Formation of molecules on stardust: what we know and what we don't know, but should

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http://physics.syr.edu/astro

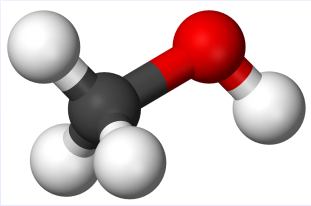
National Science Foundation
WHERE DISCOVERIES BEGIN

National Aeronautics
and Space Administration

Outline

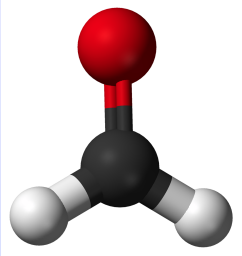
1. Formation of molecules on stardust: Molecules of interest for the evolution of the ISM
2. What we need to know
3. A two-minute primer on surface science
4. How laboratory work can help: selected results
5. Translation of experimental results to the ISM: theory, modeling, and simulations
6. What's left to know

Molecules of interest



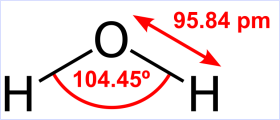
methanol

on, in ices
dense clouds/
hot cores



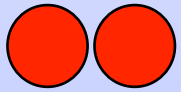
formaldehyde

on, in ices
dense clouds/
hot cores



water

on, in ices
edge dense clouds

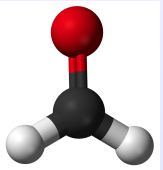


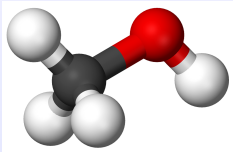
hydrogen

bare surfaces, ices
Everywhere (diffuse,
PDR, shocked
regions, dense)

What we need to know

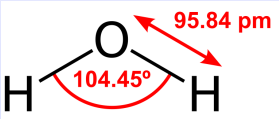
- Formation routes, products, conditions, rates





UV processing of ices
(Greenberg, Allamandola, Schutte, Linnartz…)

Cosmic rays (MeV p, keV e) into ices
(Moore, Baragiola, Palumbo, Kaiser,…)



Hydrogenation, oxidation reactions
(Watanabe,Vidali, Chutjian, ,…)

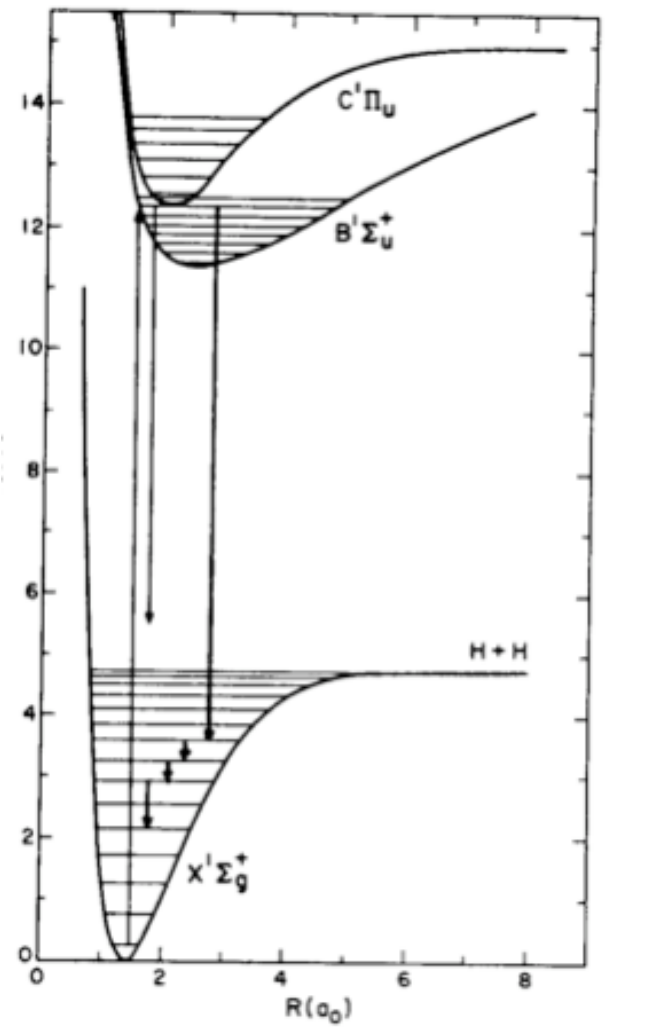
H_{gas} , O_{gas} onto grains

Herbst & van Dishoeck (2009)

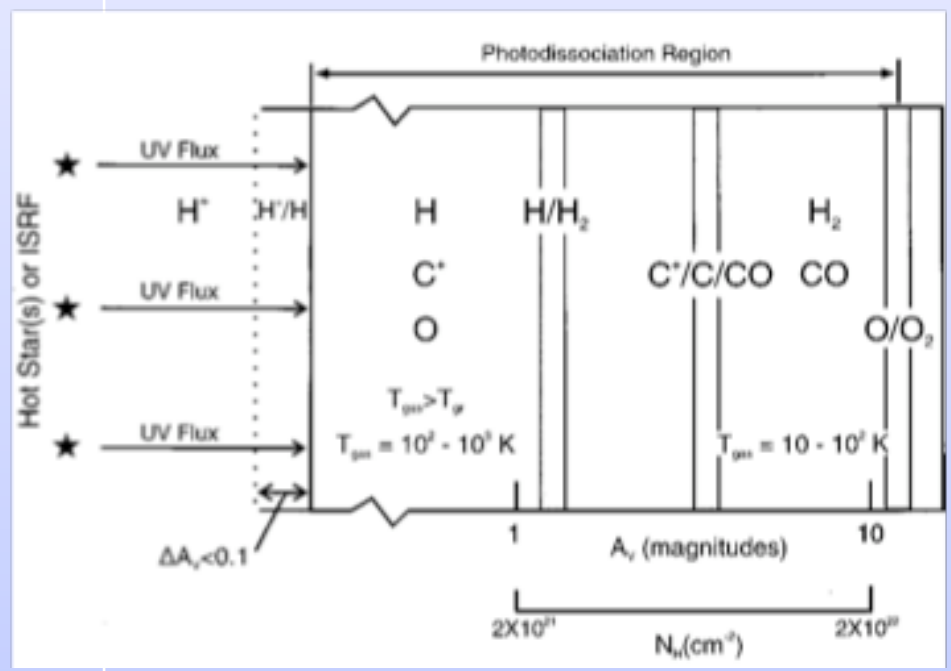
What we know — Reaction routes, products

What we don't know — Rates, comprehensive picture of which formation route prevails in which ISM environment, laboratory-ISM gap

Molecular Hydrogen in the Universe



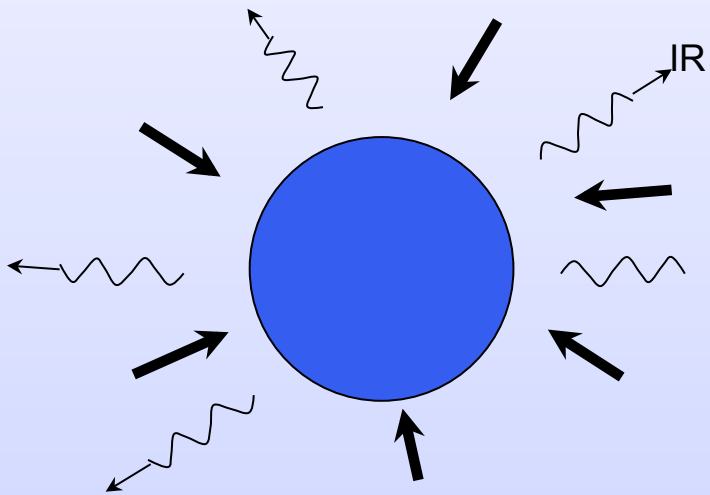
- Most abundant molecule Carruther (1970)
- Tracer of warm gas
  - collisional excitation
  - FUV excitation



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 contraction

- Promotes interstellar chemistry

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

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

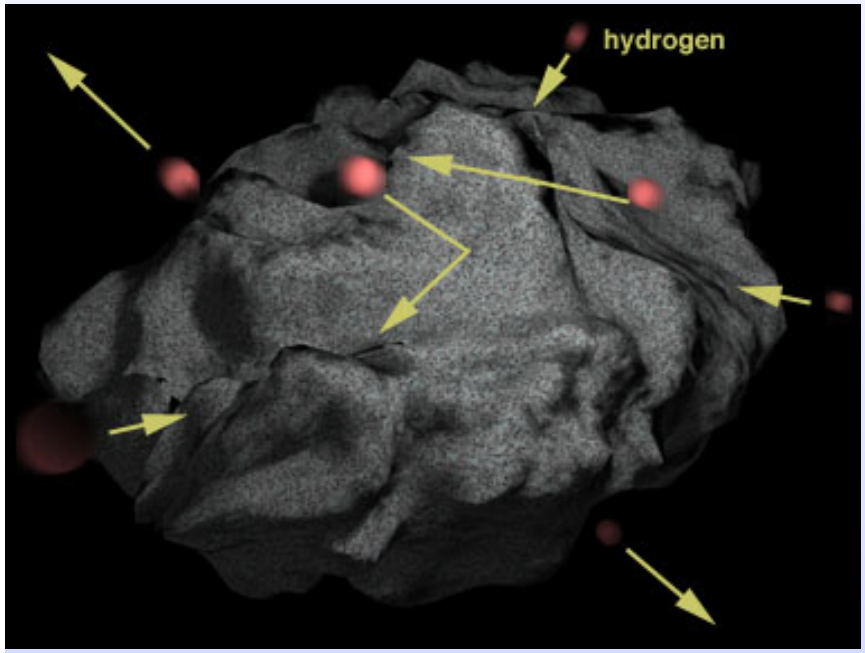
oxygen chemistry:

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

hydrocarbon chemistry:

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

Formation of H_2 in the ISM



$H+H \rightarrow H_2$ on dust grains (polycrystalline ice)
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 (H atoms are trapped at defects)

Experiments by Scoles' group in the 1970s

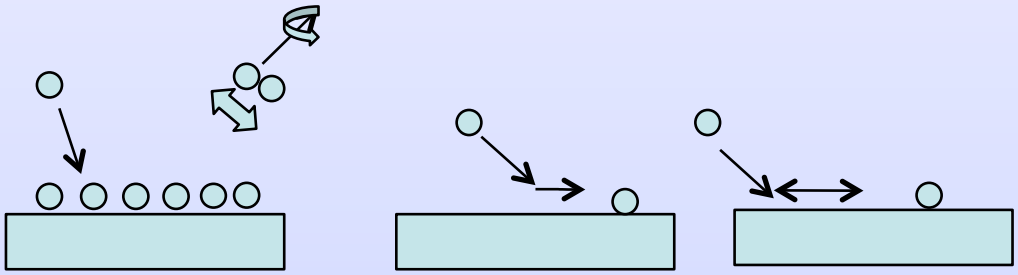
observational evidence difficult:
Herschel: correlation of H_2 emission and dust

A little of surface science: Adsorption

Atom-surface interaction

Physical adsorption
(physisorption) ~1-300 meV

Chemical adsorption
(chemisorption) ~ eV



Eley-Rideal
$\sigma \sim 10^{-15}$ cm^2
H on H+graphite
(Mennella, 2008)
Molecule not equil.

Hot-atom
H on metals
Superthermal
speed

Langmuir-
Hinshelwood,
most reactions

Adsorption

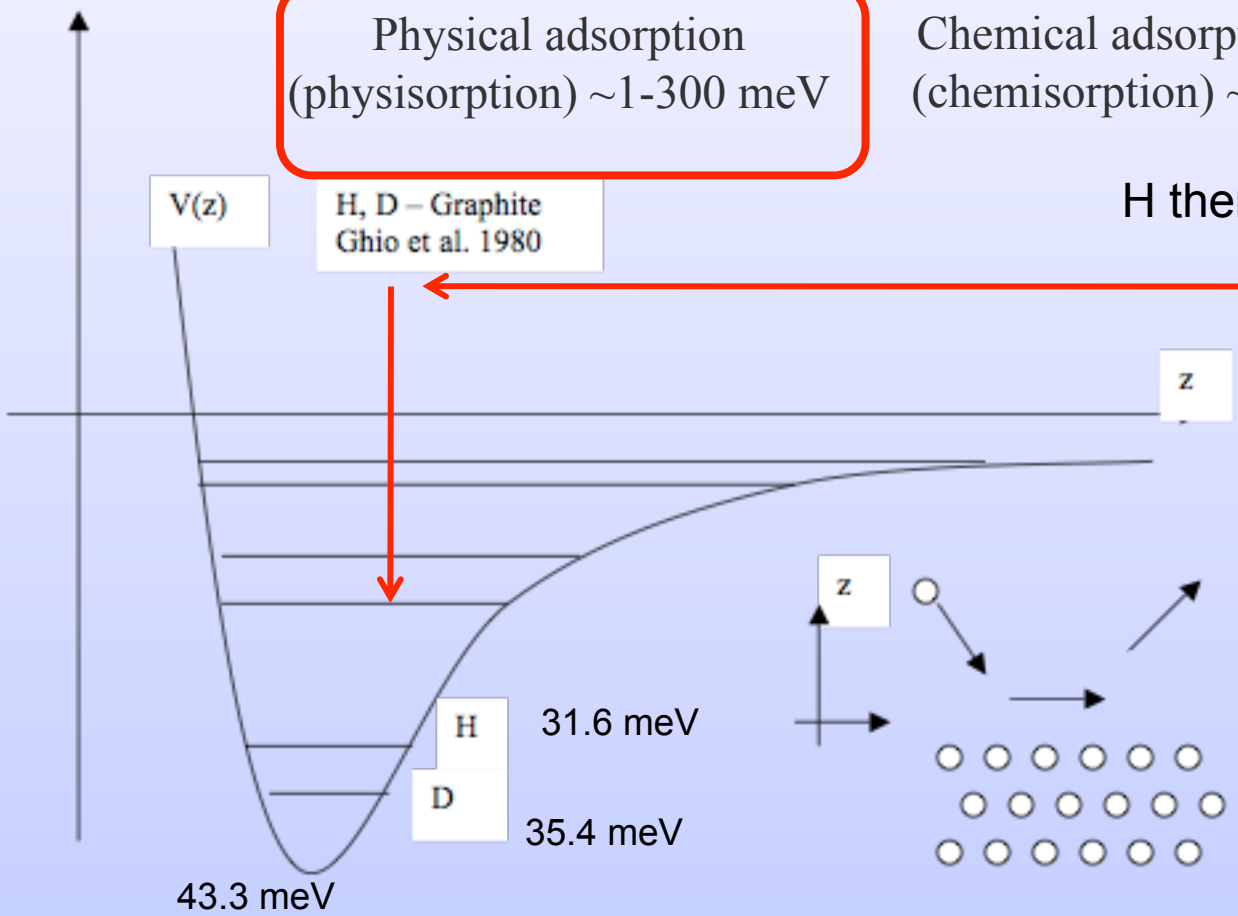
Atom-surface interaction

Physical adsorption (physisorption) ~1-300 meV

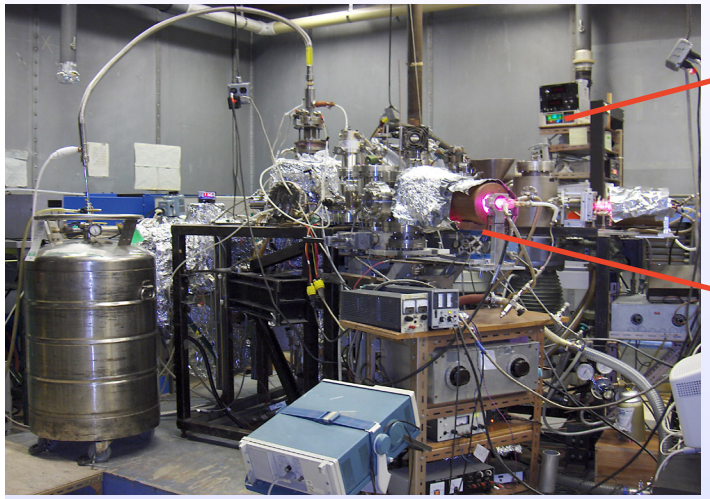
Chemical adsorption (chemisorption) ~ eV

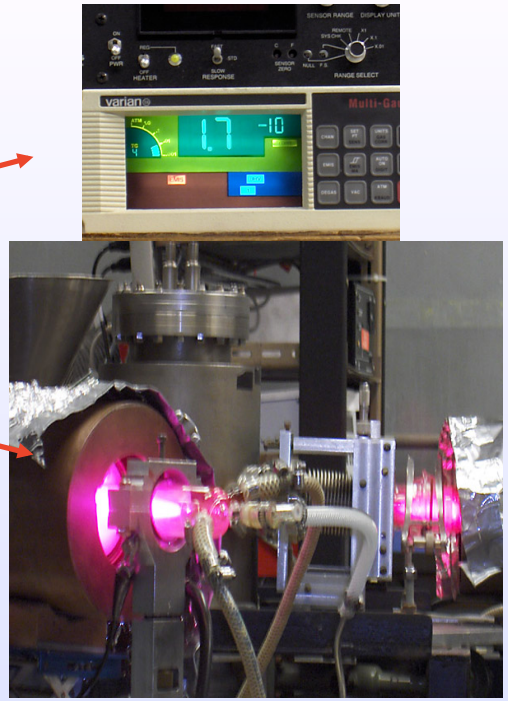
H thermal beam scattering

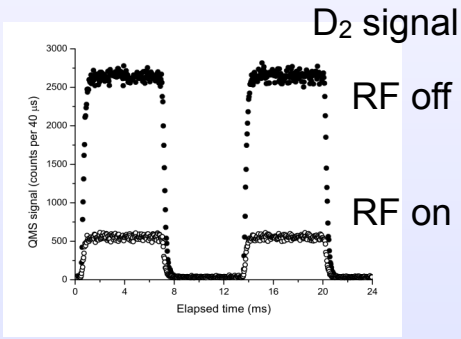
H or D

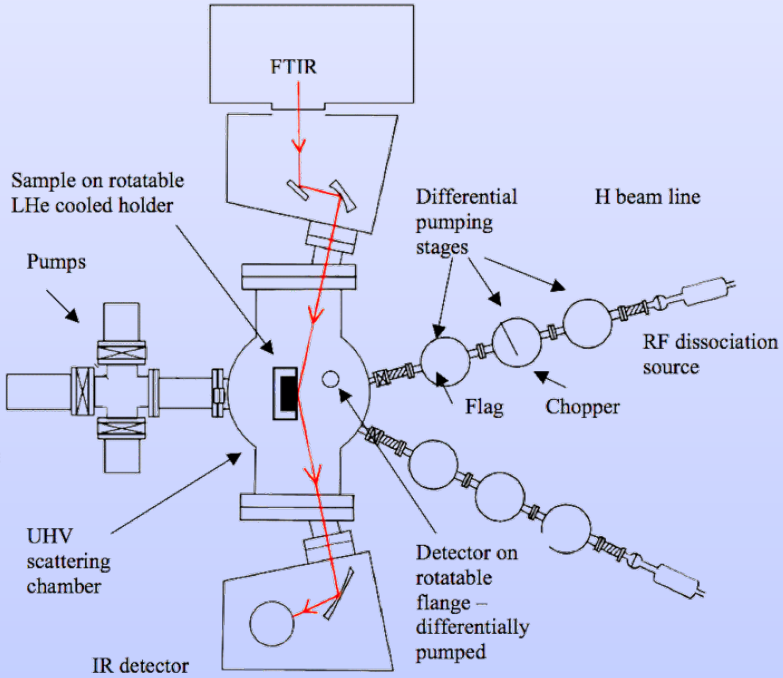


Vidali et al.
Surf .Sci. Rep. 12, 133 (1991)







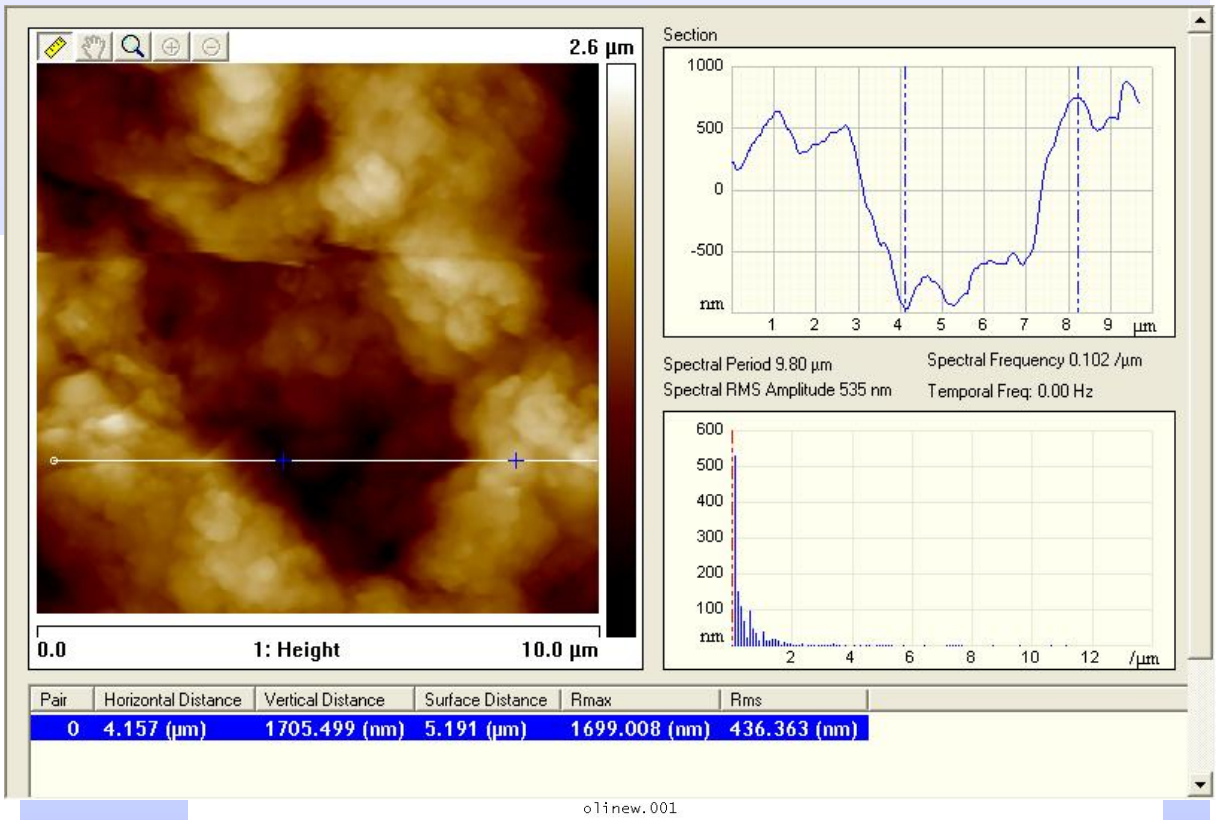


Apparatus at S.U to study molecule formation on dust grain analogues

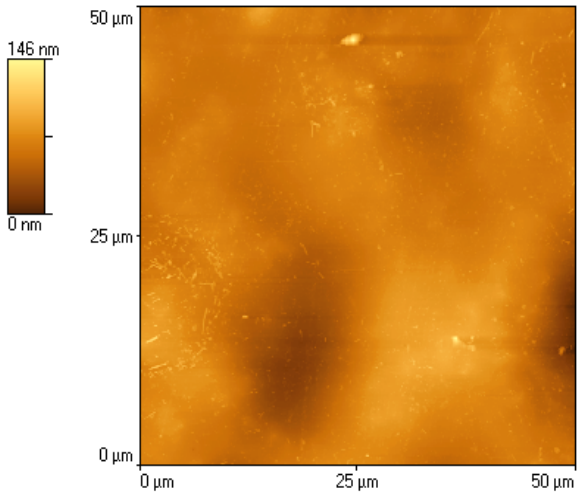
Amorphous silicate $(Mg_{0.5}Fe_{0.5})_2SiO_4$
prepared by Dr. J.Brucato
(Astronomical .Obsrv. Naples)

amorphous silicate $MgFeSiO_4$

Hebrew Univ.



Polycrystalline olivine



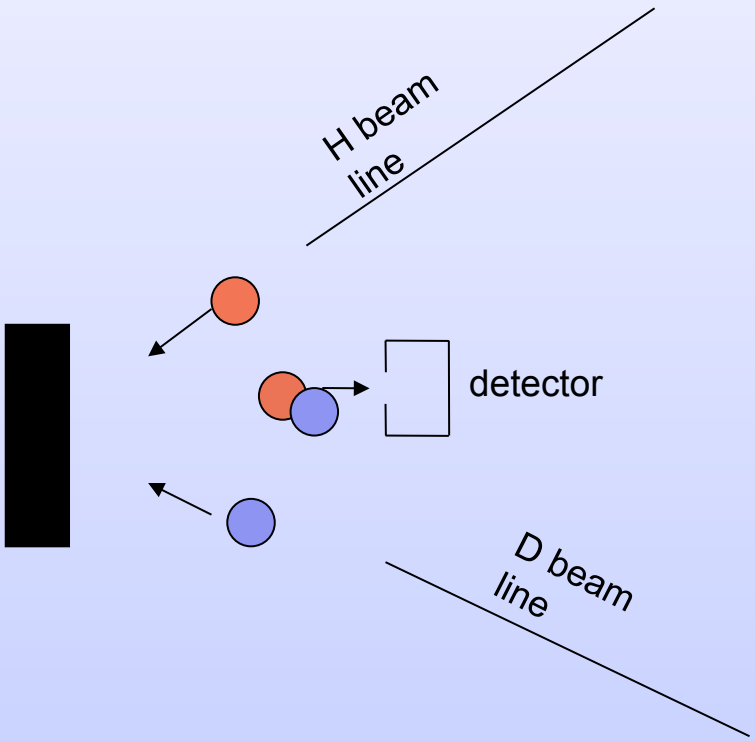
Syracuse Univ.

Prompt Reaction

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

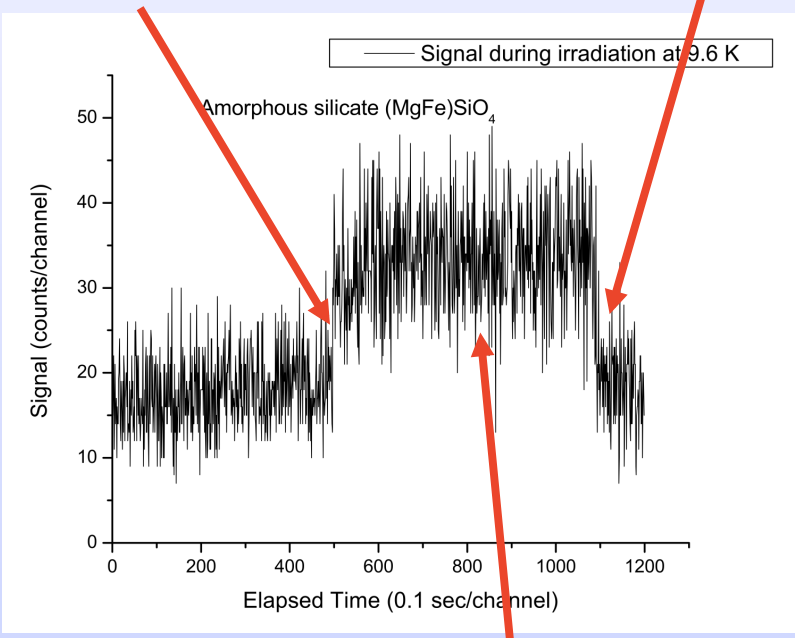
at SU

Irradiation phase



Irradiation begins

irradiation ends



Signal at mass 3 (HD) during irradiation

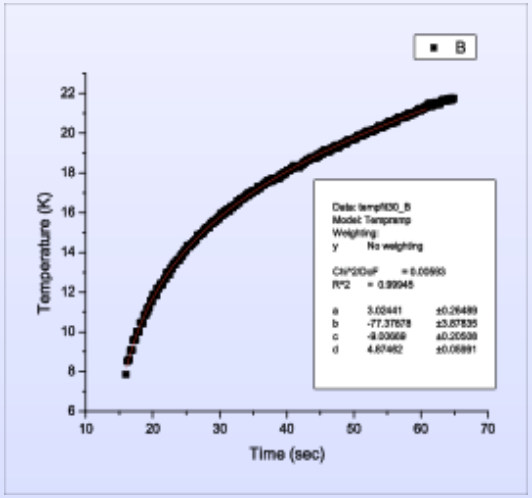
In the range of sample temperature explored, this gives little contribution to the overall HD yield -see below

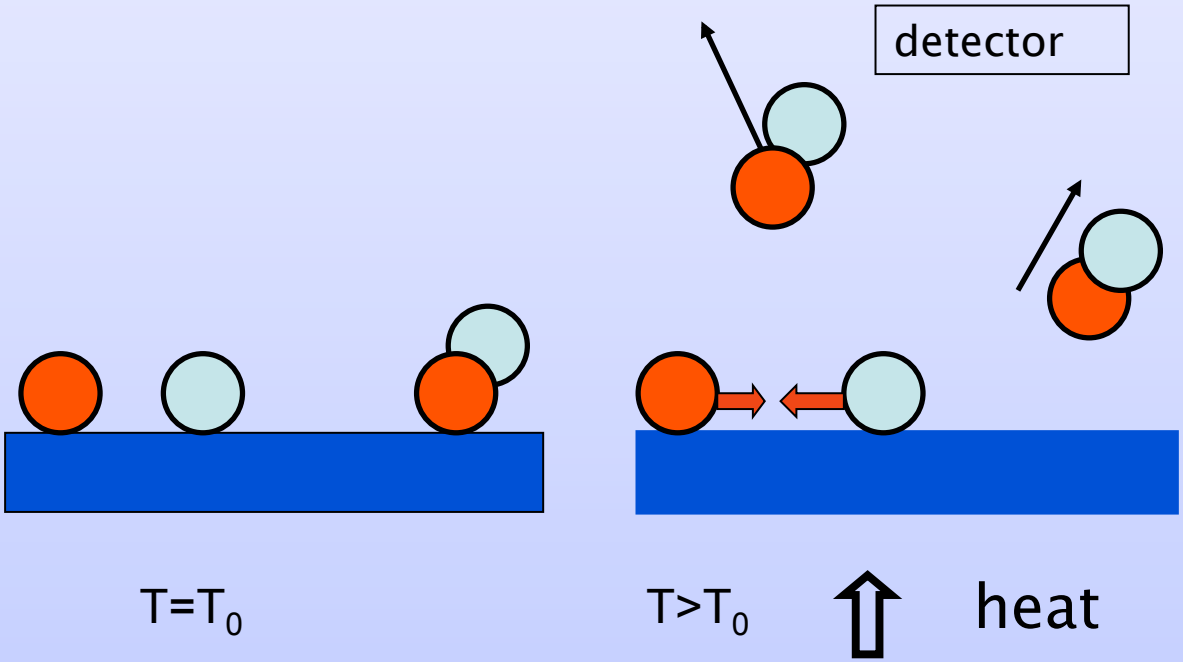
Temperature Programmed Desorption

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





Molecules of interest: H_2

THE ASTROPHYSICAL JOURNAL, 475:L69–L72, 1997 January 20
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LABORATORY SYNTHESIS OF MOLECULAR HYDROGEN ON SURFACES OF ASTROPHYSICAL INTEREST

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Received 1996 September 23; accepted 1996 November 1

ABSTRACT

We report on the first results of experiments to measure the recombination rate of hydrogen on surfaces of astrophysical interest. Our measurements give lower values for the recombination efficiency (sticking probability S times the probability of recombination upon H-H encounter, γ) than model-based estimates. We propose that our results can be reconciled with *average* estimates of the recombination rate $[(1/2)n_H n_g v_H AS\gamma]$ from astronomical observations, if the actual surface of an average grain is rougher, and its area bigger, than the one considered in models.

Subject headings: dust, extinction — ISM: abundances — ISM: molecules — molecular processes

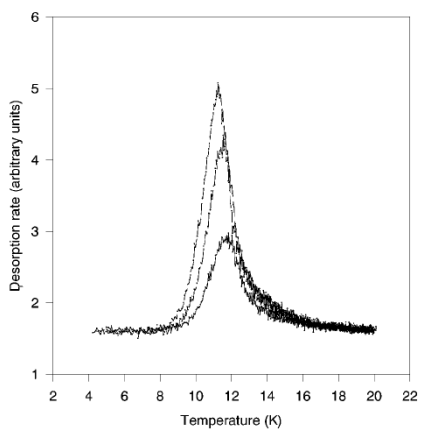


FIG. 2.—Representative thermal desorption ion curves of HD from olivine; exposure to H and D for 2, 1.5, and 1 minute (*top to bottom*) at 5 K; heating rate: ~1 K s^{-1}.

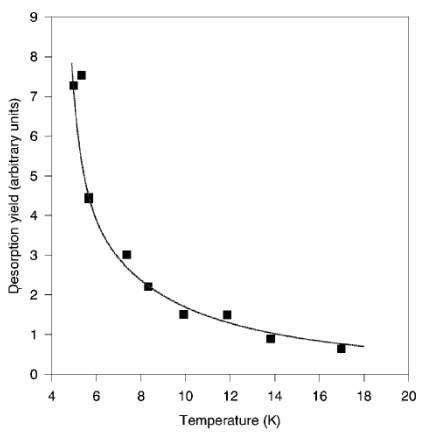
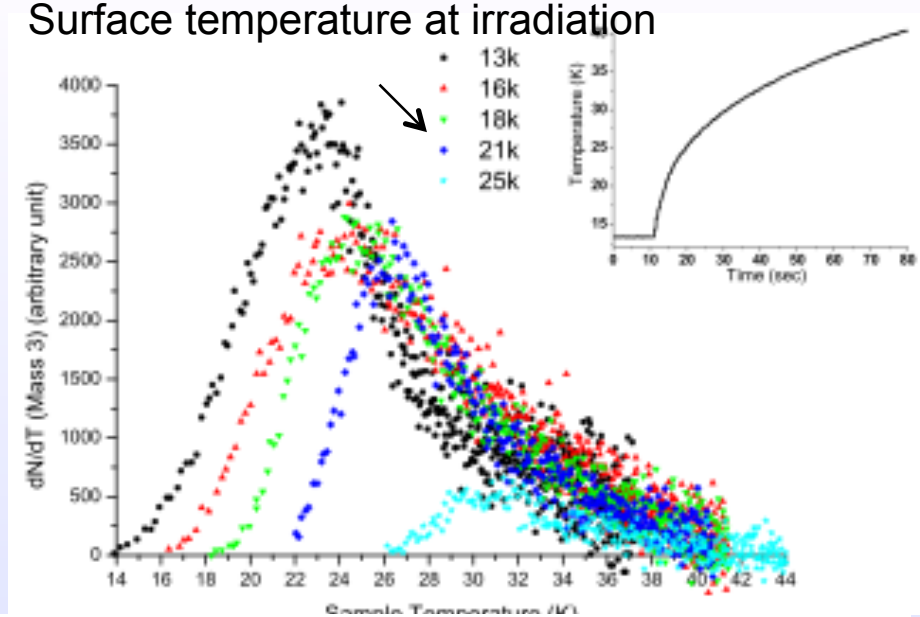


FIG. 4.—Desorption yield of HD from olivine after adsorption of H and D at the indicated temperatures. Exposure time: 1 minute (*line:* guide to the eye).

Surface: polished olivine (polycrystalline telluric sample)

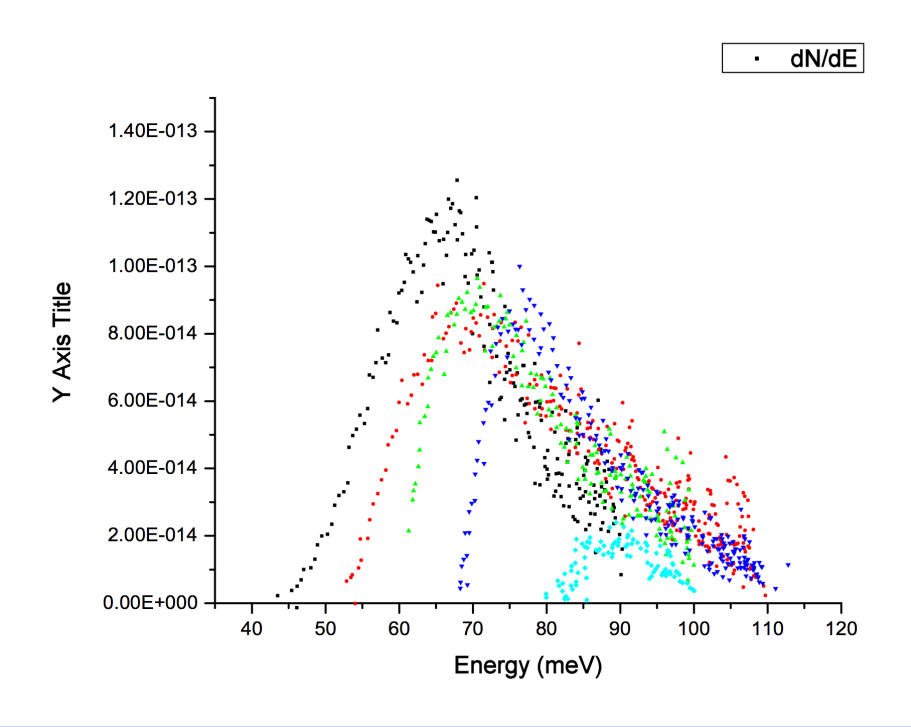
Surprise:
-Thermal activation necessary
-High efficiency drops quickly vs. temperature

Surface temperature at irradiation

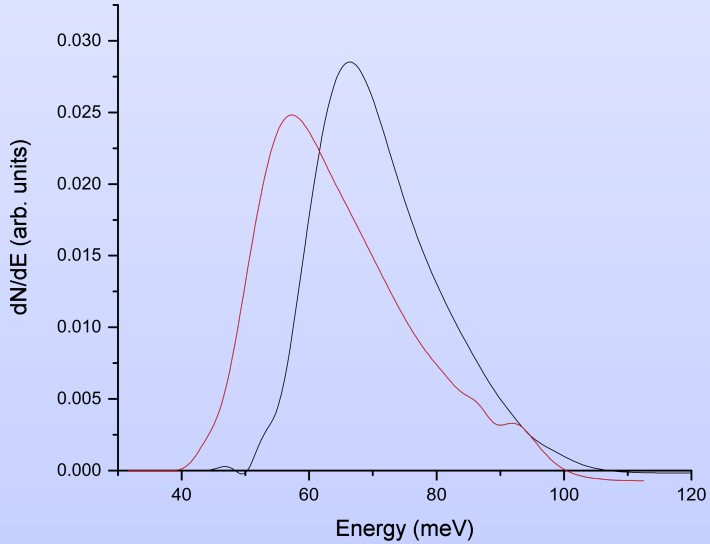


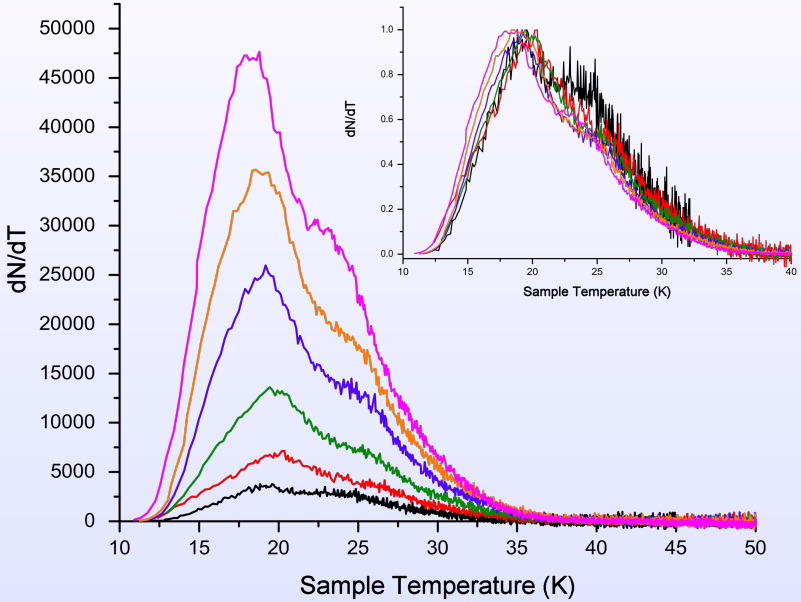
Amorphous silicate provided by
J. Brucato (Obsrv, Arcetri)

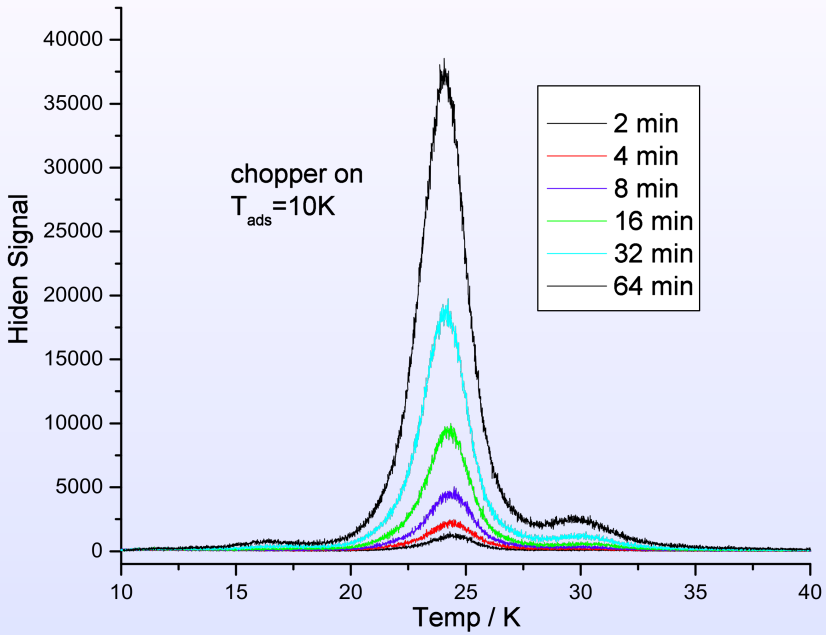
Vidali et al. Adv.Space Res. 43, 1291 (2009)



Vidali & Li J.Cond.Matt. C 22, 304012 (2010)







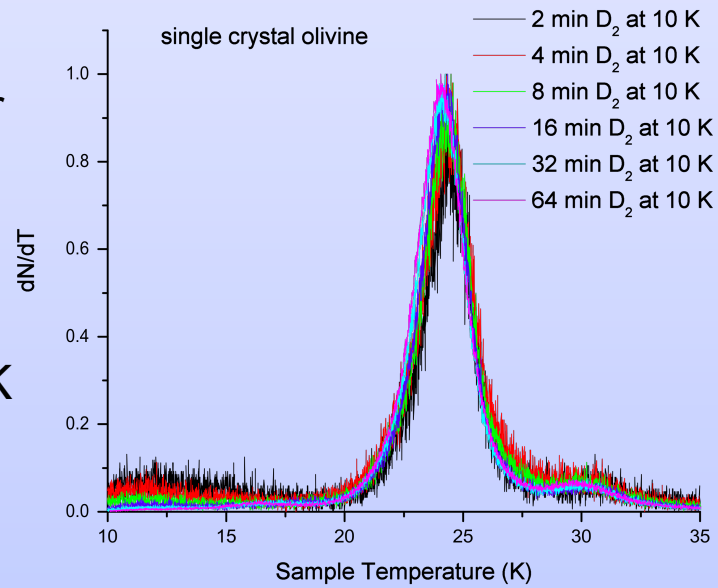
Vidali & Li J.Cond.Matt. C 22, 304012 (2010)

D_2 desorption from single crystal olivine after different irradiation times

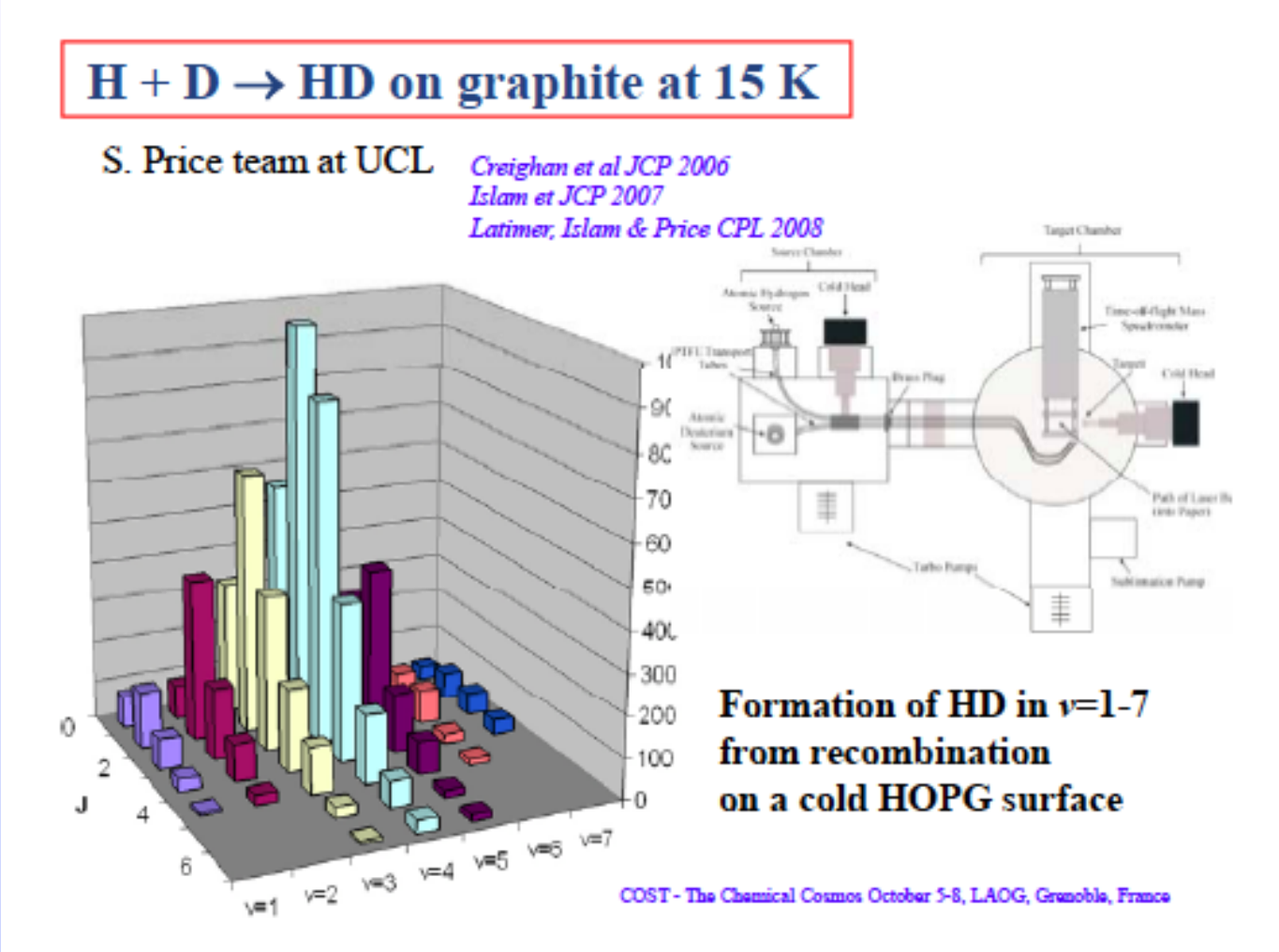
Collapse of the TPDs -> little diffusion

10 K

Frank et al. in preparation



Measuring the ro-vibrational state of the molecules formed on surfaces



Translational energy of H_2 from water ice: nearly thermal (Roser et al., 2003, Hornekaer et al. 2003, Congiu et al., 2009)

Rate Equation → Master Equation

For small grains under low flux the typical population size of H atoms on a grain may go down to

$$n \sim 1$$

Thus: the **rate equation** (mean field approximation) **fails**

One needs to take into account:

The **discreteness** of the H atoms
The **fluctuations** in the populations of H atoms on grains

→ Master Equation for the probability distribution
$P(n)$, $n=0,1,2,3,\ldots$

Master Equation

$H + H \rightarrow H_2$

$$\frac{dP(n)}{dt} = F\left[P(n-1) - P(n)\right] \quad \textbf{Flux}$$

$$+W\left[(n+1)P(n+1) - nP(n)\right] \quad \textbf{Desorption}$$

$$+A\left[(n+2)(n+1)P(n+2) - n(n-1)P(n)\right]$$

Recombination

Direct Integration:

Biham, Furman, Pirronello and Vidali, ApJ 553, 595 (2001)

Green, Toniazzo, Pilling, Ruffle, Bell and Hartquist, A&A 375, 1111 (2001)

Monte Carlo:

Charnley, ApJ 562, L99 (2001)

Cuppen & Herbst

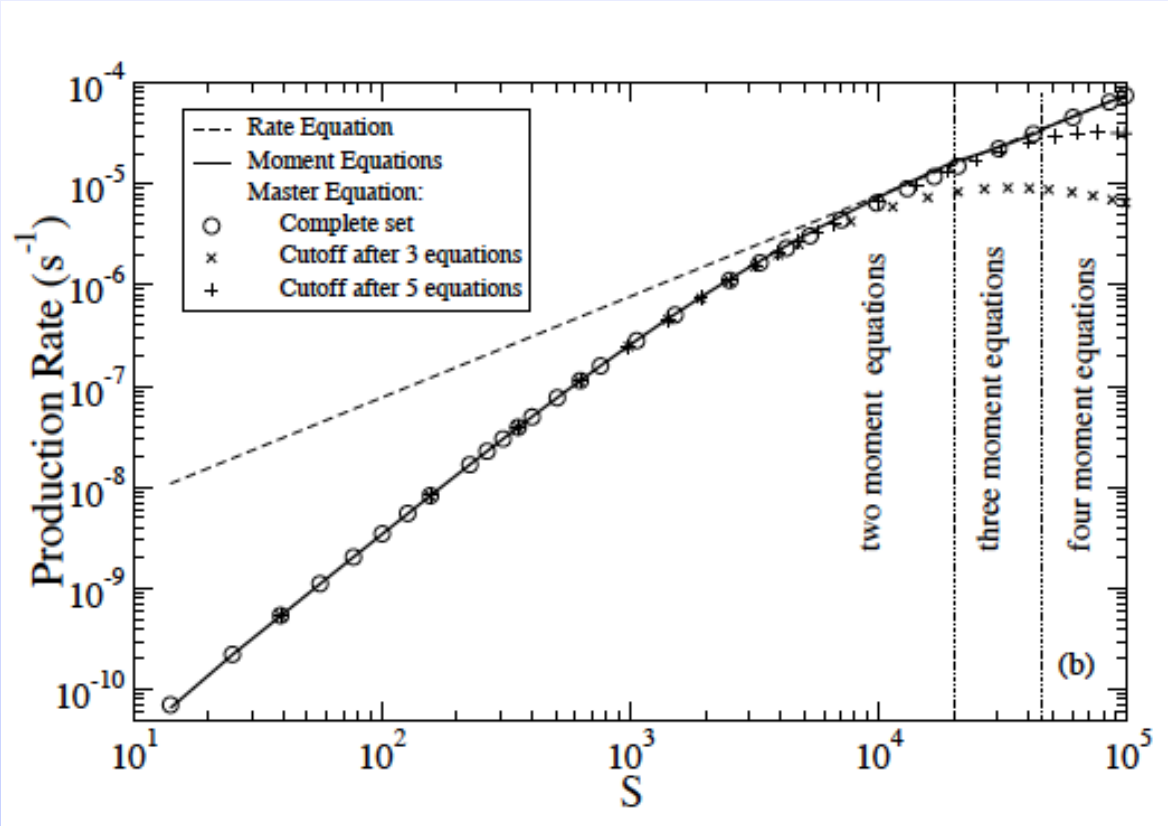
H_2 Production Rate vs. Grain Size

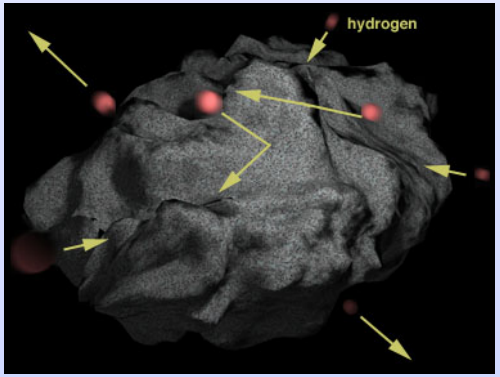
Rate equation

$$R = An^2$$

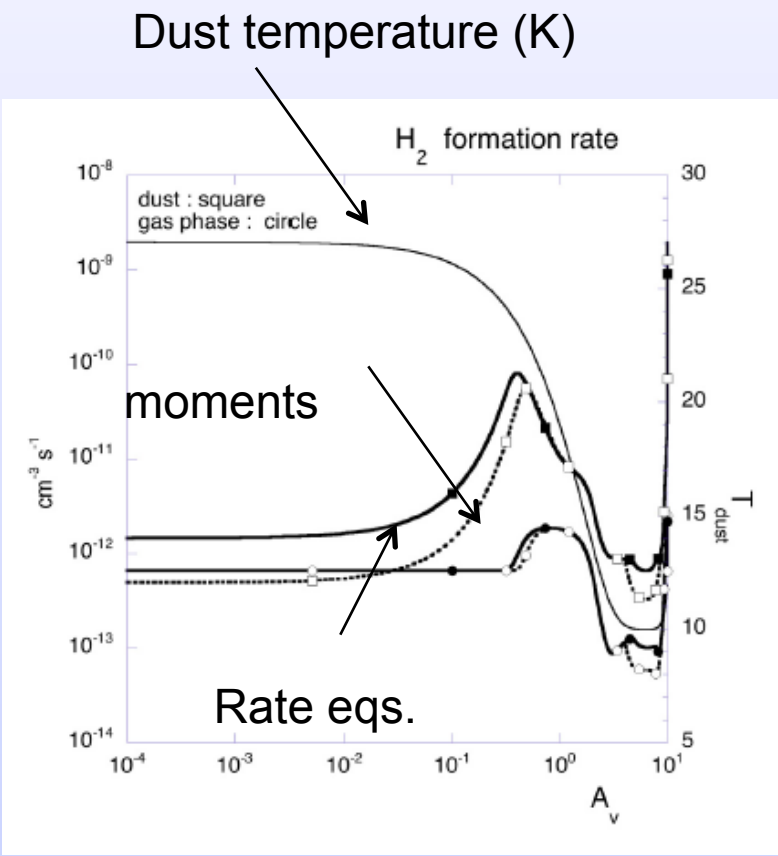
Master equation

$$R = A\sum n(n-1)P(n)$$





H_2 formation vs. A_v



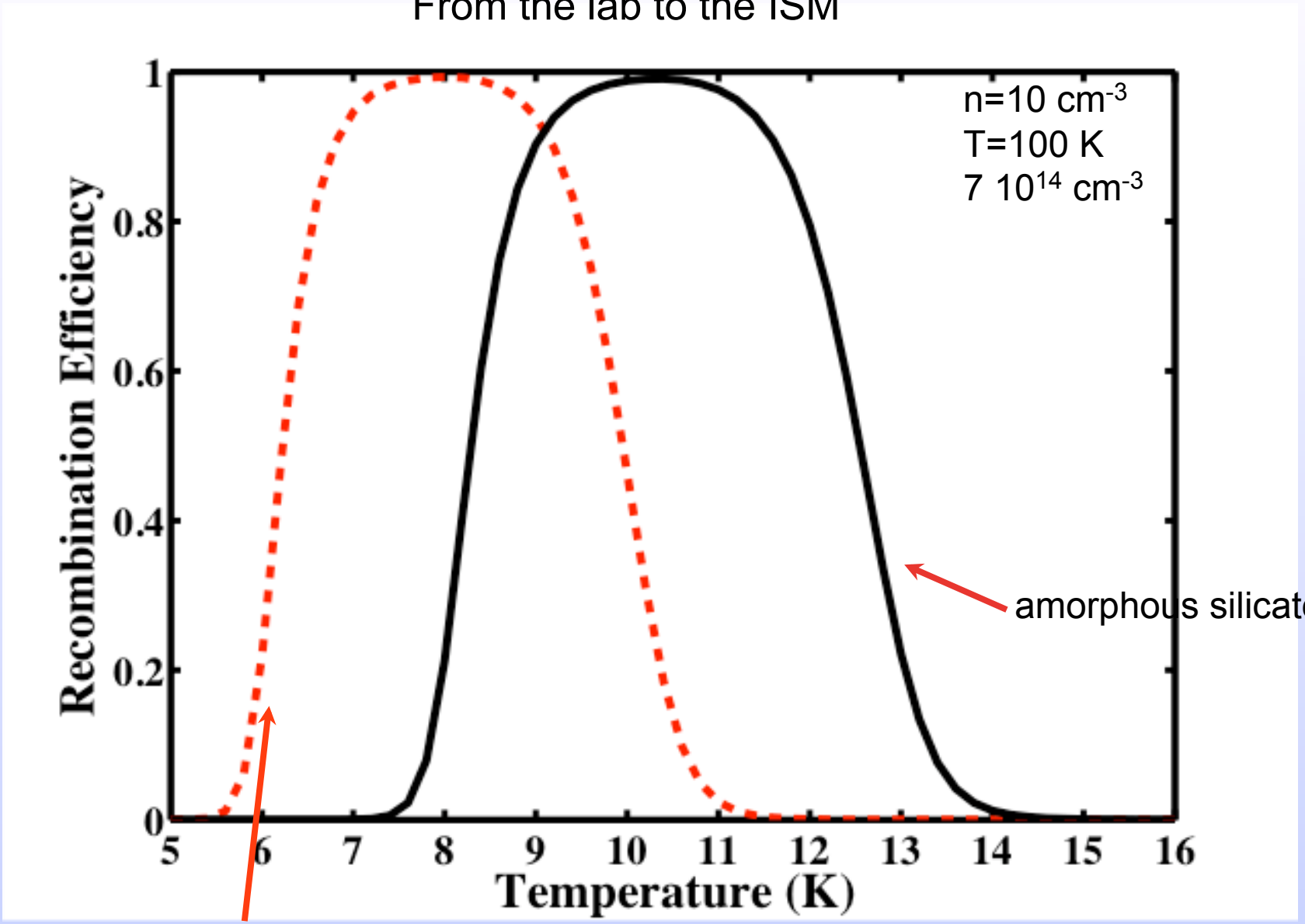
Meudon PDR code

LePetit et al. (2009)

$$\frac{d\langle N_H\rangle}{dt} = F_H + (-W_H + 2A_H)\langle N_H\rangle - 2A_H\langle N_H^2\rangle$$

$$\frac{d\langle N_H^2\rangle}{dt} = F_H + (2F_H + W_H - 4A_H)\langle N_H\rangle + (8A_H - 2W_H)\langle N_H^2\rangle - 4A_H\langle N_H^3\rangle$$

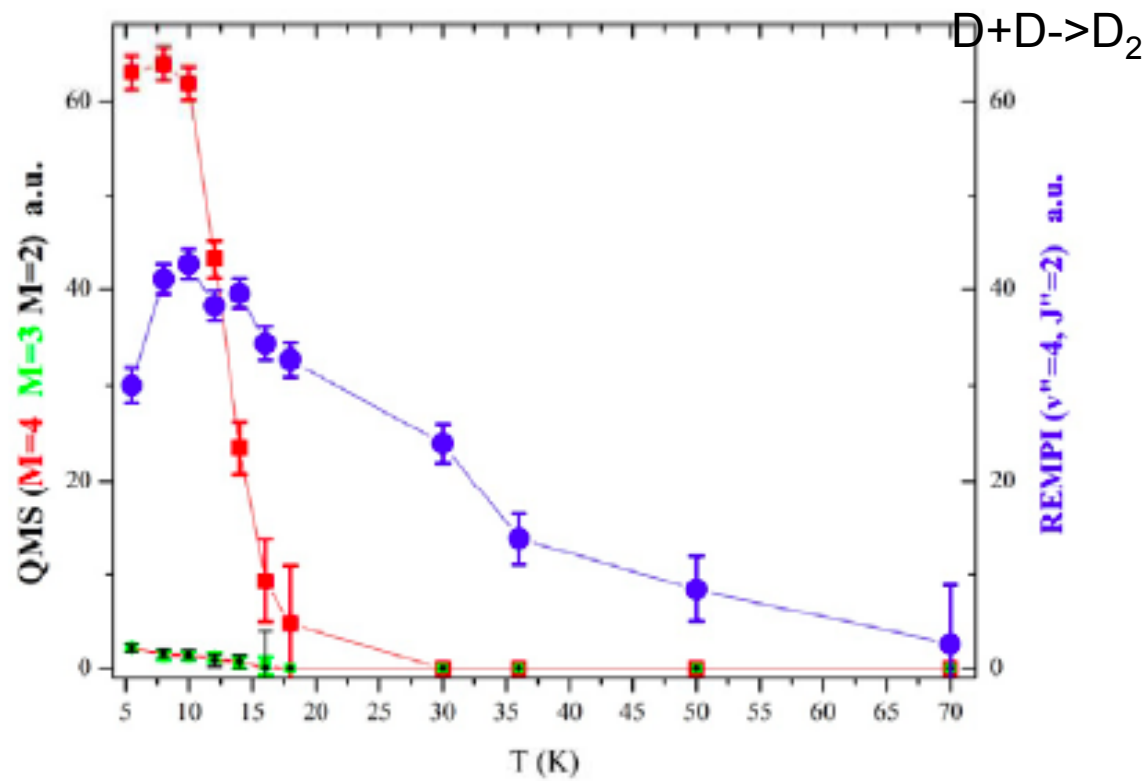
From the lab to the ISM



Perets et al. ApJ 661, L163 (2007)

Dust analog	Efficien. (exp)	T sample range	Energy T<10 K	Mechan.	Ro-vibr.	Kinetic energy	Lab
Silicate a	High High	5-30 K 5-70 K	30-50 meV >50 meV (T>13 K)	L-H L-H +prompt	 high		Vidal Lemaire
Silicate c	low	5-30 K	20-30 meV	L-H			Vidali
Carbon a	high	5-30 K 300 K	40-50 meV	L-H, prompt			Vidali Mennella
Graphite		>15 K		Prompt	high		Zecho, Hornekaer, Price
Ice a (hd)	high	5-30 K	50-70 meV	L-H prompt	thermal	~ thermal	Vidali, Hornekaer, Lemaire
Ice a (ld)	high	5-30 K	40-60 meV		high		Vidali, Lemaire

D_2 formation on silicates



- **Integrated intensities** of the REMPI (D_2) signal during irradiation and of the QMS (D_2) signal of the TPD after irradiation versus the sample temperature during irradiation.
- The HD signal is due to exchange reactions on the sample and/or walls of the apparatus.

D_2 formation on and ejection from a silicate film

Lemaire, Vidali, …. (Submitted to ApJL Sept. 2010)

Desiderata

Characterize microscopic processes (surface science)
Characterization of surfaces; know more about actual dust
Measure the activation energy for diffusion, desorption
Measure rates

Comparison of rates obtained in molecule formation using beams (hydrogenation), UV and energetic particles

Theory, models and simulations of processes in the ISM using laboratory data

Database – is it possible? Potentials of Physical Adsorption Vidali et al Surf Sci Rep 12, 133 (1991)