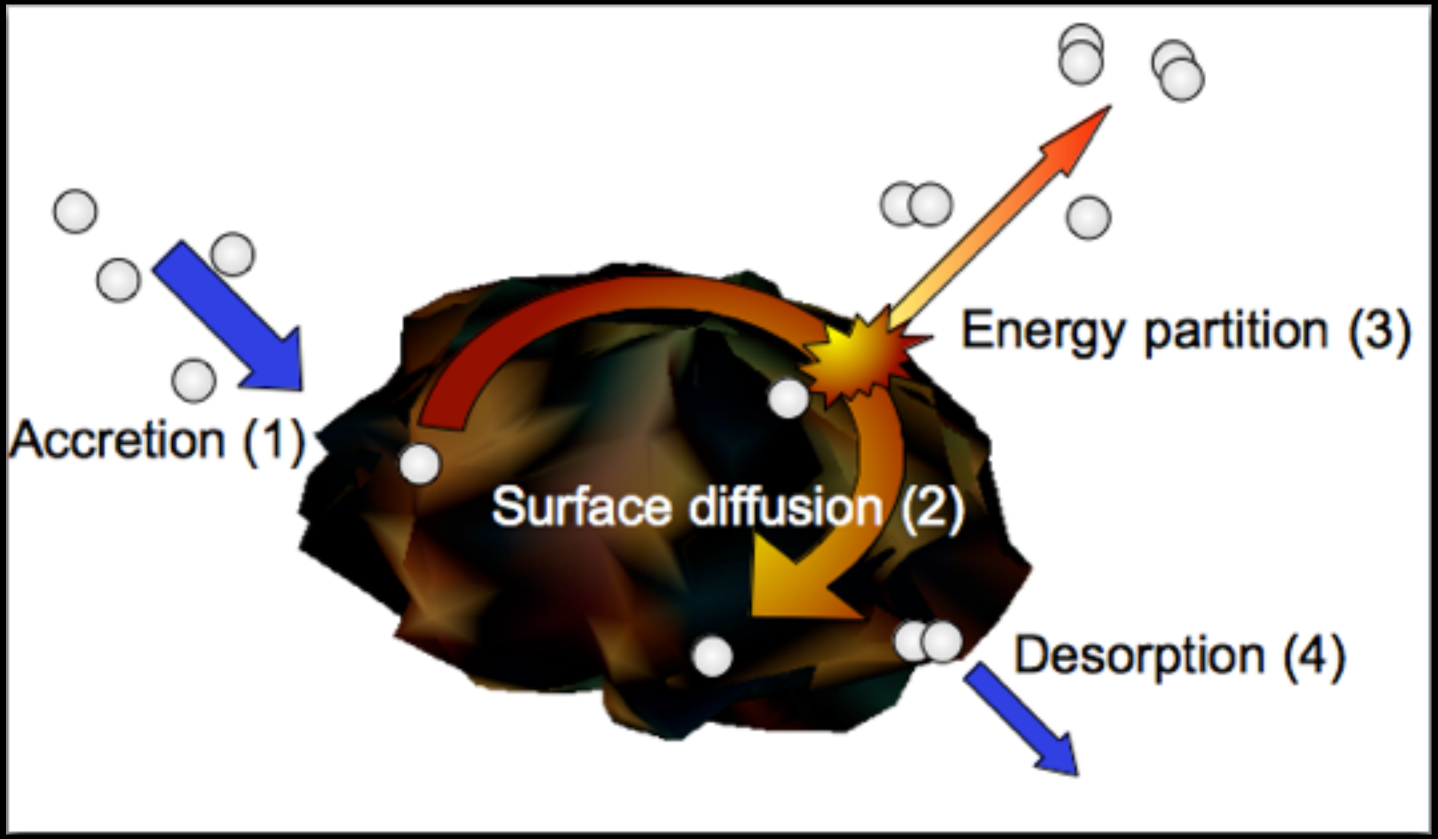
FORMATION DE H_2 SUR LES SURFACES : REVUE ET PERSPECTIVES

FRANCOIS DULIEU - LERMA

THE PHYSICS OF H2 IN SPACE WITH THE JAMES WEBB SPACE TELESCOPE - IAP - NOV. 2016

QUELS MÉCANISMES ?

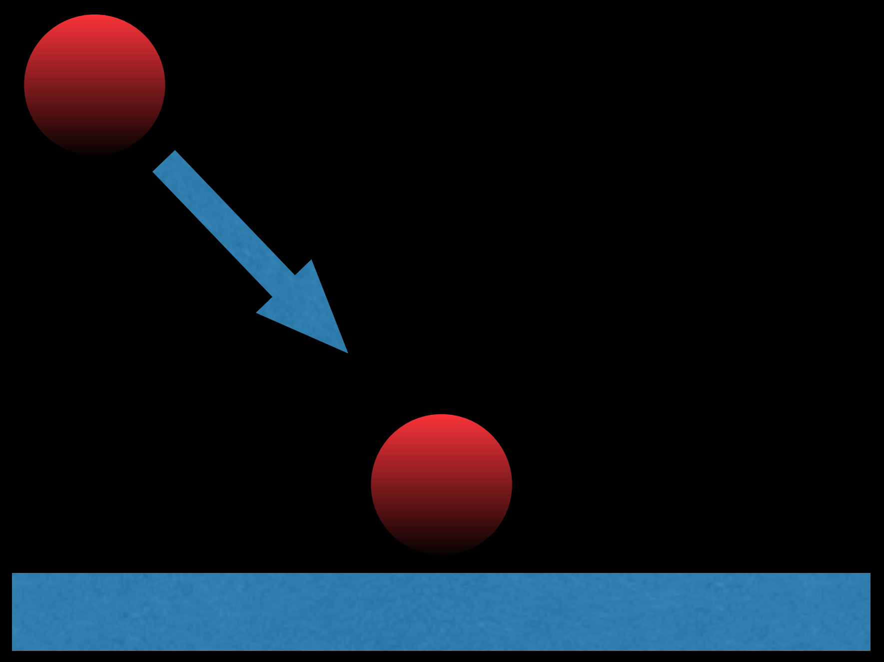
- Collage (oui mais physisorption ou chemisorption)
- H_2 prompt release : quelle répartition énergétique H_2*?
- Diffusion (quel mécanisme ? physisorption, thermal hopping, Q. tunneling, chemisorption)
- Desorption - Induced desorption
- OPR - Nuclear spin conversion



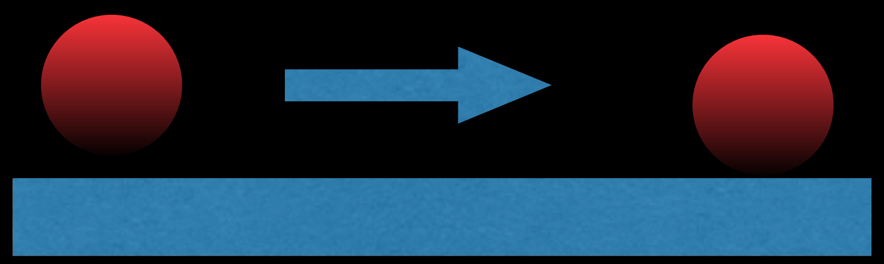
THERE ARE (MAINLY) TWO MECHANISMS

REJECTION MECHANISM (??)
HOT ATOM (??)

- Eley-Rideal : varies with coverage

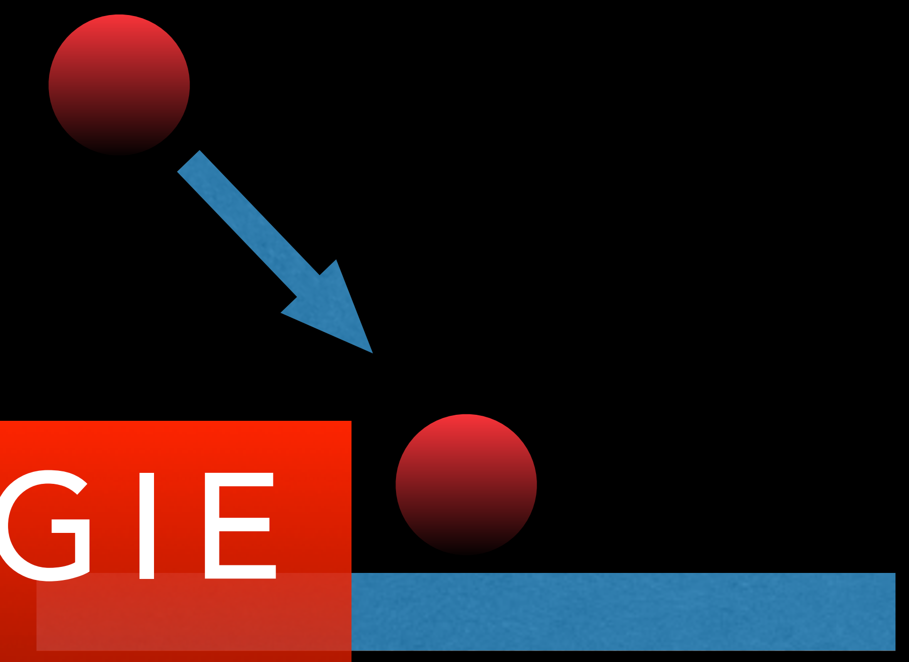


- Langmuir- Hinshelwood : is the diffusive process which depends on the surface temperature (exponential?).



THERE ARE (MAINLY) TWO MECHANISMS

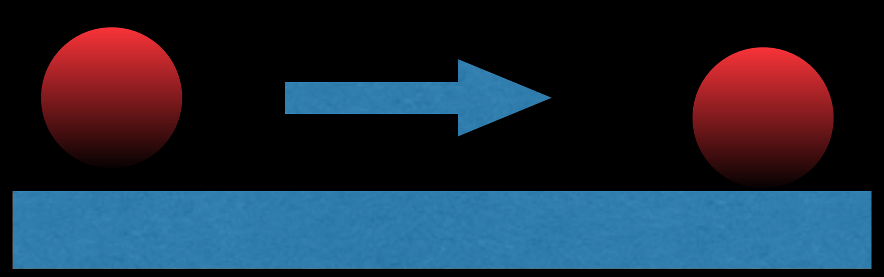
REJECTION MECHANISM (??)
HOT ATOM (??)



- Eley-Rideal : varies with coverage

MORPHOLOGIE
TEMPERATURE

- Langmuir- Hinshelwood : is the diffusive process which depends on the surface temperature (exponential?).



QUELLES SURFACES?
QUELLES ÉTUDES ?

Most of the studies
italic : <2006
roman <2011
bold >2011

Surfaces	Collage	Physisorption	Chimisorption	H	Opr
Glaces (Am., Por., Crist…)	Oui	**Oui**	- -	Oui	**Oui**
Graphite	?	Oui	Oui	Oui	?
Carbones Armorphes Oignons	Oui (Chem)	?	Oui	Oui (!)	???
PAH/PAH	**Sigma**	?	**Oui**	?	???
Silicates Armorphes Crystallins Poreux	**Oui**	*Oui*	Non	Oui	?

see review by Wakelam et al (Arcachon meeting)

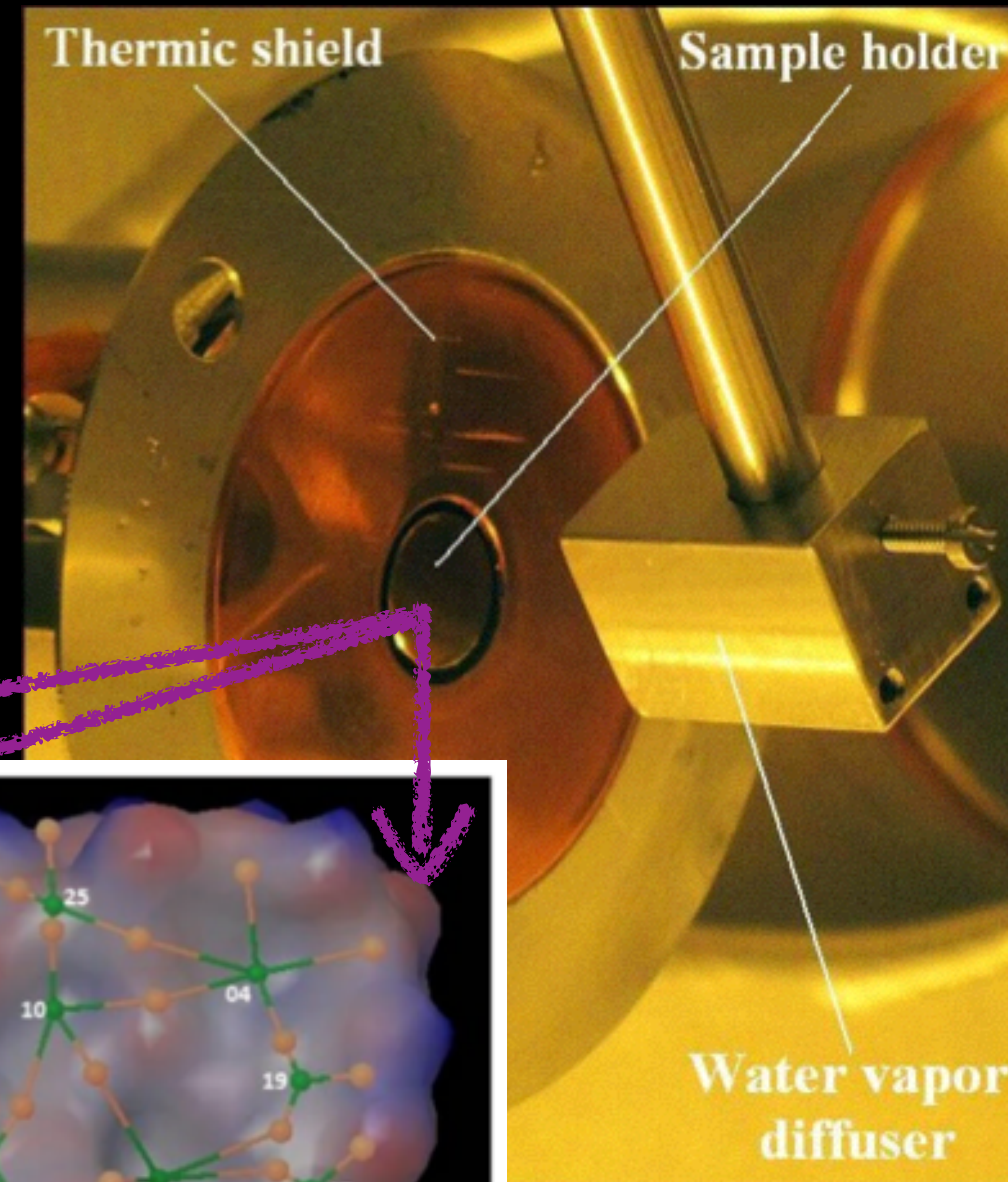
LERMA - Cergy

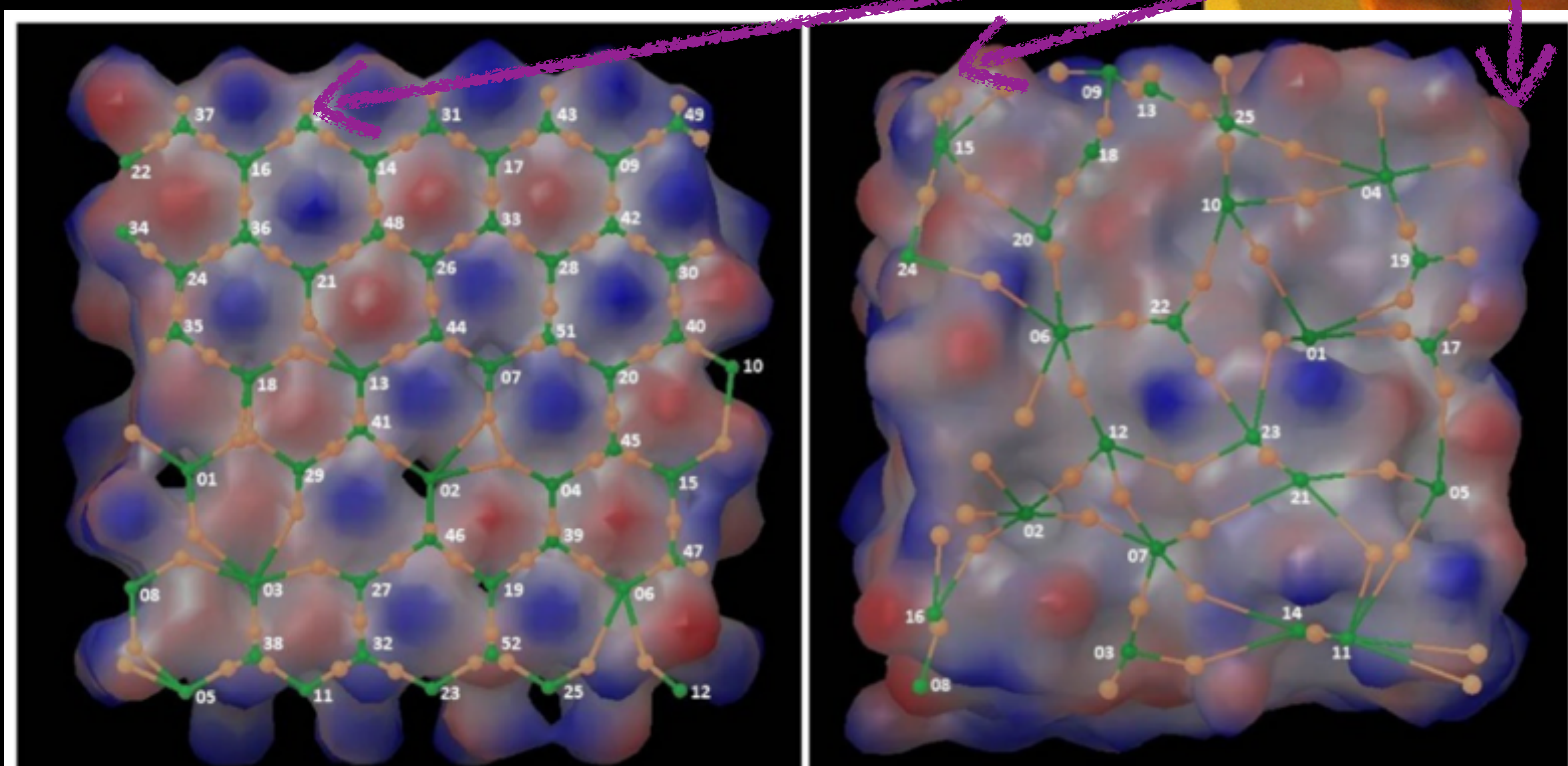
OUTLINE

- Sticking
- Diffusion
- H_2*
- OPR
- Perspectives

La glace d’eau

- **Versatile, bien caractérisable**





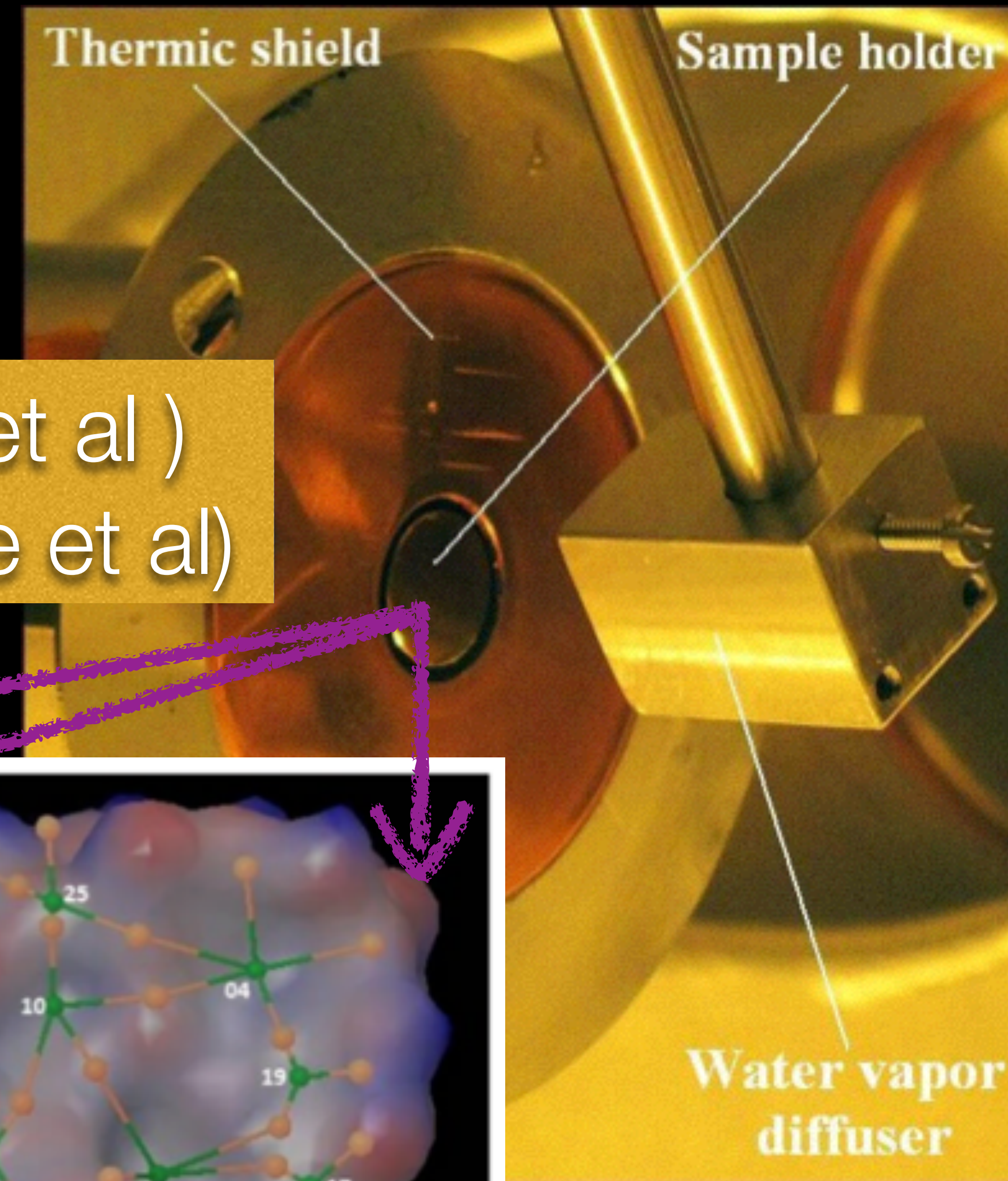
© Senevirathne et al, *submit. to PCCP*

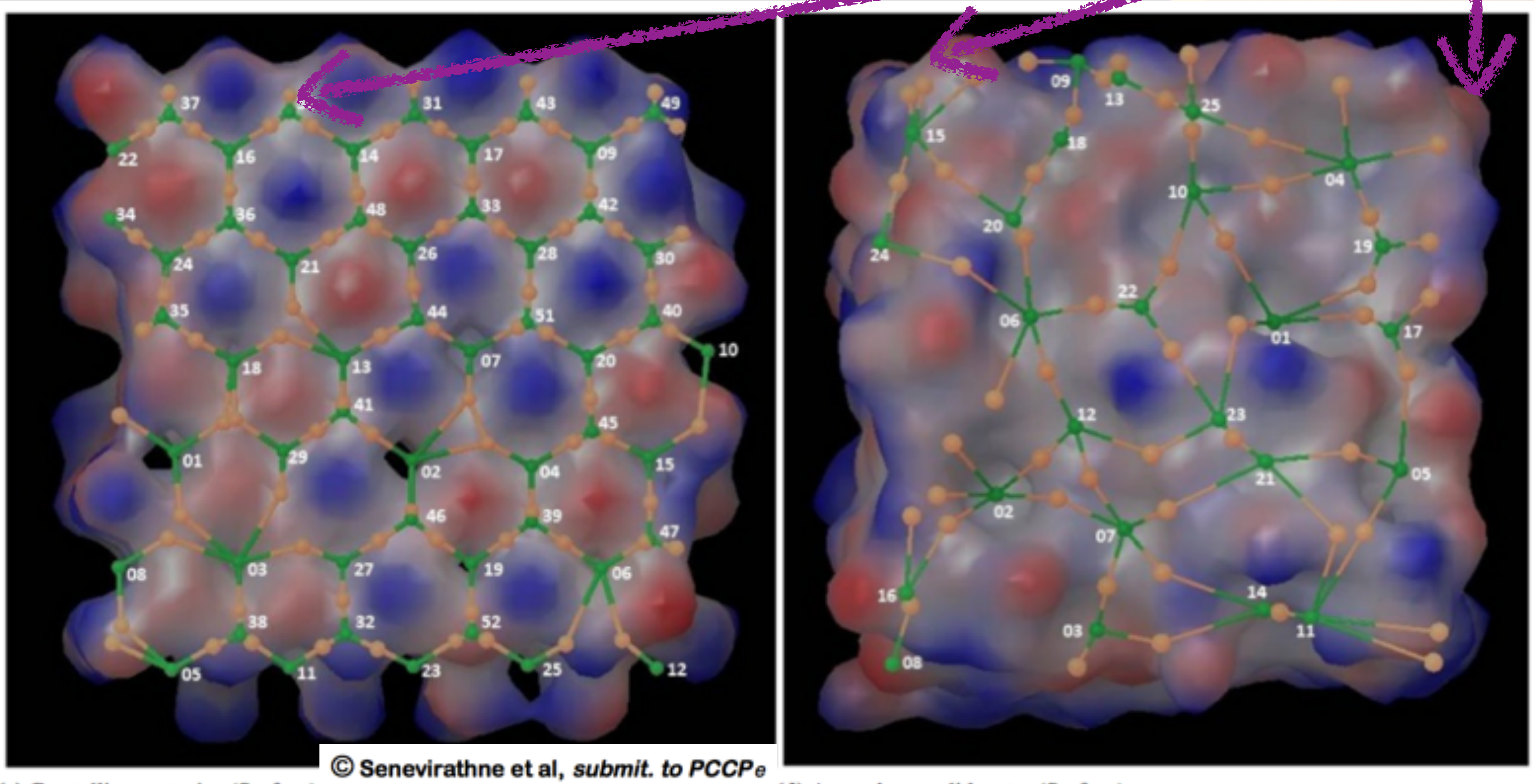
(c) Crystalline water ice (Surface)

(d) Amorphous solid water (Surface)

La glace d'eau

- Très beaux calculs (Senevirathne et al)
- Très belles expériences (Watanane et al)



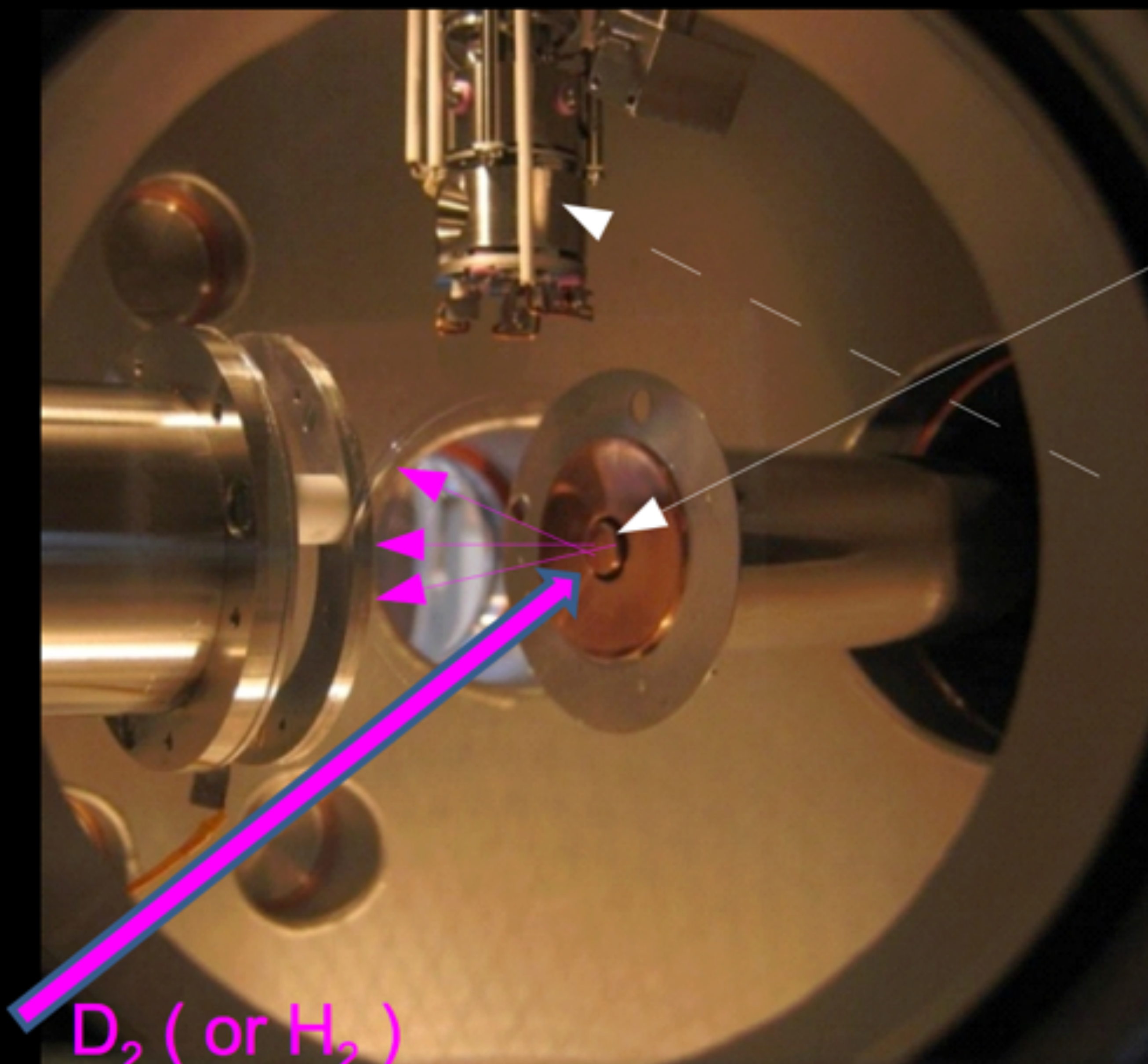


(c) Crystalline water ice (Surface)

(d) Amorphous solid water (Surface)

1200 K*
100 meV
10 kJ/mol
2.4 kCal/mol
834 cm-1

Sticking measurements of H_2 and D_2



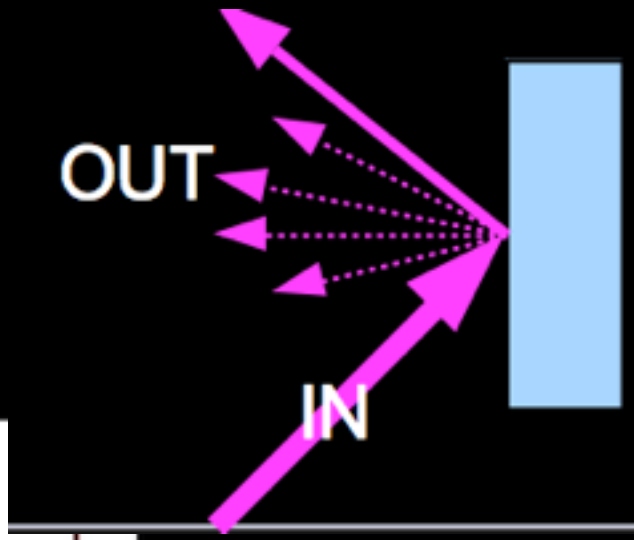
0 – UHV chamber

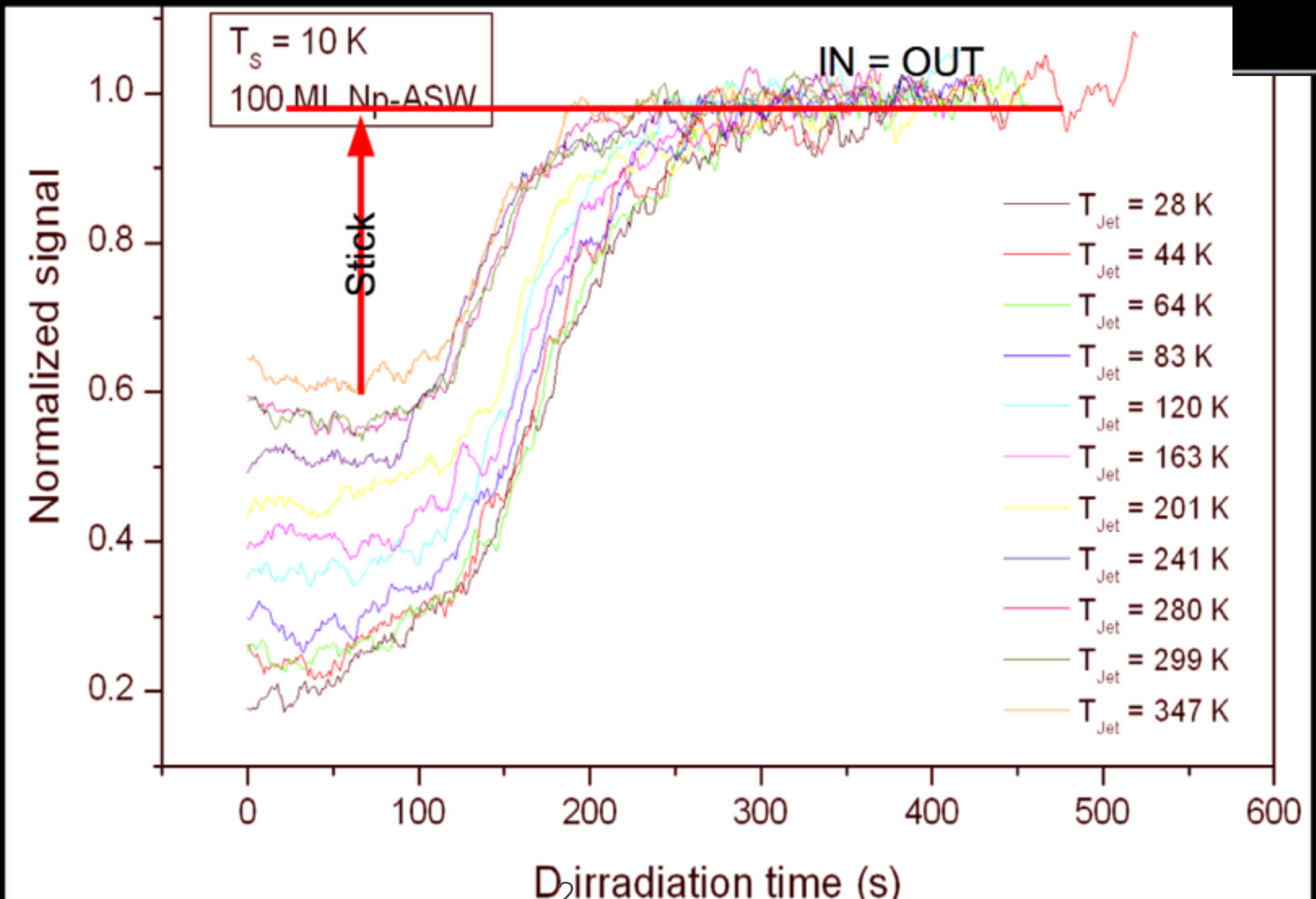
1 – Ice sample (np) Ts = 10 K

2 – D_2 beam (T_b 30– 350 K)

3 – Monitor (real time)
partial pressure of D_2

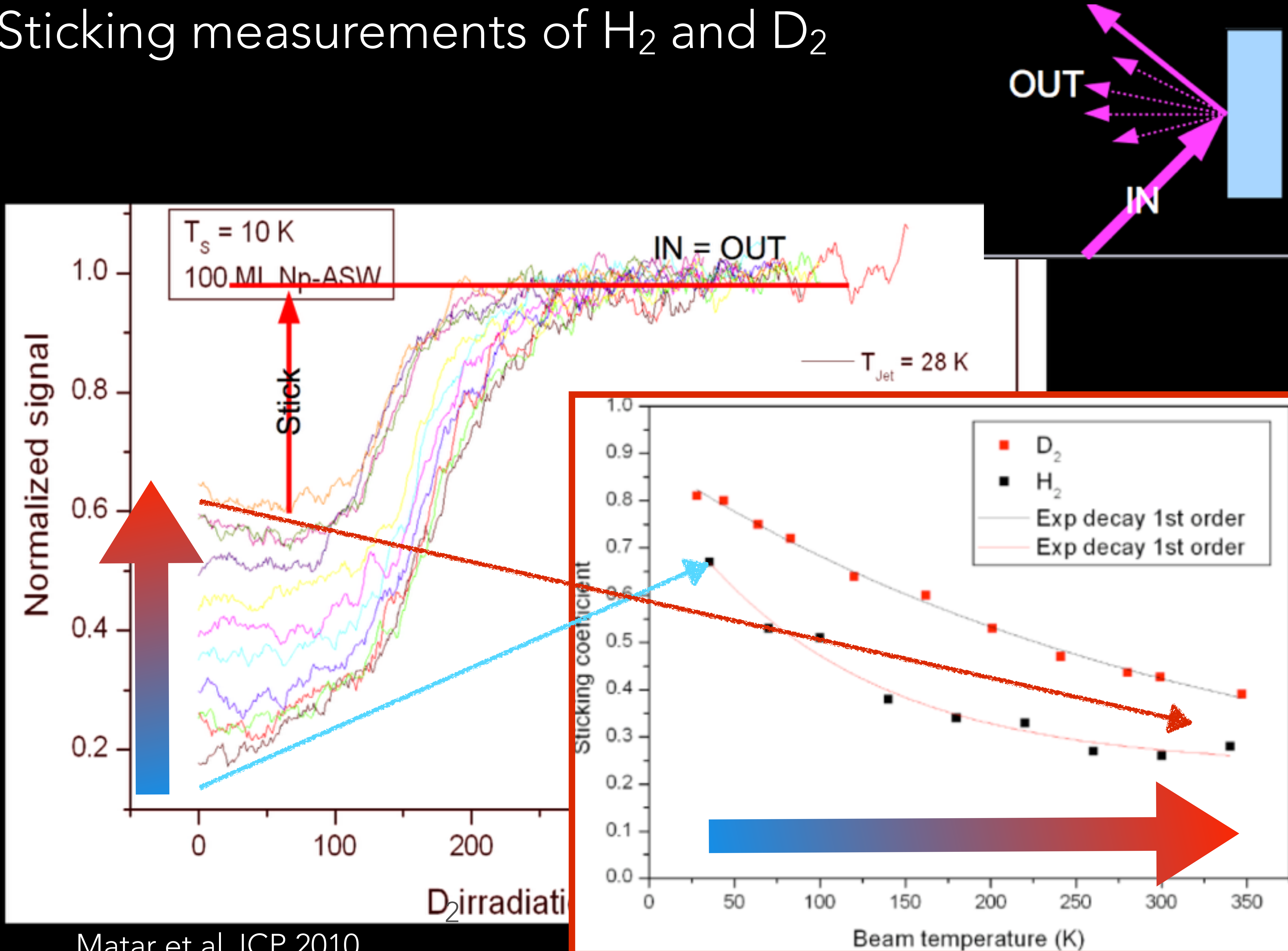
Sticking measurements of H_2 and D_2





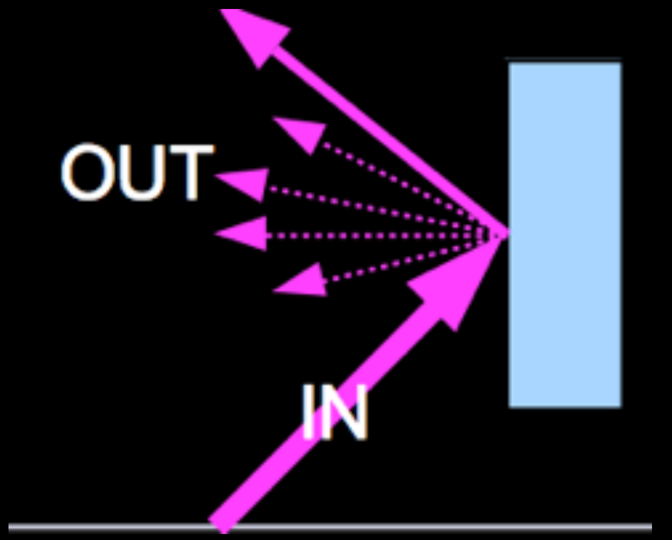
Matar et al JCP 2010

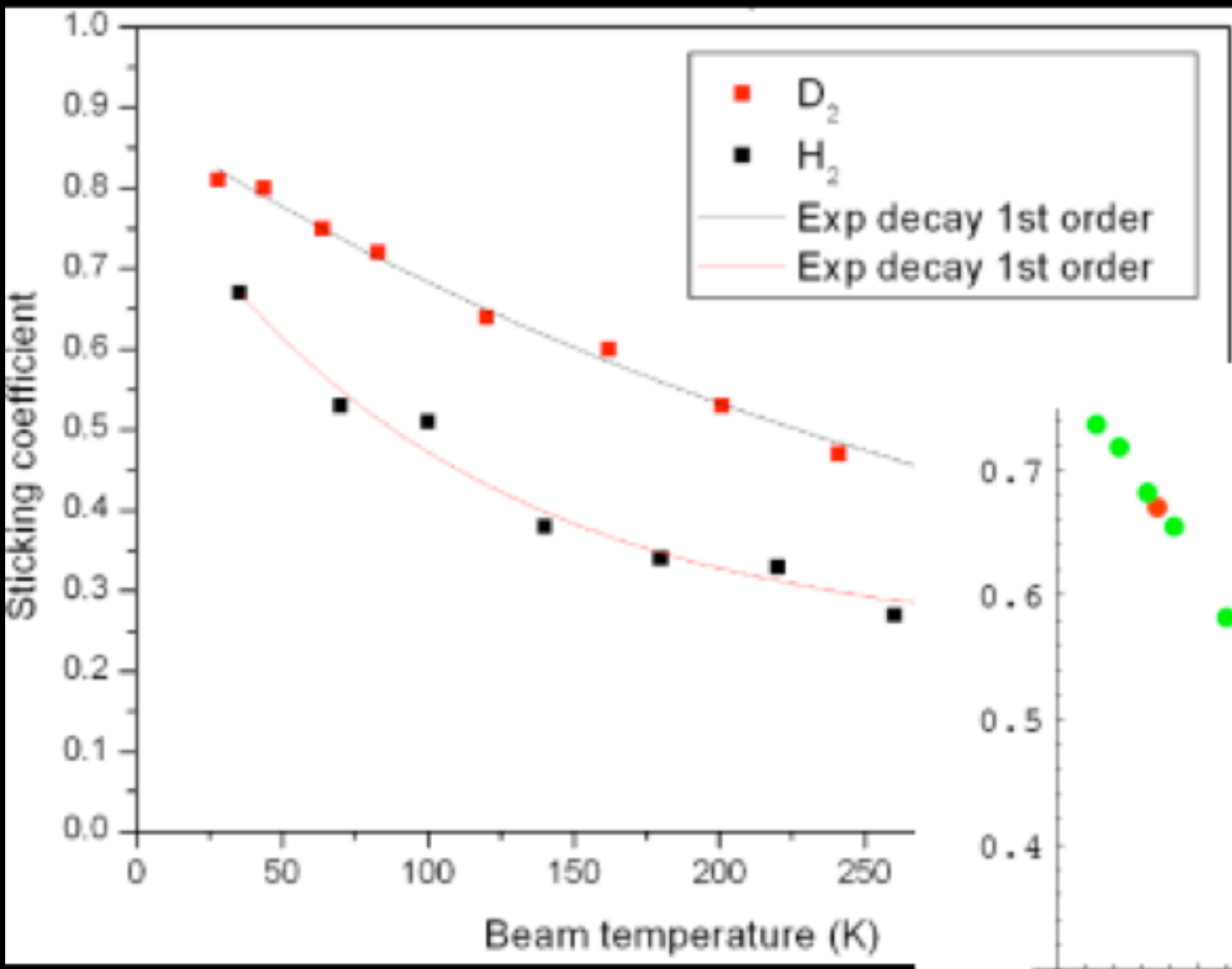
Sticking measurements of H_2 and D_2

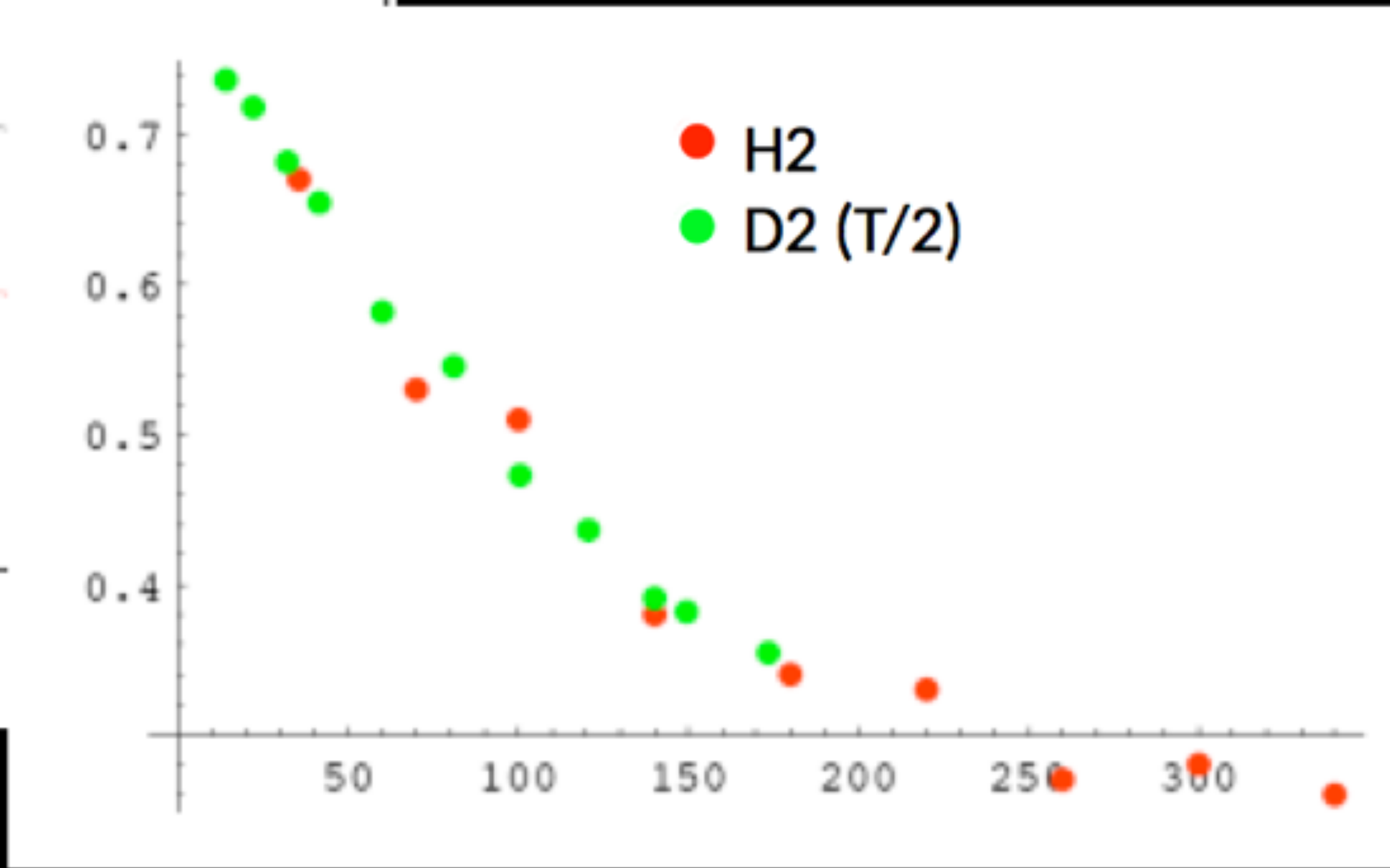


Matar et al JCP 2010

Sticking measurements of H_2 and D_2

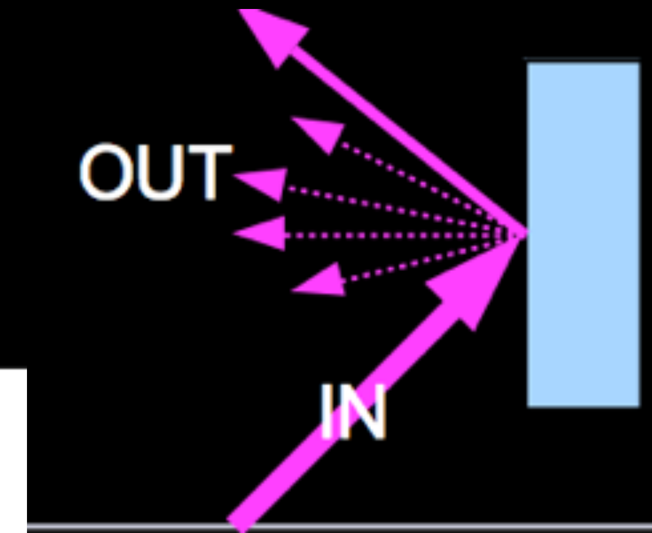




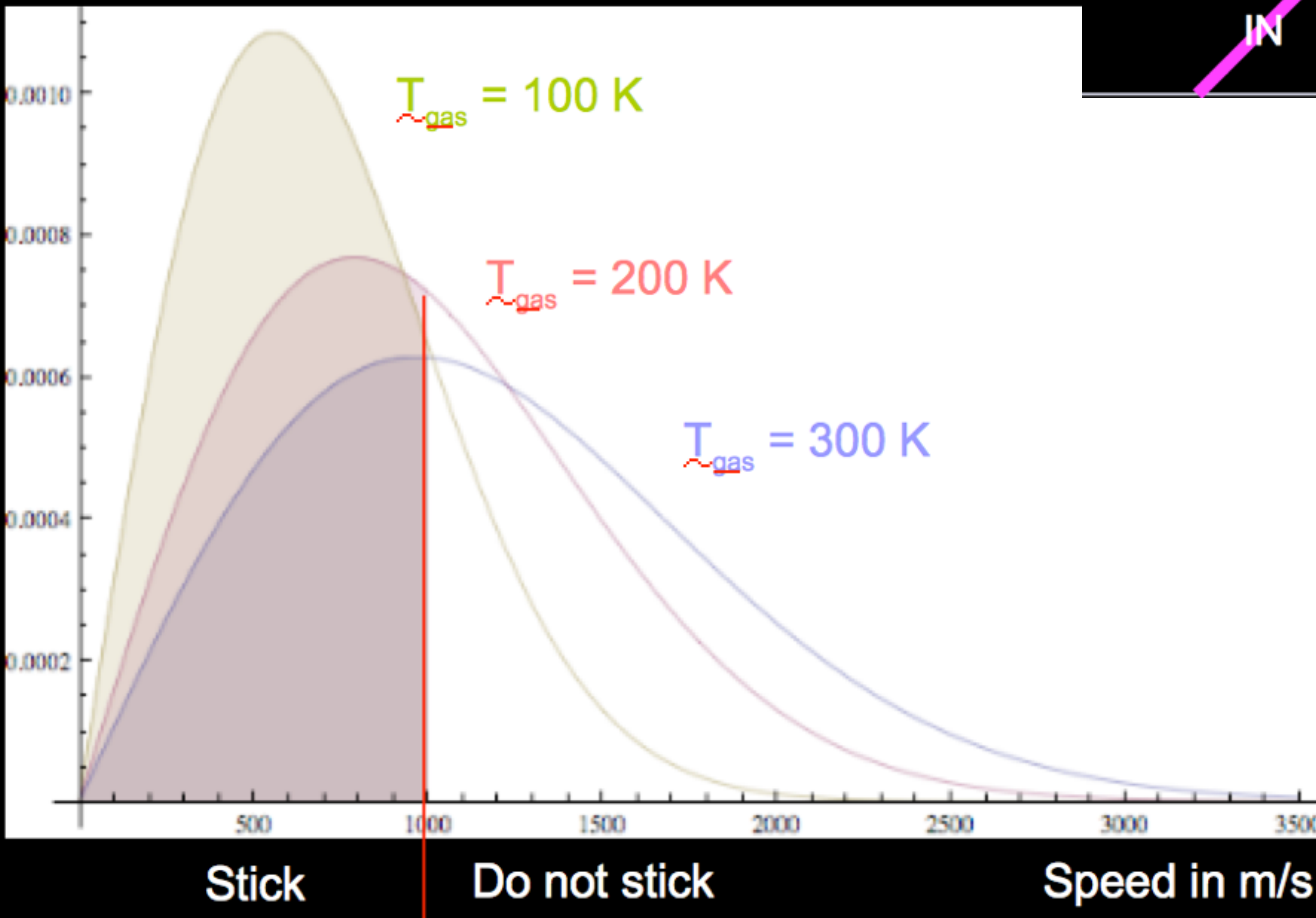


If T for D2 is divided by a factor 2 … the law is the same

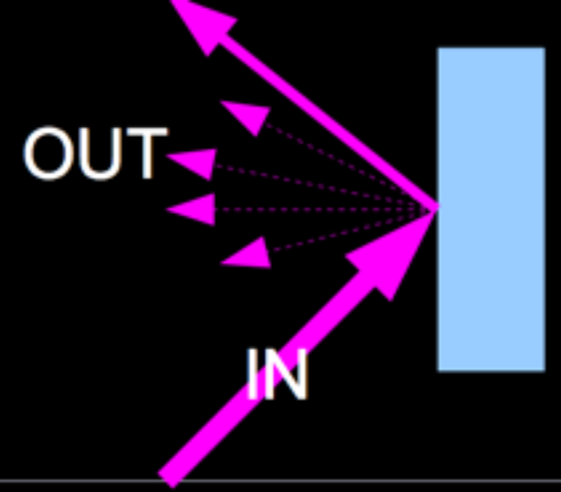
Sticking measurements of H_2 and D_2



Temperature distribution



Sticking of light species



$$S(T) = S_0 \frac{(1 + \beta\, T/T_0)}{(1 + T/T_0)^{\beta}}$$

ß = 2.5 for isotropic thermal distribution

Substrates	Species	S_0	T_0 (K)	References
np-ASW ice	H	1	52	1
	D	1	104	1
	H_2	0.76	87	2
	D_2	0.80	174	2
	HD	0.83	130.5	Prediction
Silicate	H	1	25	Extrapolation
	D	1	50	Extrapolation
	H_2	0.95	56	This study
	D_2	0.82	112	This study
	HD	0.87	84	Prediction

Chaabouni et al *A&A*, 2012; Matar et al, *JCP*, 2010,

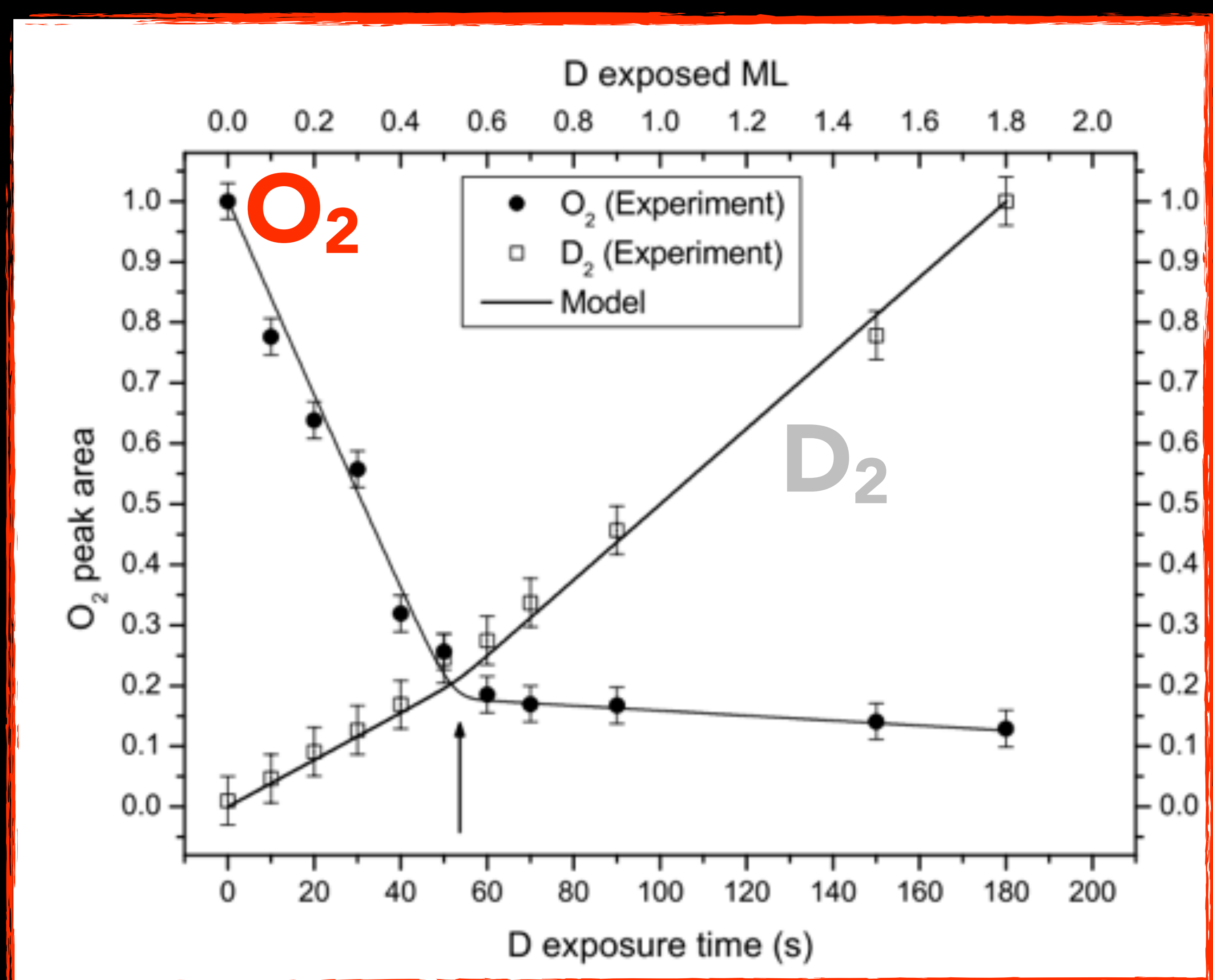
- Large isotopic effect H and D, never took into account (T_g > 50K)
- Amorphous silicate is “harder” than ASW ice

STICKING : SUMMARY

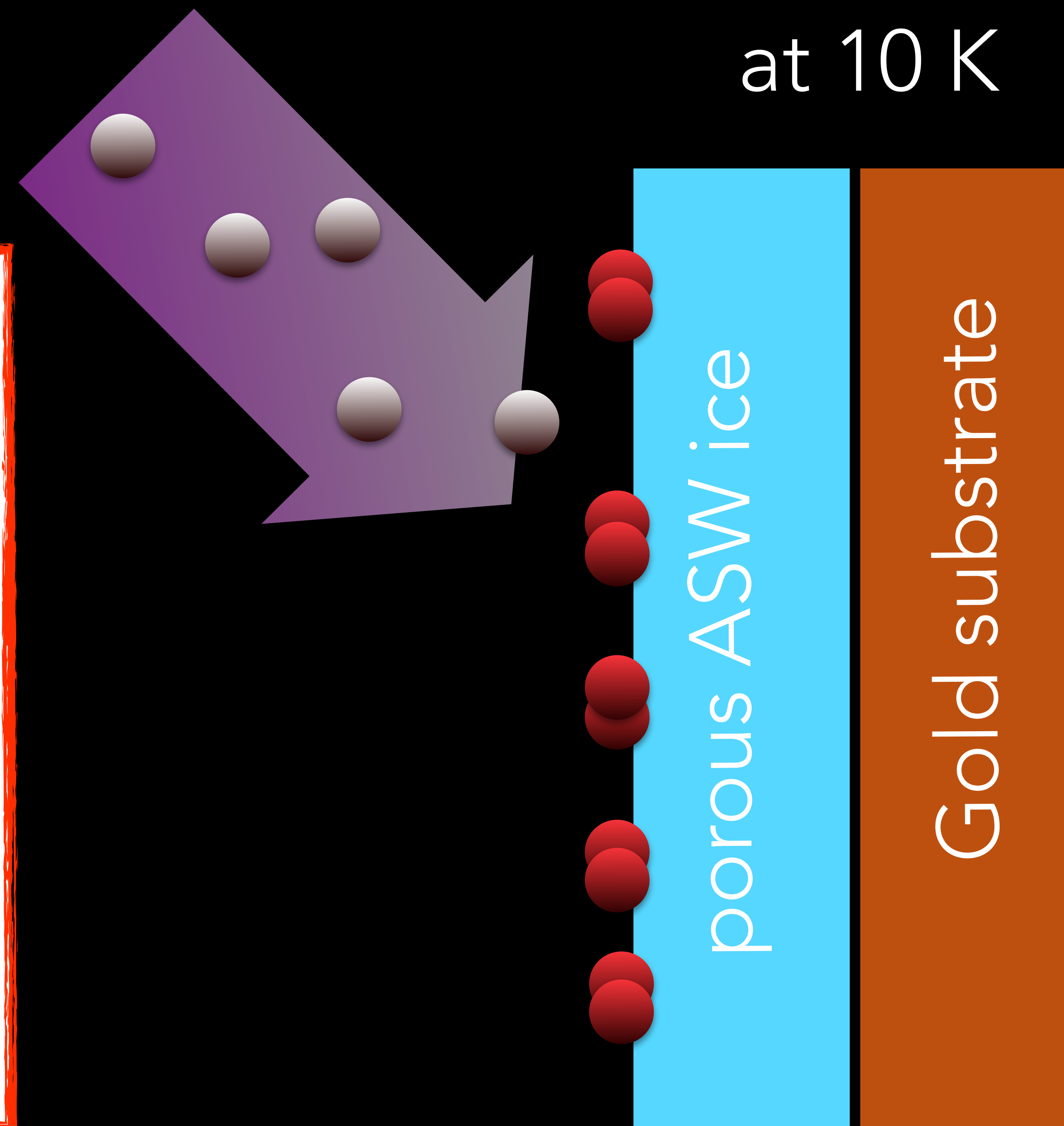
- Sticking on amorphous surfaces is mainly governed by Tgas, and mass of species
- Light species (H, H2, D, D2 He) may have a sticking coefficient lower than unity ==> Strong isotopic effect H/D (Chaabouni+ A&A 2012, Matar+ JCP 2010)
- See some astro effects and new calculations (Cazaux+A&A 2011)
- Heavier species have a sticking coefficient close to unity. (higher mass + higher binding energy) (i.e. Acharyya+ A&A 2007, Fillion + EPJ web conf 2011)

DIFFUSION OF H (ON WATER ICE)

Matar+ A&A (2008)



at 10 K



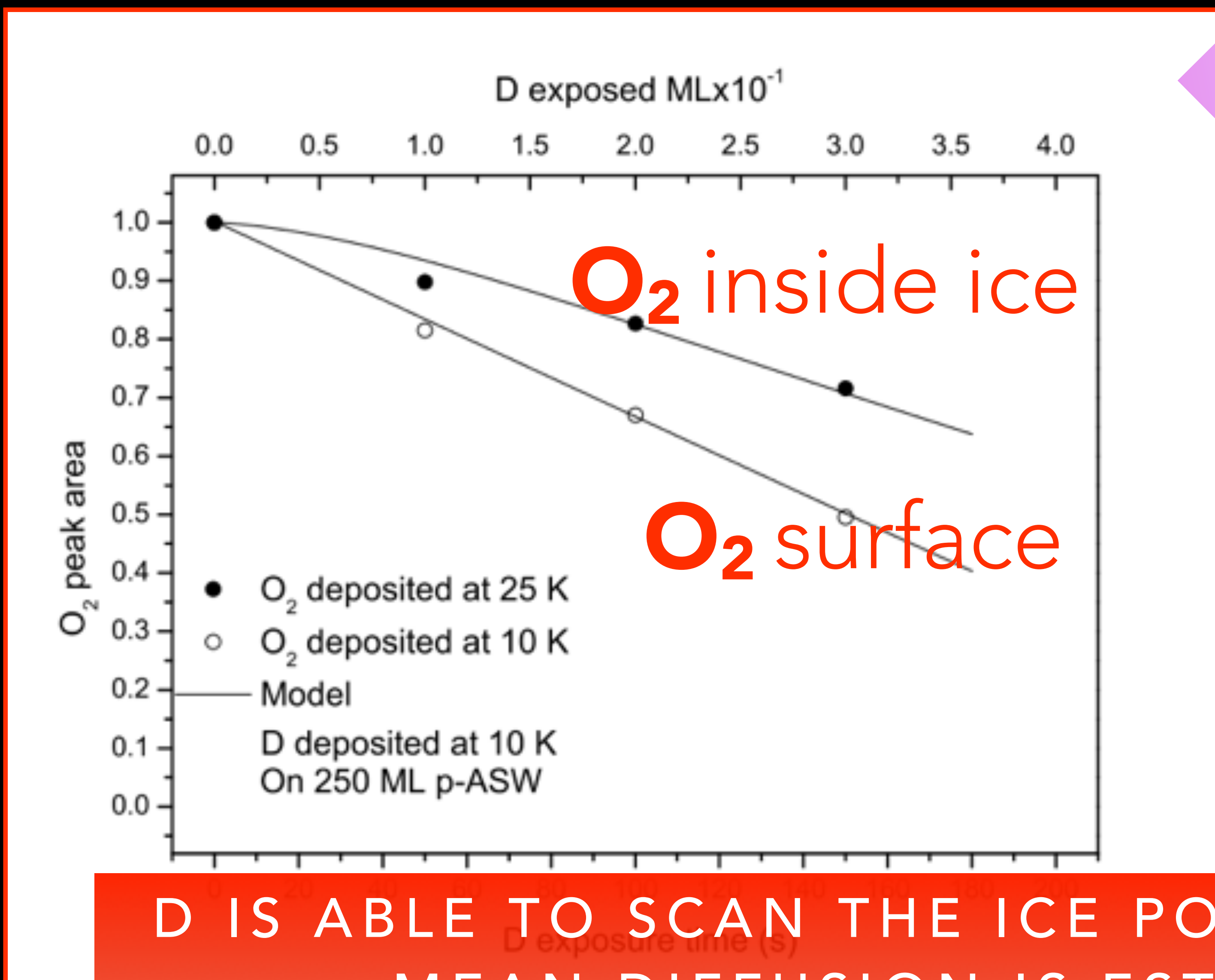
Thin layer of O_2, tracer of presence of D (reactivity)

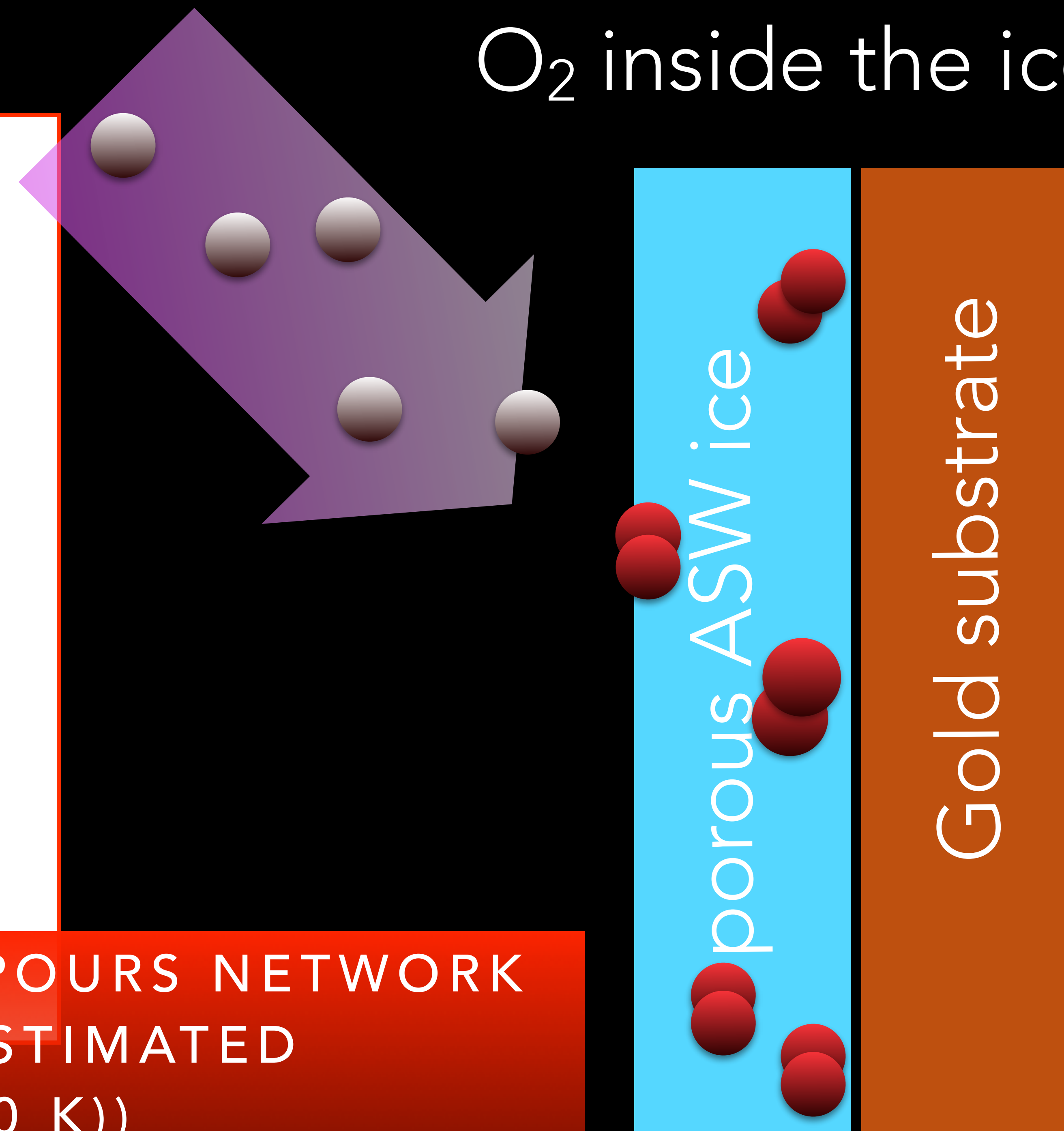
DIFFUSION OF H (ON WATER ICE)

Matar+ A&A (2008)

at 10 K

O_2 inside the ice

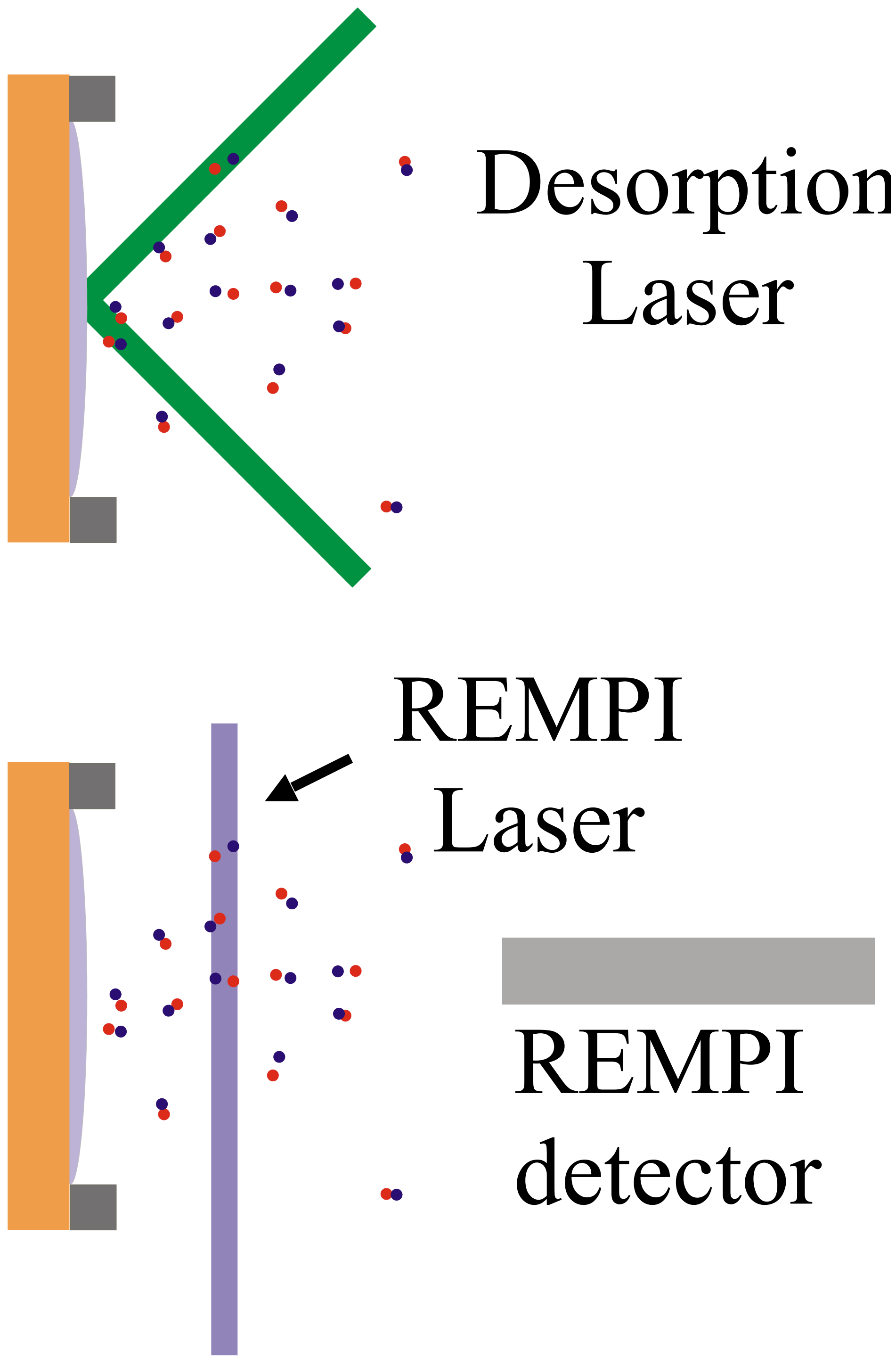


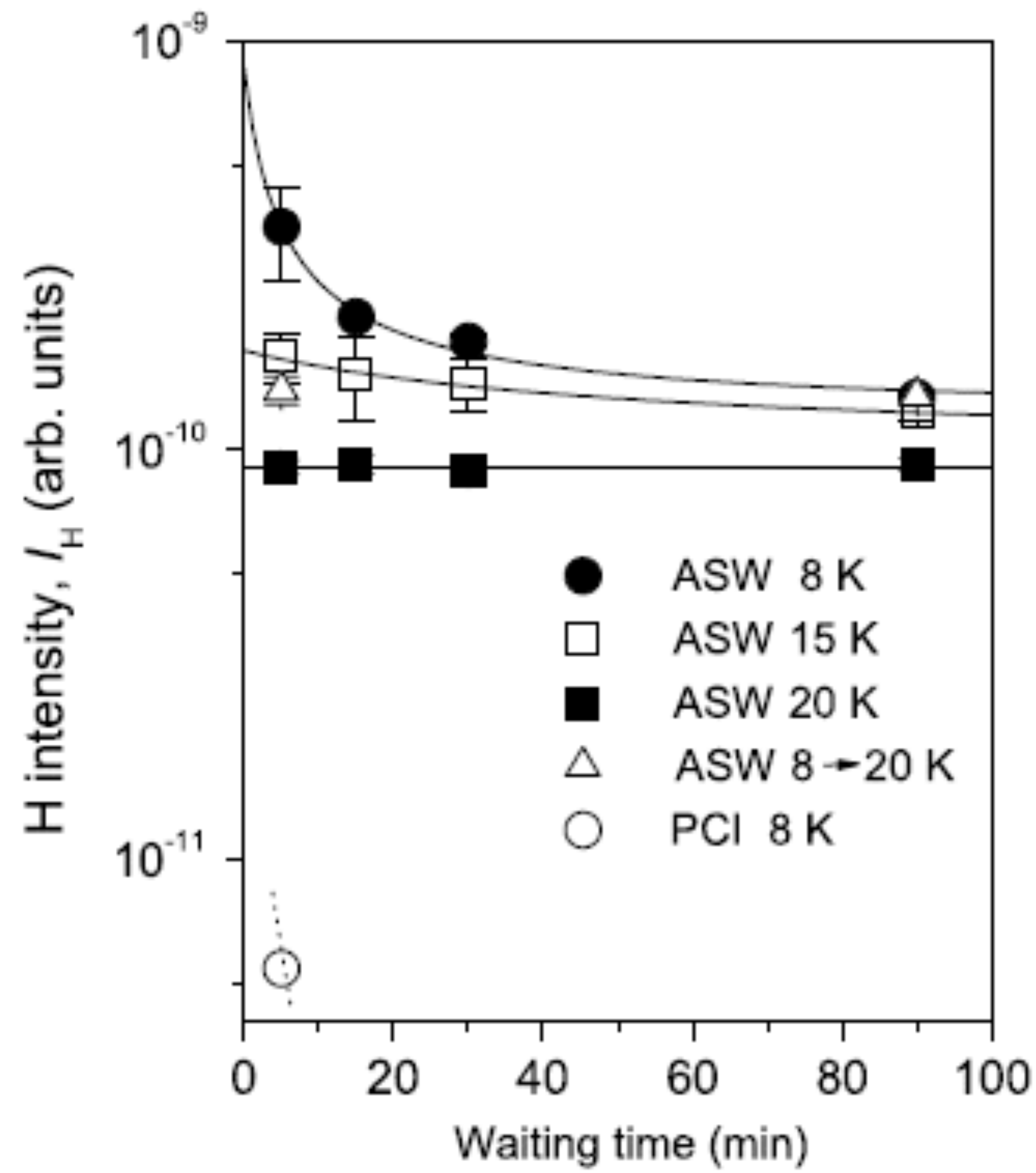


D IS ABLE TO SCAN THE ICE POURS NETWORK
MEAN DIFFUSION IS ESTIMATED
(E_{DIFF}=22 meV (230 K))

Thin layer of O_2, tracer of presence of D (reactivity)

H mobility





Binding sites: ~20 meV and >50 meV

Watanabe et al. Ap. J. 714:L233–L237 (2010)

!! H2 HAS TO BE FORMED ON GRAINS - H RULES THE HYDROGENATION !!

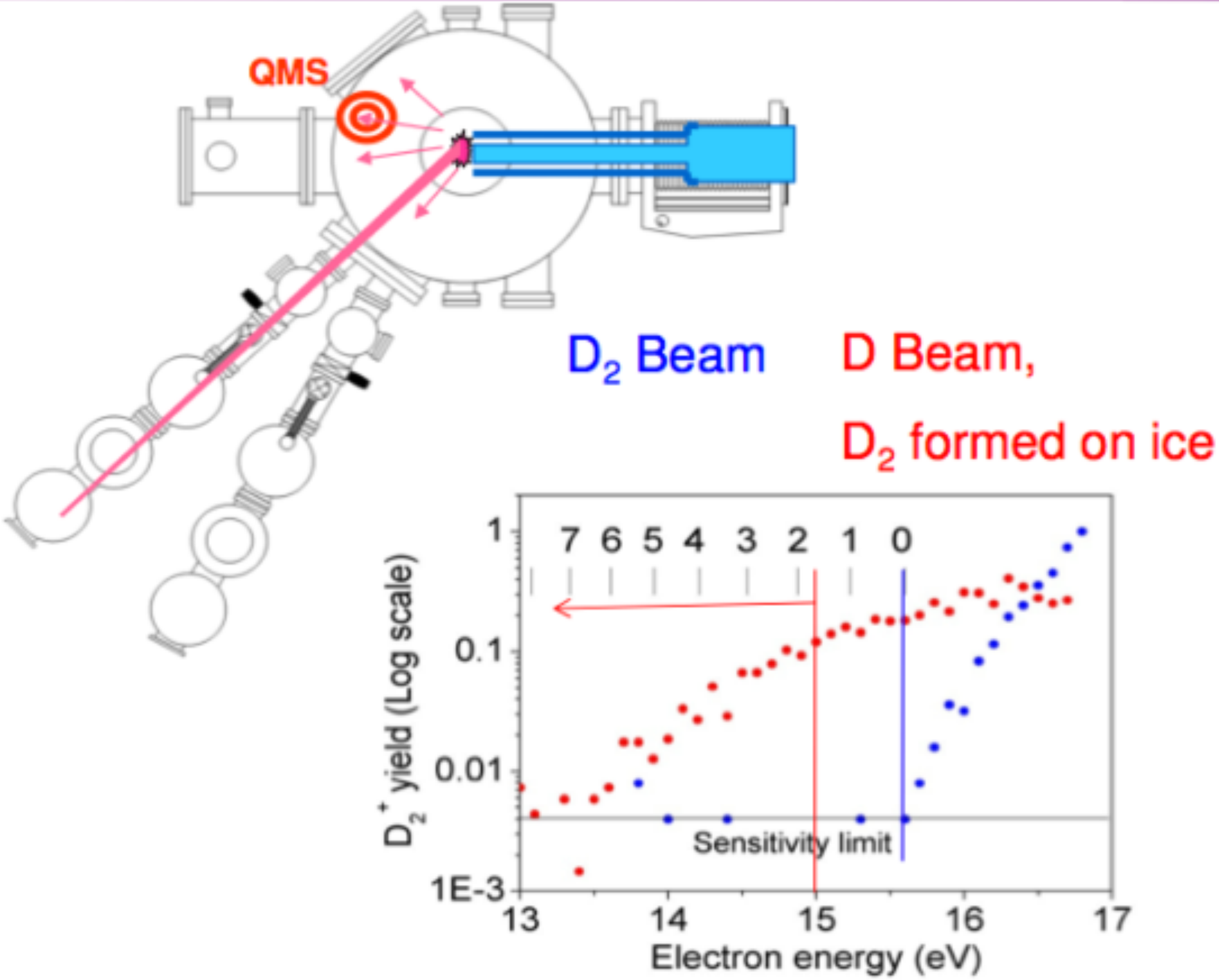
DIFFUSION OF H (ON WATER ICE)

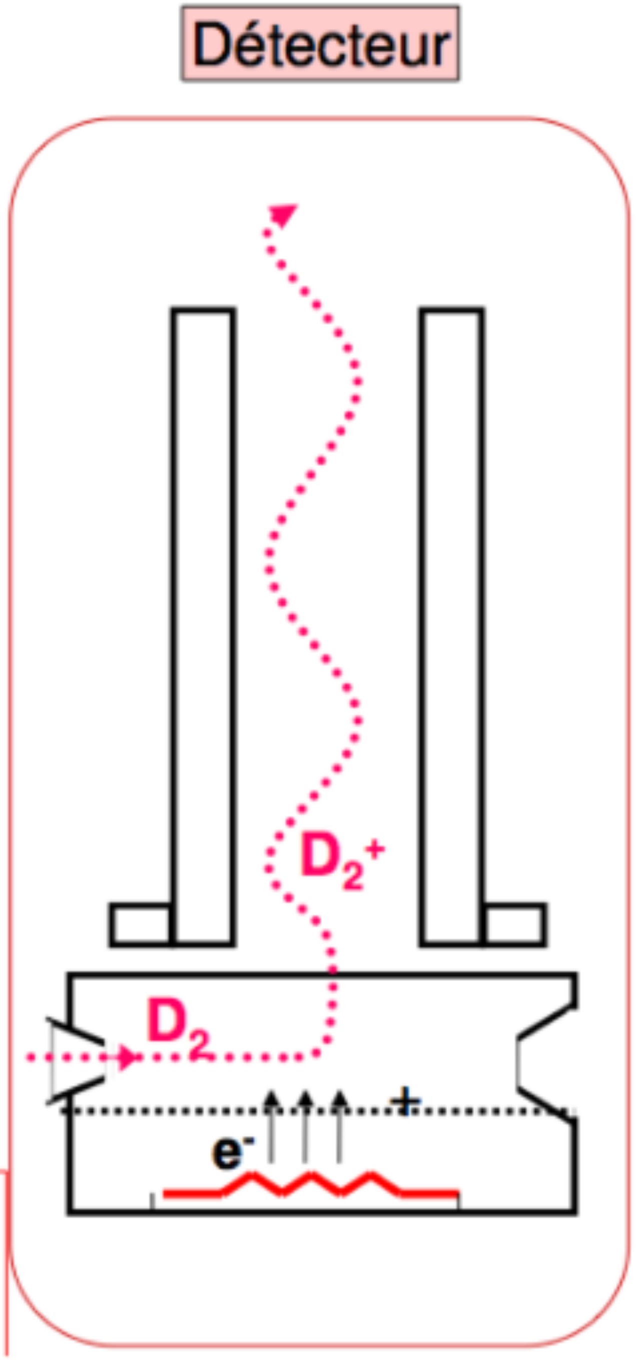
- Manico+ ApJL 2001; Perets+2005 : High barrier diffusion (51 meV)
- Calculations (Buch&Zhang 1991; experiments : Hornekaer+ Science 2003 : H is mobile.
- Matar+ A&A 2008 (see later) Ediff (D) ==> 22 meV
- Hama+ApJ 2012, Kuwahata + PRL 2015, Distribution of binding energies peaked around 22 meV
- Calculations : Senevirathne+ submitted : Confirmation of late experiments.

FOR H ON OTHERS SURFACES SEE VIDALI'S REVIEW, 2013
ONE OTHER COMING SOON ? (WAKELAM+).

D_2 PROMPT RELEASE

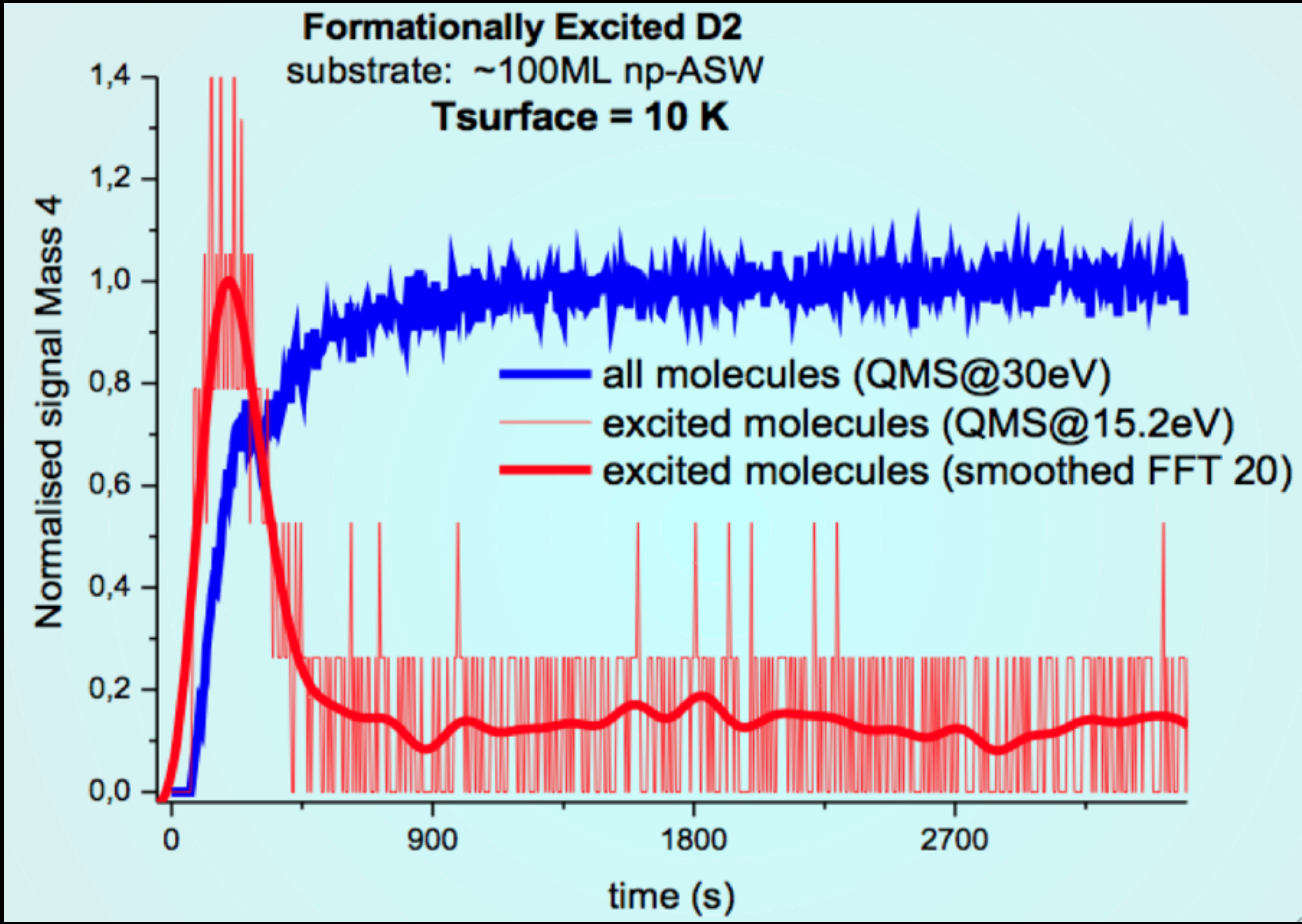
NP **Tunning the kinetic energy of the ionosing electrons**



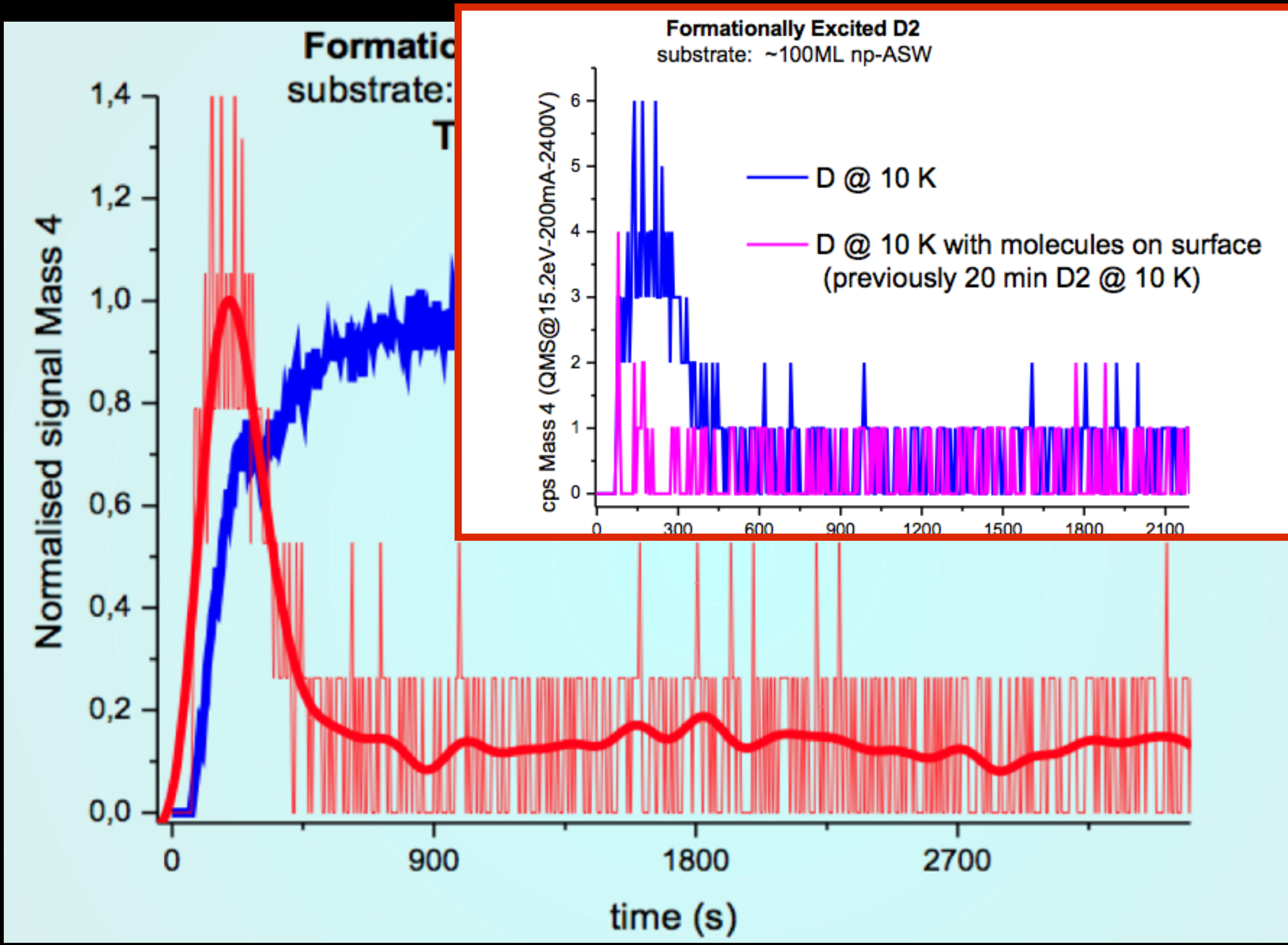


15 eV → only excited molecules
30 eV → All the molecules (excited or not)

D_2* RELEASED QUENCHED BY NEIGHBORS



D_2* RELEASED QUENCHED BY NEIGHBORS



SUMMARY H DIFF (AND REACTIVITY)

- H and D can diffuse on ice.
- There is a distribution of barrier to diffusion
- a typical value of 22 meV can be used
- On time scale experiments, H self-react in H_2. If the surface is not porous, and free of H_2 ==> Excited H_2 is promptly released.

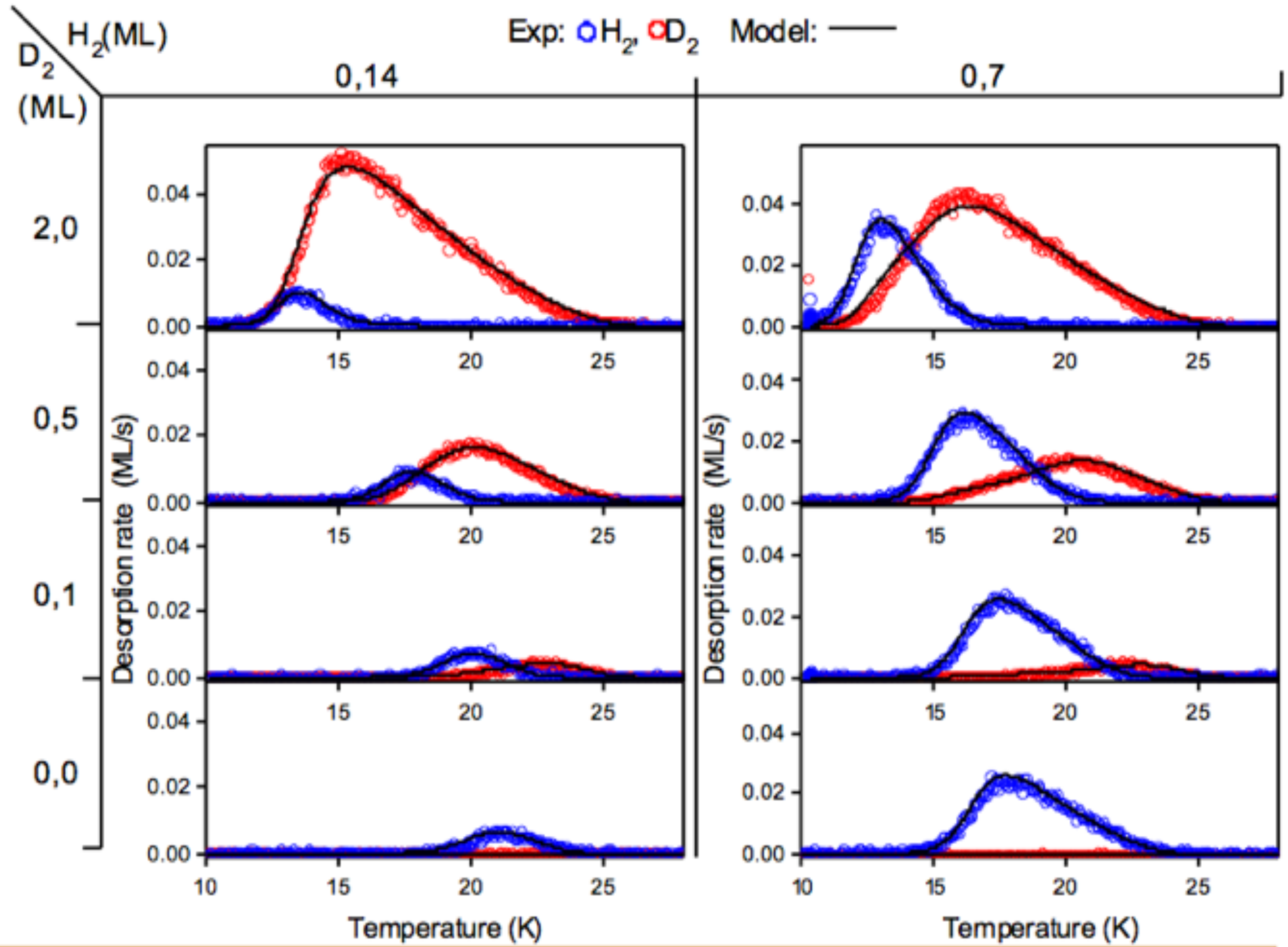
H2*

- Graphite : medium v, high J, insensitive to surface temperature
- Presence of co-adsorbed H2 ‘kill’ the H2*
- Porosity or bulky material , ==> no internal energy

FERMI-DIRAC STATISTICS:
TEST CASE OF ISOTOPES

(c) Amiaud et al *PCCP* 2015

ISOTOPIC SHIFT —> ISOTOPIC SEGREGATION



Set of 30 experiments with variable proportions of H_2:HD:D_2

Model : one unique fit of the 30 experiments

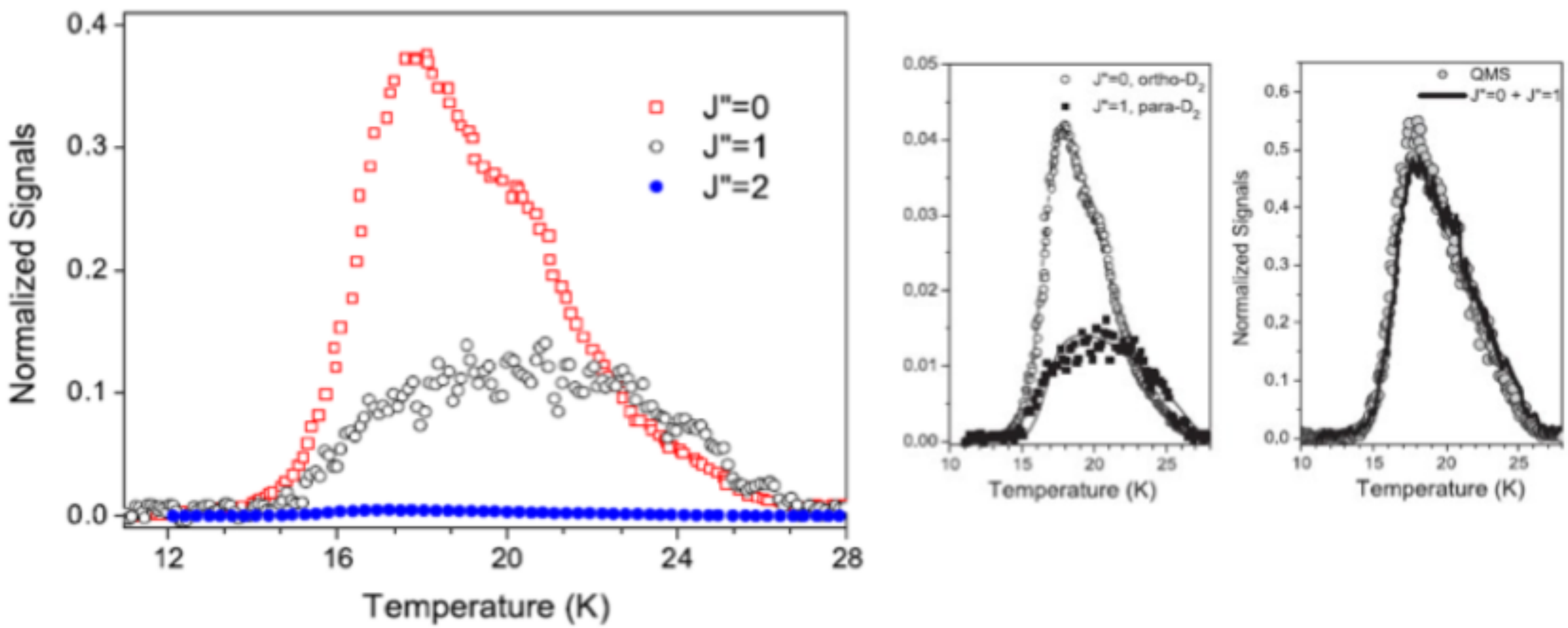
2 + 2 free parameters describing the energy distribution (+ scaling factor)

FERMI-DIRAC STATISTICS: TEST CASE OF **DIFFERENT *J* STATES**

PRL **100**, 056101 (2008) PHYSICAL REVIEW LETTERS week ending 8 FEBRUARY 2008

Measurement of the Adsorption Energy Difference between *Ortho*- and *Para*-D_2 on an Amorphous Ice Surface

L. Amiaud,* A. Momeni, F. Dulieu,† J. H. Fillion,‡ E. Matar, and J.-L. Lemaire



Ortho and para state do not desorb identically !

Energy difference :1.4 ± 0.3 meV

MOLECULES IN *J*=1 STATES HAVE HIGHER BINDING ENERGIES !

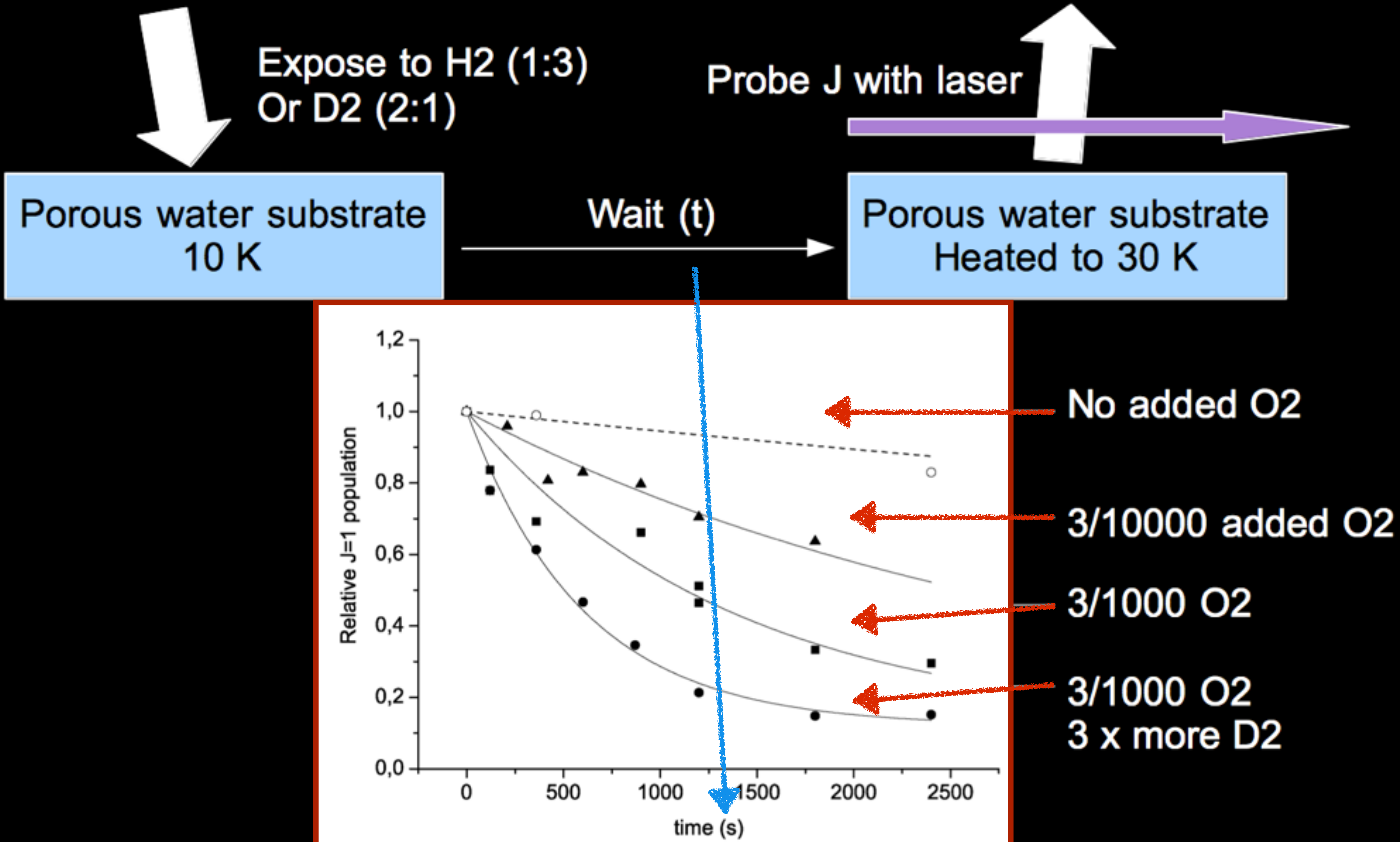
See also poster by D. Ivanov (H2 on Pd)

CONCLUSION ON ADSORPTION AND DESORPTION PROCESSES

- DISTRIBUTION OF BINDING ENERGIES
- INFLUENCE OF OTHERS ADSORBATES
- SMALL DIFFERENCES IN BINDINGS ENERGIES CAN MAKE ORDERS OF MAGNITUDE IN DESORPTION RATES AT A GIVEN TEMPERATURE

NUCLEAR SPIN CONVERSION OF D_2 (AND H_2) ON ASW IN PRESENCE OF O_2 TRACES

(c) Chehrouri et al PCCP 2011



O_2 TRACES SPEED-UP THE NSC

QUELLES SURFACES?
QUELLES ÉTUDES ?

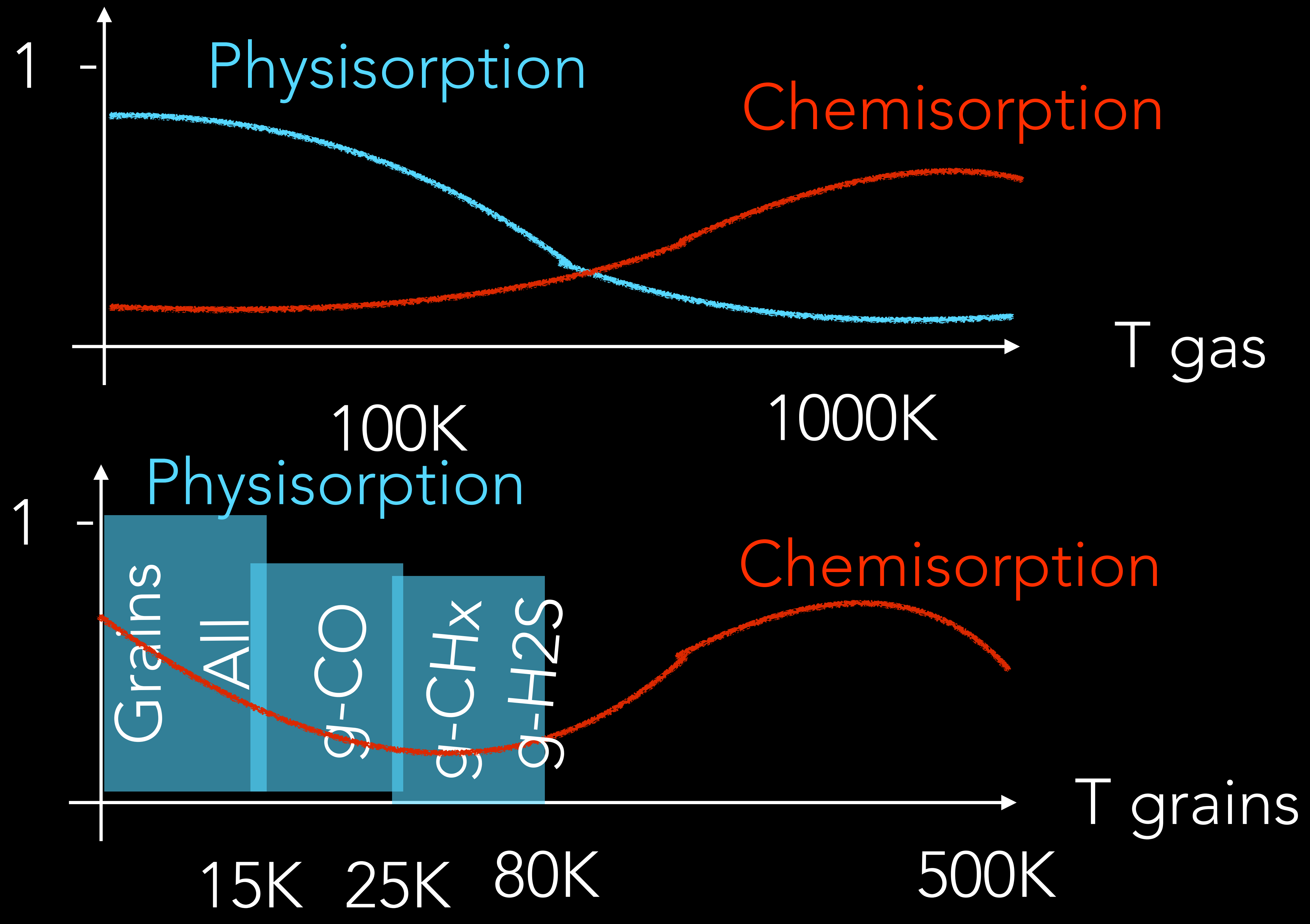
Most of the studies
italic : <2006
roman <2011
bold >2011

Surfaces	Collage	Physisorption	Chimisorption	H	Opr
Glaces (Am., Por., Crist…)	Oui	**Oui**	- -	Oui	**Oui**
Graphite	?	Oui	Oui	Oui	?
Carbones Armorphes Oignons	Oui (Chem)	?	Oui	Oui (!)	???
PAH/PAH	**Sigma**	?	**Oui**	?	???
Silicates Armorphes Crystallins Poreux	**Oui**	*Oui*	Non	Oui	?

see review by Wakelam et al (Arcachon meeting)

ENJEUX : LIENS ENTRE TOUS LES MÉCANISMES ?

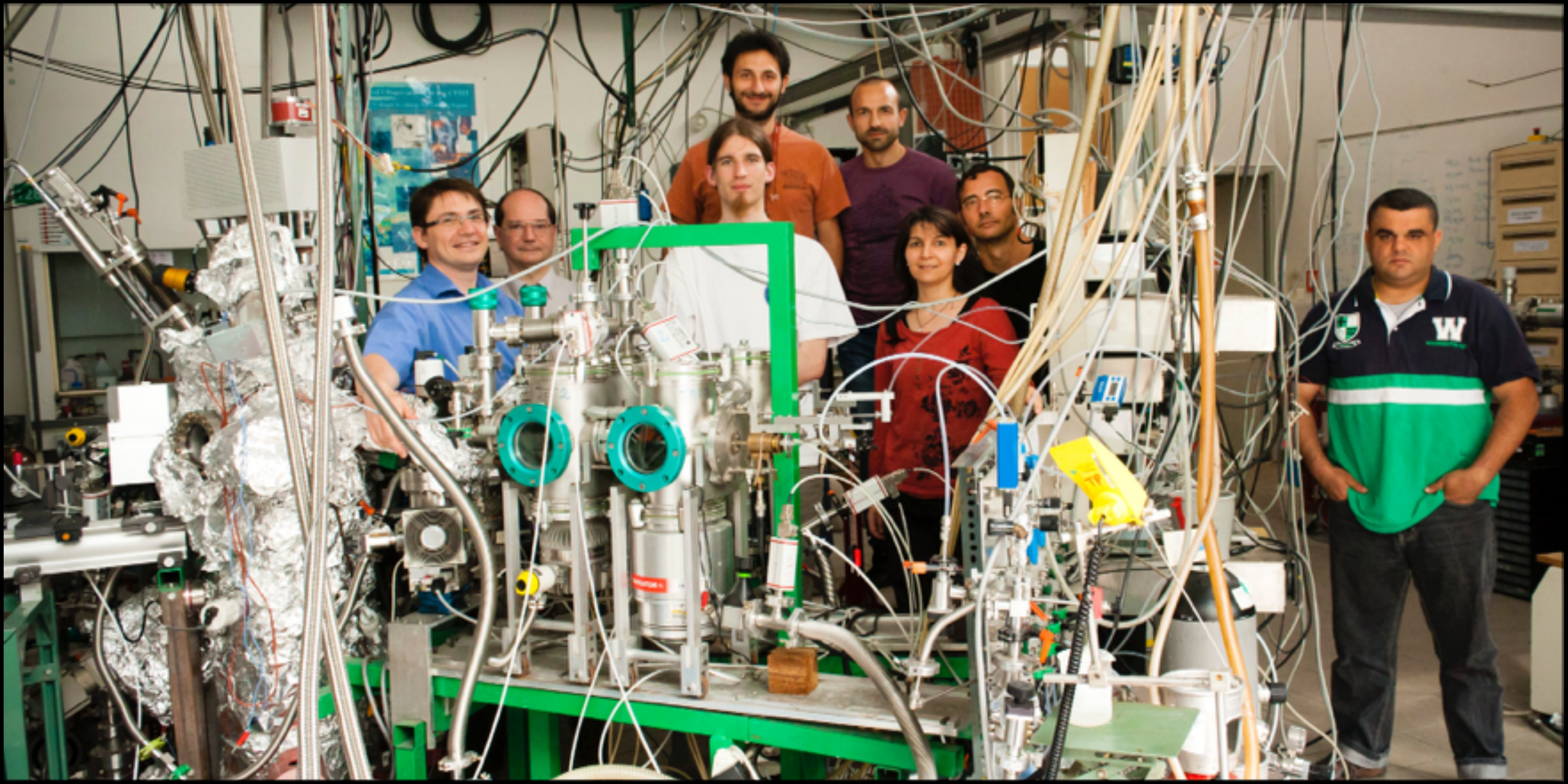
Efficacité intégrée



OUR LAB IS HERE! (50km...)

Merci !

Juin 2014



Collaborations: S. Cazaux, J. Noble, P. Theulé + Pirronello et al, Linnartz et al, Loison, Parent&Laffon…

ACAV

îledeFrance

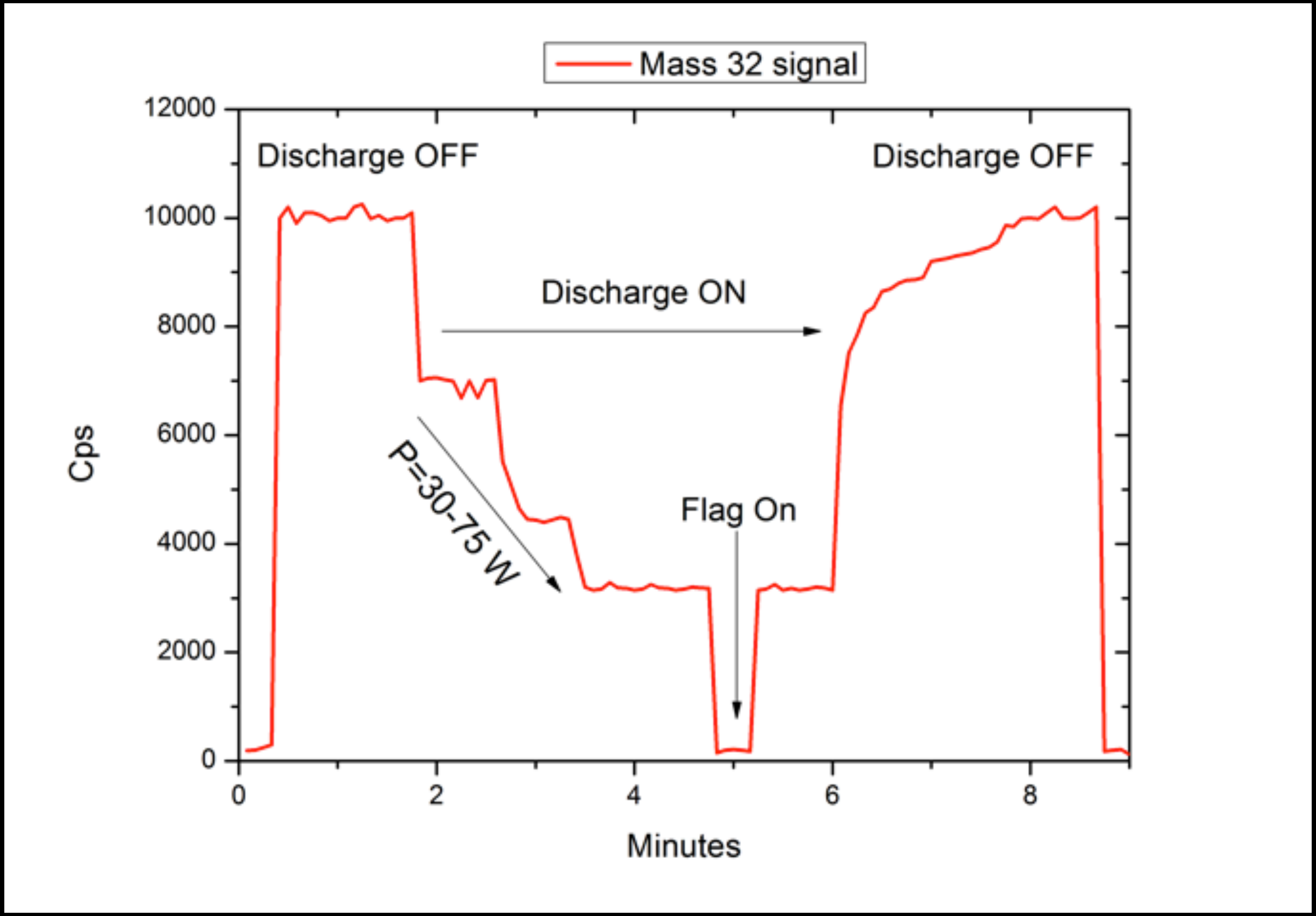
pcmi

FP 7 ITN LASSIE

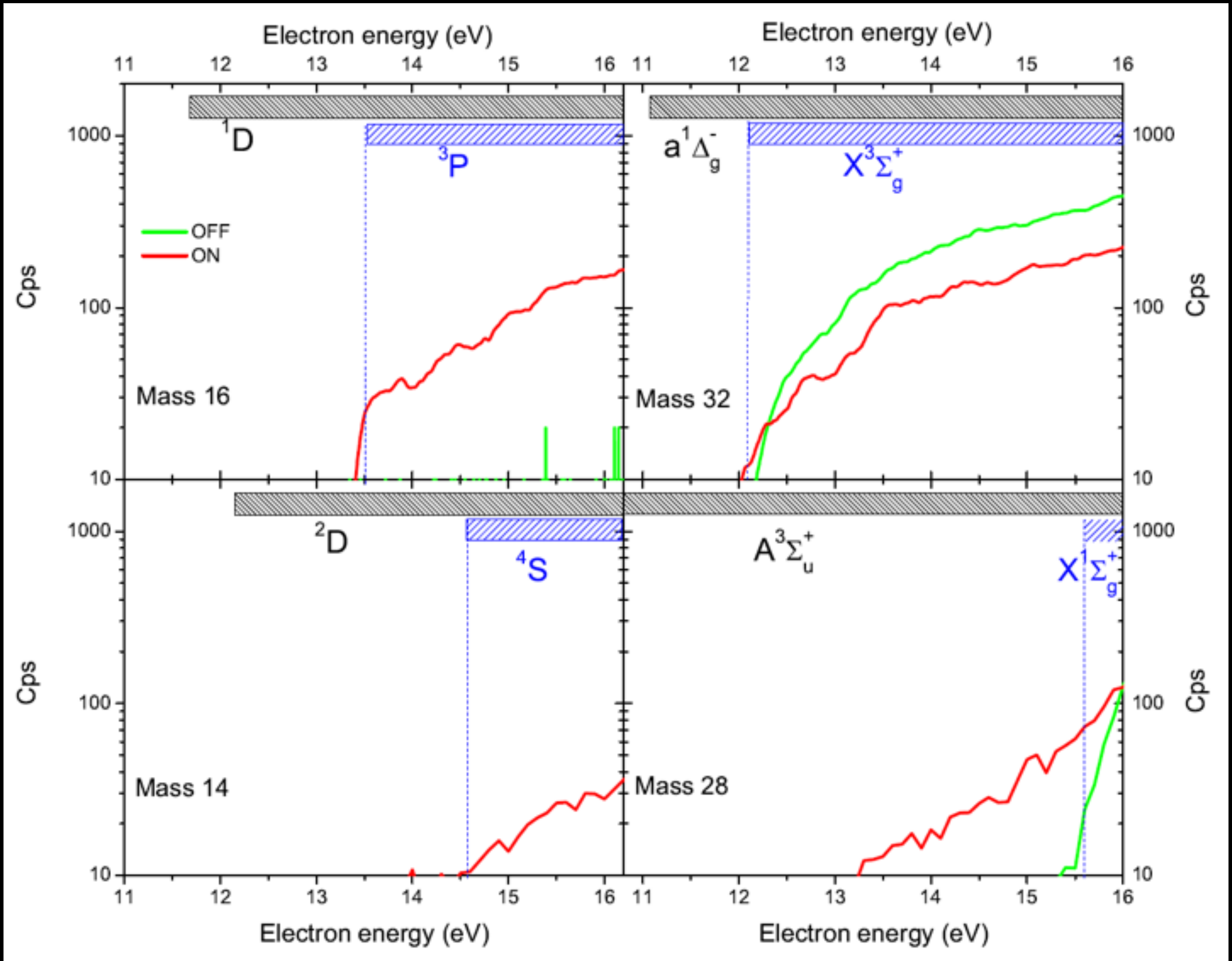
l'Observatoire de Paris

UNIVERSITÉ de Cergy-Pontoise

BEAM DISSOCIATION EFFICIENCY

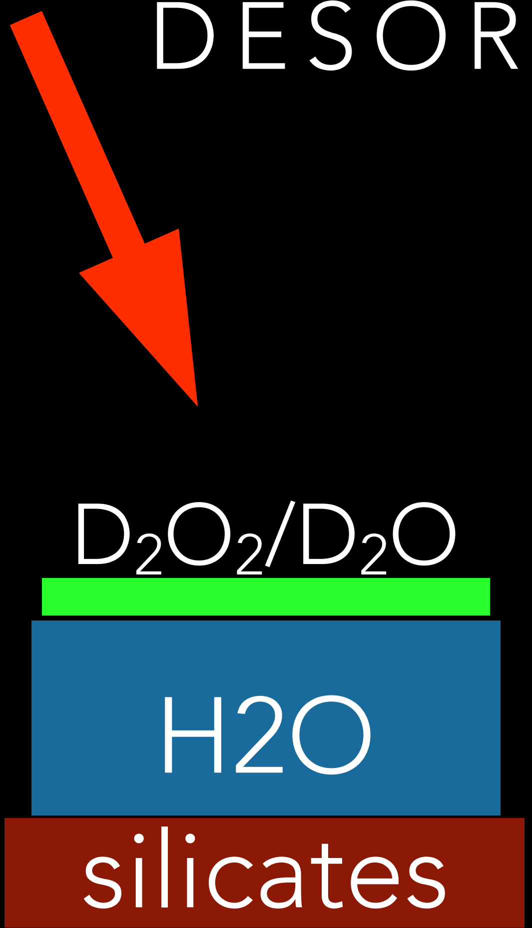


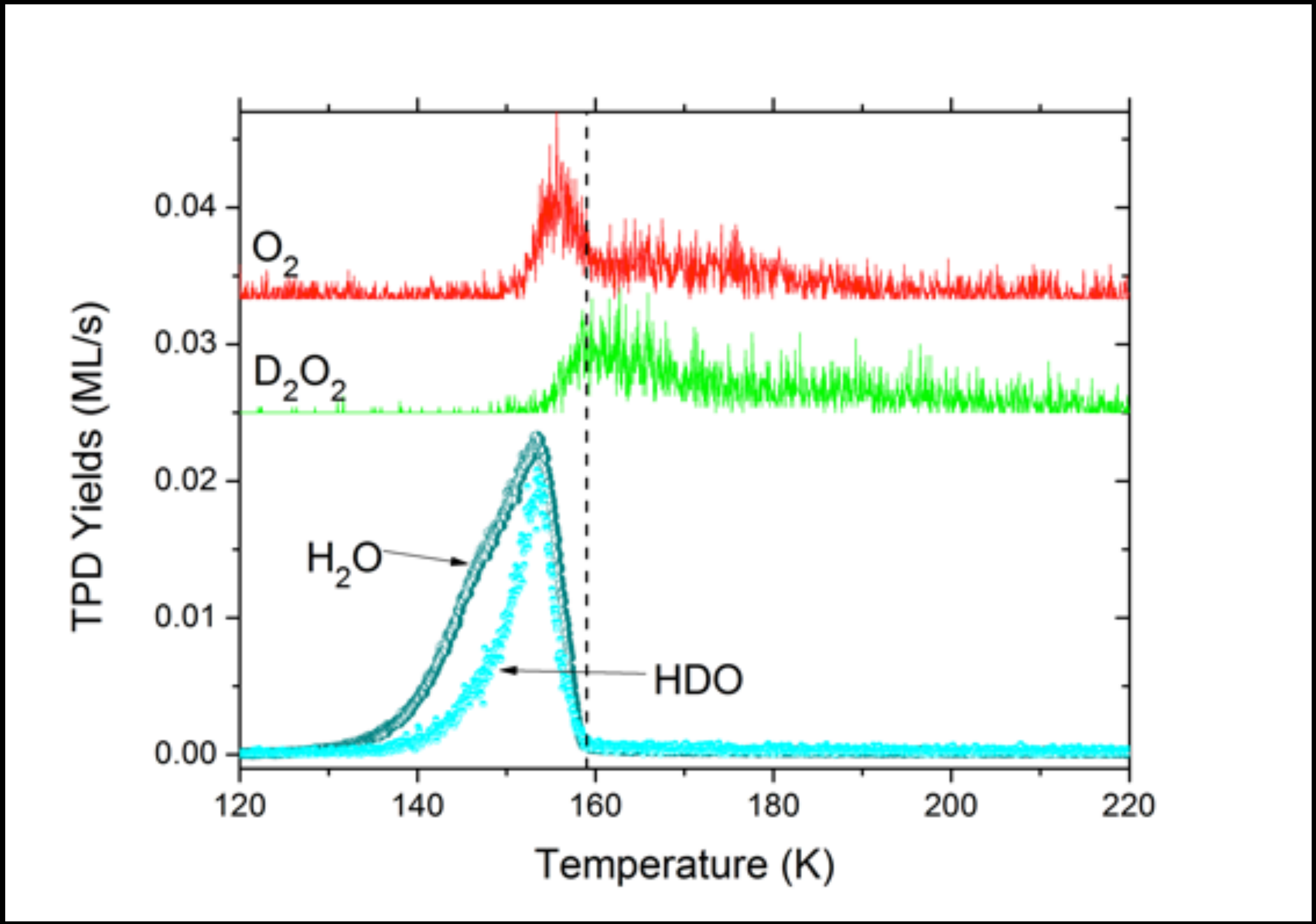
BEAM INTERNAL ENERGY OF O AND N DISCHARGES



H_2O/D_2O_2 MIXTURE (95/5%) MADE FROM [O_2+D] ON H_2O LAYERS

DESORPTION OF MIXED H_2O/H_2O_2 LAYERS

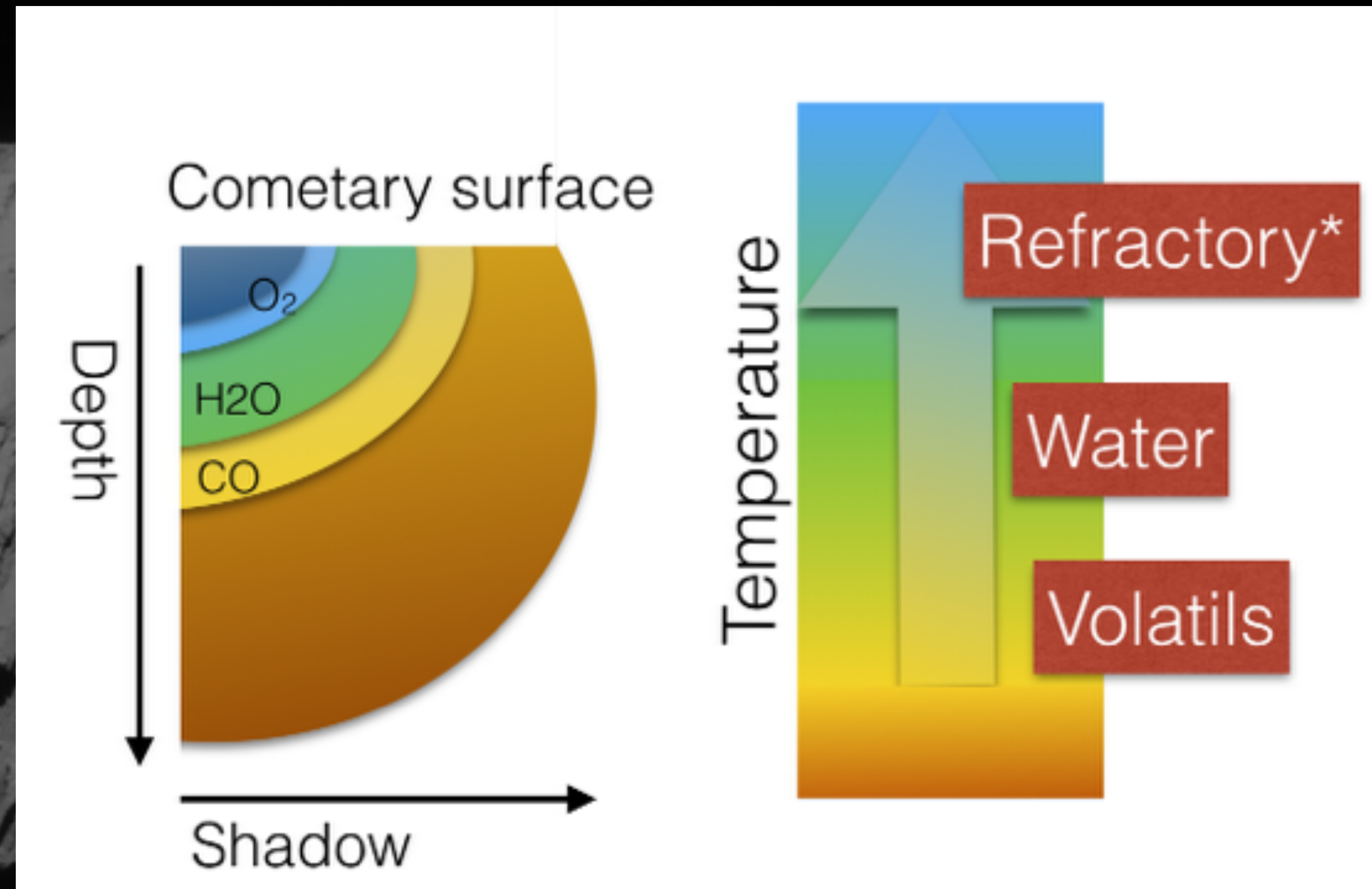




$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2.$$

YES, DISMUTATION OCCURS AT 155 K, AND COMPLETE*

DESORPTION OF MIXED H_2O/H_2O_2 LAYERS



YES, DISMUTATION OCCURS, AND IS COMPLETE AT THE VERY END OF WATER DESORPTION

It is possible that 7% of initial H_2O_2 release 3.5 % of O_2 just after the final desorption of water ice

O_2 IN THE ISM ?

O_2 and H_2O_2 is/was over predicted
O_2 and H_2O_2 are sparsely detected

H_2O_2 only detected where O_2 is detected (see Parise et al 2014)

THE ASTROPHYSICAL JOURNAL, 737:96 (17pp), 2011 August 20 doi:10.1088/0004-637X/737/2/96
© 2011. The American Astronomical Society. All rights reserved. Printed in the U.S.A.

Goldsmith et al 2011

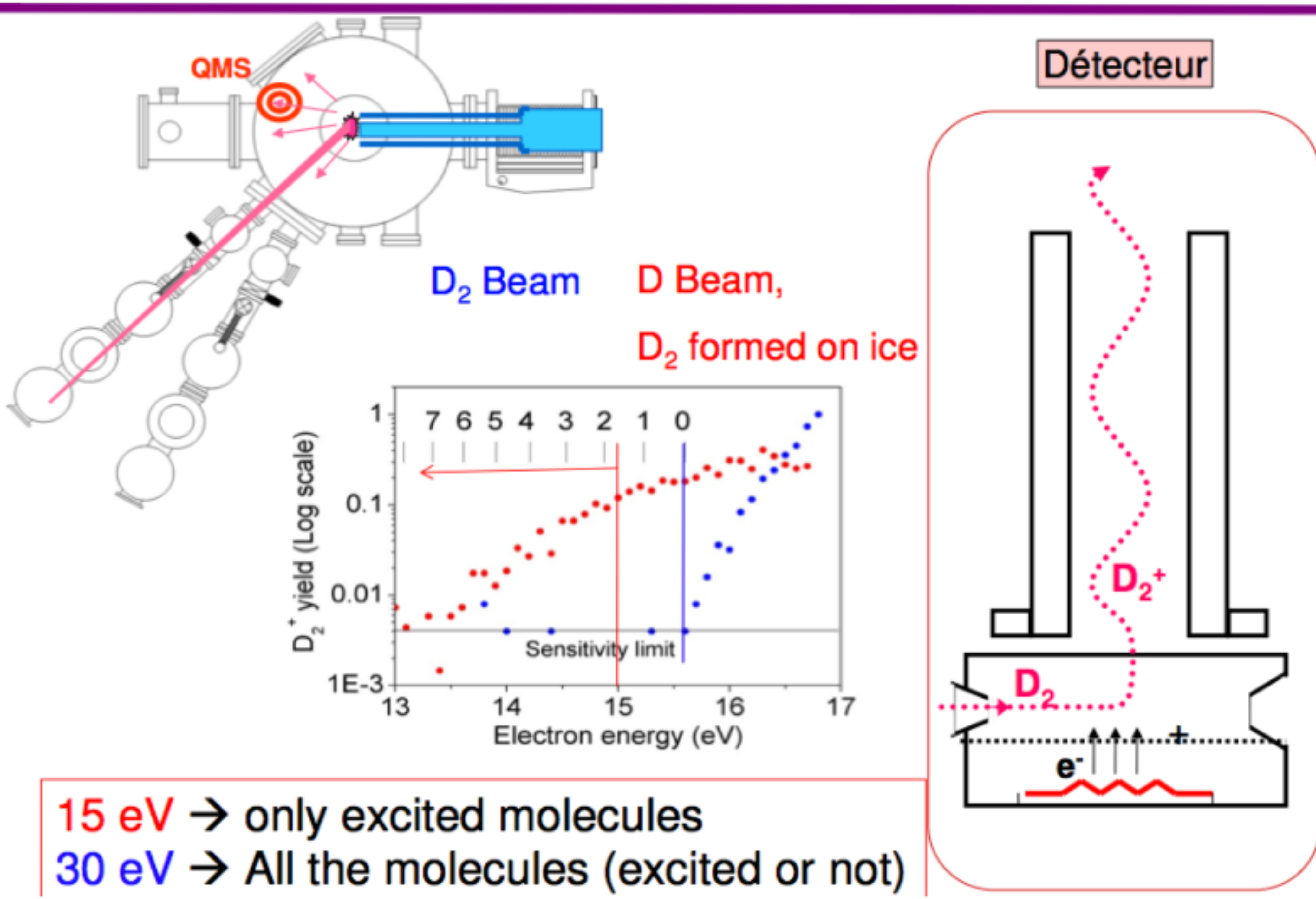
*HERSCHEL** MEASUREMENTS OF MOLECULAR OXYGEN IN ORION

denoted Peak A, the Western Clump, or MF4. The mass of this source is $\sim 10\,M_\odot$ and the dust temperature is $\gtrsim 150$ K. Our preferred explanation of the enhanced O_2 abundance is that dust grains in this region are sufficiently warm ($T \gtrsim 100$ K) to desorb water ice and thus keep a significant fraction of elemental oxygen in the gas phase, with a significant fraction as O_2. For this small source, the line ratios require a temperature $\gtrsim 180$ K. The inferred

- Many new molecules have been synthesized at low T on amorphous surfaces
- Reaction networks are looping, and an experiment is only the measure of a chemical equilibrium
- Complex organic molecules can be form, but how and how much is the current problem
- **Ongoing efforts** to couple reasonable models to experimental facts
- Desorption is more complex than previously thought
- Isotopic effects, nuclear spin conversion (OPR), also happen in the solid phase …

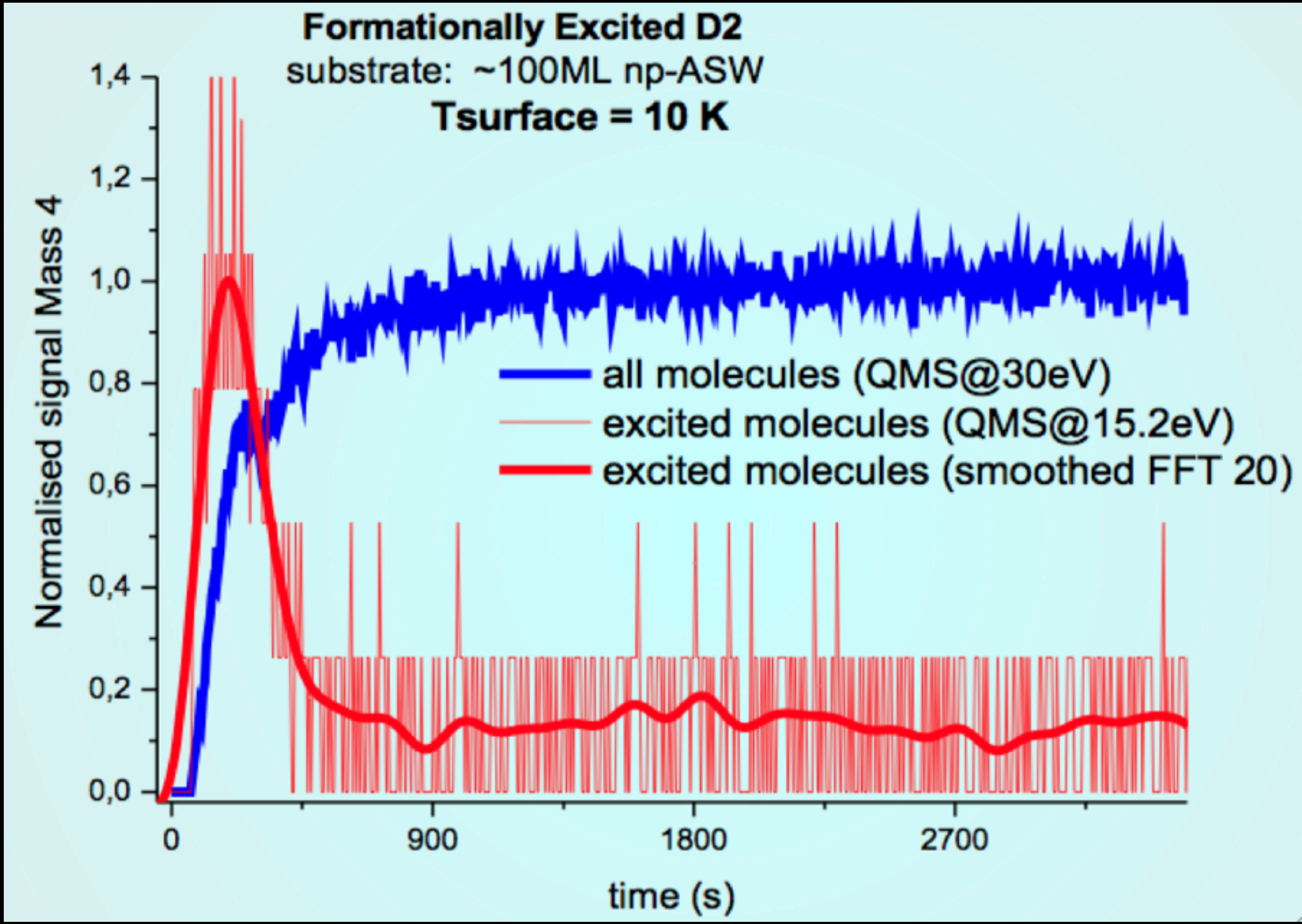
D2 PROMPT REALEASE

NP Tunning the kinetic energy of the ionosing electrons

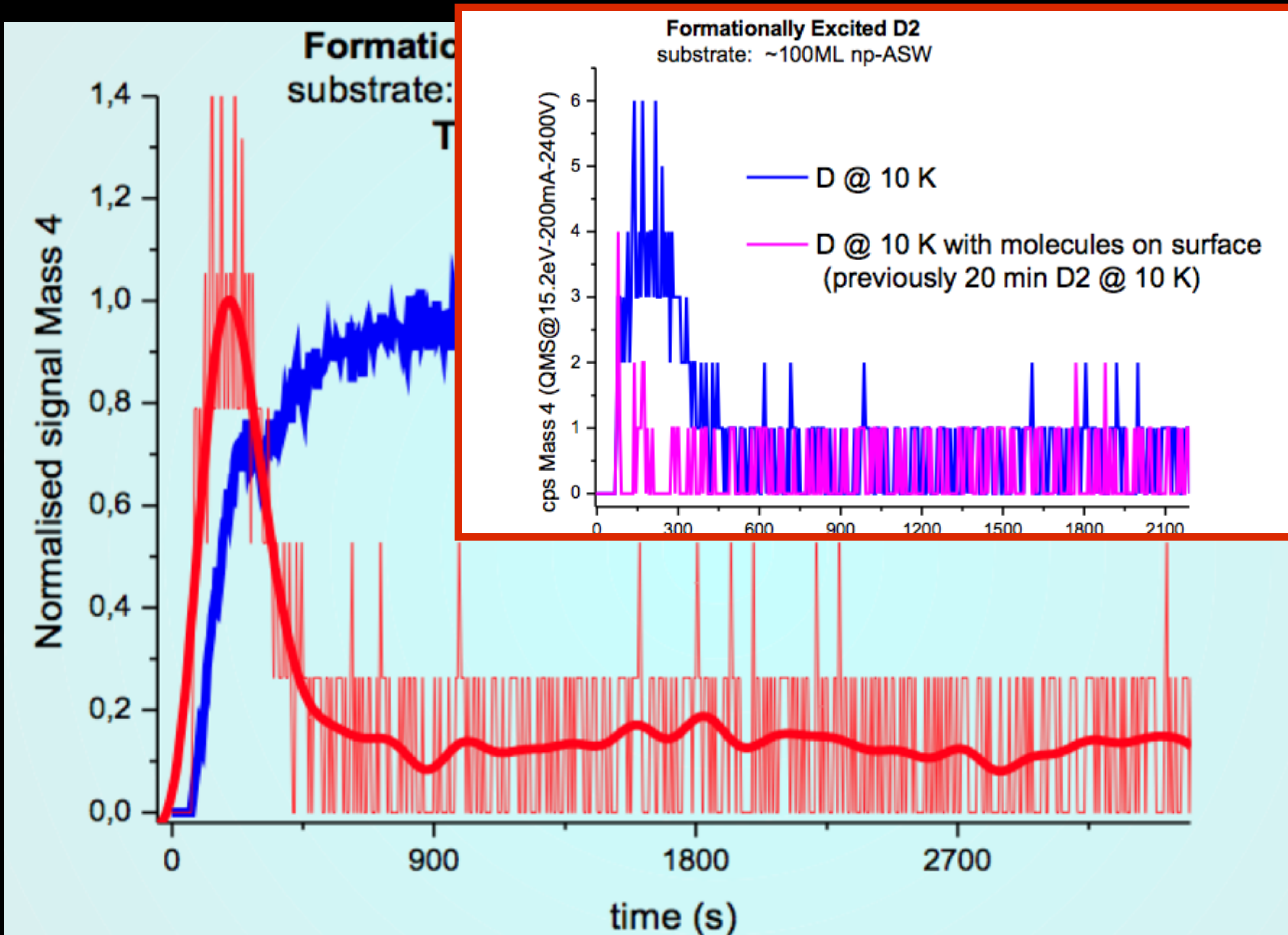


15 eV → only excited molecules
30 eV → All the molecules (excited or not)

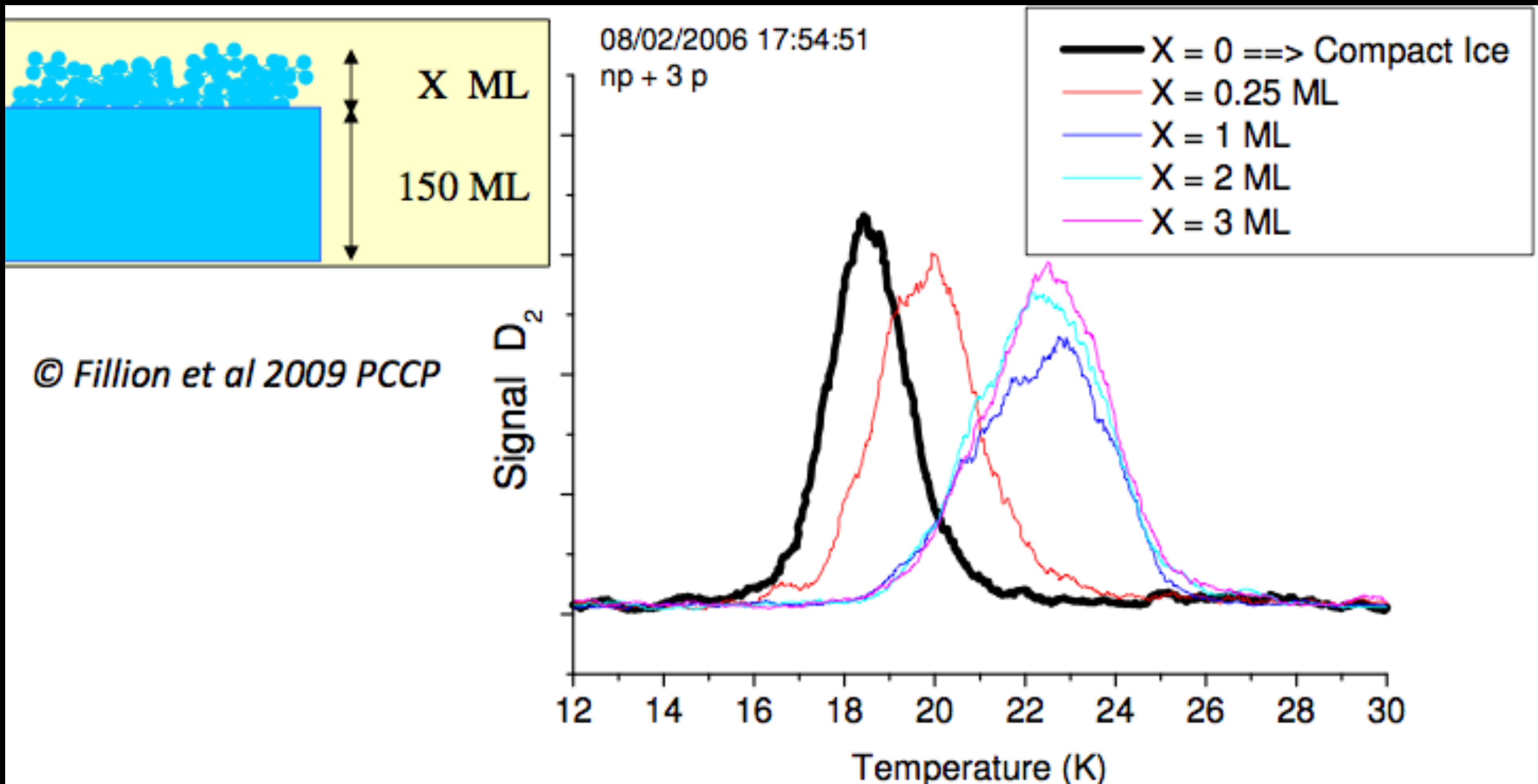
D_2* RELEASED QUENCHED BY NEIGHBORS



D_2* RELEASED QUENCHED BY NEIGHBORS



D_2 TPD: A VERY SENSITIVE TOOL TO PROBE THE WATER ICE MORPHOLOGY

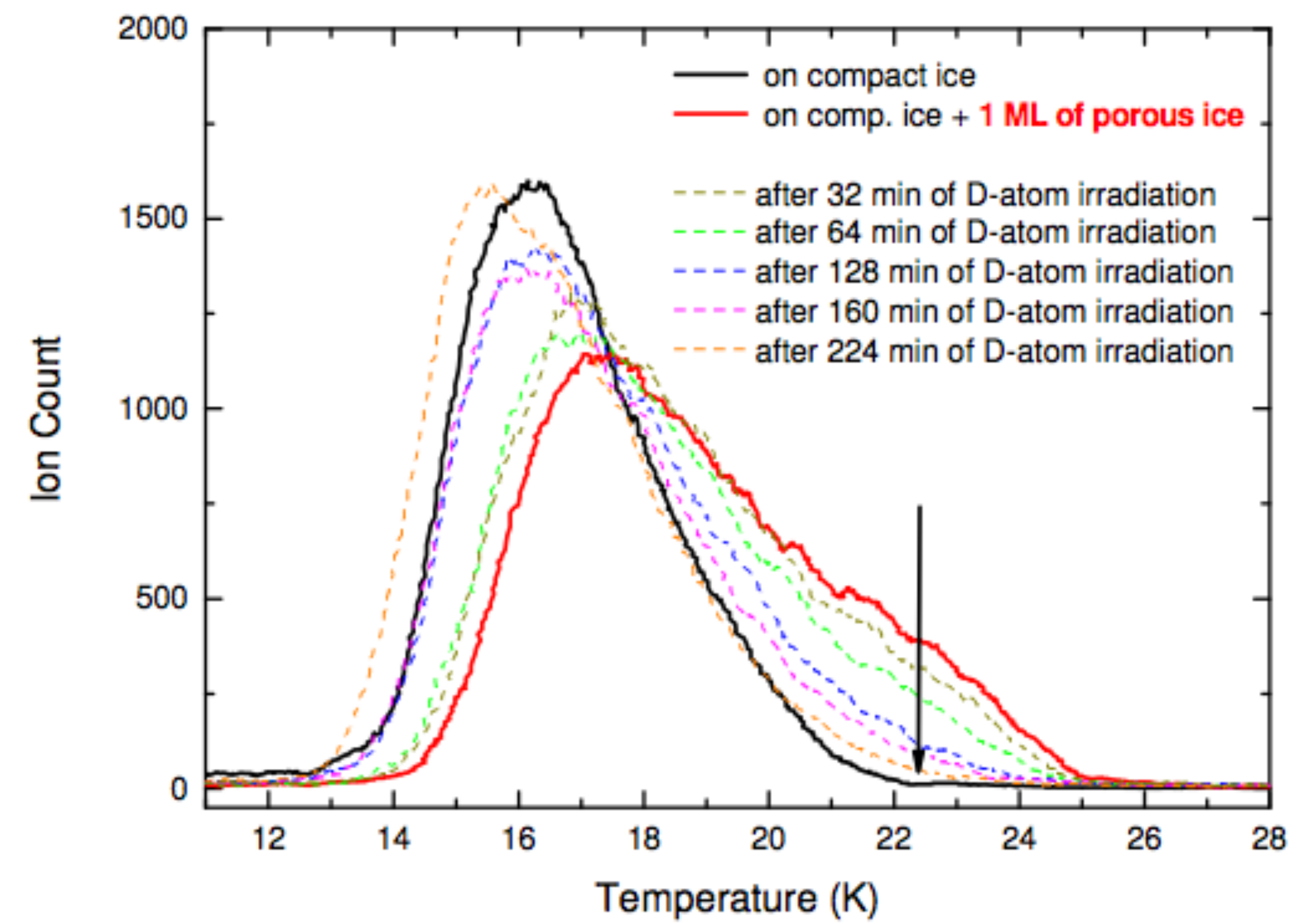


One over - layer of « porous ice » is enough to get energetical properties of « thick » porous ice.

5 layers required to « hide » the ice substrate properties.

POROSITY REDUCTION DUE TO D RECOMBINATION

Experiments: overlayer of porous ice is exposed to D (or H)



O2 calibration