Recombinaison d'atomes d'hydrogène physisorbés sur des surfaces à basses températures

Réunion interdisciplinaire interactions hydrogène/surface
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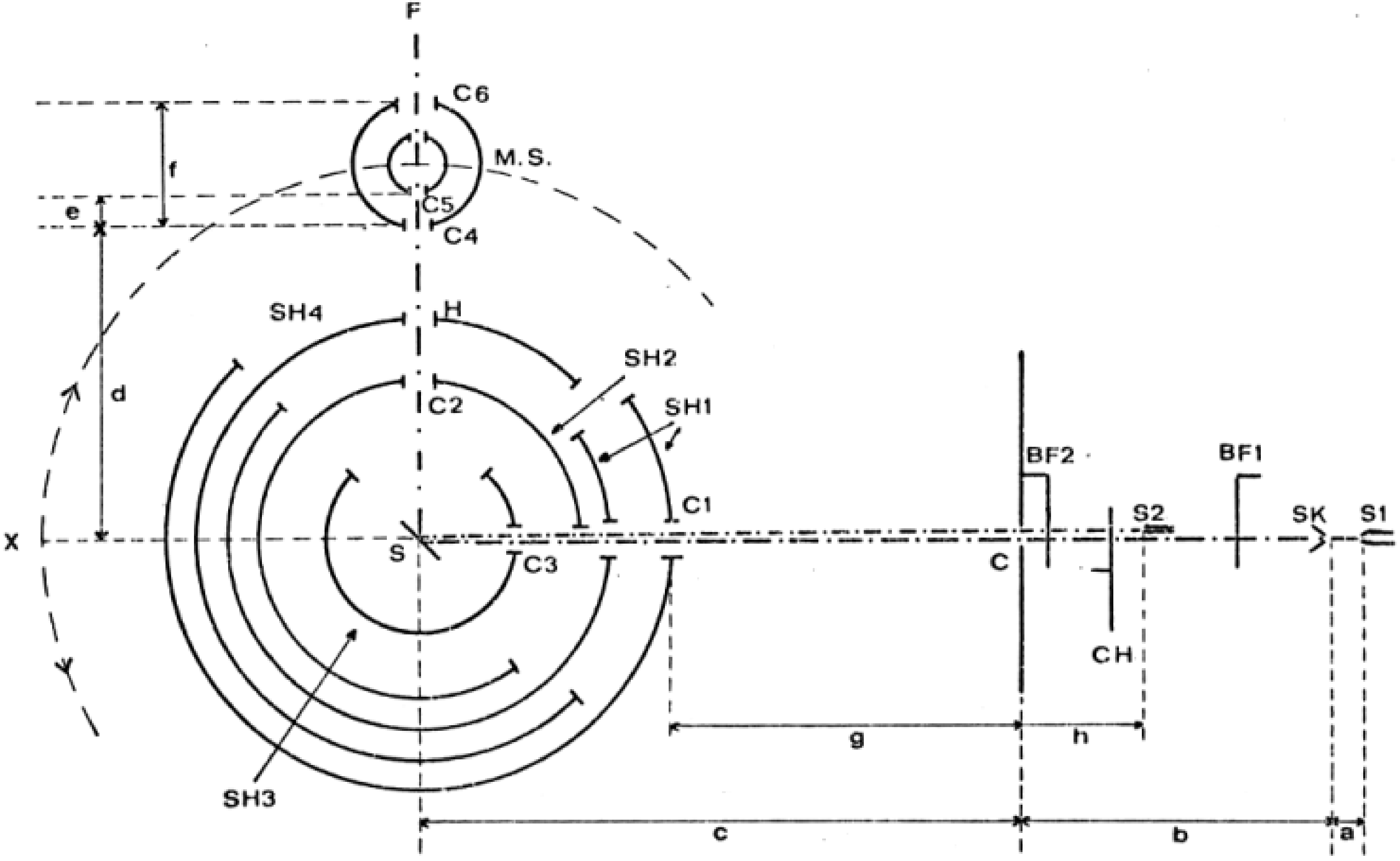
Basé sur des résultats extraits de :

Lorenzo Mattera, Ph.D. Thesis, University or Waterloo (Ontario, Canada), 1978

T.R.Govers, L. Mattera and G.Scoles, J. Chem. Phys. 72, 5446 (1980)

Manuscrit et présentation accessibles sur : www.aecono.com

T.A.Rector (NOAO/AURA/NSF) and Hubble Heritage Team (STScI/AURA/NASA)


F
C6
M.S.
f
e
C5
C4
d
SH4
H
SH2
SH1
C2
BF2
BF1
C1
X
S2
SK
S1
S
C3
C
CH
SH3
g
h
c
b
a

Doped amorphous silicon bolometer serves as substrate
and as energy detector

Surface is covered by polycrystalline water ice deposited
during cooldown of the cryostat

and is well controlled in terms of temperature
(3 to 10 °K)
and of hydrogen coverage (H_2 or D_2)

Mass spectrometer measures density (= flux / velocity)
of molecules released
from or reflected by the bolometer surface

1 eV = 11606 K ; 100 K = 8.6 meV

Average speed of H in 100 K Maxwell gas = 1.46 10^5 cm s^{-1}

At H density on 10^3 cm^{-3} H impact rate is 3.64 10^7 cm^{-2} s^{-1}

If one defines 1ML = 10^{15} cm^{-2},

it takes 2.72 10^7 s to impact the equivalent of a monolayer,

i.e. 10 months + 11 days

In the lab H beam intensities are typically 4 10^{14} cm^{-2} s^{-1},

it takes 5 seconds

Define sticking coefficient S as fraction of molecules that equilibrate to the surface temperature, so that their residence time can be expressed under the form:

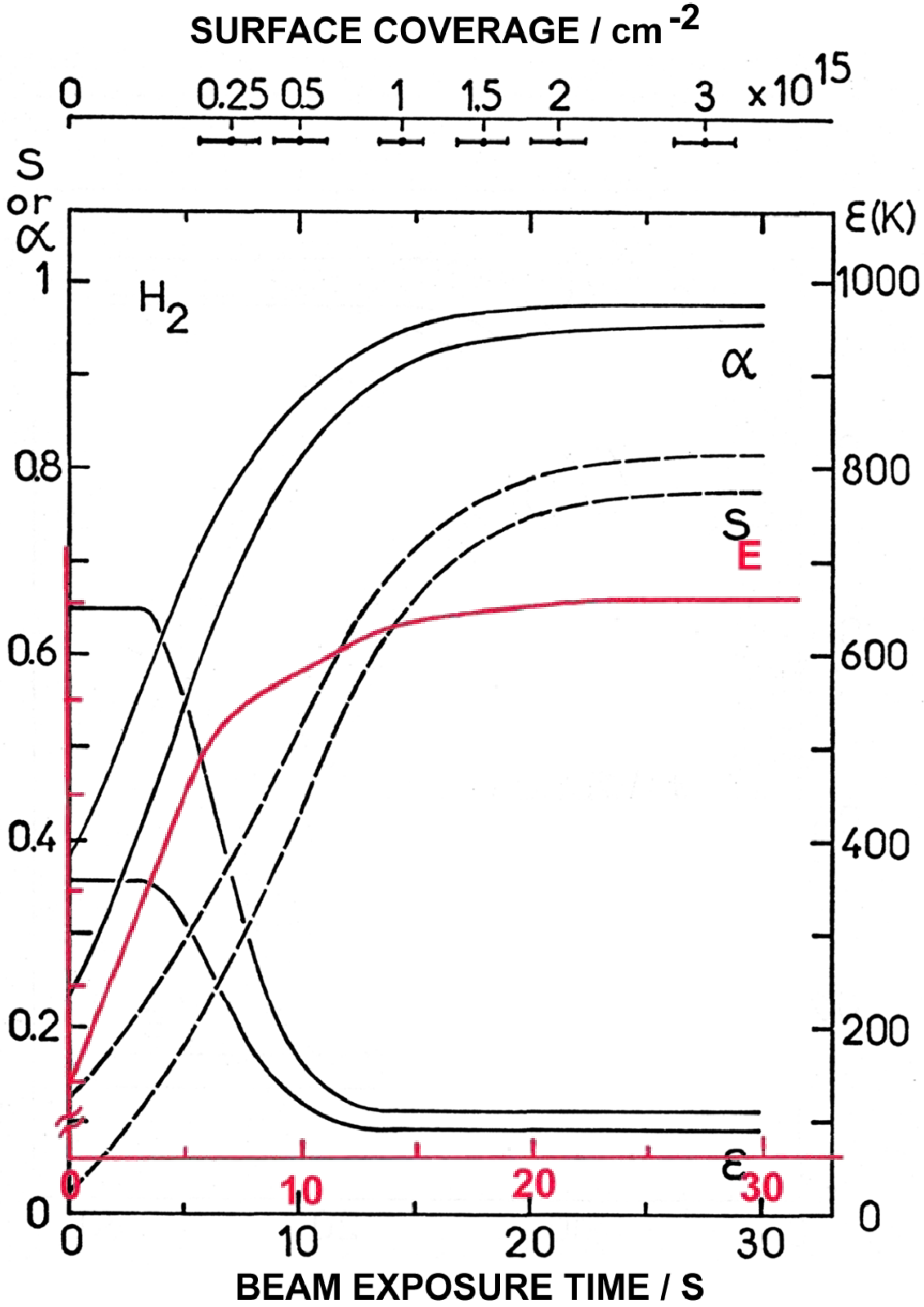
$$\tau = \tau_o \exp (\varepsilon/kT_s),$$

where (1/ τ_o) is the caracteristic vibration frequency of adsorbed molecules, and ε the binding energy.

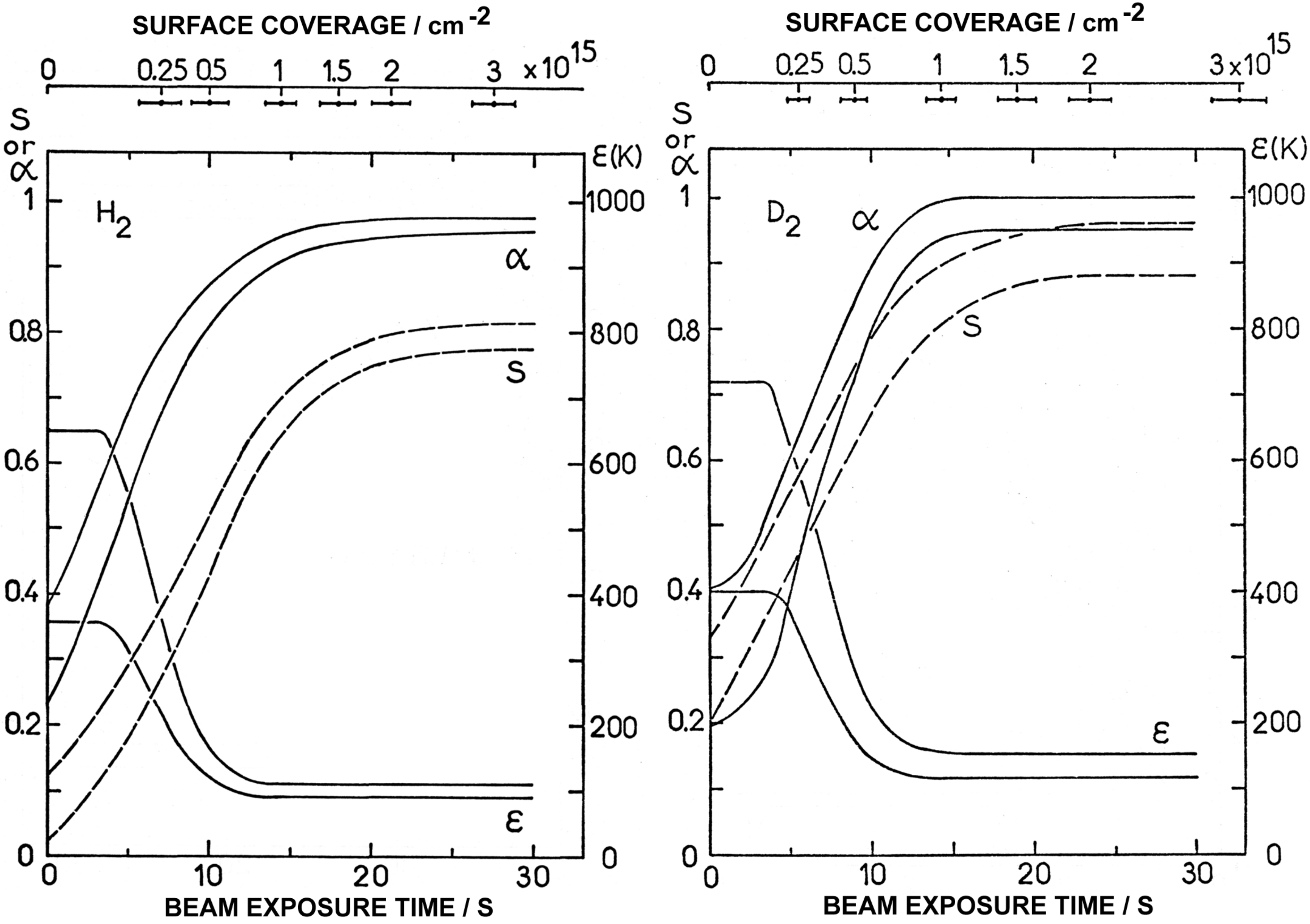
$\tau = 10^{-13} \exp \varepsilon/kT_s$ (sec)

	T_s (K)			
ε/k	3	4	5	10
40	6.17E-08	2.20E-09	2.98E-10	5.46E-12
80	3.81E-02	4.85E-05	8.89E-07	2.98E-10
100	3.00E+01	7.20E-03	4.85E-05	2.20E-09
120	2.35E+04	1.07E+00	2.65E-03	1.63E-08
140	1.85E+07	1.59E+02	1.45E-01	1.20E-07
160	1.45E+10	2.35E+04	7.90E+00	8.89E-07
180	1.14E+13	3.49E+06	4.31E+02	6.57E-06
200	8.97E+15	5.18E+08	2.35E+04	4.85E-05
240	5.54E+21	1.14E+13	7.02E+07	2.65E-03
300	2.69E+30	3.73E+19	1.14E+13	1.07E+00
400	8.05E+44	2.69E+30	5.54E+21	2.35E+04
500	2.41E+59	1.94E+41	2.69E+30	5.18E+08
600	7.23E+73	1.39E+52	1.30E+39	1.14E+13

N.B. : Beam modulation period is 7.4×10^{-3} sec


SURFACE COVERAGE / cm -2
0
0.25
0.5
1
1.5
2
3
x10 15
S or α
1
0.8
0.6
0.4
0.2
0
H2
α
S
E
ε
ε(K)
1000
800
600
400
200
0
0
10
20
30
0
10
20
30
BEAM EXPOSURE TIME / S

MOLECULAR HYDROGEN ON INITIALLY HYDROGEN-FREE SURFACE



FROM MOLECULAR HYDROGEN EXPERIMENTS ONE CONCLUDES:

- ☞ **Strong initial changes of ε, α and S over narrow coverage range : ½ ML H_2 increases α and S and decreases ε by a factor 2 or more (1 ML ≡ 10^{15} molecules/cm^2)**

- ☞ **H_2 build-up limited to ½ ML when T_s is raised above 3.5 K, confirming that ε has already decreased to 120 K at such limited coverage**

- ☞ **Should expect strong influence of molecular hydrogen coverage on sticking and binding of atomic hydrogen, and therefore on recombination probability**

BINDING ENERGIES

ε/k (K)

Ref.			This work
1	90	H_2/H_2	105±10
2	615	H_2/H_2O	500±150
3	555±35	$H_2/(H_2O\text{-}CH_3OH)$	
4	320 to 1400	$H_2/(H_2O)_{450}$	
	most prob. 650		

References:

(1) Silvera, Rev. Mod. Phys. 1980

(2) Hollenbach & Salpeter, JCP 1970, with revised gas phase well: 130 instead of
100 K (Duquette 1977)

(3) Sandford & Allamandola, Astrophys. J. 1993

(4) Hixson et al., JCP 1992

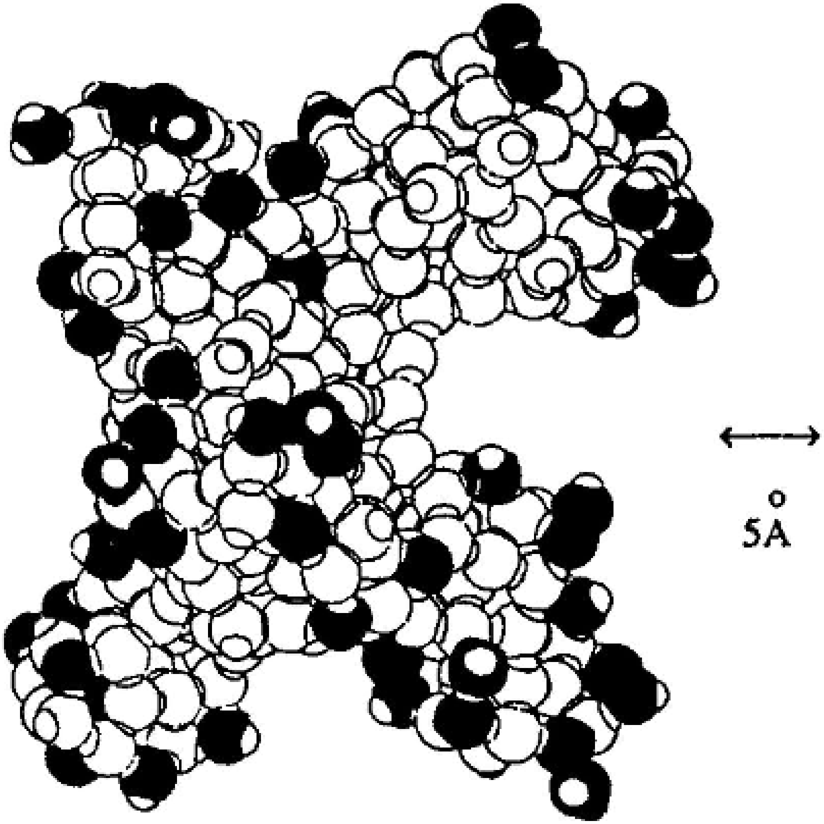
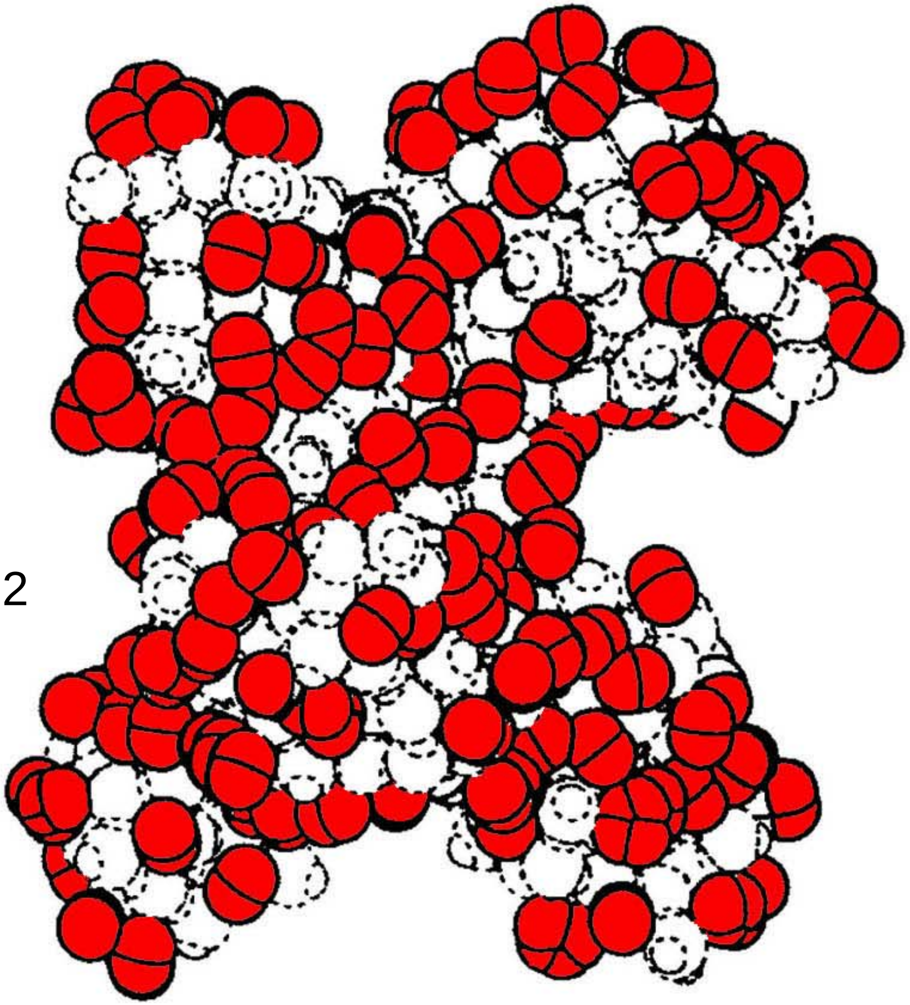


FIG. 6. The $(H_2O)_{450}$ amorphous ice cluster. Dangling oxygen atoms are marked in black. (A dangling O atom participates in one hydrogen bond only.)

Hixson et al., JCP 1992



Hixson et al., JCP 1992

FIG. 7. Distribution of potential minima with respect to H_2 coordinates. A H_2 molecule is displayed in each minimum location. H_2 are drawn in a continuous line; cluster atoms in a dashed line. Note: the minima shown in the figure were calculated for *isolated* H_2.

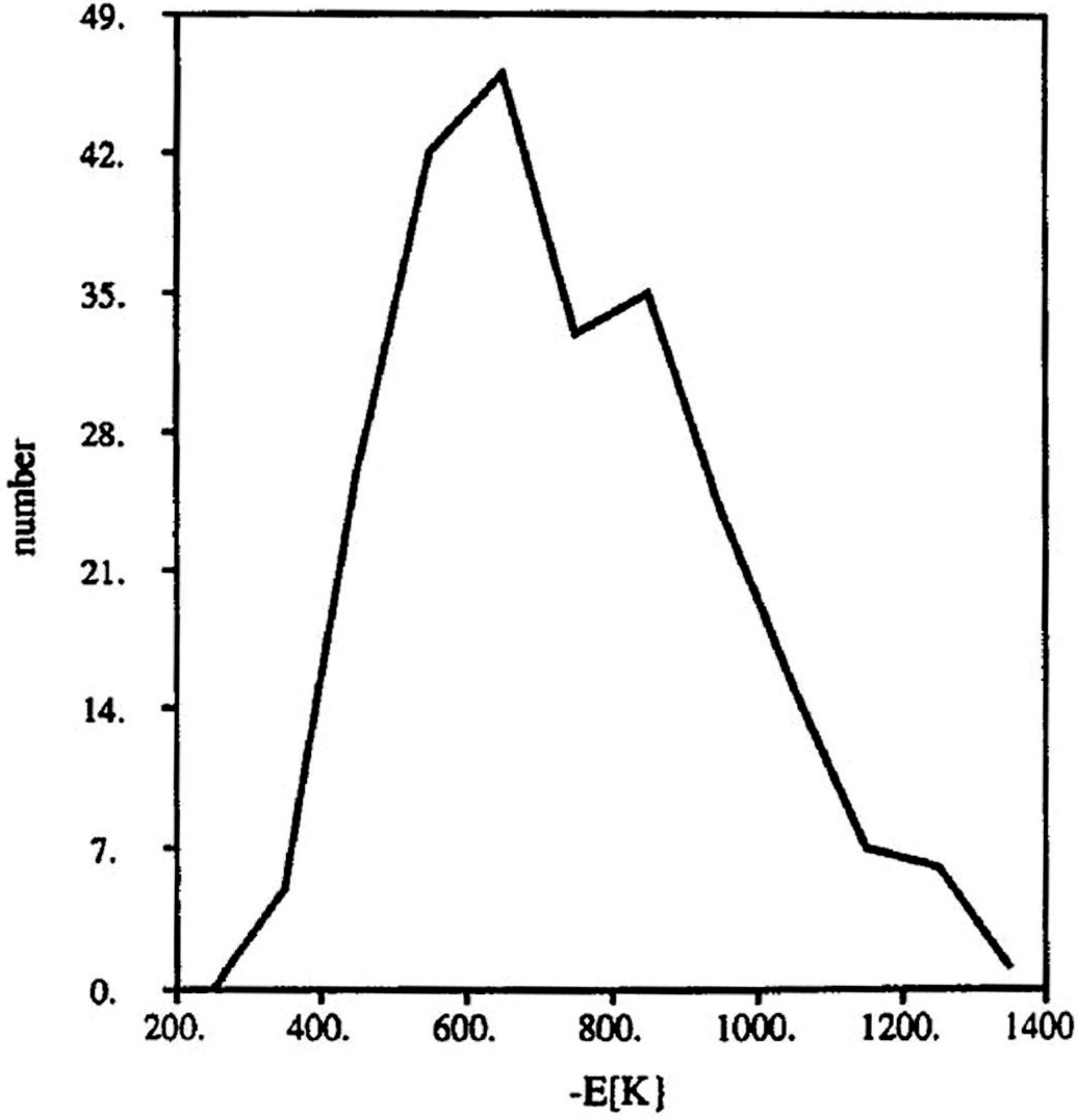
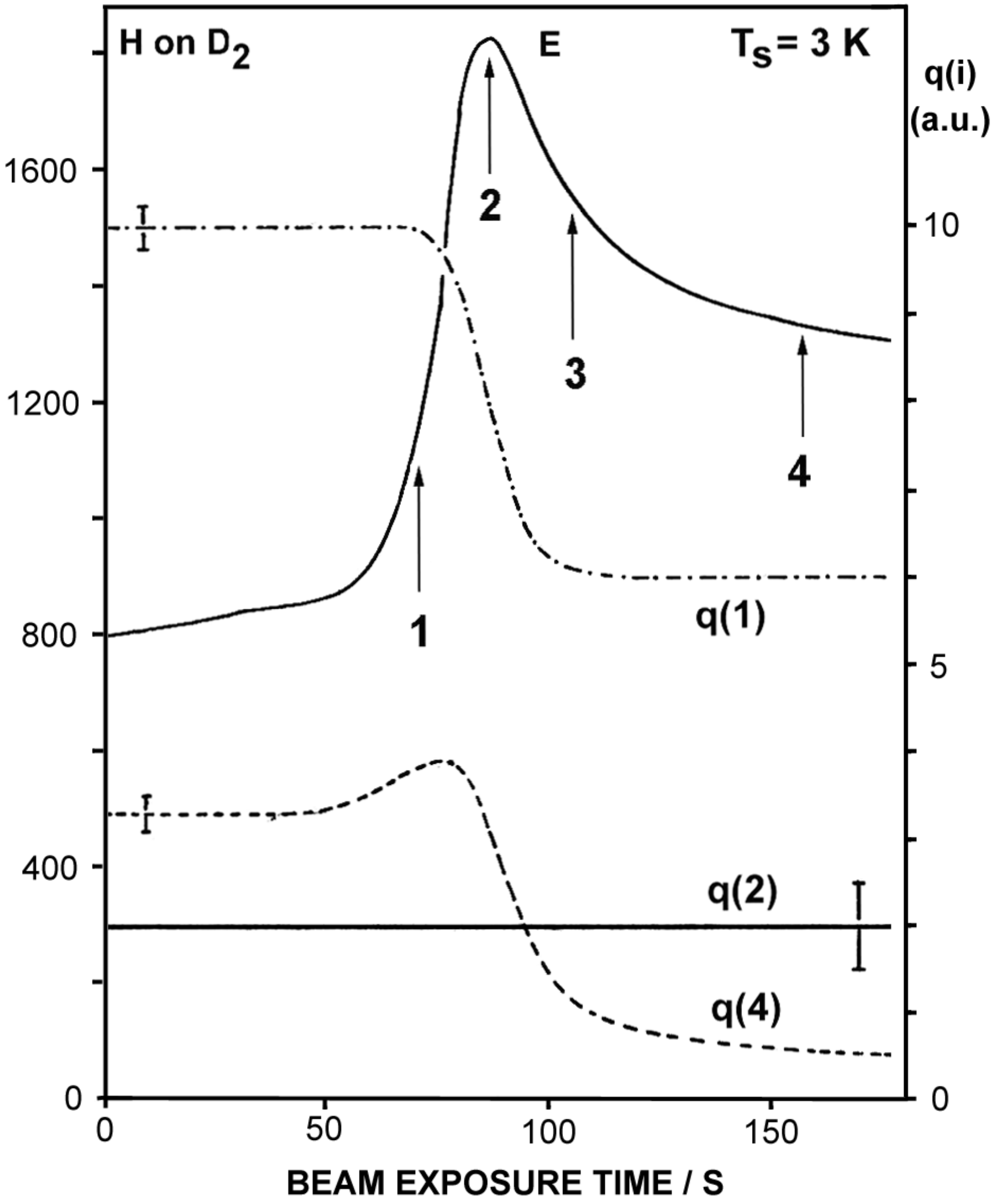


FIG. 8. Distribution of minimum energies for the 240 minima.

ATOMIC HYDROGEN ON INITIALLY HYDROGEN-SATURATED SURFACE



- **Low E compared to recomb. energy 25 980 K / atom**
- **First order in H**
- **No mass 3**
- **Recombination ejects D_2**
- **Strong influence of D_2 coverage**
- **No significant impact of coverage by N_2, CO_2, H_2O: only H_2 or D_2matter**

H RECOMBINATION "BOILS OFF" PRE-ADSORBED D_2

- **Response to D_2 beam is used to determine D_2 coverage: intially 3×10^{15} molecules cm^{-2} ; arrows (1) 9×10^{14} cm^{-2}, (2) 1.9×10^{14} cm^{-2}, (3) 1.6×10^{14} cm^{-2}, (4) 4.5×10^{13} cm^{-2}**

- **Incident H flux is 3.8×10^{14} atoms cm^{-2} s^{-1}**

- **Recombining fraction is about 0.15 or less (see below)**

- **Each H_2 molecule formed ejects at least 1 D_2 molecule**

H RECOMBINATION ANALYSIS

Energy to bolometer per incident H atom

$$E = S\,(\,2kT + \varepsilon\,) + 2kT\,(\,1 - S\,)\,\alpha$$

$$+ \tfrac{1}{2}\,S\beta\,(\,\varepsilon_{rec} - \varepsilon_2 - 2kT_2 - E_{int})$$

$$-\varphi_4/\,\varphi_i\,(\,2kT_4 + \varepsilon_4\,)$$

$$-\varphi'_1/\varphi_i\,(\,2kT'_1 + \varepsilon\,)$$

where S is fraction of H atoms that stick to the surface,
and β the fraction thereof that recombines
φ represents total flux, and ’ refers to ejected atoms

H RECOMBINATION ANALYSIS

Quadrupole MS signals per incident H atom

$$Q_1 = C_1 \{ (1 - S)[T - \alpha (T - T_s)]^{-1/2} + \varphi'_1/\varphi_i \, T'_1{}^{-1/2}\}$$

$$Q_2 = C_2 \times ½ \, S\beta T_2^{-1/2}$$

$$Q_4 = C_4 \times \varphi_4 / \varphi_i \times T_4^{-1/2}$$

Know φ_i ,T, C_1, C_2, C_4 and measure φ_4, E, Q_1, Q_2, Q_4
as a function of time, i.e. D_2 coverage
Know ε_4 and extrapolate α, and ε from H_2 and D_2 expts
Unknowns are S, β, φ'_1/φ_i , T'_1, T_2, T_4, and E_{int}

4 equations, 7 unknowns

H RECOMBINATION ANALYSIS

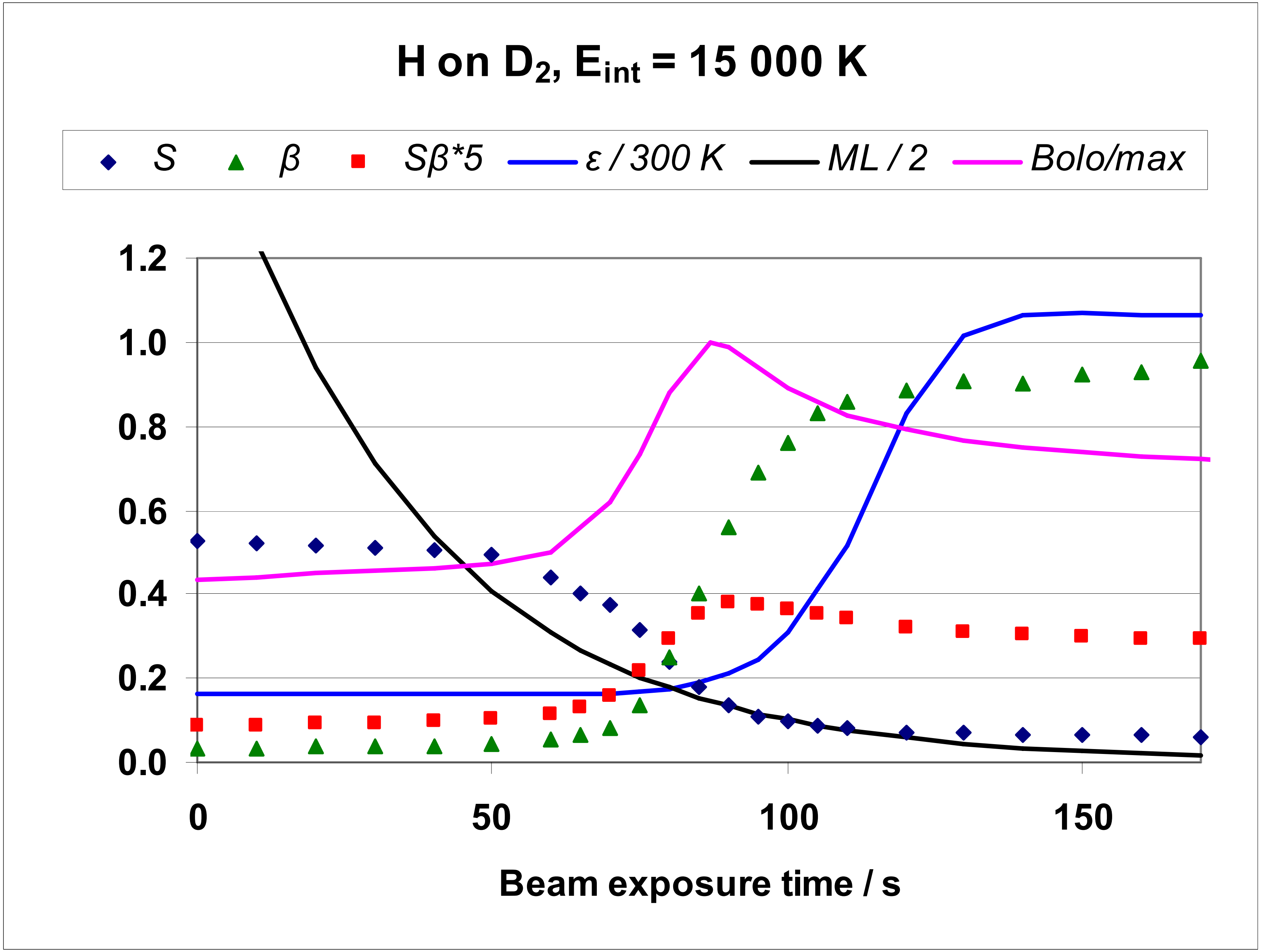
Treat internal energy of recombined H_2 as parameter

Assume $\varphi'_1/\varphi_i = S\,(1 - \beta)$
i.e. all H atoms that stick but do not recombine
are ejected in phase with the incident beam

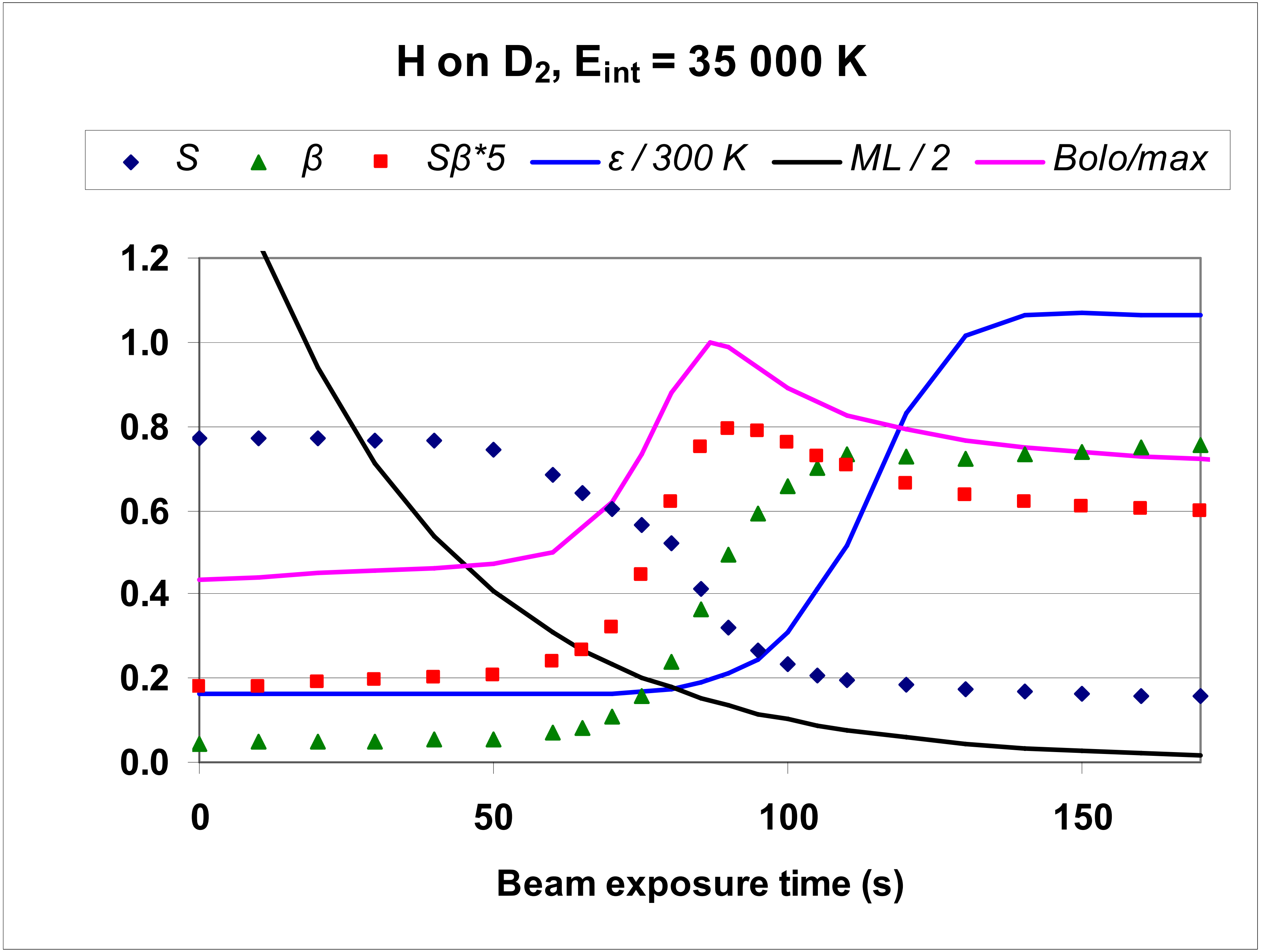
Assume $2\,kT'_1 + \varepsilon = 2\,kT_4 + \varepsilon_4$
i.e. equipartition of energy between ejected H and D_2

Can now determine S,β, and the recombination probability Sβ
as a function of D_2 coverage with the internal energy E_{int}
as a parameter

LOWER LIMIT TO E_{int} FROM S at t = 0 (D_2- saturated surface)



UPPER LIMIT TO E_{int} FROM S at t = ∞ (D_2- free surface)



BINDING ENERGIES

	ε/k (K)		
Ref.			This work
5	36	H/H_2	
6	42	H/D_2	
5 + 6	44	H/D_2	50±15
7	400±50	H/H_2O	320±70
8	250 to 800 most prob. 550	$H/(H_2O)_{115}$	

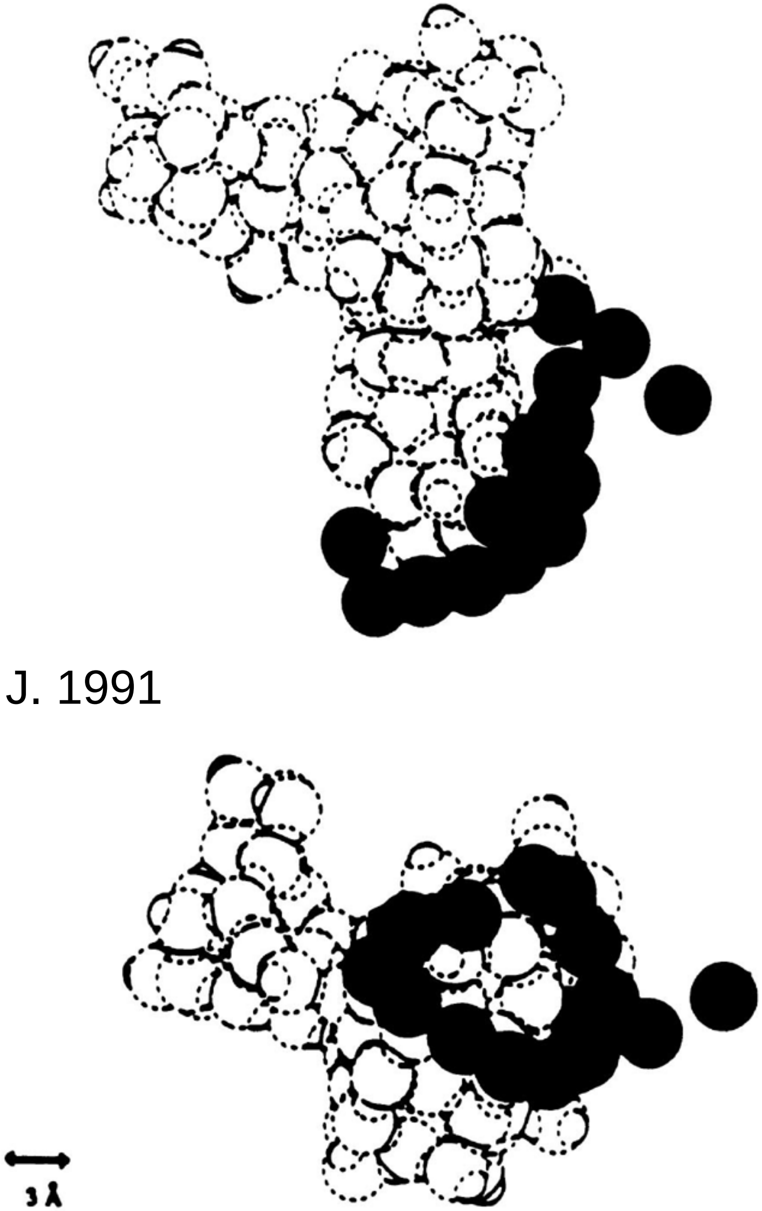
References:

(5) Crampton et al. Phys. Rev.B 1982 (exp.)

(6) Pierre et al. JCP 1985

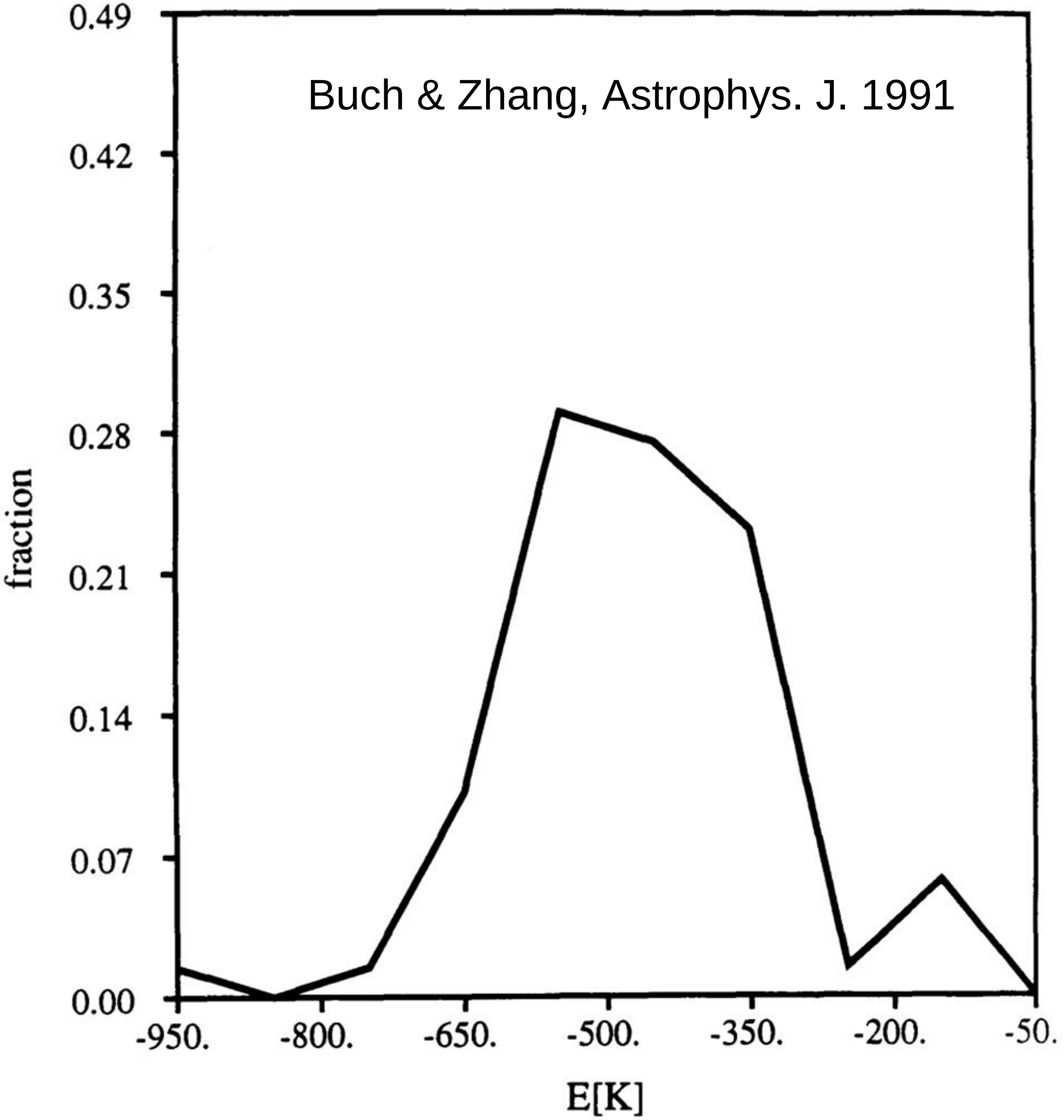
(7) Al-Halabi et al. J.Phys.Chem.B 2002

(8) Buch & Zhang, Astrophys. J. 1991



Buch & Zhang, Astrophys. J. 1991

FIG. 1.—Two views on an amorphous ice particle composed of 115 water molecules. The dark circles trace a sticking trajectory of an H atom of initial energy $E = 200$ K, until its energy decreases to -100 K; this trajectory happens to make a loop on the particle. The circles correspond to snapshots at intervals of 0.25 picosecond.



Buch & Zhang, Astrophys. J. 1991

FIG. 2.—The distribution of minimum energies of the H atom on the cluster shown in Fig. 1.

ATOMIC HYDROGEN ON INITIALLY D_2-SATURATED SURFACE

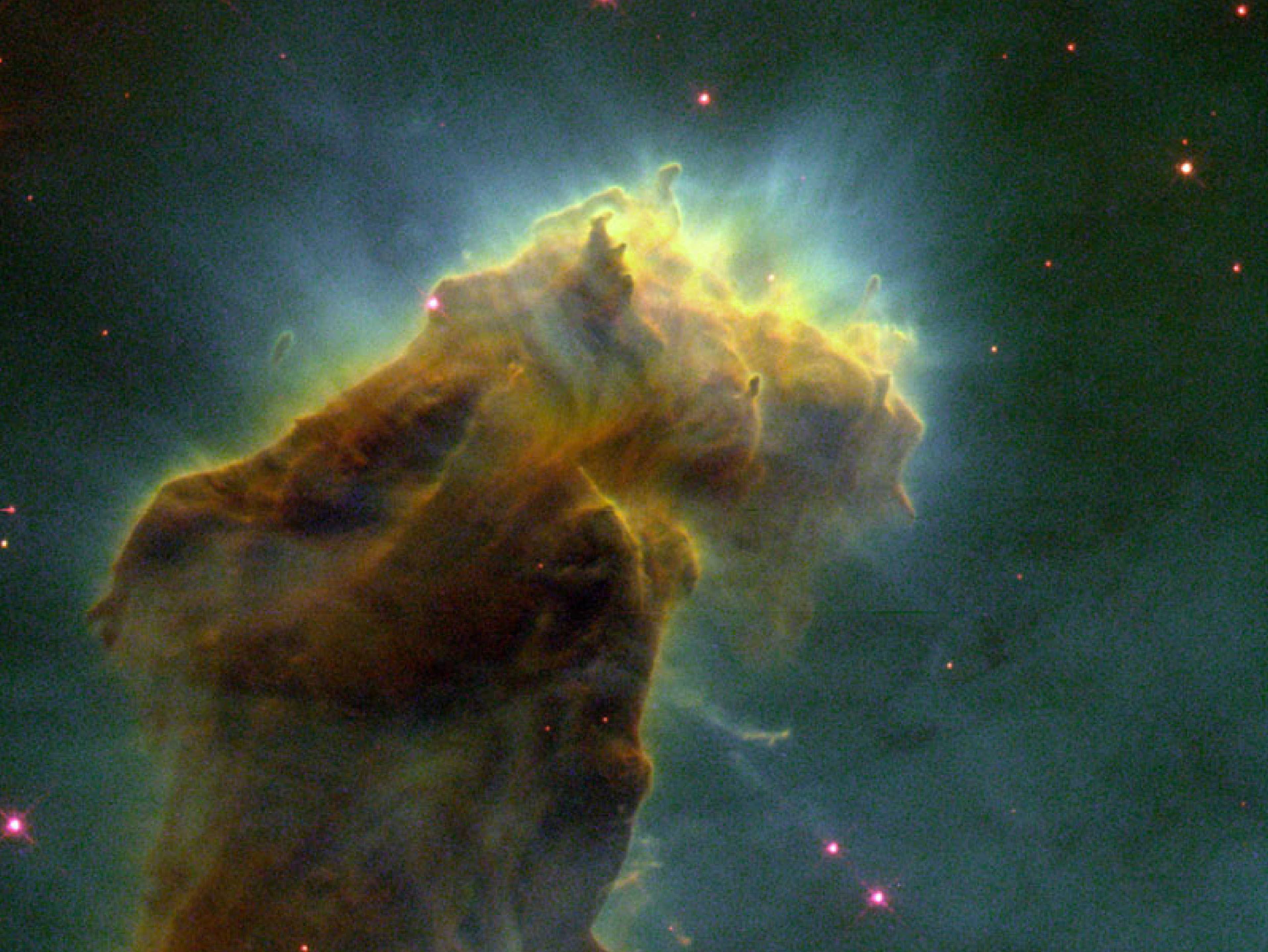
- **Maximum in bolometer signal reflects maximum in recombination probability Sβ**

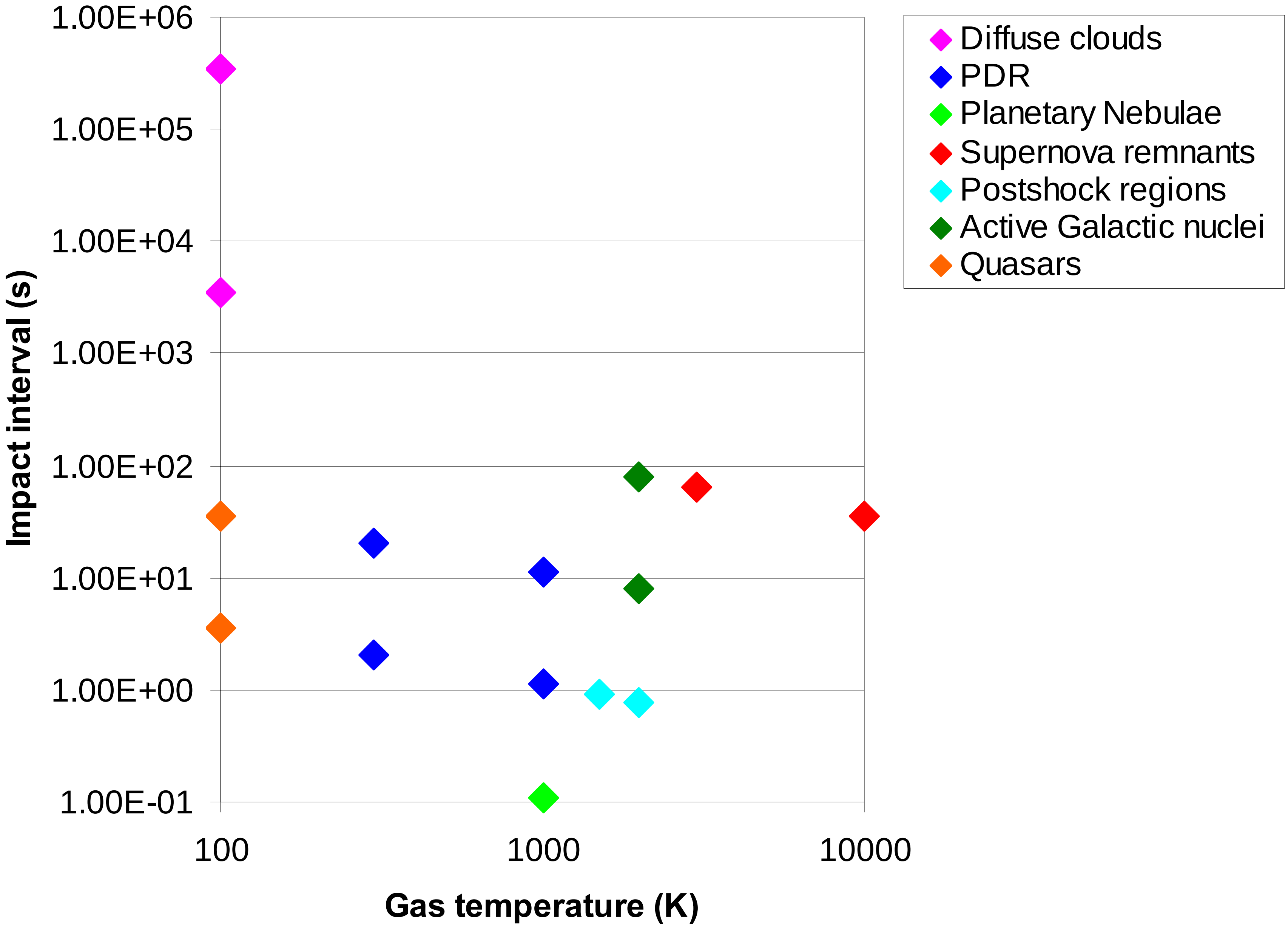
- **At "high" D_2 coverage, S is rather large (0.5 to 0.8), but β is small, because residence time of H is low (small binding energy)**

- **At low D_2 coverage, S is small (0.06 to 0.16), while β approaches 1**

- **Optimum at about 0.25 ML D_2 coverage, with S = 0.15 to 0.3 and β ~ 0.5**

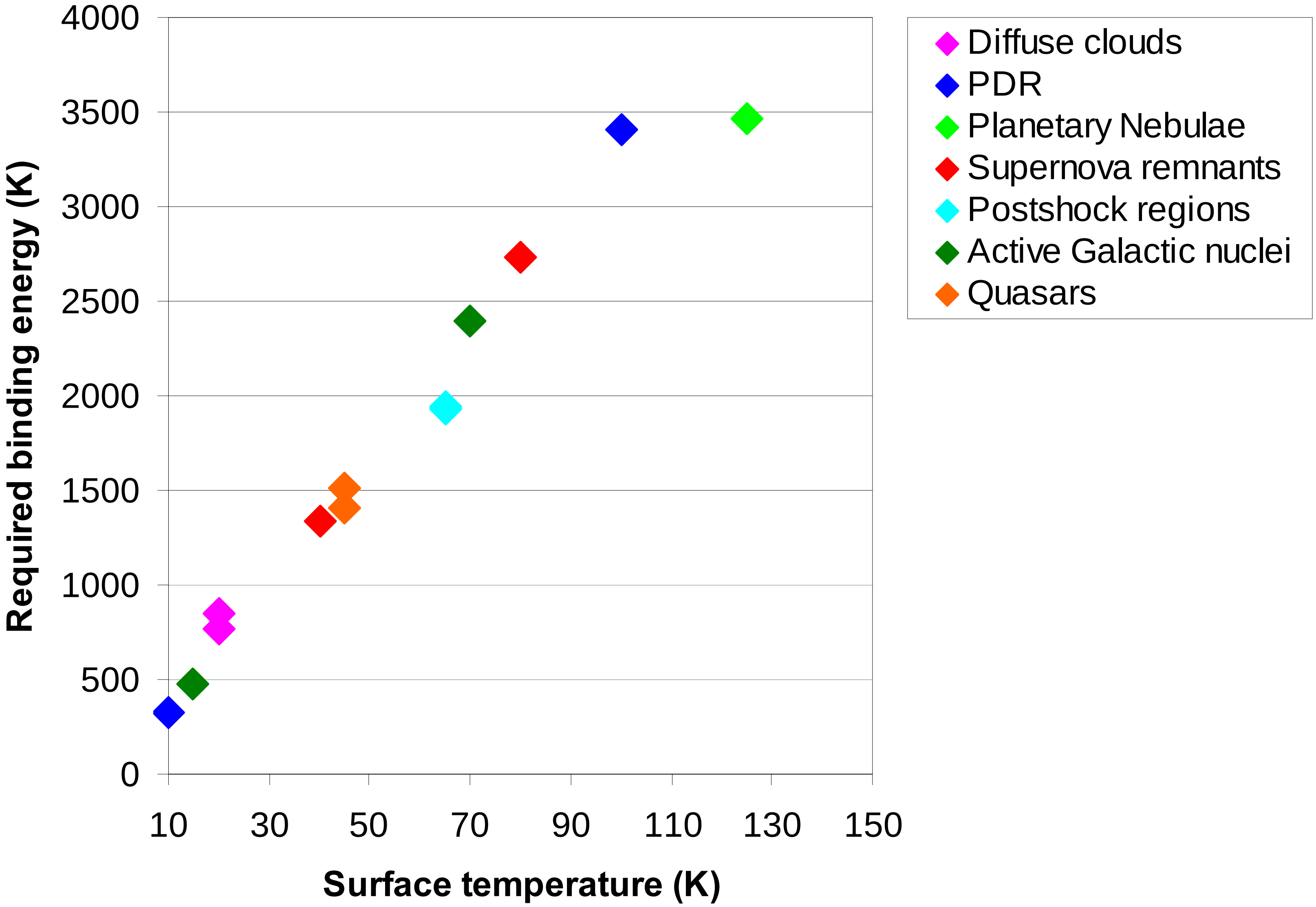
- **Recombination produces internally excited H_2 (most likely about 35 000 K)**





Hydrogen atom impact on 0.1 µm grains

Hydrogen atom impact on 0.1 µm grains



In dense clouds, H_2 will accumulate on the grains until the binding energy becomes low enough for evaporation to balance renewal:

$$10^{13} \exp - \varepsilon/kT_s = (S \times nv / 4) / 10^{15}$$

For T = 100 K, $v\ (H_2) = 1.03 \times 10^5$ cm/s

$\varepsilon / kT_s = \ln (3.88 \times 10^{23} / n)$ gives limiting ε

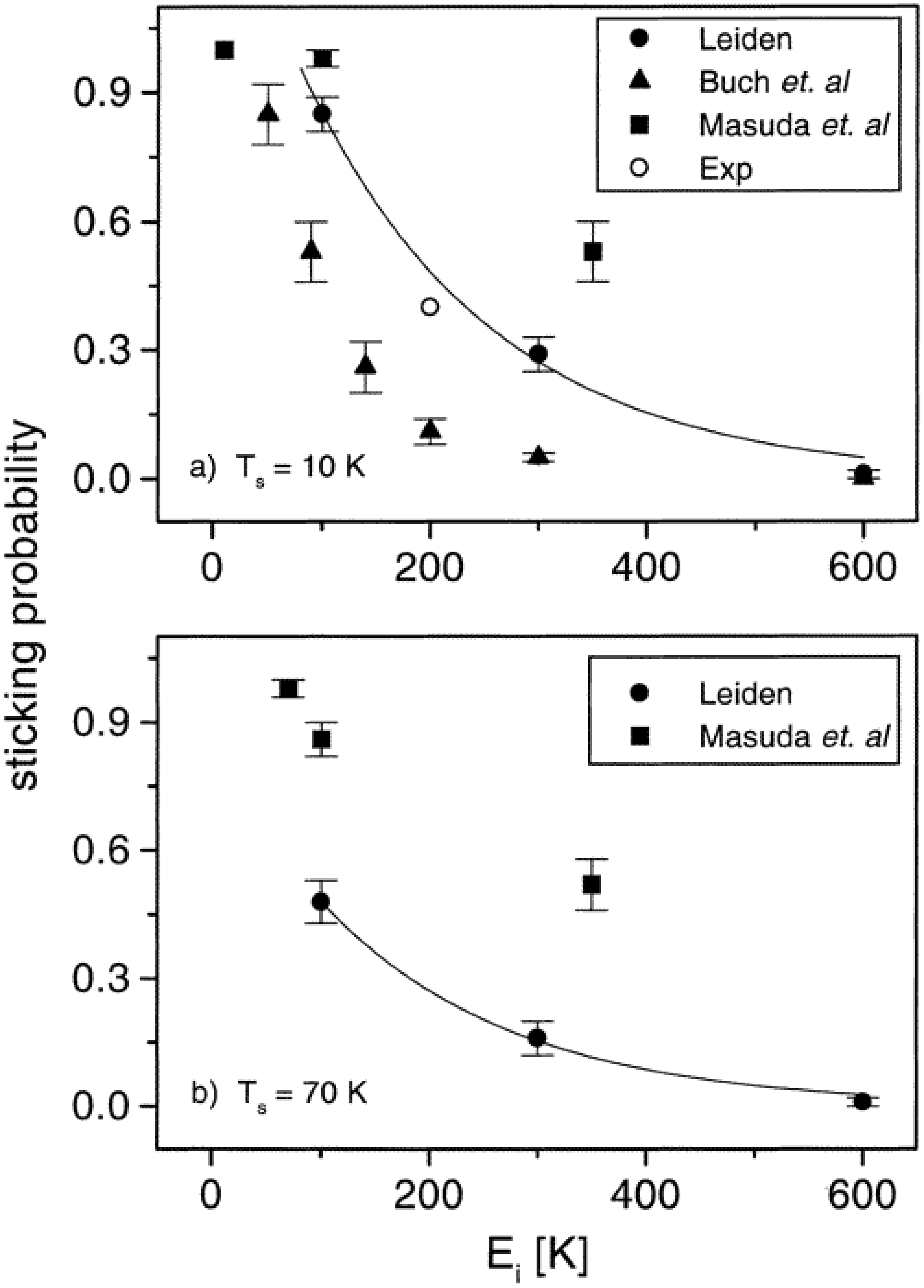
$$\varepsilon / kT_s \approx (54.4 - \ln n)$$

For grains in dense clouds ($T_s \approx 10$ K, $n_{H2} \approx 5 \times 10^3$)
one finds $\varepsilon \approx 460$ K

Since these grains are probably covered by water ice,
we can use our H_2 measurements to infer the
corresponding H_2 coverage

The result is ≈ 0.2 ML H_2 coverage, i.e. close to optimum
conditions for H recombination: $\beta \approx 0.5$

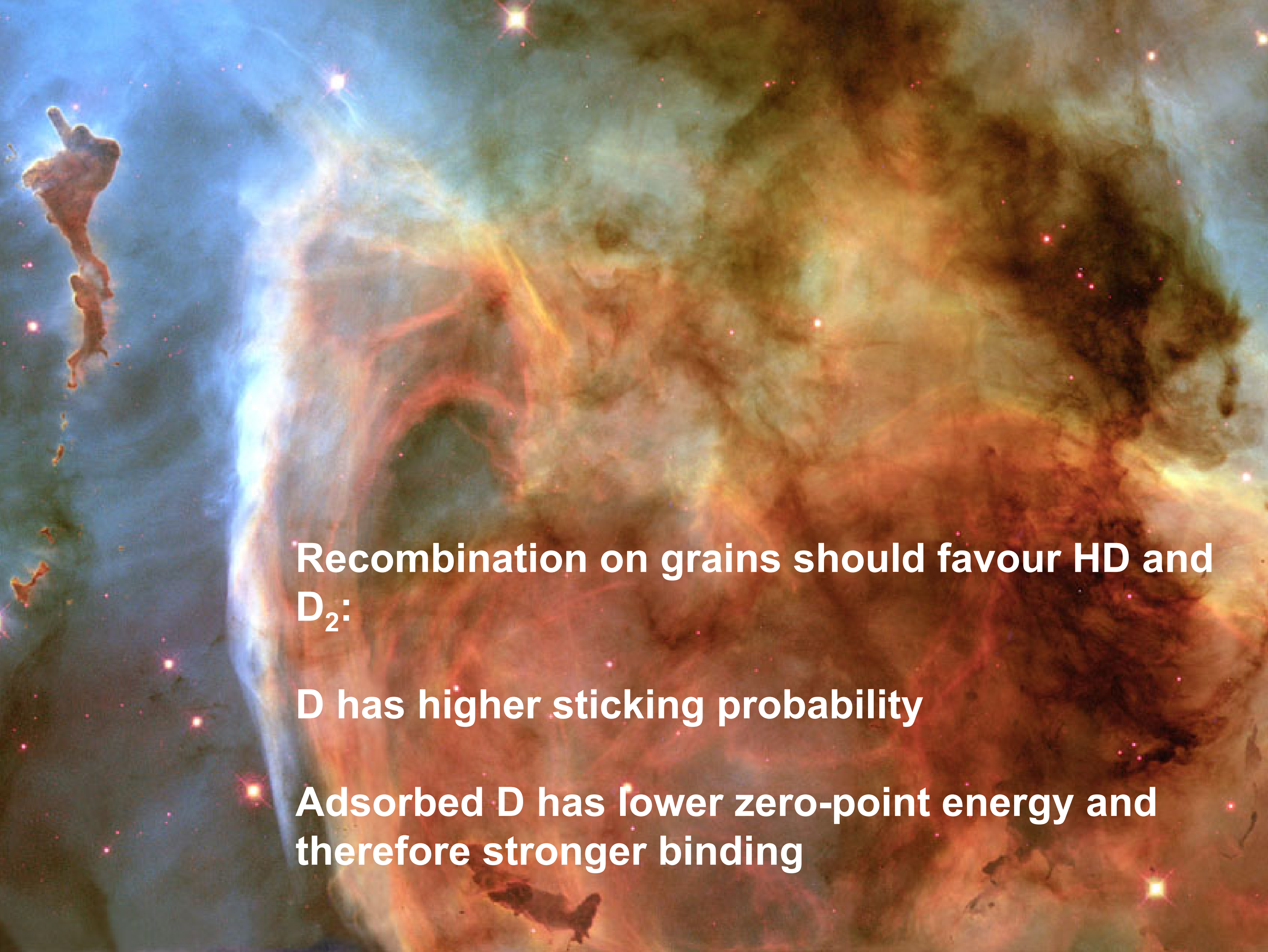
S = 0.15 to 0.4 for present T = 350 to 400 K,
expect S ≈ 0.9 for T = 100 K (see El Halabi et al.)
► $S\,\beta \approx 0.5$ for grains
in dense clouds



sticking probability
Leiden
Buch et. al
Masuda et. al
Exp
a) T_s = 10 K
b) T_s = 70 K
0.0
0.3
0.6
0.9
0
200
400
600
E_i [K]

On hydrogen-free grains, recombination is determined by the sticking probability, which is rather small unless the hydrogen atoms are "cold". But those that do stick may recombine with high probability if enhanced-binding sites are available.

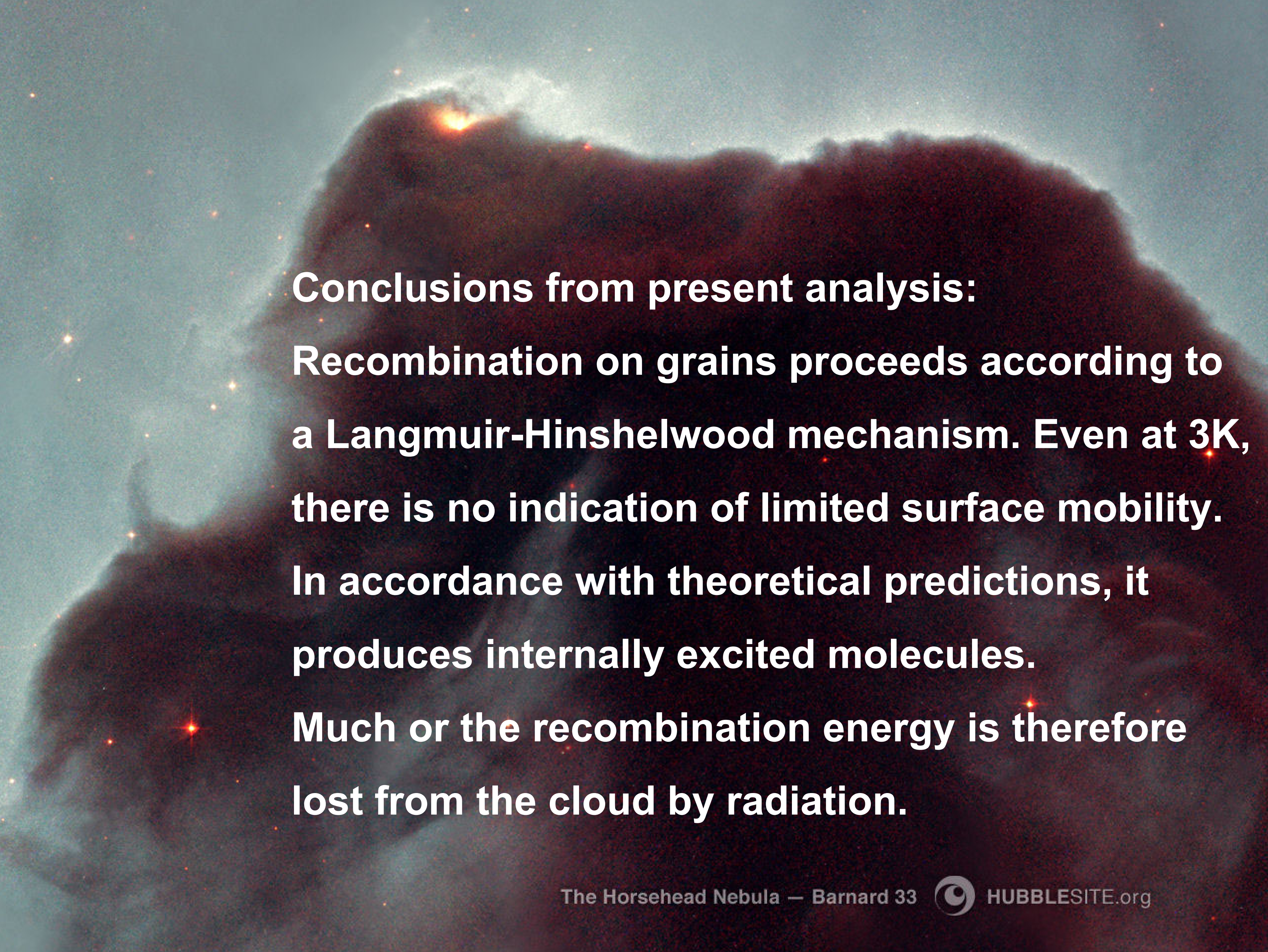
On hydrogen-saturated grains, the sticking probability can approach unity, but recombination will be limited by the low binding energy, as molecular hydrogen will effectively compete for the enhanced-binding sites.



Recombination on grains should favour HD and D_2:

D has higher sticking probability

Adsorbed D has lower zero-point energy and therefore stronger binding



Conclusions from present analysis:

Recombination on grains proceeds according to a Langmuir-Hinshelwood mechanism. Even at 3K, there is no indication of limited surface mobility.

In accordance with theoretical predictions, it produces internally excited molecules.

Much or the recombination energy is therefore lost from the cloud by radiation.

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