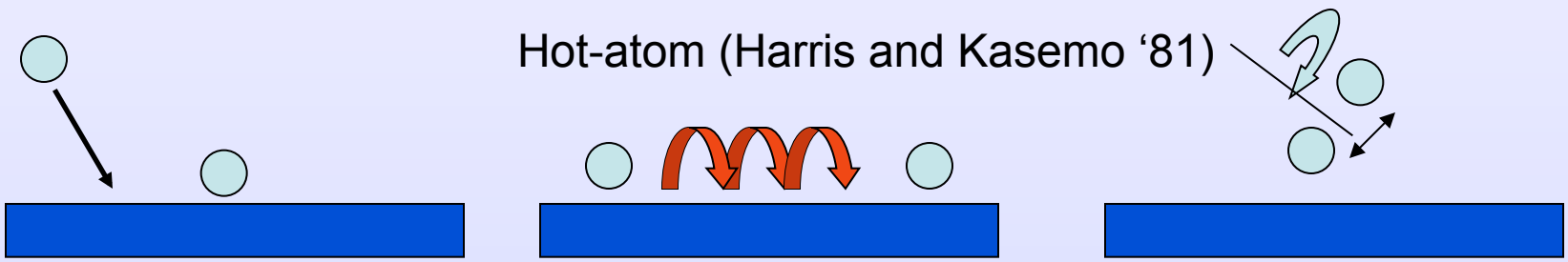

Cuppen et al. MNRAS 367, 1757 (20006)

# Mechanisms of reaction

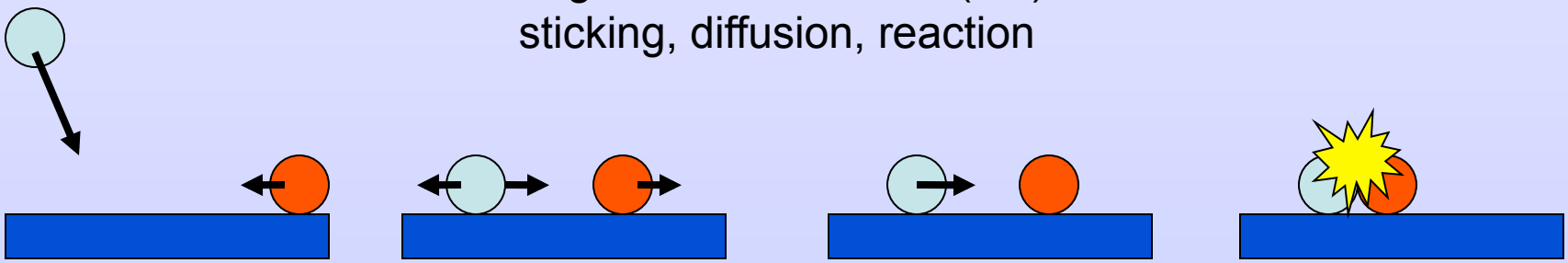
Eley-Rideal ('40)



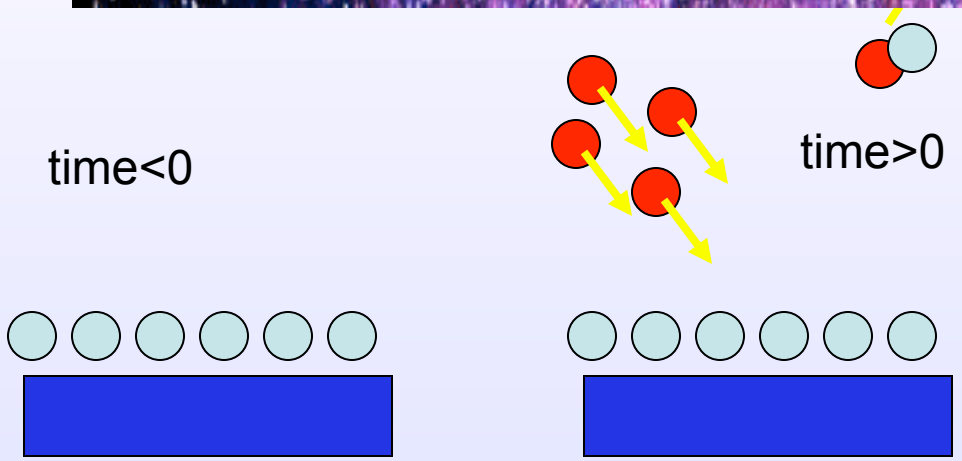
Hot-atom (Harris and Kasemo '81)

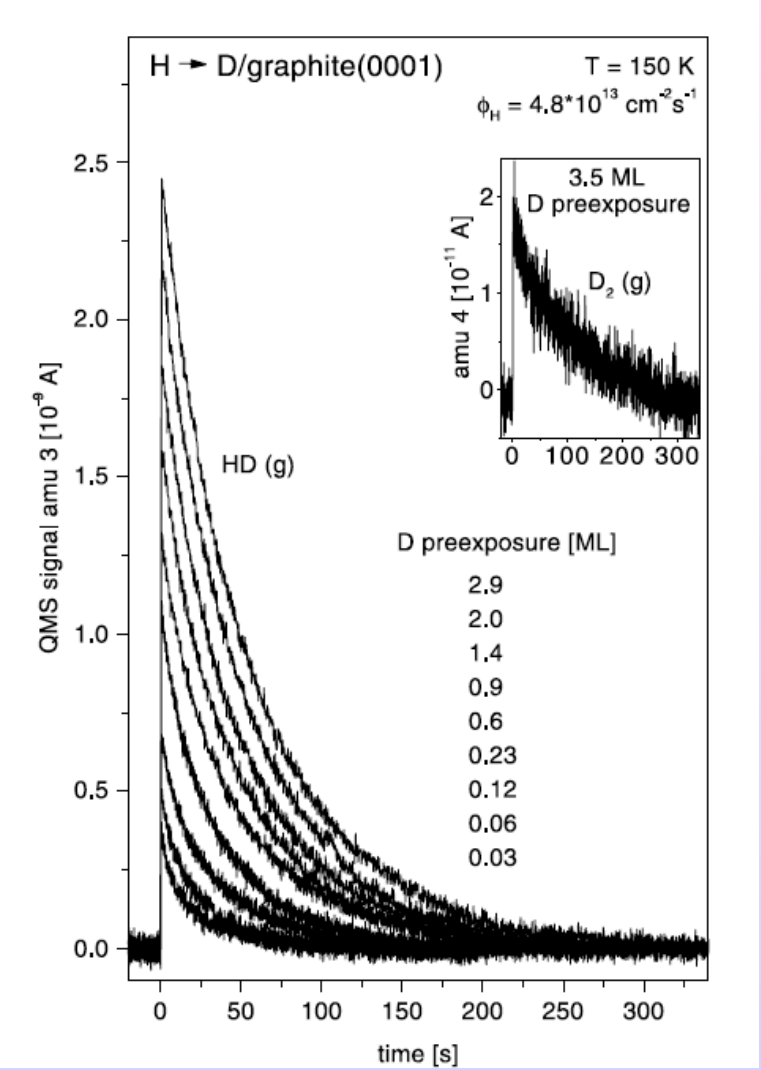


Langmuir-Hinshelwood ('22):
sticking, diffusion, reaction



# Eley-Rideal/hot-atom reactions



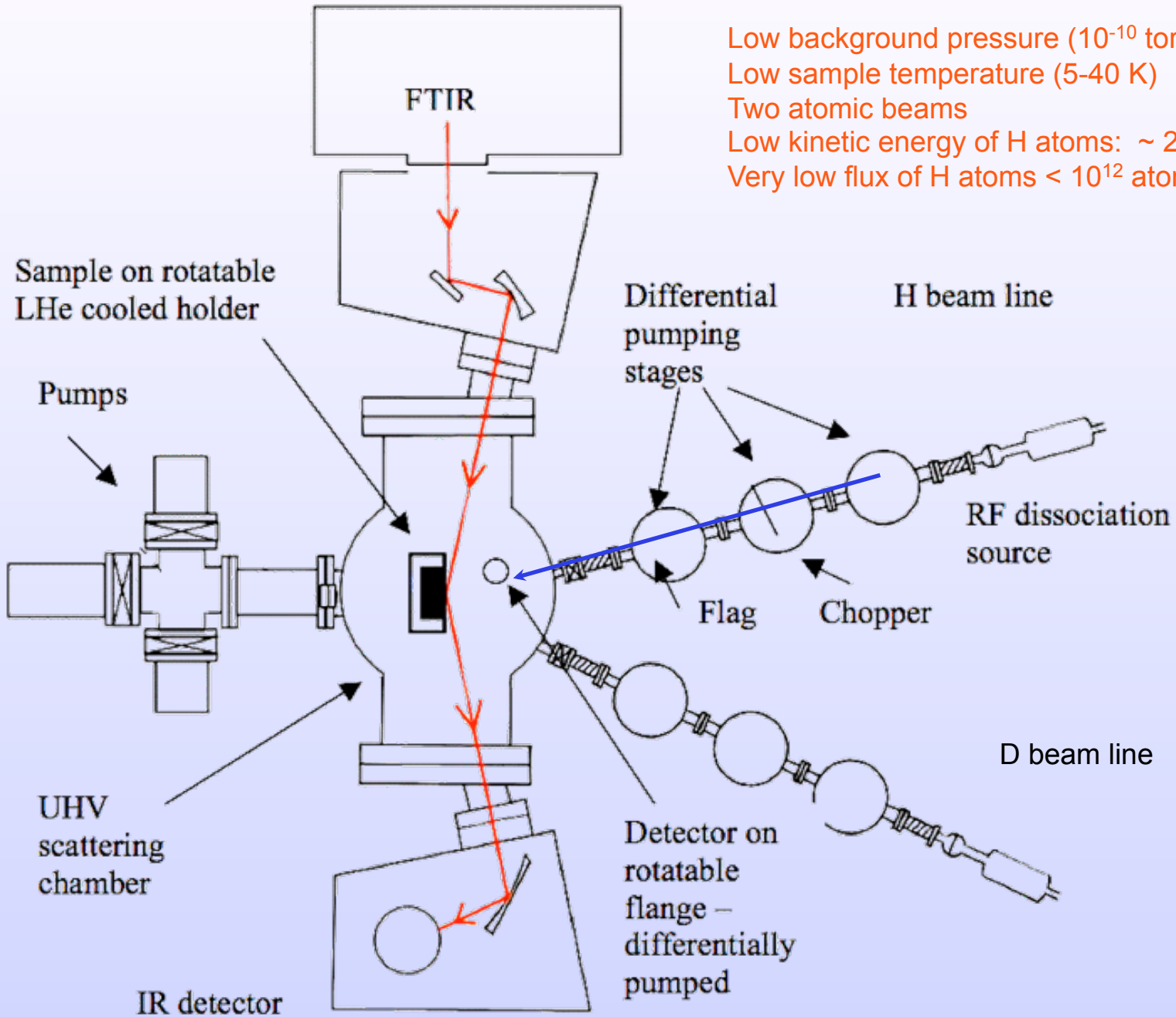



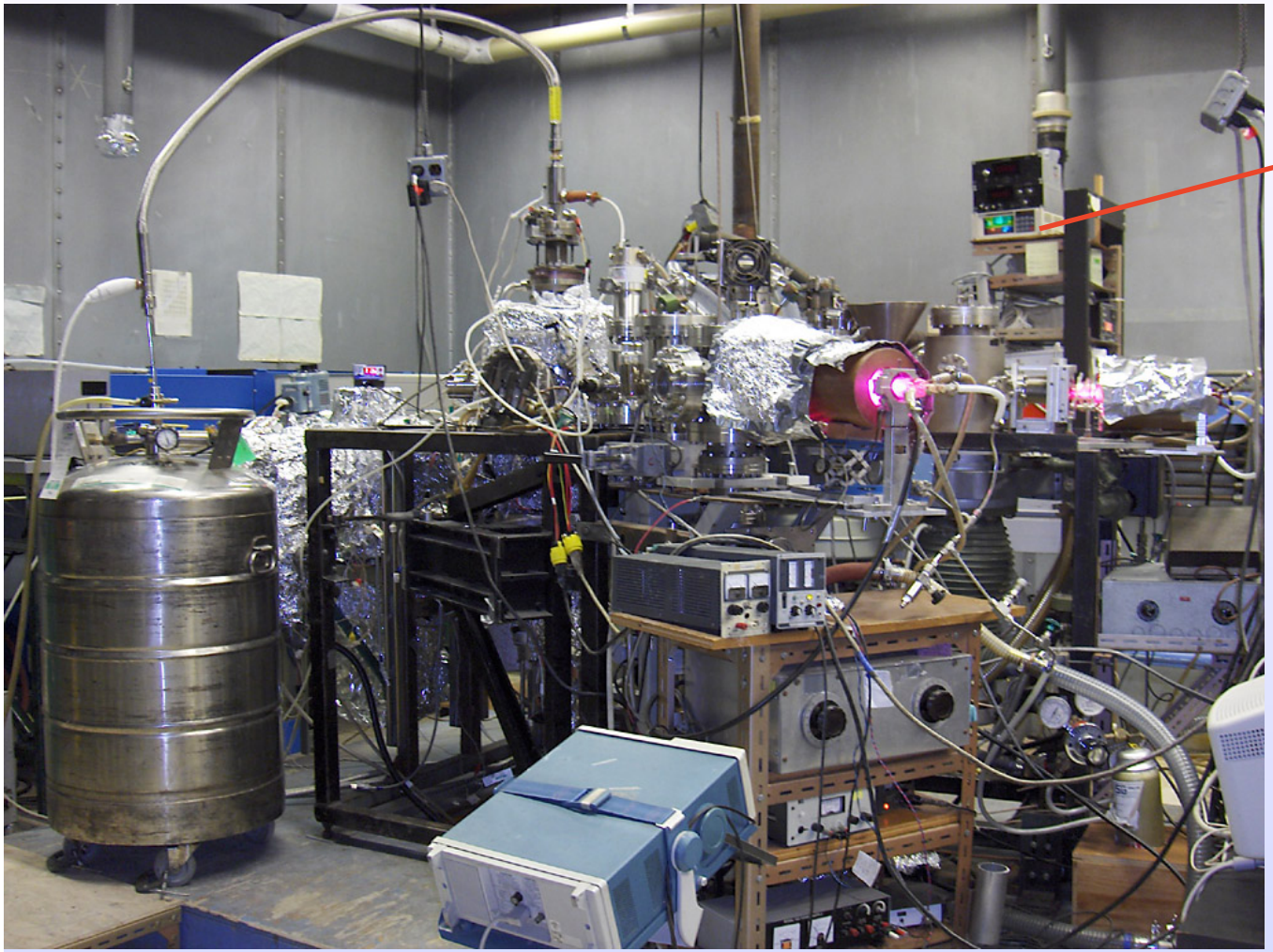

- Incomplete accommodation
  - Poor inelastic coupling
- Sizable condensation energy
- Sizable coverage
- Signature
  - Small cross-section
  - Energy partition

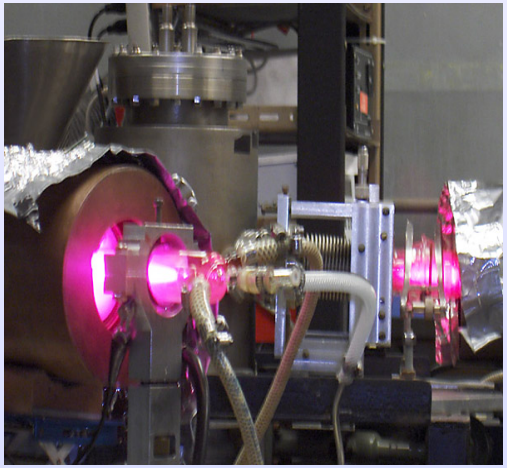
$R \sim e^{-\sigma \phi t}$

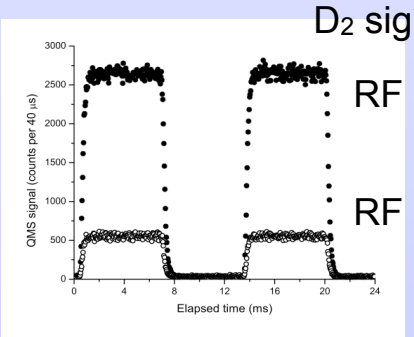
Zecho et al. Chem.Phys.Lett. 366, 188 (2002)

Low background pressure ($10^{-10}$ torr)
Low sample temperature (5-40 K)
Two atomic beams
Low kinetic energy of H atoms: ~ 200-300 K
Very low flux of H atoms < $10^{12}$ atoms/cm$^2$/sec



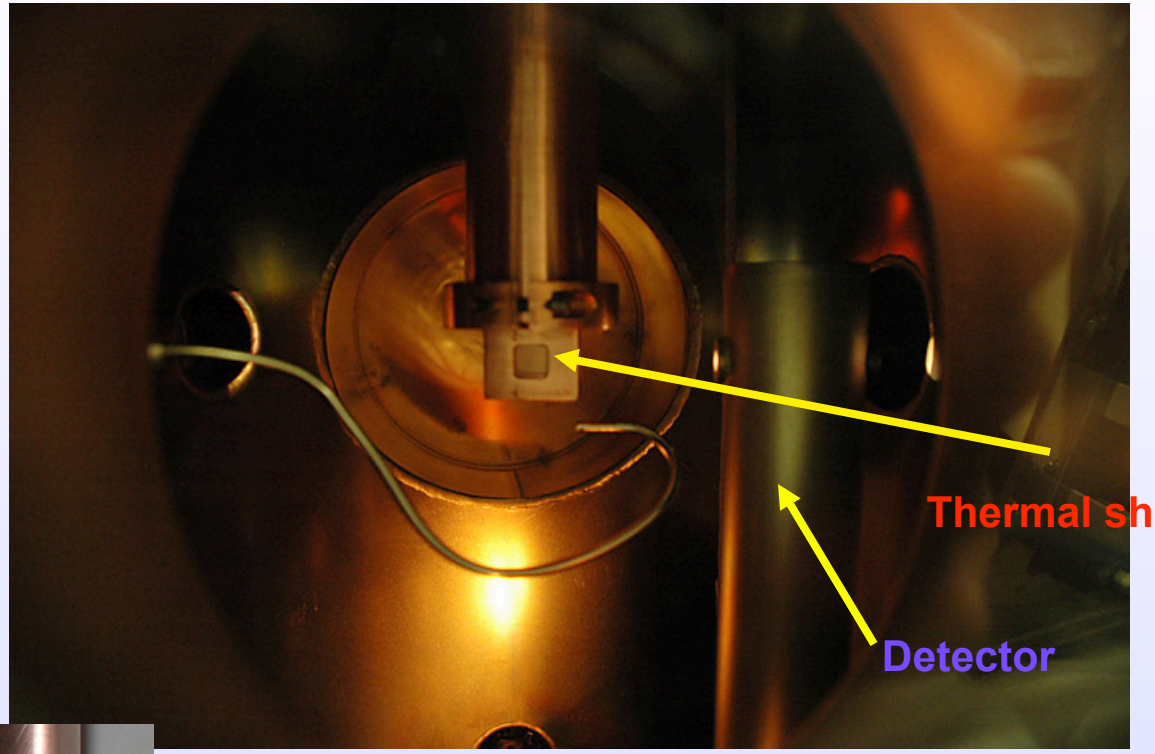


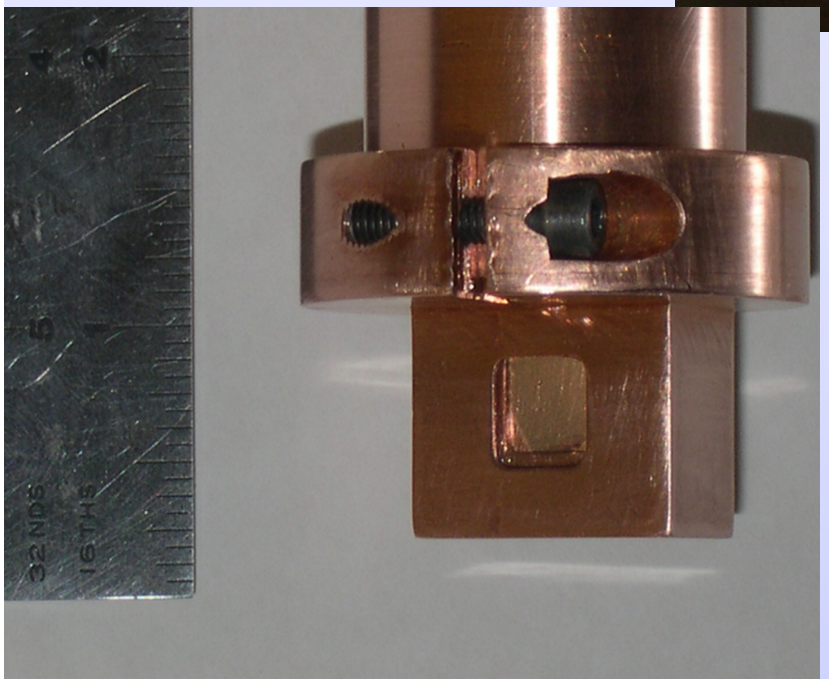





# Apparatus at S.U. to study molecule formation on dust grain analogues

# Apparatus: Details

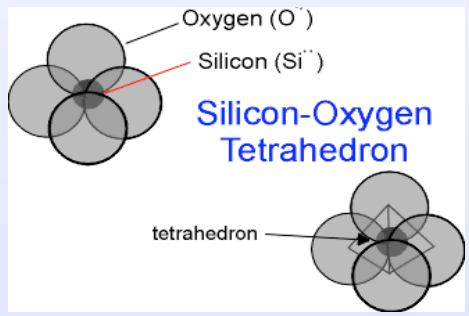


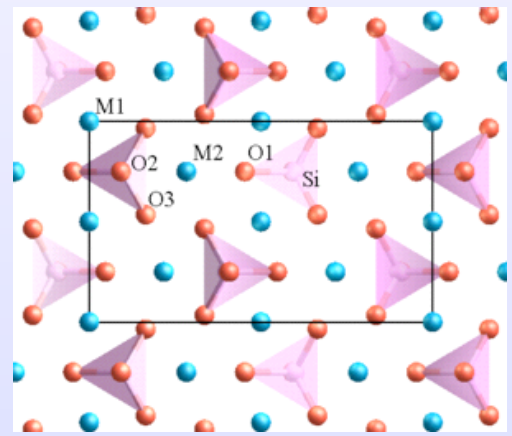



# Types of Dust

- Silicates $(Mg_x, Fe_{1-x})_2\ SiO_4$

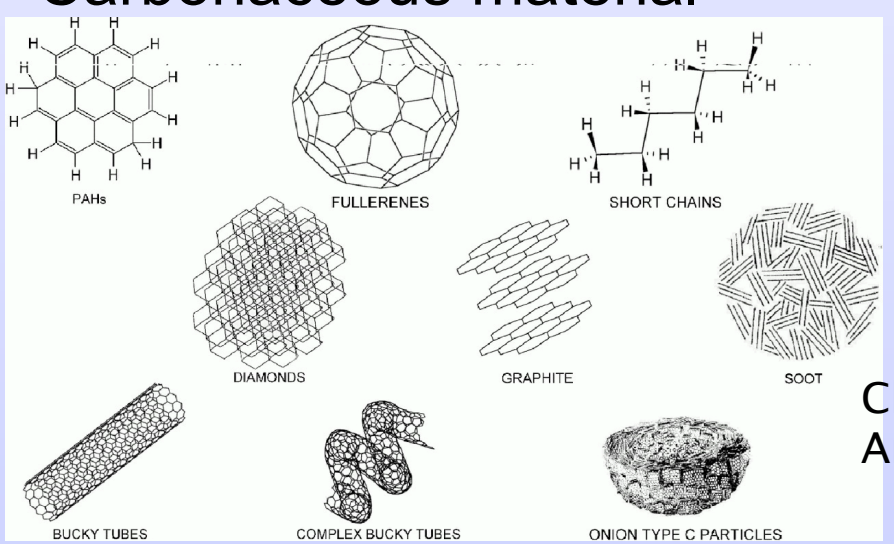
Simple silicate (olivine)



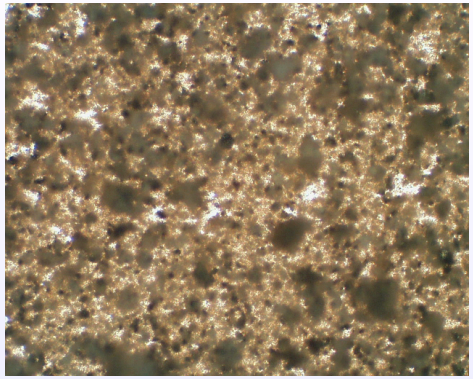

Carbonaceous Material

- Carbonaceous material




Also: SiC, nanodiamonds, aluminosilicates

Charnley and Ehrenfreund, Ann.Rev.Astron.Astrophys.



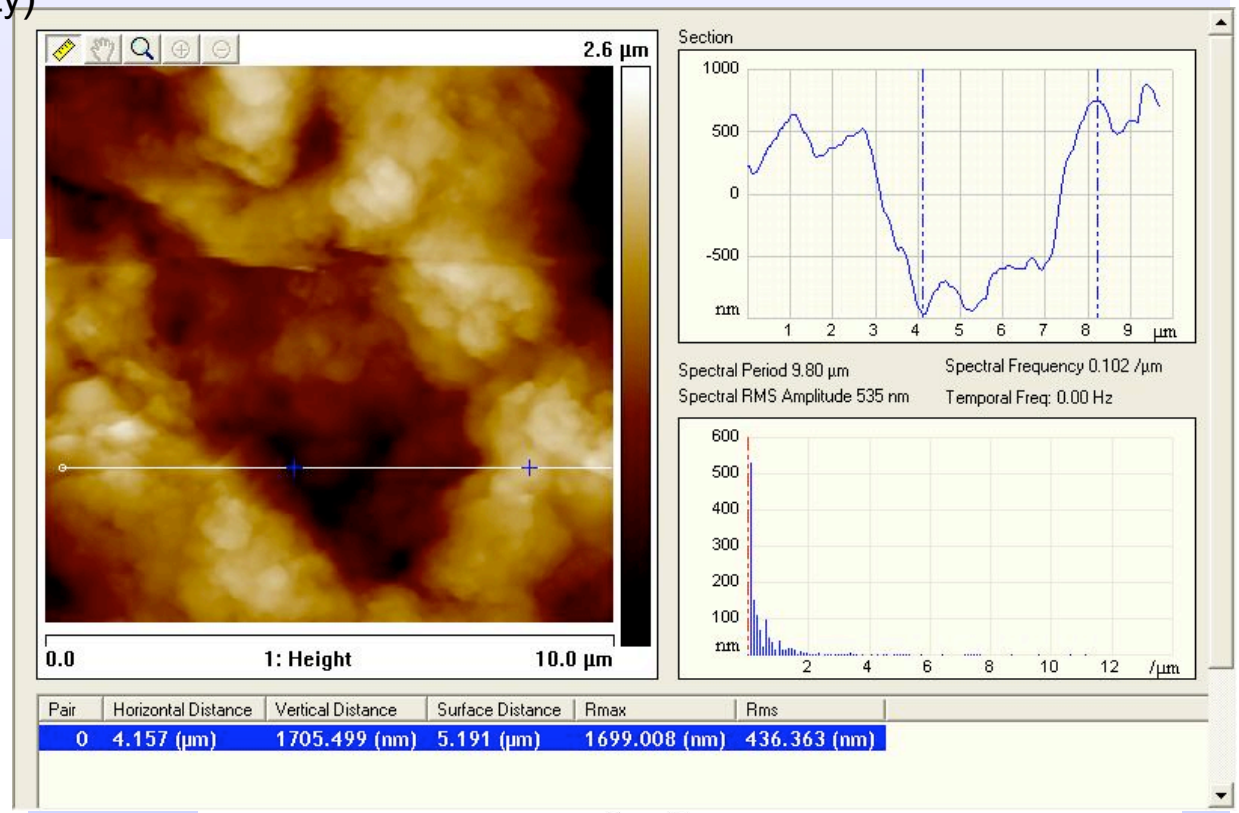
Optical x10

Amorphous silicate $(Mg_{0.5}Fe_{0.5})_2SiO_4$
prepared by Dr. J.Brucato
(Astronomical .Obsrv. Naples)

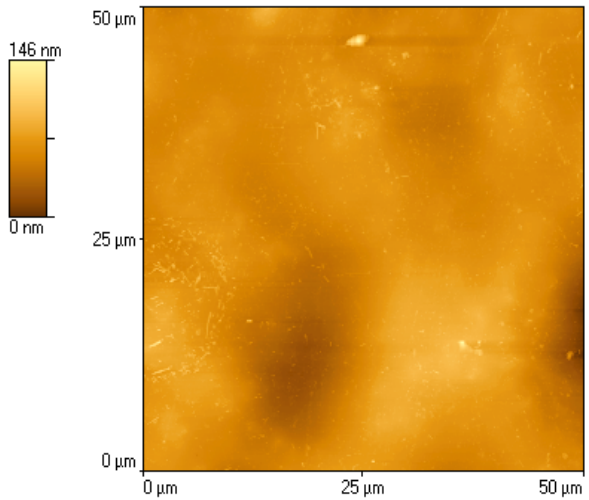
optical images taken by
Dr. Herma Cuppen (Ohio State University)

amorphous silicate $MgFeSiO_4$

Hebrew Univ.

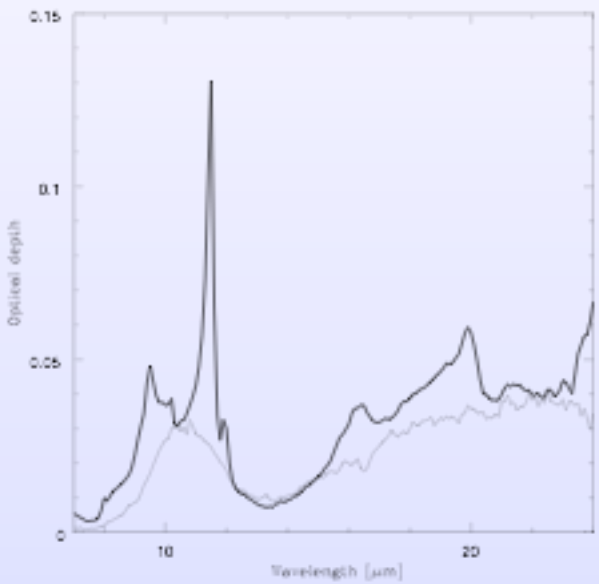



Polycrystalline olivine

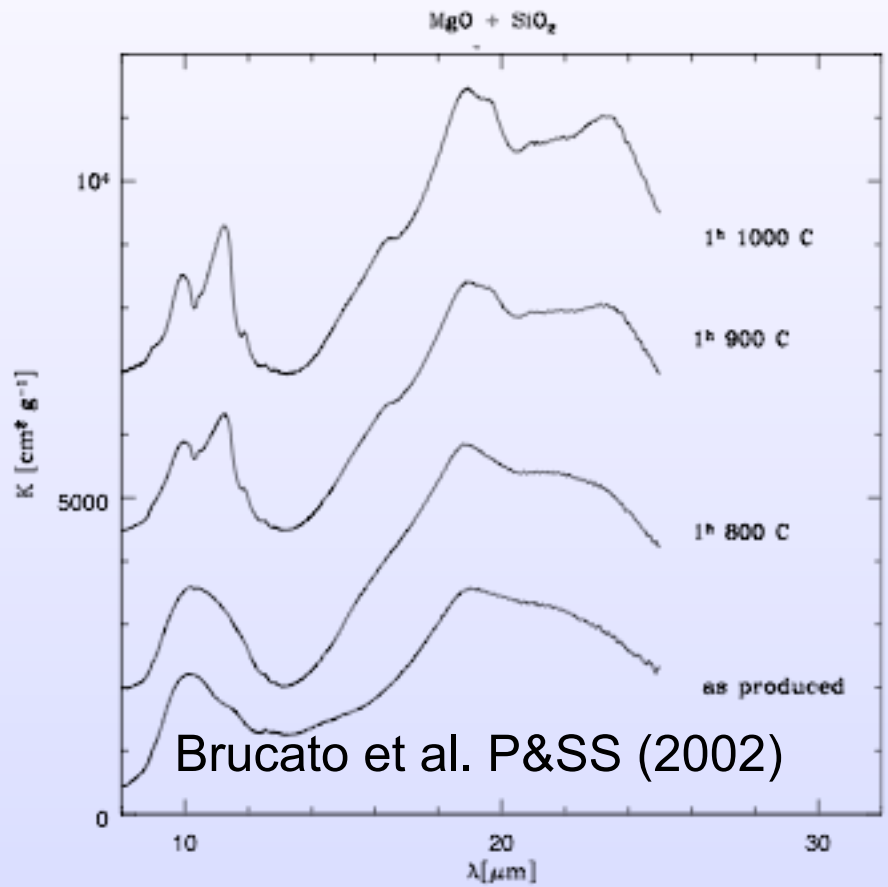



Syracuse Univ.

Amorphous silicate $(Mg_{0.5}Fe_{0.5})_2SiO_4$
prepared by Dr. J.Brucato
(Astrophys.Obsrv. Naples)




Samples used



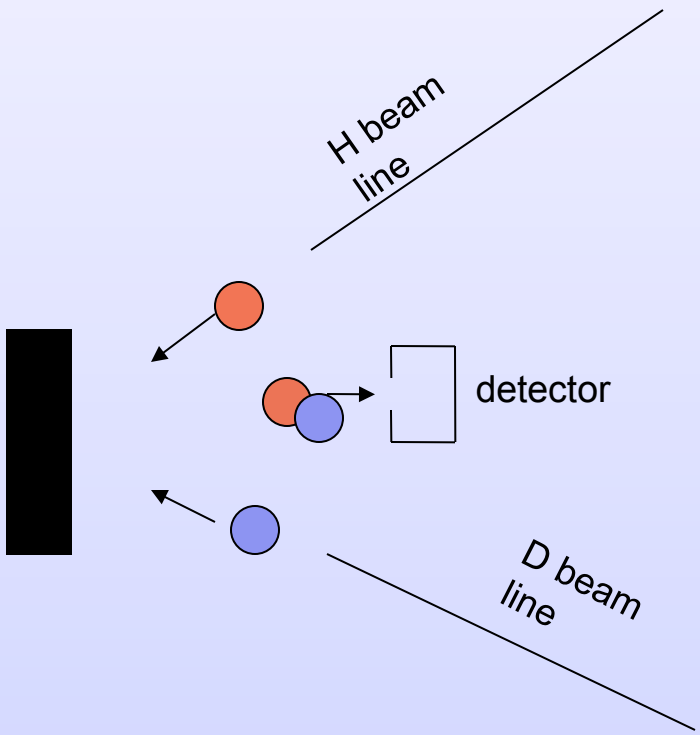

Brucato et al. P&SS (2002)

# Prompt Reaction

Detection of HD formation via
Ealy-Rideal, hot atom mechanisms

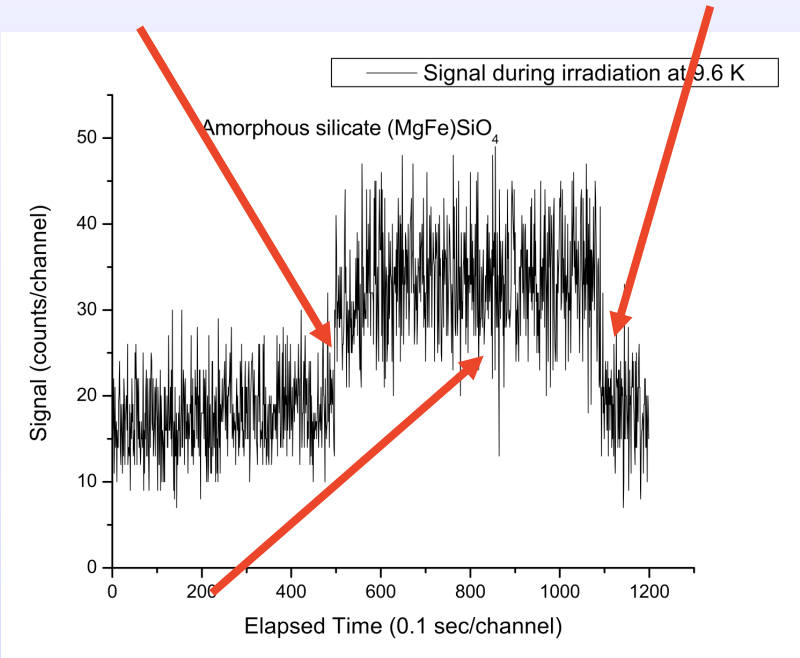
at SU

Irradiation phase




Irradiation begins

irradiation ends




Signal at mass 3 (HD) during irradiation

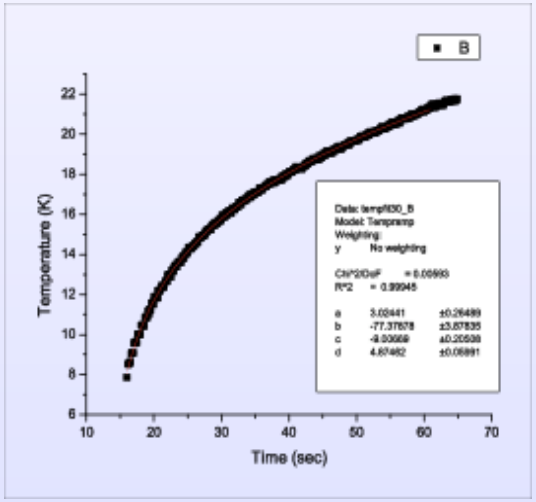
In the range of sample temperature explored, this gives little contribution to the overall HD yield -see below

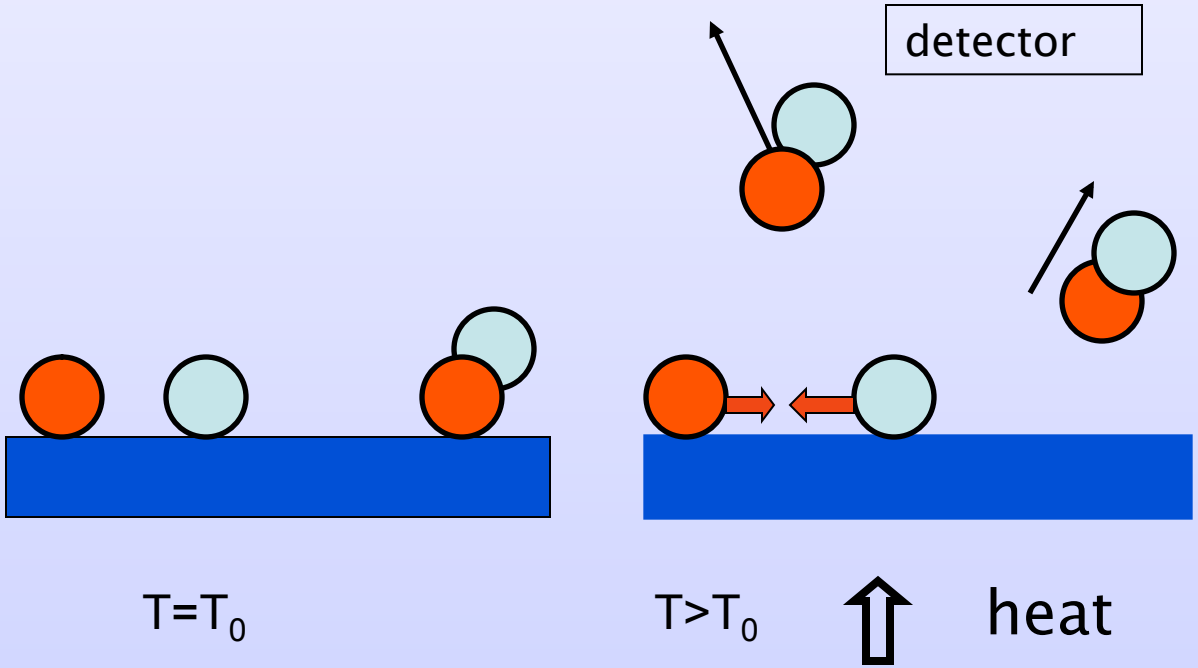
# Temperature Programmed Desorption

Detection of HD formation via the Langmuir-Hinschelwood mechanism

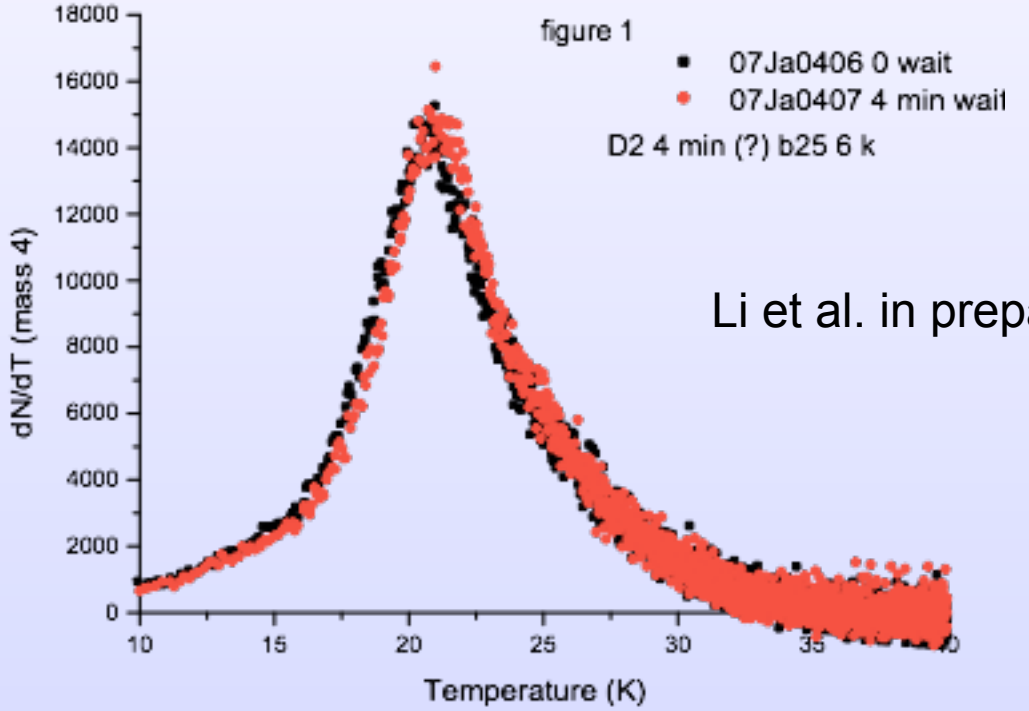
The purpose of the second part of the experiment is to:

1. Set atoms in motion that are still on the sample
2. Desorb molecules already formed on the surface

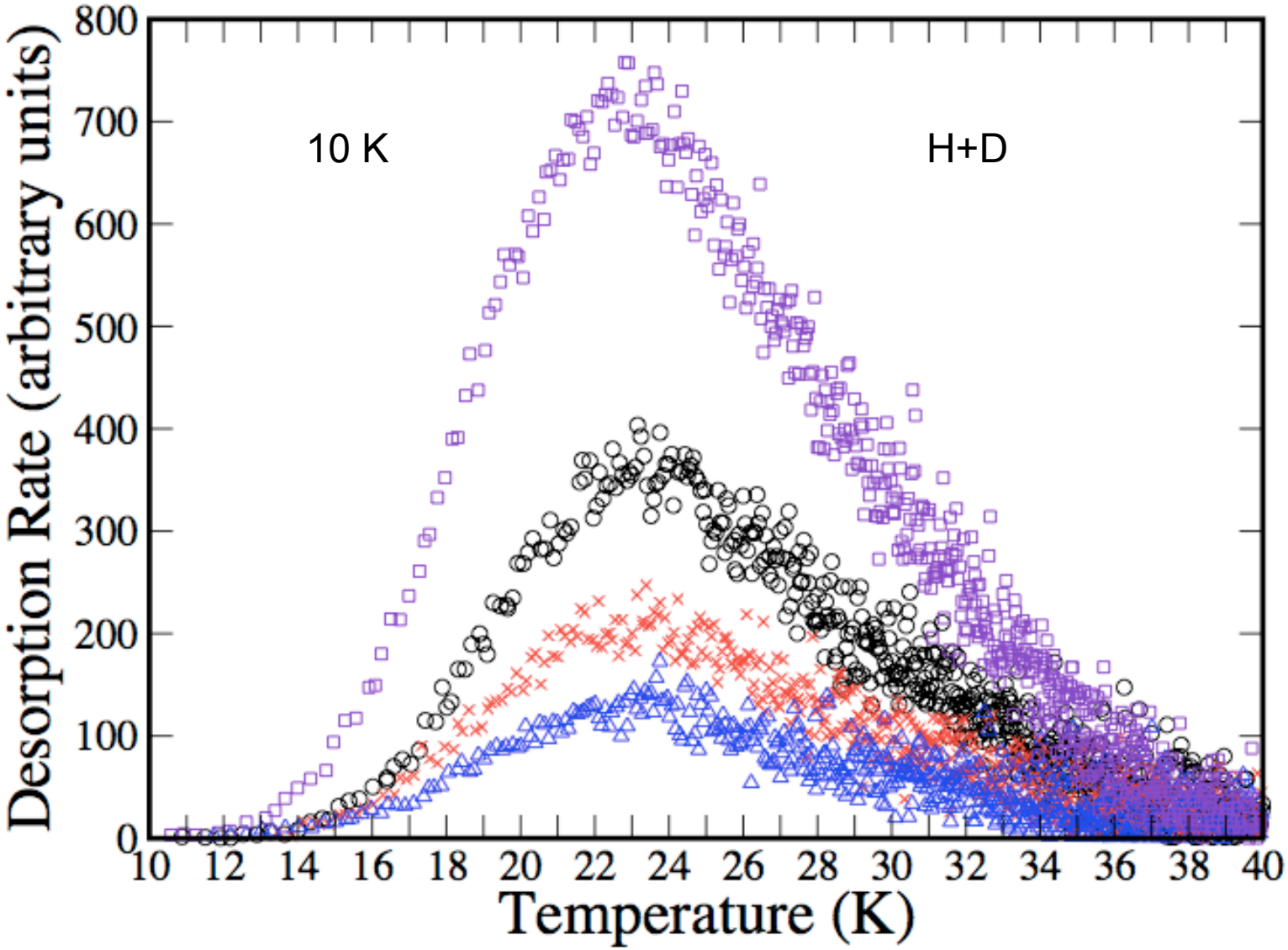


# There is hardly desorption of molecules at low temp. (A similar result for H atoms)

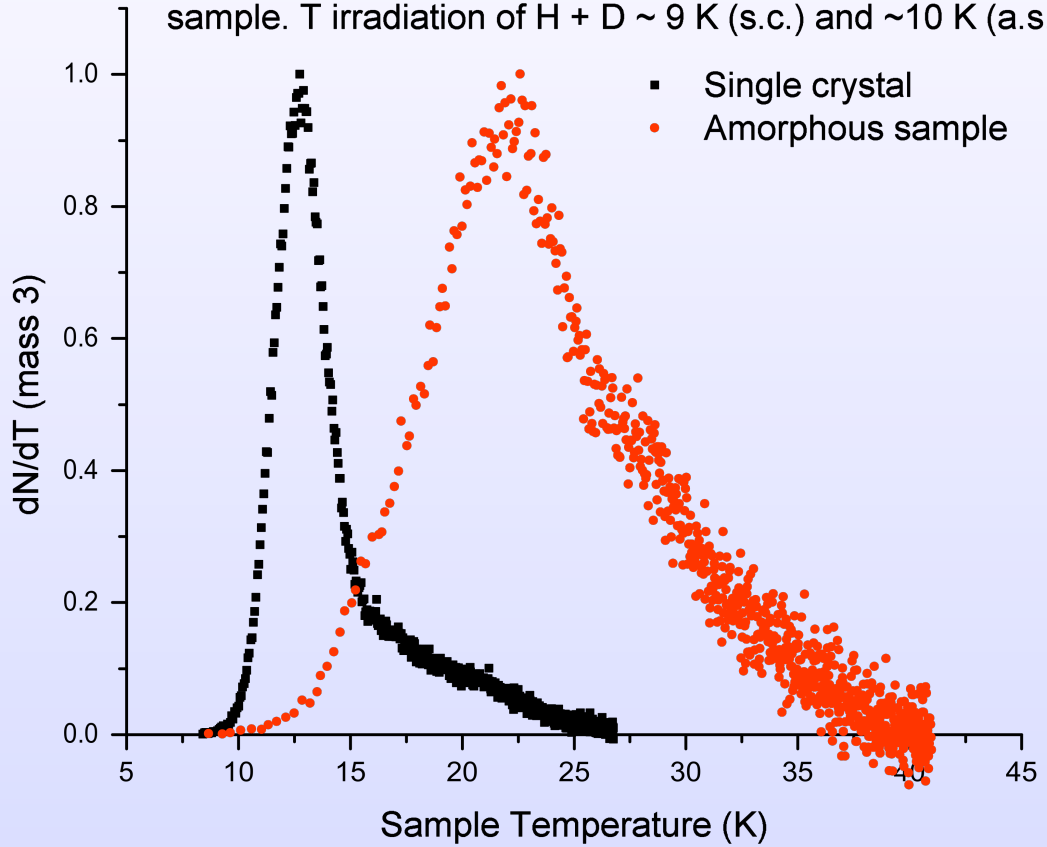



Li et al. in preparation




Vidali et al. - J.Phys Chem A 111 12611 (2007)

Comparison of TPDs from a single crystal and an amorphous sample. T irradiation of H + D ~ 9 K (s.c.) and ~10 K (a.s.)




Li et al., in preparation

A similar result for ice, Vidali et al., JGR 109 E07S104 (2004); Al-Halabi et al., MNRAS (2007)

$$\frac{dn_{\mathrm{H}}}{dt} = f_{\mathrm{H}} - W_{\mathrm{H}} n_{\mathrm{H}} - 2a_{\mathrm{H}} n_{\mathrm{H}}^2 - (a_{\mathrm{H}} + a_{\mathrm{D}}) n_{\mathrm{H}} n_{\mathrm{D}}$$

$$\frac{dn_{\mathrm{D}}}{dt} = f_{\mathrm{D}} - W_{\mathrm{D}} n_{\mathrm{D}} - 2a_{\mathrm{D}} n_{\mathrm{D}}^2 - (a_H + a_D) n_{\mathrm{H}} n_{\mathrm{D}}.$$

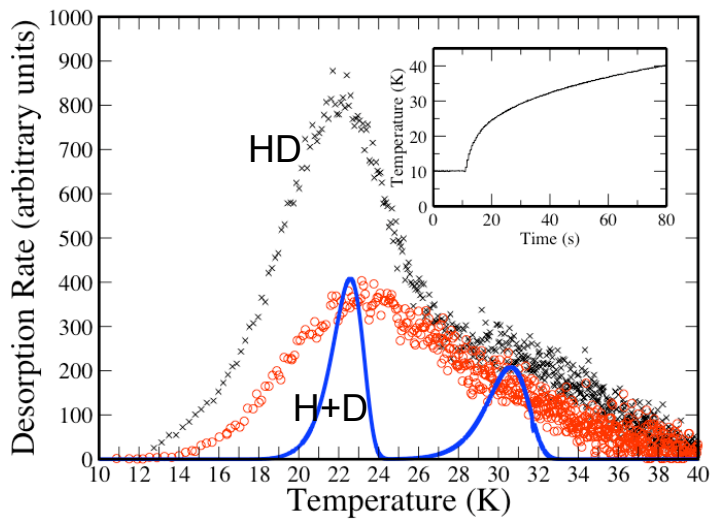
$$\frac{dn_{\mathrm{H_2}}}{dt} = a_{\mathrm{H}} n_{\mathrm{H}}^2 - W_{\mathrm{H_2}} n_{\mathrm{H_2}}$$

$$\frac{dn_{\mathrm{D_2}}}{dt} = a_{\mathrm{D}} n_{\mathrm{D}}^2 - W_{\mathrm{D_2}} n_{\mathrm{D_2}}$$

$$\frac{dn_{\mathrm{HD}}}{dt} = (a_{\mathrm{H}} + a_{\mathrm{D}}) n_{\mathrm{H}} n_{\mathrm{D}} - W_{\mathrm{HD}} n_{\mathrm{HD}}$$

$$W_{\mathrm{X}} = \nu \exp(-E_{\mathrm{X}}^{\mathrm{des}}/k_{\mathrm{B}}T)$$

$$a_{\mathrm{X}} = \nu \exp(-E_{\mathrm{X}}^{\mathrm{diff}}/k_{\mathrm{B}}T)$$

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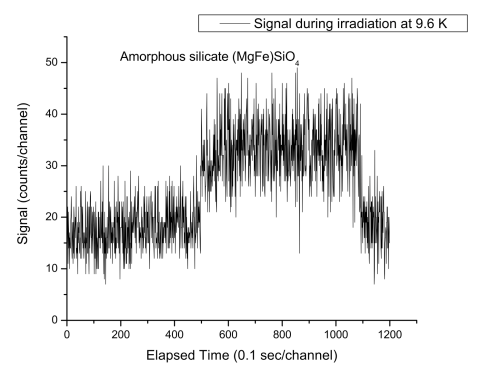
energies in meV

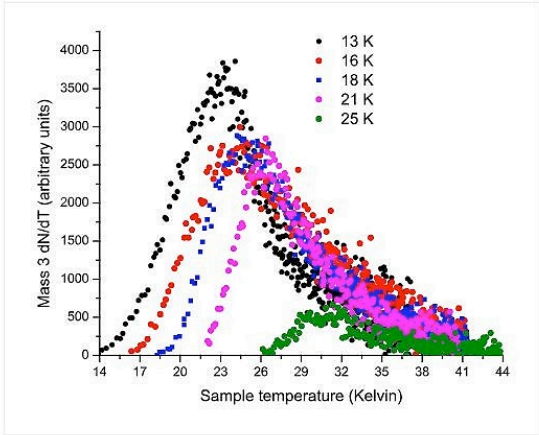
| material | $E_{diff}$(H) | $E_{des}$(H) | $E_{des}$(HD) | $E_{des}$(HD) | $E_{des}$(HD) | sites |
|---|---|---|---|---|---|---|
| a-silicate | 35 | 44 | 35 | 53 | 75 | $7\ 10^{14}$ |
| p-cryst. | 25 | 32 | 27 | | | |

# Calculation of molecule formation efficiency

The number of molecules coming off during irradiation is proportional to the area under the trace



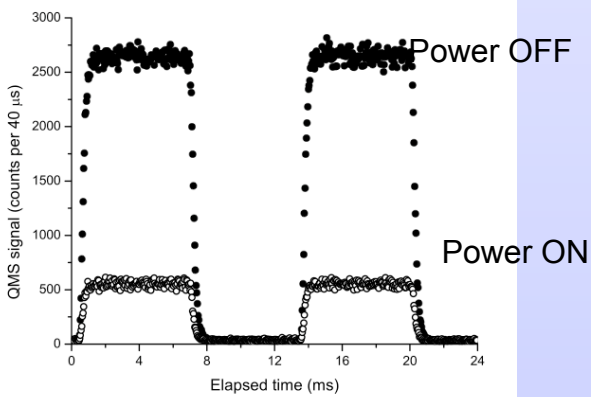

The number of molecules coming off during the temperature programmed desorption is proportional to the area under the curve




$$R = \frac{N_{irr} + N_{des}}{N_{beam}}$$

*Number of atoms going to the sample during the irradiation phase*

Change in the signal level of $D_2$ with RF power ON and OFF in the dissociation source; from this, the number of atoms in the beam can be calculated.



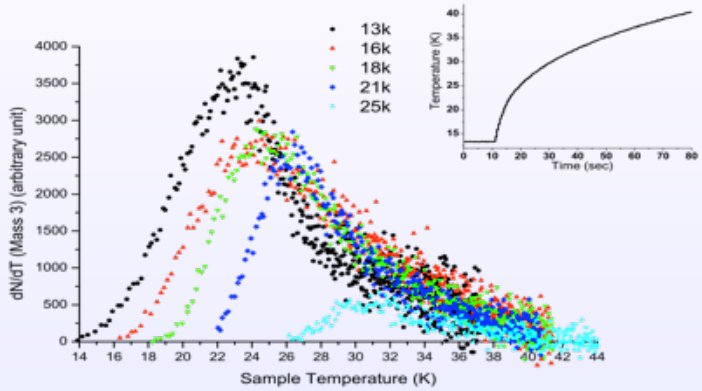



Fig. 3. TPD of HD desorption after H and D atom irradiation at different sample temperatures. Irradiation is for 4 minutes with hydrogen and deuterium atoms on an amorphous silicate sample $(Fe_xMg_{(1-x)})_2$ $SiO_4$, $x$=0.5. A temperature ramp following irradiation at 13 K is shown in the top right corner.

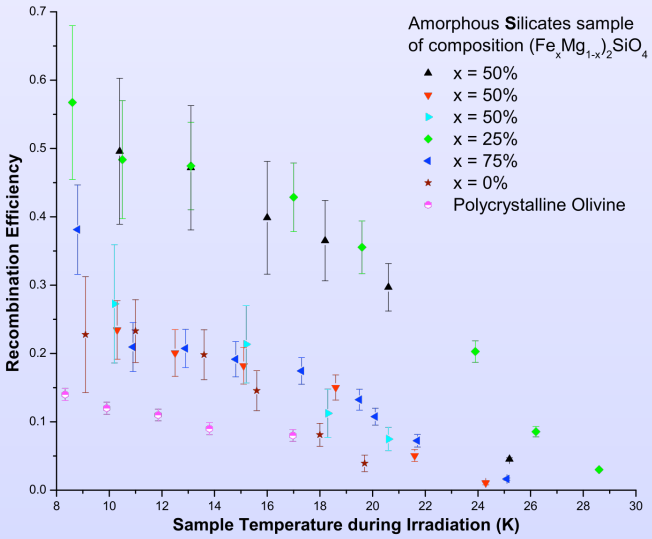



Fig. 4. HD formation efficiency after irradiation of amorphous silicate and polycrystalline samples with hydrogen and deuterium atoms. Data form a representative set of samples of different composition are shown.

Table 1
Desorption energy of HD obtained from TPD runs at different irradiation temperatures from an amorphous silicate of composition $(Fe_xMg_{(1-x)})_2$ $SiO_4$, $x$=0.5.

| Irradiation Temperature | E(meV) | Relative Coverage |
|---|---|---|
| 13 K | 59 | 1 |
| 16 K | 61 | 0.9 |
| 18 K | 64 | 0.8 |
| 21 K | 69 | 0.7 |
| 25 K | 80 | 0.4 |

Table 2
Desorption energy of HD from amorphous silicates of different composition $(Fe_xMg_{(1-x)})_2$ $SiO_4$. Energies in meV.

| Sample | E at T∼13K | E at T∼25-26 K |
|---|---|---|
| $x$=0.25 | 65 | 81 |
| $x$=0.5 | 59 | 80 |
| $x$=0.75 | 58 | 76 |

1

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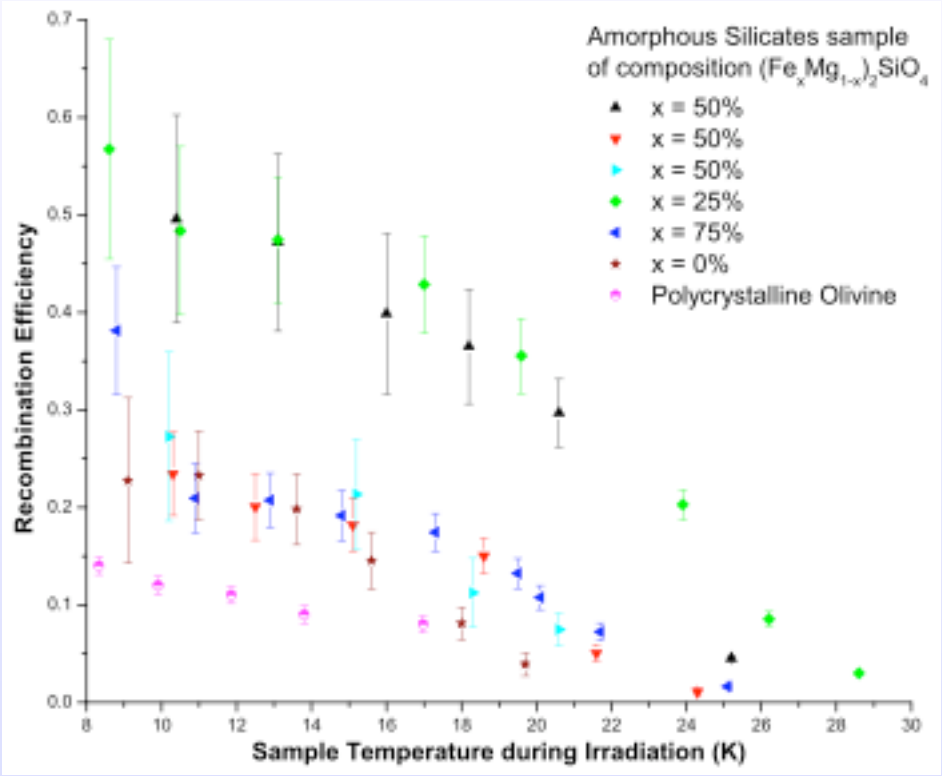
o State

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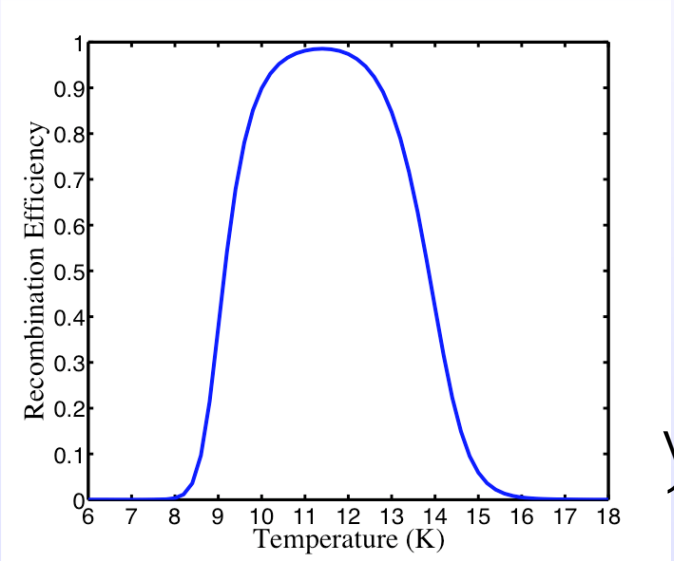
# Theory

- Katz et al., Astrophys.J. **522** 305 (1999): rate equations, physisorption, Langmuir-Hinshelwood
- Cazaux & Tielens, Astrophys.J. **575** 29 (2002); ibid. **604** 222: rate equations, plus chemisorption, isotopes
- Biham & Lipshtat Phys.Rev. E 055103: master eq. approach - stochastic effects for small grains
- Cuppen and Herbst, Mon.Not.R. Astron. Soc. **361** 565 (2005): Monte Carlo, influence of surface roughness

- See also: Biham, Lipshtat & Perets, IAU No231 Proceedings

# From the laboratory to space

Results of rate equations




$n=100\ cm^{-3}$
$T_g=100\ K$
$f=5\ 10^{-9}$ ML/sec

ML=monolayer

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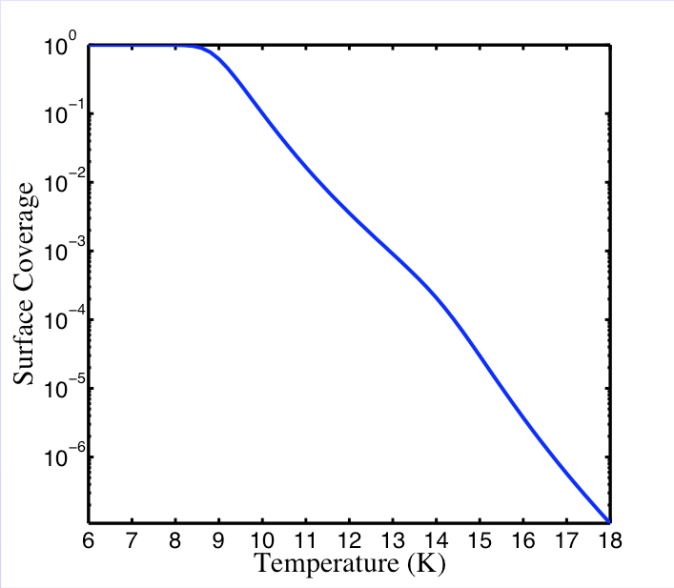
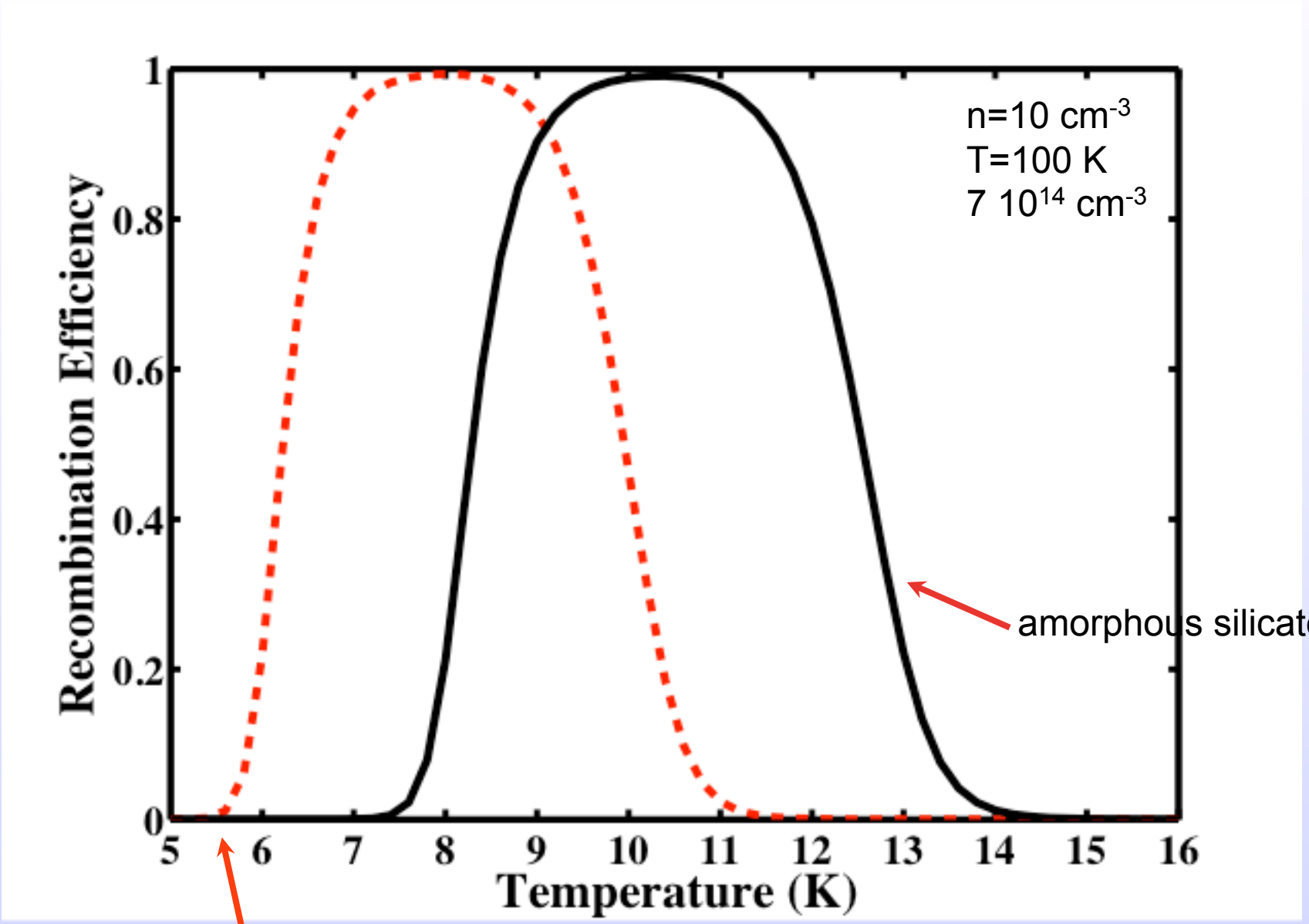
Simulation under steady state conditions




Amorphous silicate




Perets et al. ApJ 661, L163 (2007)

# Summary of results from experiments

- System: formation of $H_2$ on dust grain analogues under simulated ISM conditions
- Information obtained:
  - **Mechanism**: Langmuir-Hinshelwood, hot atom (depending on circumstances)
  - **Atom/molecule - surface interactions**: physisorption
  - **Formation Efficiency**: higher for amorphous surfaces
  - **Energetics**: diffusion and desorption energies
  - **Kinetic Energy** of just-formed molecules: nearly thermal from a-ice

- Collaborators:
  - Profs. O.Biham (Hebrew Univ.), V.Pirronello (Univ. of Catania)
  - L. Li, H.Zhao, E.Congiu (now at U. Cergy-Pontoise), J.Roser (now at NASA-Ames), H.Perets (now at the Weizmann Inst.)
- Sponsors: NASA-APRA, NSF-Planetary Astronomy, BSF, Israel Science Foundation, Adler Foundation, Italian Ministry of Research