H_2 ortho-para conversion on amorphous solid water

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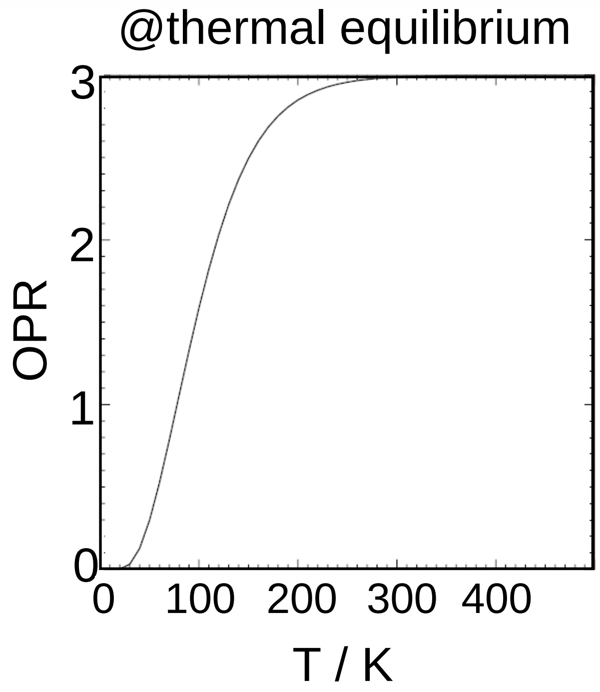
- Ortho, Para, Ortho-to-para ratio (OPR) of H_2
- Astronomical importance of H_2-OPRs
- What we know for OPR on ice
- Experiment, Results & Discussion
- Summary

Ortho-to-para ratio (OPR) of H_2



Total spin	I=1（ortho）	↮	I=0（para）
Spin multiplicity	3		1
Rotation	J=1, 3, 5, …		J=0, 2, 6, …

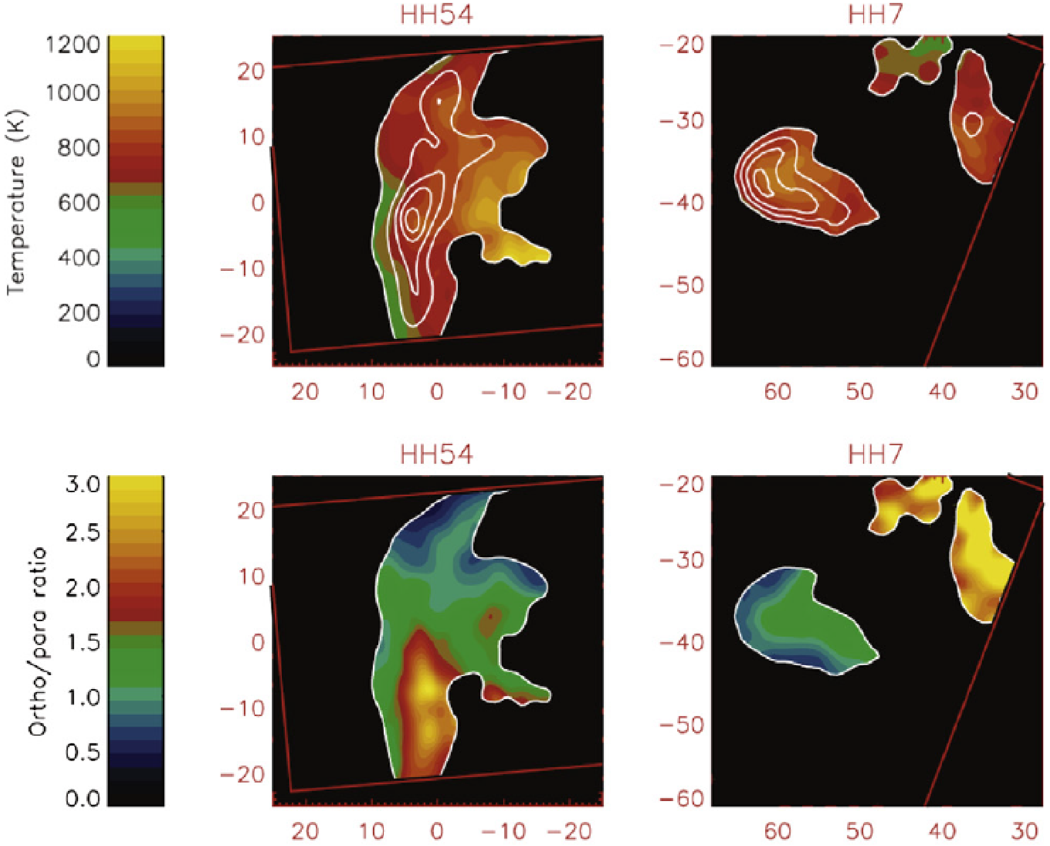
$$\mathrm{OPR} = \mathrm{N}_{\mathrm{ortho}} / \mathrm{N}_{\mathrm{para}} = \frac{\sum\limits_{v,\,J=odd} g_I (2J+1)\exp(-E_{v,J}/kT)}{\sum\limits_{v,J=even} g_I (2J+1)\exp(-E_{v,J}/kT)}$$

For example,

OPR = 0.01 → nuclear spin temperature = 30 K @thermal equilibrium

Observations of OPRs for H_2

@ Shock regions



Upper : rotational 600-1000 K

Lower : OPR 0.5-3   spin and rotational temps inconsistent

Neufeld *et al*. *ApJ* 649, 816 (2006)

@ Photodissociation regions

OPRs ~ 1

lower than 3 expected from rotational temps.

e.g. Harbart *et al.* 2003, 2011

Fleming *et al.* 2010

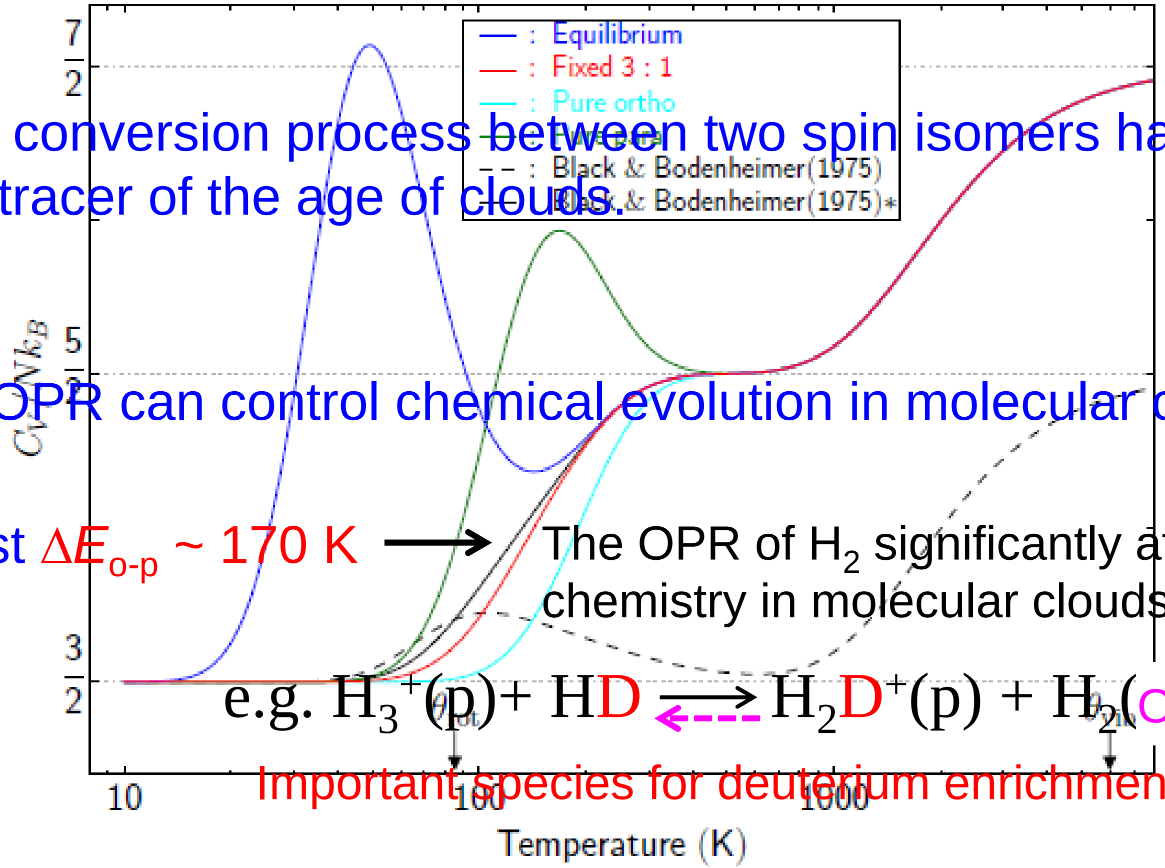
The OPRs are out-of-equilibrium !

Importance of OPR for H_2

☆ The OPR affects dynamics of core formation in star-forming region.

☆ Slow conversion process between two spin isomers has been used as a tracer of the age of clouds.

☆ The OPR can control chemical evolution in molecular clouds.



The lowest $\Delta E_{o\text{-}p}$ ~ 170 K → The OPR of H_2 significantly affects chemistry in molecular clouds

$$\text{e.g. } H_3^+(p) + HD \rightleftarrows H_2D^+(p) + H_2(o) + 230\text{ K}$$

Important species for deuterium enrichment in molecules

Heat capacity of H_2 gas with different OPRs
(Vaytet *et al.* A&A 563, A85 (2014))

Motivation

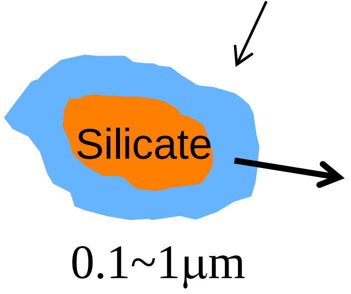
What { is the meaning of / controls } the observed OPR (spin temperature) ?

🚫 radiative process ⟶ *spin temp can be a tracer of physicochemical history of molecules…*

☆ OPR can change in gas phase by spin exchange reaction, but slow.

$$\text{e.g. } H_3^+(o) + H_2(o) \longrightarrow H_3^+(o) + H_2(p)$$

☆ Little is known about how the OPR behaves on ice grains (temp., structure, composition, etc).

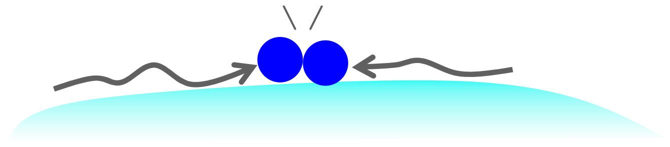


Amorphous Water Ice (ASW)

Look at how the OPRs of H_2 behave on ice dust at ~10 K !

Recent findings in OPR of H_2 on ice at ~10 K

OPR of nascent H_2 on ASW

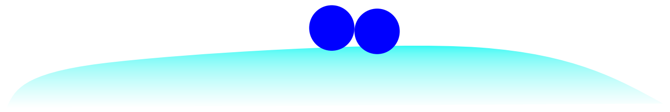


OPR of nascent H_2 formed by H-H recombination is ~3

Watanabe *et al.* 2010

Gavilan *et al.* 2012

OP conversion on ASW with time



First observed by IR

Buch & Devlin 1993

OPR of H_2 decreases significantly for several minutes

Watanabe *et al.* 2010

Large isotope effect on conversion rate

H_2 (~370s) >> D_2

Sugimoto & Fukutani 2011

Hama *et al.* 2012

Trace O_2 molecules accelerate the OP conversion for D_2

Chehrouri *et al.* 2011

Today's topic

Temperature dependence of OP conversion

↓

Important information about the rate-limitted process

Requirements for OP conversion

1. Energy difference exists between ortho and para states

→ Rotation required

Lowest $\Delta E_{\text{o-p}}$ in gas phase: ~ 170 K for H_2 (v=0, J=0;1)

$\Delta E_{\text{o-p}}$ ↘ when rotation hindered on the surface

Cf. $\Delta E_{\text{o-p}} \rightarrow 0$ for H_2O OP conversion? See poster #40 by Hama et al. tomorrow!

2. State mixing between ortho and para states induced by perturbation

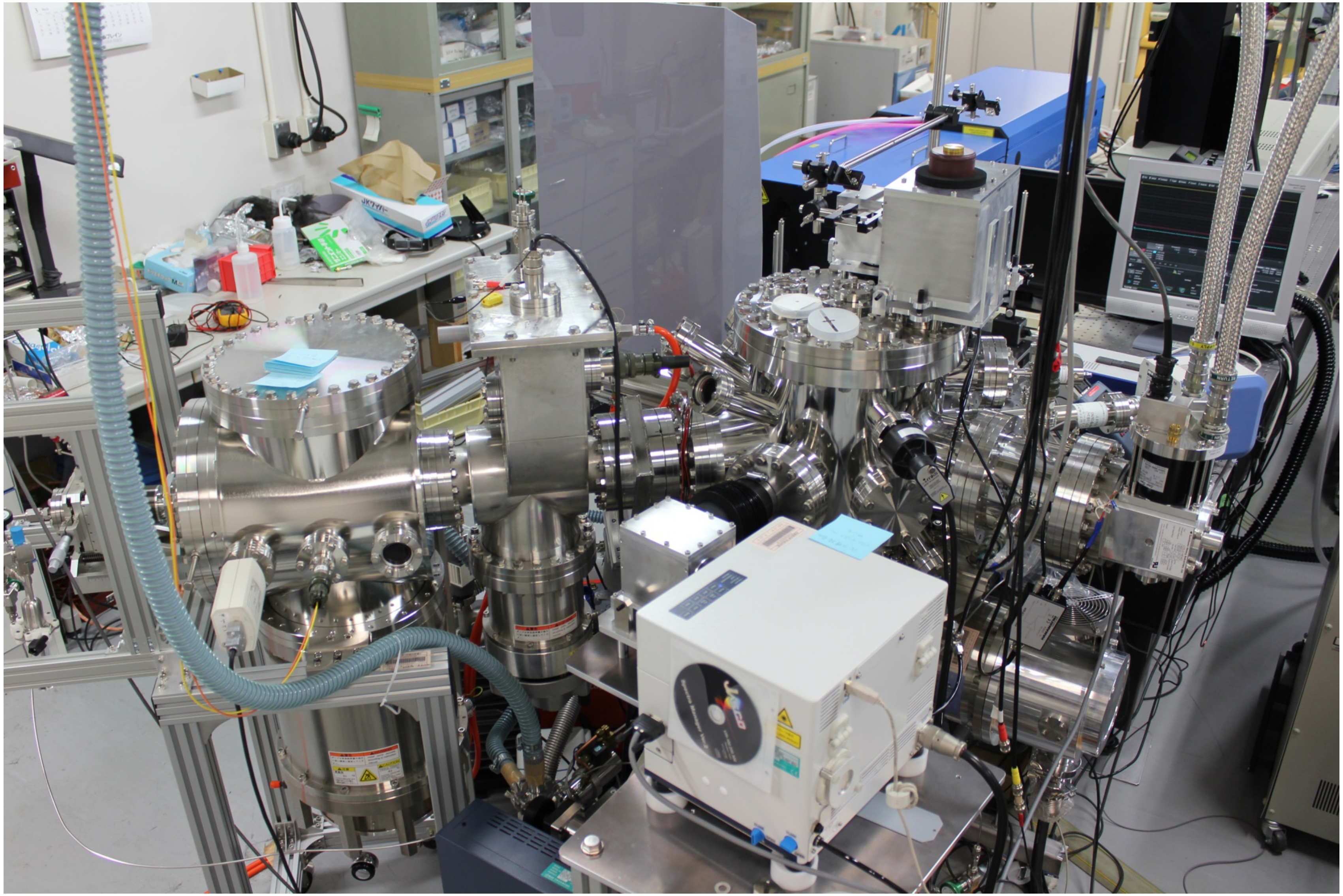
*e.g. intra-(or inter-)*molecular nuclear magnetic dipole-dipole interaction,
Fermi contact, etc

→ For H_2 on ice (Sugimoto & Fukutani 2010, in Nature Phys.)

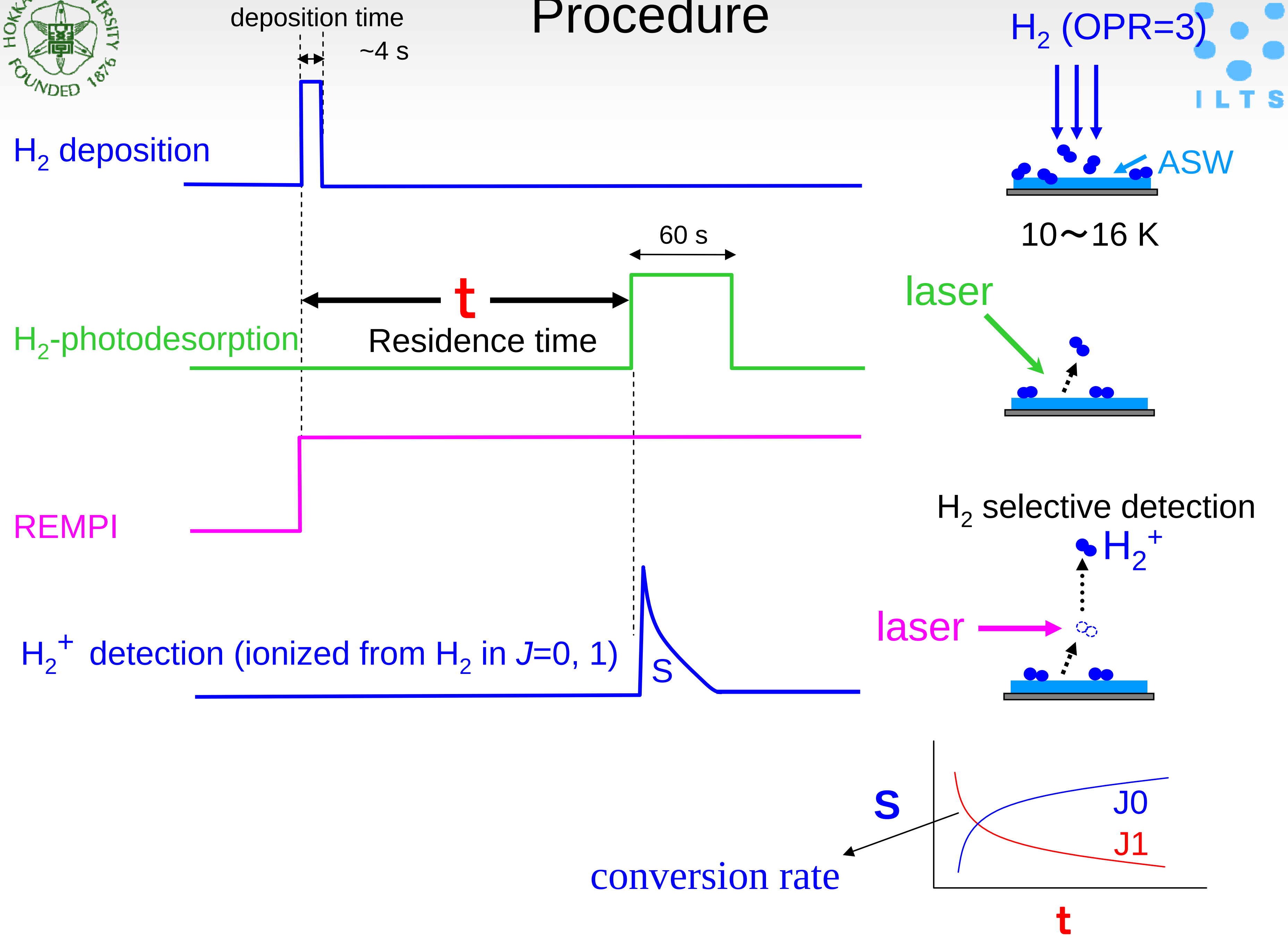
3. Energy release (relaxation) at the OP conversion

Energy dissipation by phonons in solid → Significant temp dependence of the conversion rate

Apparatus



Procedure



deposition time

~4 s

H_2 deposition

60 s

t

Residence time

H_2-photodesorption

REMPI

H_2^+ detection (ionized from H_2 in J=0, 1)

S

H_2 (OPR=3)

ASW

10～16 K

laser

H_2 selective detection

H_2^+

laser

S

conversion rate

REMPI (2+1) transition in H_2

$E,F^1\Sigma_g^+(v'=0, J'=J'') \leftarrow\leftarrow X^1\Sigma_g^+(v'', J'')$

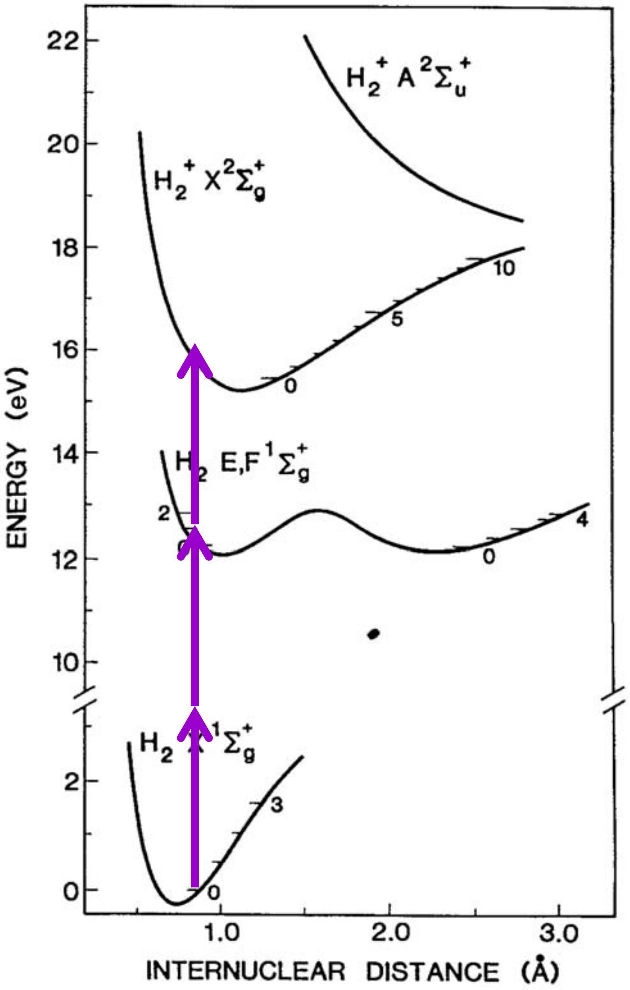
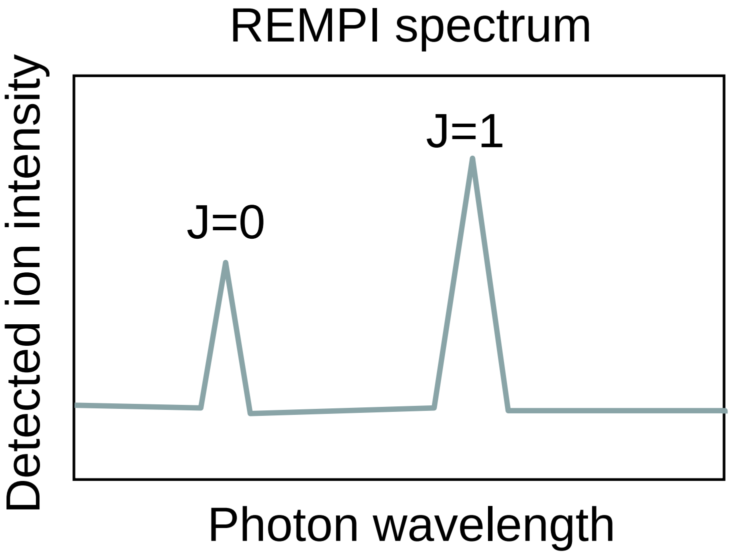


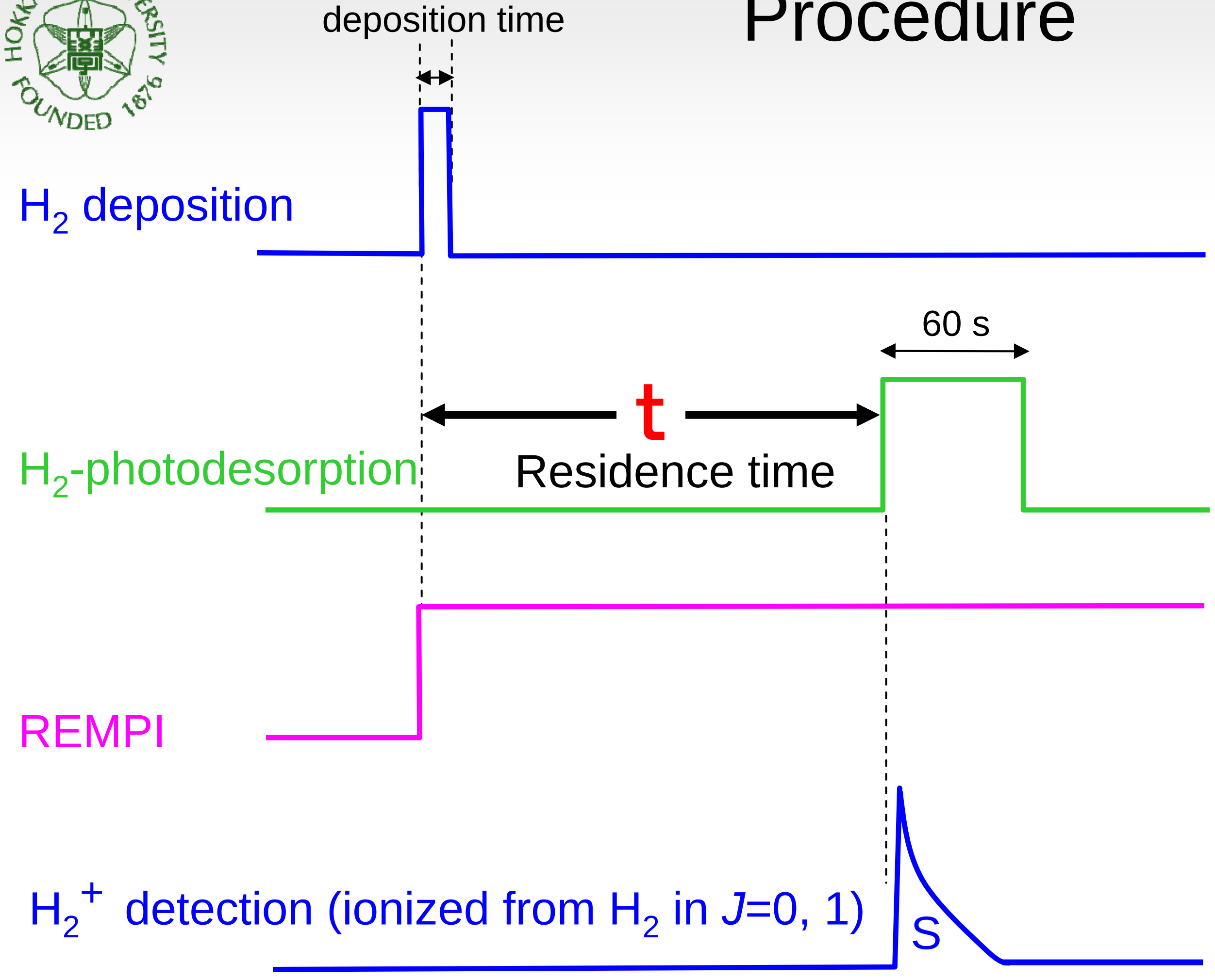
FIG. 1. Potential energy curves relevant to (2 + 1) REMPI of molecular hydrogen.

3-photon absorption ionizes H_2 in the specific rovibrational states.



We monitored the peak heights

Procedure



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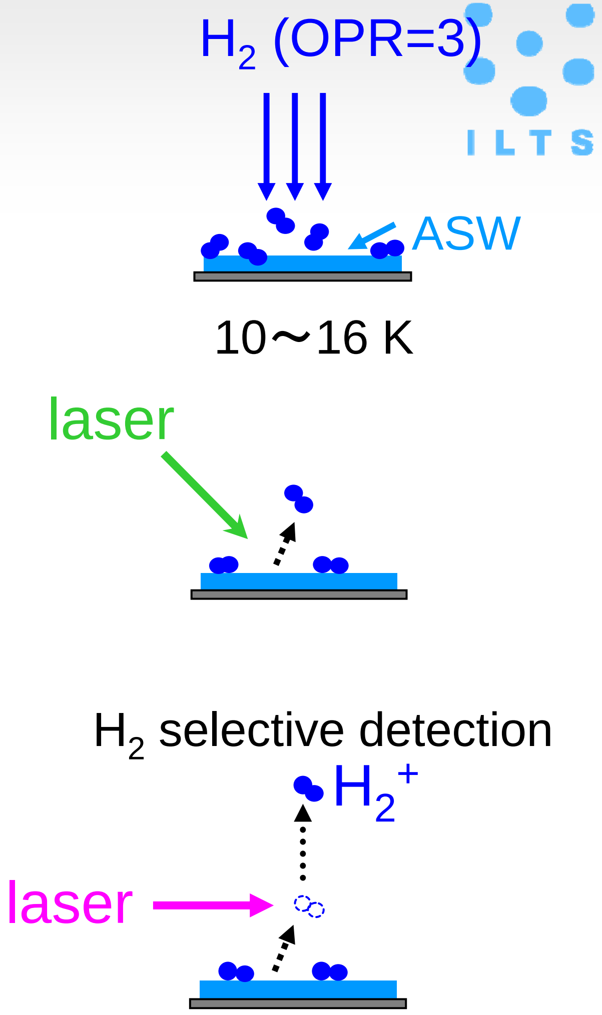


H_2 (OPR=3)

ASW

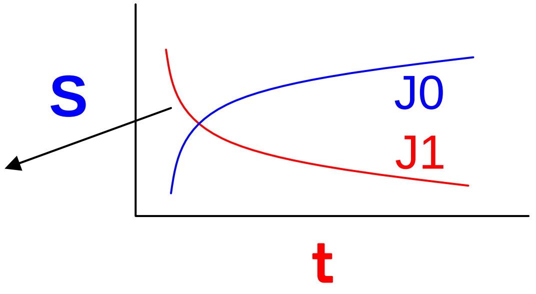
10～16 K

laser

H_2 selective detection

H_2^+

laser



S

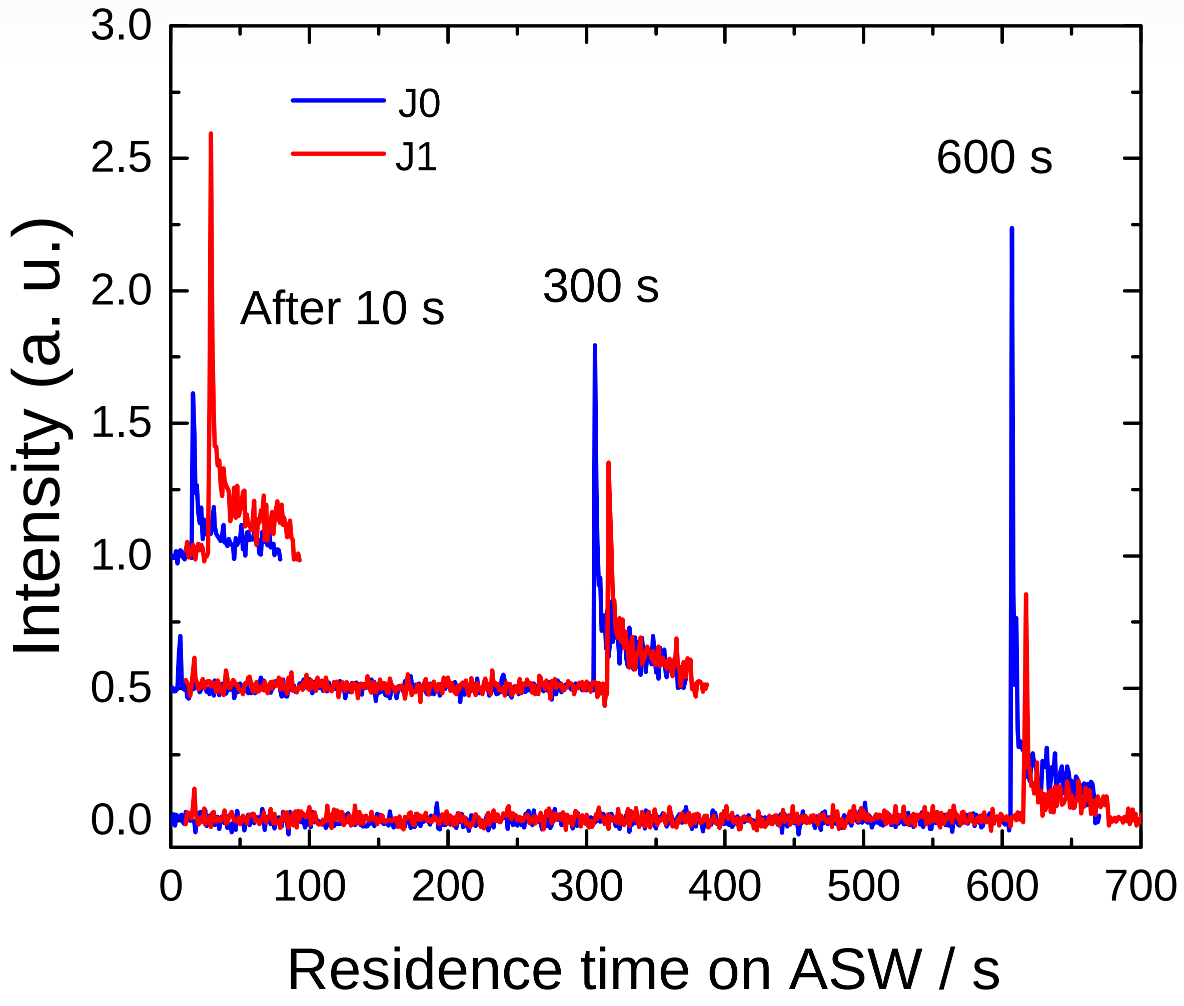
J0

J1

t

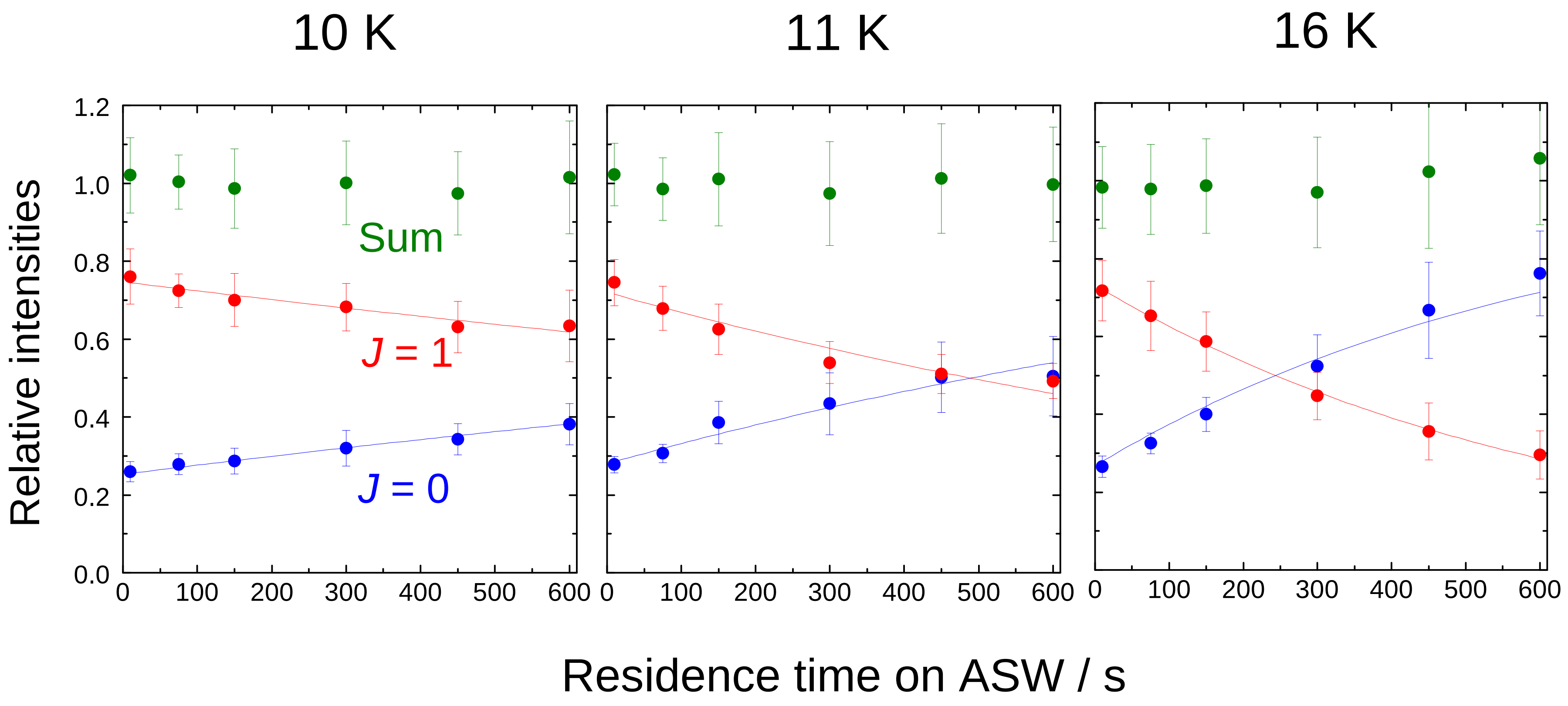
conversion rate

REMPI signals after the H_2-deposition on ASW at 16 K

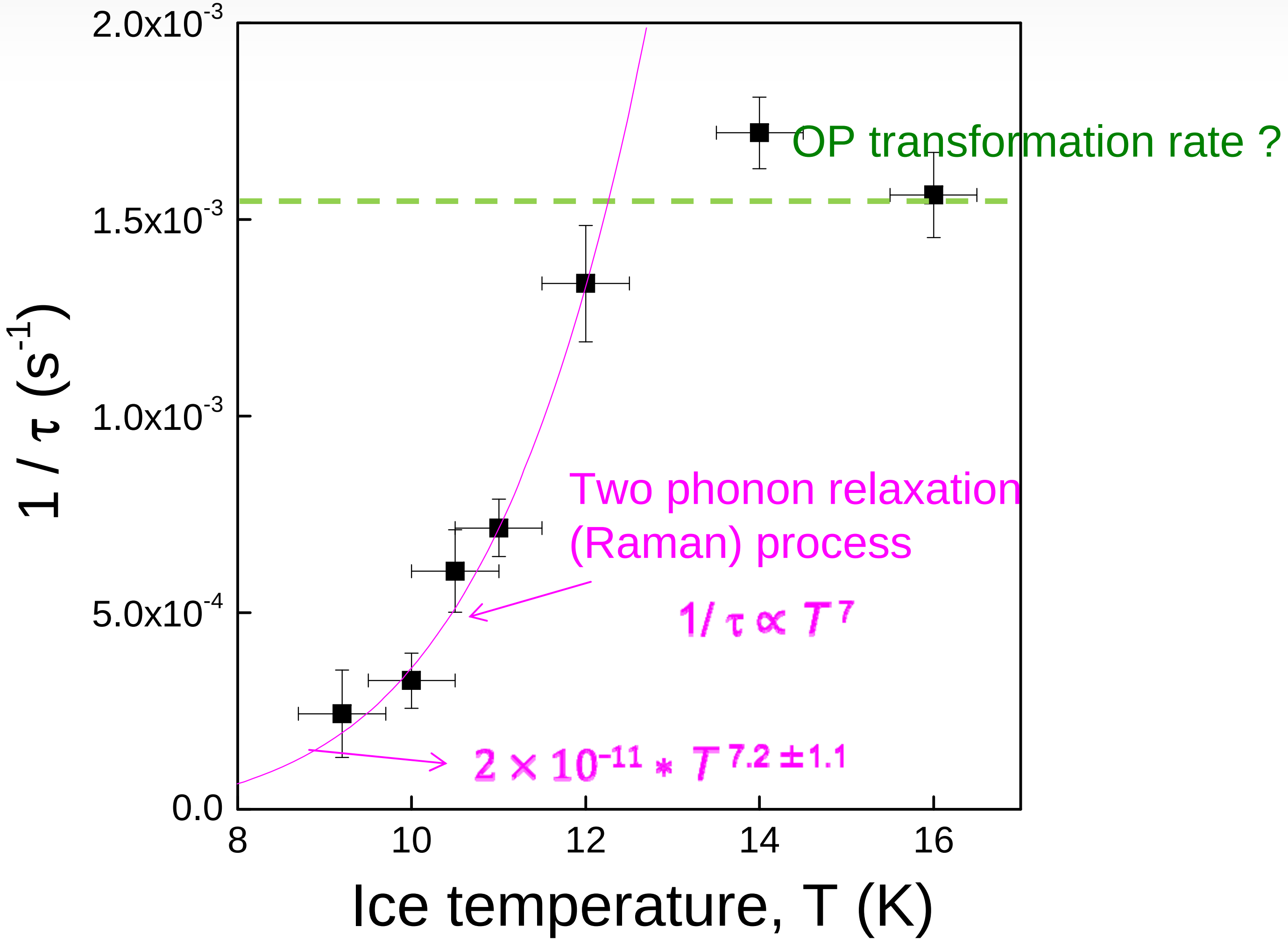


REMPI laser was fixed at the resonance wavelength.

OP conversion of H_2 on ASW



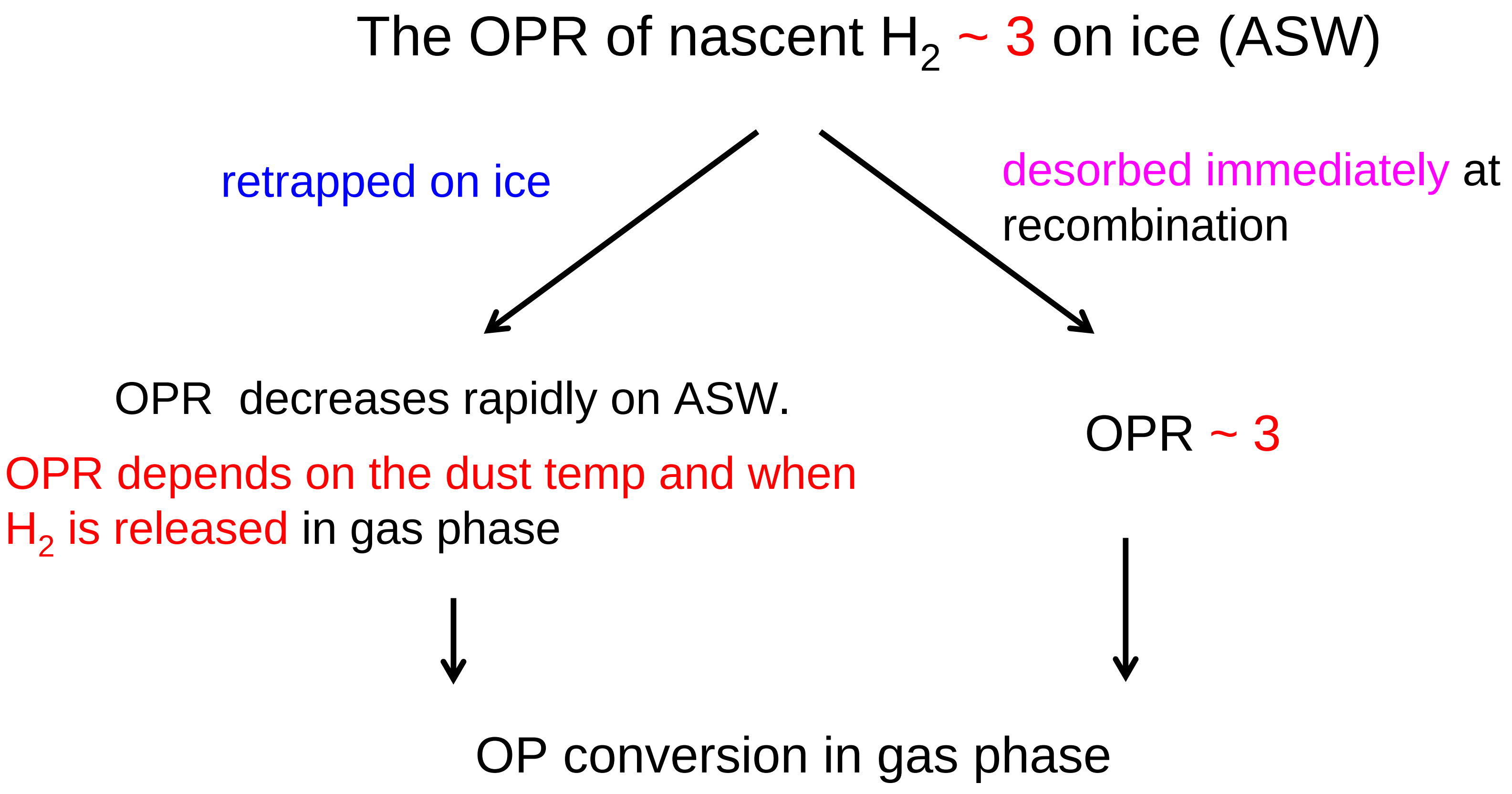
OP conversion rate vs surface temperature



Steep increase of conversion rate cannot be explained by state-mixing alone.

Energy dissipation process should be considered.

Astrochemical story for OPR of H_2 molecule starting from the ice grain



The OPR of nascent H_2 ~ 3 on ice (ASW)

retrapped on ice

desorbed immediately at recombination

OPR decreases rapidly on ASW.

OPR depends on the dust temp and when H_2 is released in gas phase

OPR ~ 3

OP conversion in gas phase

e.g. *for the gas phase reactions,see*

D. Gerlich *et al*., *Philos. Trans. A. Math. Phys. Eng. Sci.* **364**, 3007 (2006).

Summary

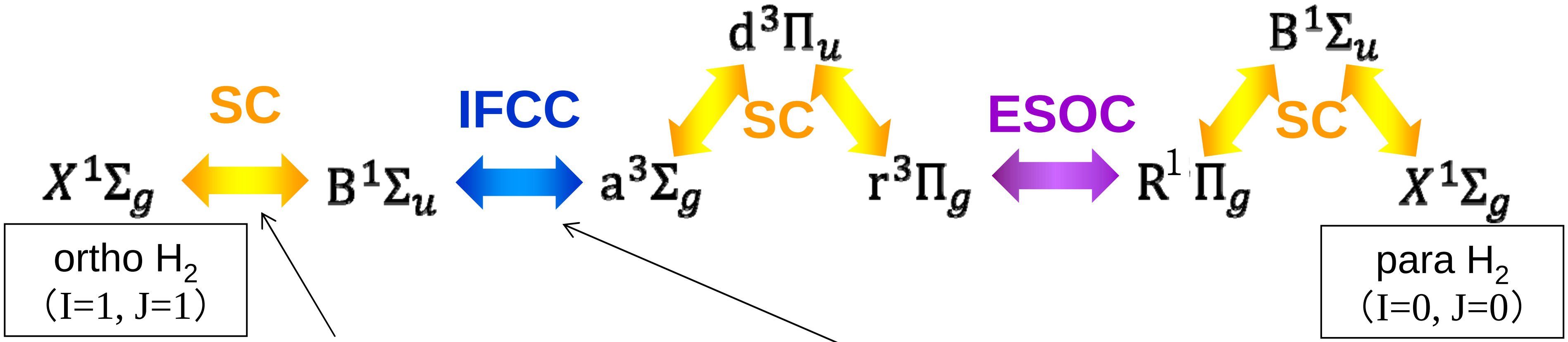
- The OPR of H_2 varies rapidly on ice, sensitively depending on the ice temperature

  Steep increase of OP conversion at lower temperature can be explained by two phonon Raman process.

→ In molecular clouds, the OPR of H_2 at desorption into the gas phase depends on when it is released and temperature of dust.

The OP conversion mechanism on ASW

(Sugimoto & Fukutani in Nature Physics, 2011)



$d^3\Pi_u$ $B^1\Sigma_u$

SC IFCC SC ESOC SC

$X^1\Sigma_g$ $B^1\Sigma_u$ $a^3\Sigma_g$ $r^3\Pi_g$ $R^1\Pi_g$ $X^1\Sigma_g$

ortho H_2
(I=1, J=1)

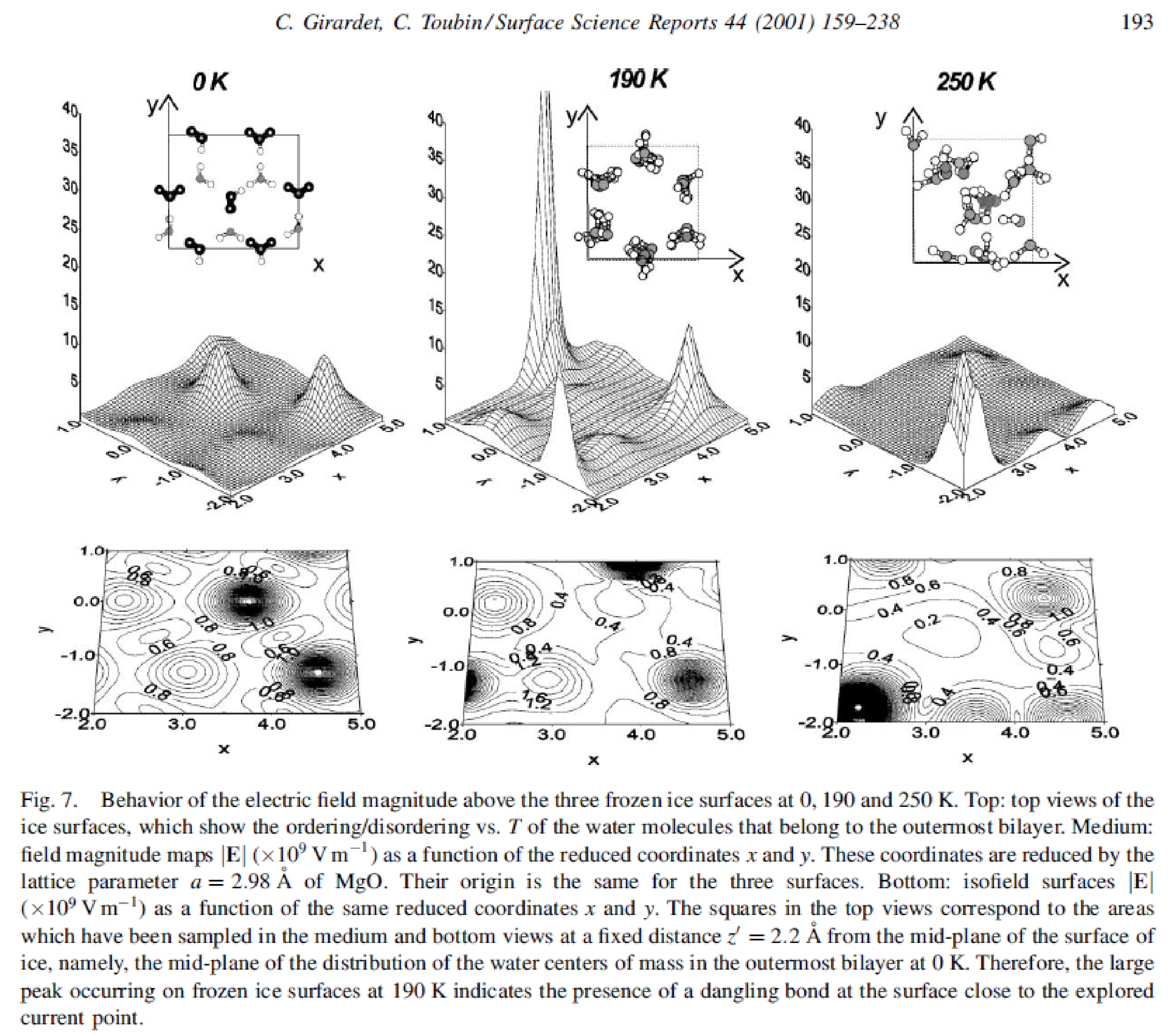
para H_2
(I=0, J=0)

ASW may locally produce
~10^{11} V/m on the surface.

Isotope effect appears due to the difference of vibrational state mixing between H_2 and D_2.

$H_2 >> D_2$

SC : Stark mixing
IFCC : Fermi contact interaction
ESOC : Spin-orbit interaction



C. Girardet, C. Toubin / Surface Science Reports 44 (2001) 159–238 193

Fig. 7. Behavior of the electric field magnitude above the three frozen ice surfaces at 0, 190 and 250 K. Top: top views of the ice surfaces, which show the ordering/disordering vs. T of the water molecules that belong to the outermost bilayer. Medium: field magnitude maps $|\mathrm{E}|$ ($\times 10^9$ V m^{-1}) as a function of the reduced coordinates x and y. These coordinates are reduced by the lattice parameter $a = 2.98$ Å of MgO. Their origin is the same for the three surfaces. Bottom: isofield surfaces $|\mathrm{E}|$ ($\times 10^9$ V m^{-1}) as a function of the same reduced coordinates x and y. The squares in the top views correspond to the areas which have been sampled in the medium and bottom views at a fixed distance $z' = 2.2$ Å from the mid-plane of the surface of ice, namely, the mid-plane of the distribution of the water centers of mass in the outermost bilayer at 0 K. Therefore, the large peak occurring on frozen ice surfaces at 190 K indicates the presence of a dangling bond at the surface close to the explored current point.

$$\mathrm{E(V/m)} = 1.9 \times 10^{3}\sqrt{I(\mathrm{W/cm^{2}})}$$

1 x 10^{10} (V/m) → 2.7 x 10^{13} (W/cm^{2})

Phonon modes of ice

(Osamura et al. JCP (2001))

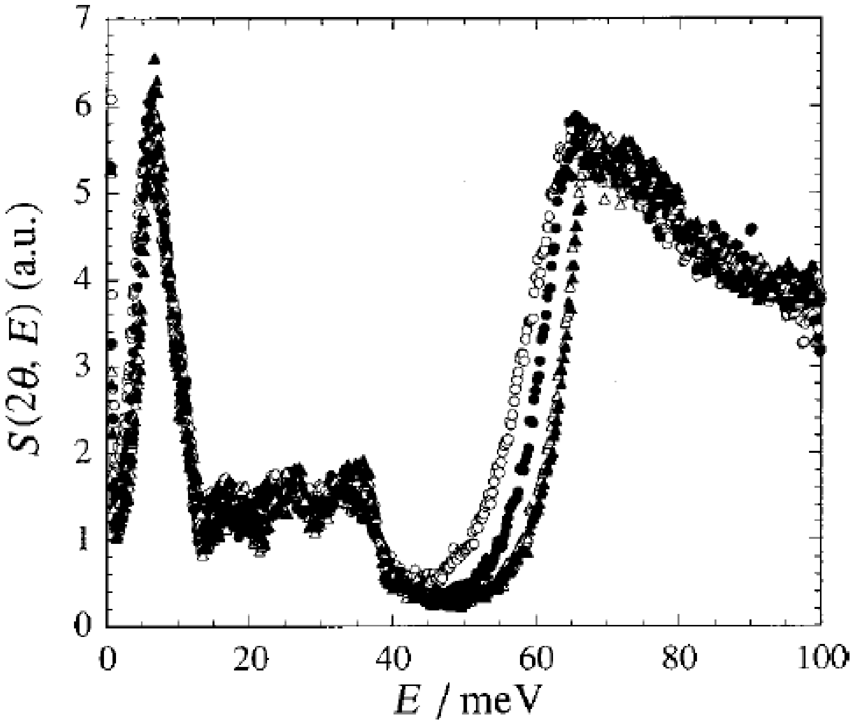


FIG. 3. Inelastic neutron scattering spectra $S(2\theta,E)$ of as-deposited amorphous ice (○), annealed amorphous ice (●), ice I_c, (△) and ice I_h (▲) measured at 50 K by the detectors at $2\theta=85°$. The Q value for the elastic scattering was 2.0 Å^{-1}.

~7, 17, 27, 36 meV for TA, LA, LO, and TO modes

Phonon relaxation rates

Kranendonk (1952)

One phonon process

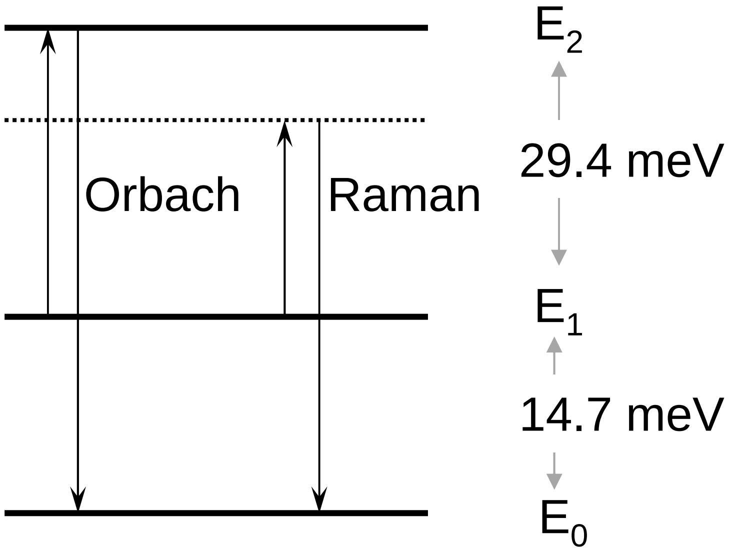
$$f_{one} \propto \coth\left(\frac{\delta}{2kT}\right)$$

Temperature independent at low temperatures for H_2

Two phonon processes

Orbach process $$f_{orbach} \propto \exp\left(-\frac{\delta}{kT}\right)$$

Raman process $$f_{raman} \propto T^n$$



NSC of H_2 and D_2 on pure ASW at 10 K

(Sugimoto & Fukutani 2011)

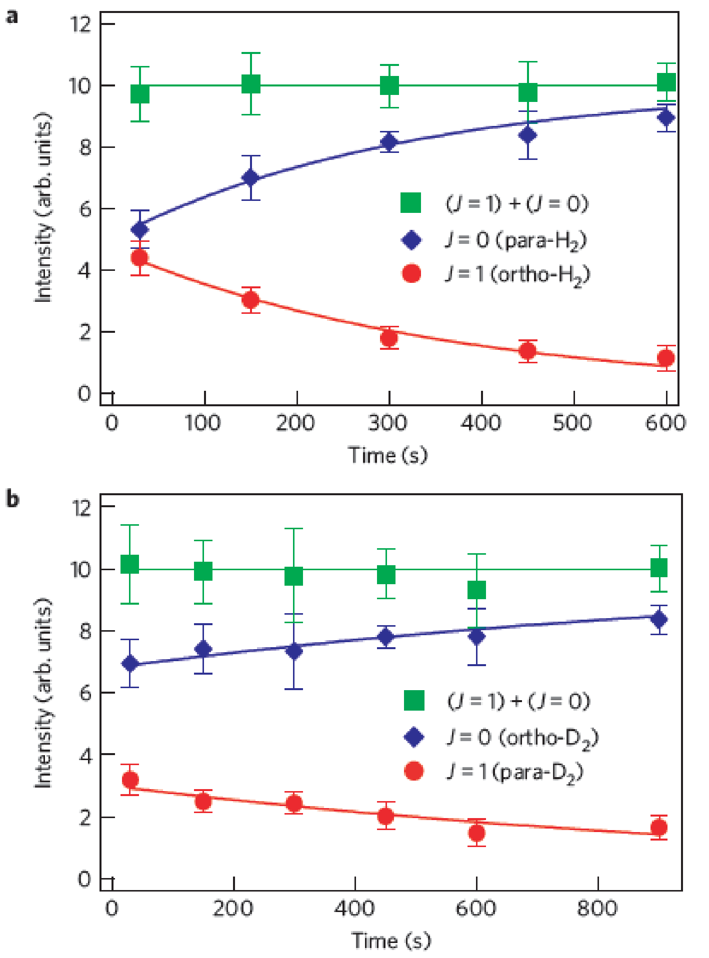


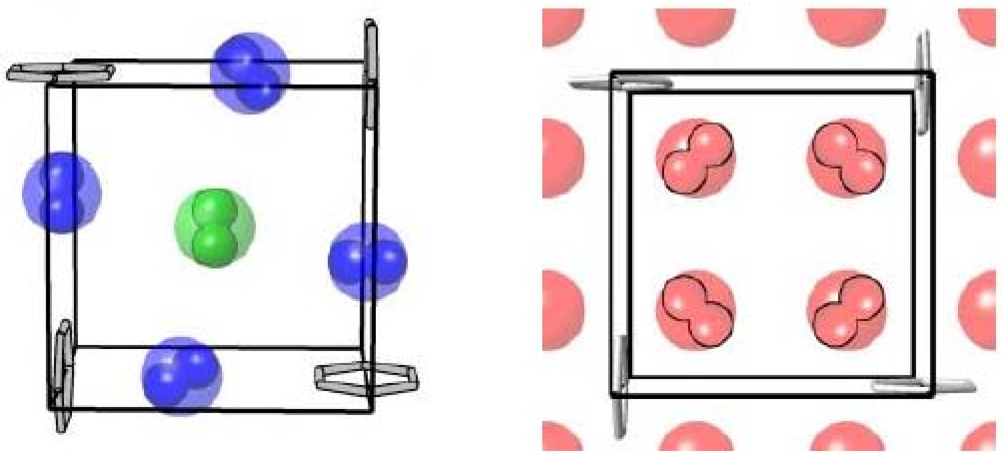
Figure 3 | Time evolution of the desorption intensities for J = 0 and J = 1 and their sum. a,b, H_2 (**a**) and D_2 (**b**) on the amorphous ice at 10 K (see Supplementary Section SC). The error bars represent the standard deviation of several independent measurements. The solid curves are fits using an exponential function, and the upper and lower limits of the time constant are evaluated by the chi-square test with a confidence level of 95% (see text).

NSC rates

H_2 : 370^{+340}_{-140} s

D_2 : 1220^{+2980}_{-580} s

Site-dependence of H_2 OP-conversion in porous polymer



(a)65K　　(b)35K

図 3　多孔性配位高分子内の水素分子の配列の模式図。(a)は 65K (b) は 35K を示す。65Kでは、水素分子は緑色のサイトⅠと青色のサイトⅡを主に占める。35K では赤色のサイトⅢを主に占めるようになる。

Kosone et al. Royal Soc. Open Sci. (2015)

Electric field depends on H_2-trapped sites

→ the OP conversion rate depends on the site.

Ortho-to-para conversion of CH_4 in p-H_2 matrix

Miyamoto et al. JCP (2008)

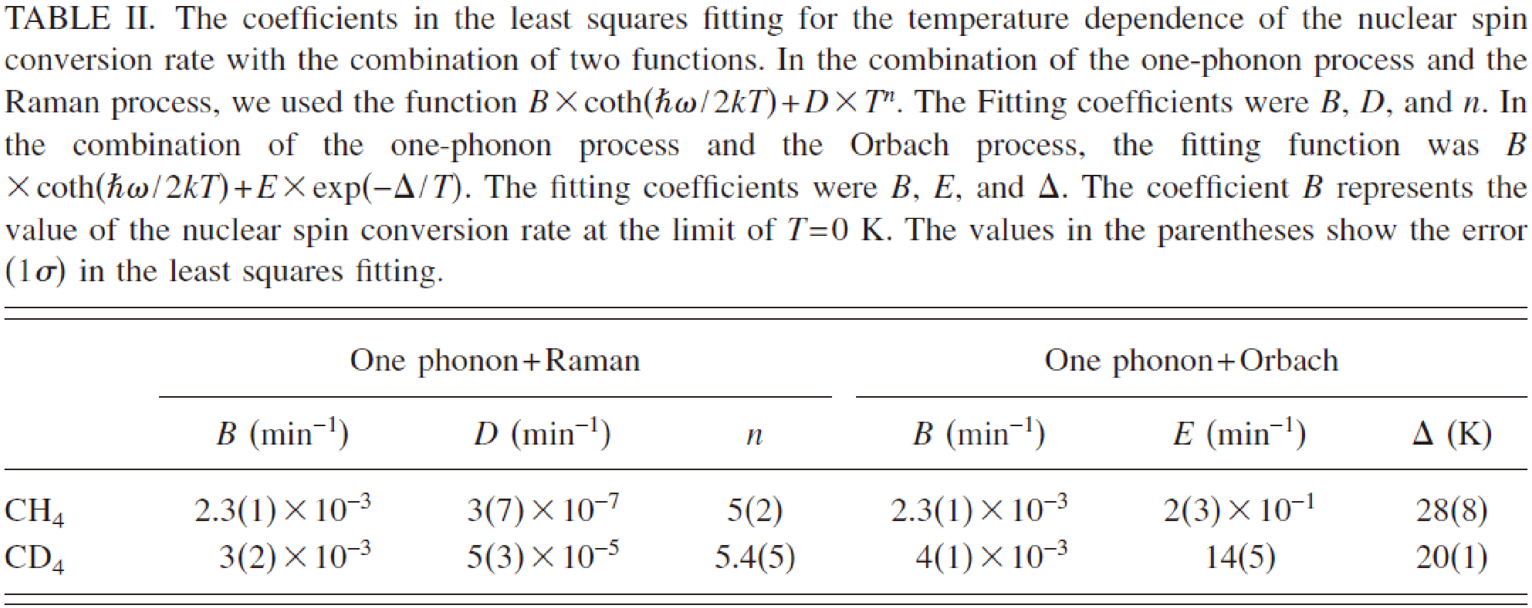


TABLE II. The coefficients in the least squares fitting for the temperature dependence of the nuclear spin conversion rate with the combination of two functions. In the combination of the one-phonon process and the Raman process, we used the function $B \times \coth(\hbar\omega/2kT) + D \times T^n$. The Fitting coefficients were B, D, and n. In the combination of the one-phonon process and the Orbach process, the fitting function was $B \times \coth(\hbar\omega/2kT) + E \times \exp(-\Delta/T)$. The fitting coefficients were B, E, and Δ. The coefficient B represents the value of the nuclear spin conversion rate at the limit of $T=0$ K. The values in the parentheses show the error (1σ) in the least squares fitting.

	One phonon+Raman			One phonon+Orbach		
	B (min^{-1})	D (min^{-1})	n	B (min^{-1})	E (min^{-1})	Δ (K)
CH_4	$2.3(1) \times 10^{-3}$	$3(7) \times 10^{-7}$	5(2)	$2.3(1) \times 10^{-3}$	$2(3) \times 10^{-1}$	28(8)
CD_4	$3(2) \times 10^{-3}$	$5(3) \times 10^{-5}$	5.4(5)	$4(1) \times 10^{-3}$	14(5)	20(1)

Origin of ortho and para states

H_2 case

$$\underset{A}{\Psi_{total}} = \underset{S}{\psi_e(\Sigma_g^+)}\ \underset{S}{\psi_{trans}}\ \underset{S}{\psi_{vib}}\ \underset{A \text{ or } S}{\psi_{rot}}\ \underset{A \text{ or } S}{\psi_{nspin}}$$

ψ_{rot} rotational wavefunction (spherical harmonics)

rotational quantum number J＝even → S

J= odd → A

ψ_{nspin} nuclear spin wavefunction

$$\left.\begin{array}{l} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{array}\right\}$$

T = 1 （ortho) S ⟶ **odd J**

multiplicity: 3

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

T = 0 （para) A ⟶ **even J**

multiplicity: 1

☆ **T = 1 $\nleftrightarrow$ T = 0 frobidden**

Nuclear spin conversion of H_2 and H_2O in gas phase

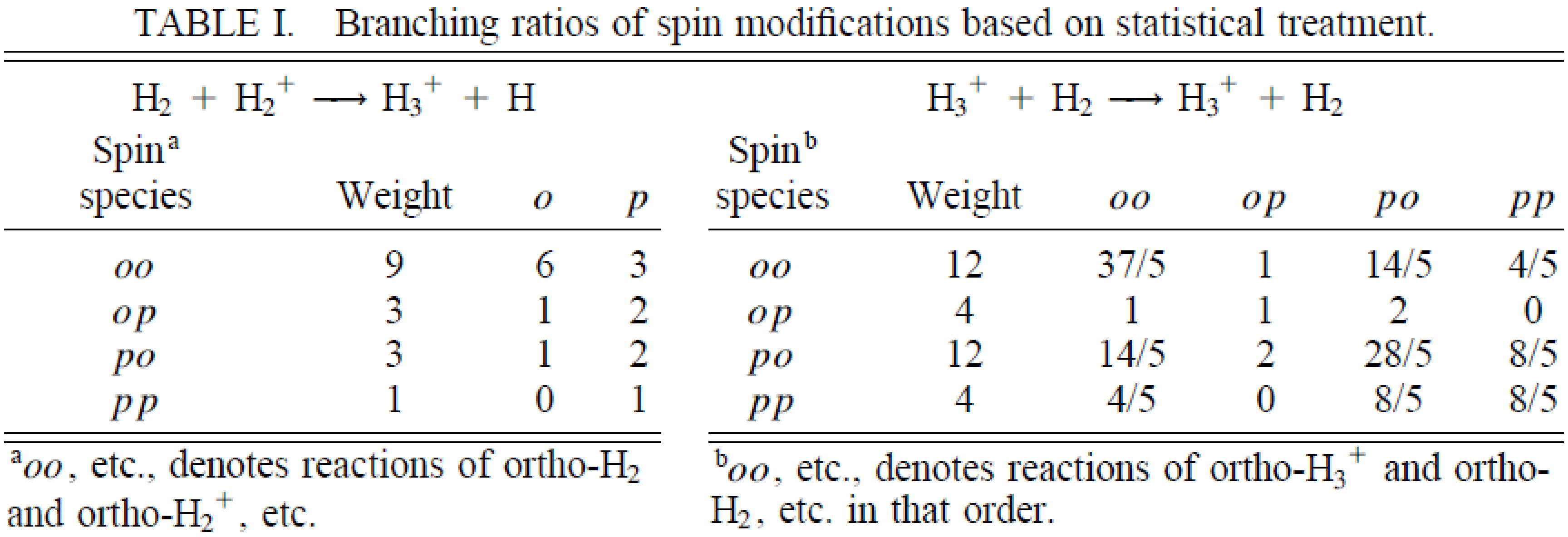


TABLE I. Branching ratios of spin modifications based on statistical treatment.

$H_2 + H_2^+ \longrightarrow H_3^+ + H$

Spin[a] species	Weight	*o*	*p*
oo	9	6	3
op	3	1	2
po	3	1	2
pp	1	0	1

[a] *oo*, etc., denotes reactions of ortho-H_2 and ortho-H_2^+, etc.

$H_3^+ + H_2 \longrightarrow H_3^+ + H_2$

Spin[b] species	Weight	*oo*	*op*	*po*	*pp*
oo	12	37/5	1	14/5	4/5
op	4	1	1	2	0
po	12	14/5	2	28/5	8/5
pp	4	4/5	0	8/5	8/5

[b] *oo*, etc., denotes reactions of ortho-H_3^+ and ortho-H_2, etc. in that order.

cf. $H_3^+(p) + HD \longrightarrow H_2D^+ + H_2(p) + 230\ K$ Uy et al. PRL 78, 3844 (1997)

$$\text{ortho-}H_2O + H^+ \rightarrow \text{para-}H_2O + H^+$$

$$\text{ortho-}H_2O + H_3O^+ \rightarrow H_3O^+ + \text{para-}H_2O$$

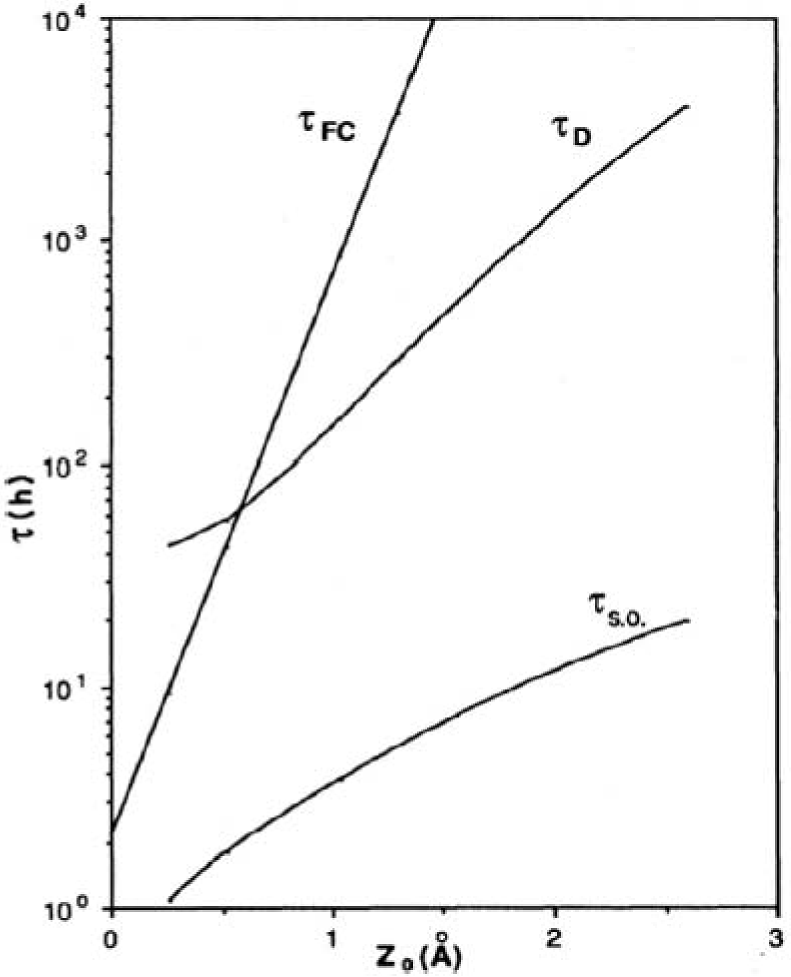
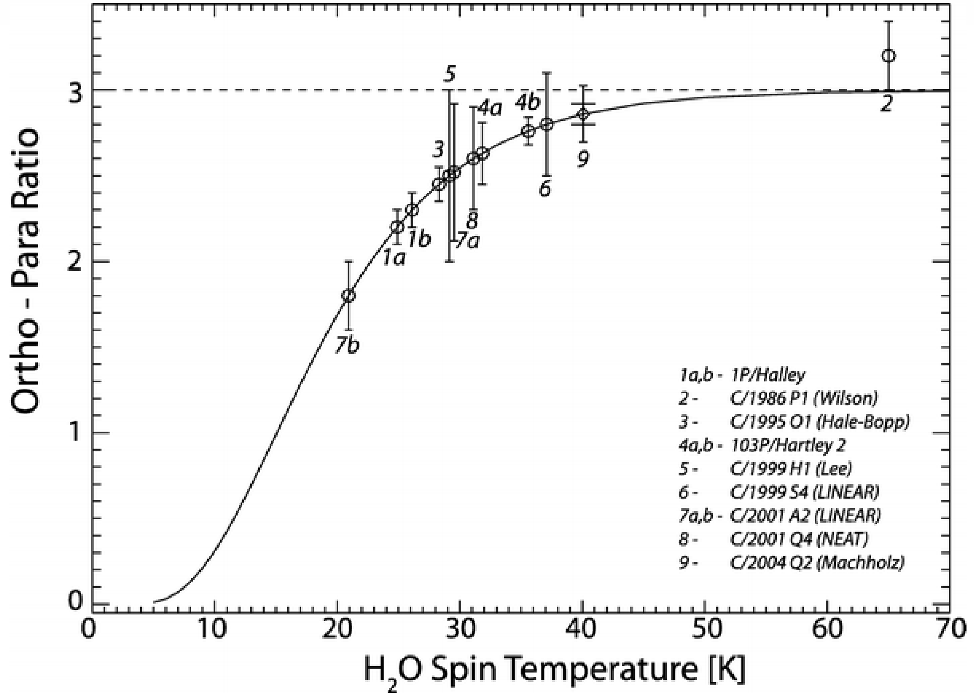


Fig. 18. The ortho–para conversion times as a function of the metal-molecule distance z_0 on a Cu surface for different processes of the magnetic dipole (τ_D), Fermi contact (τ_{FC}) and electron motion (τ_{SO}) calculated by Yucel. Reproduced by permission from [24]. Copyright (1989) by the American Physical Society.

OPR of H_2O



Bonev *et al.* 2007

OPR at high temperature limit = 3

$T_{spin} > \sim 50$ K

$8 < T_{spin} < 27$ K

star forming regions

$20 < T_{spin} < 40$ K in comet comae

Question: Does the OPR tell us the temperature of molecules' birth place (grain)?

What we did,

- the OPR measurements of thermal desorbed H_2O from ices formed at ~10 K

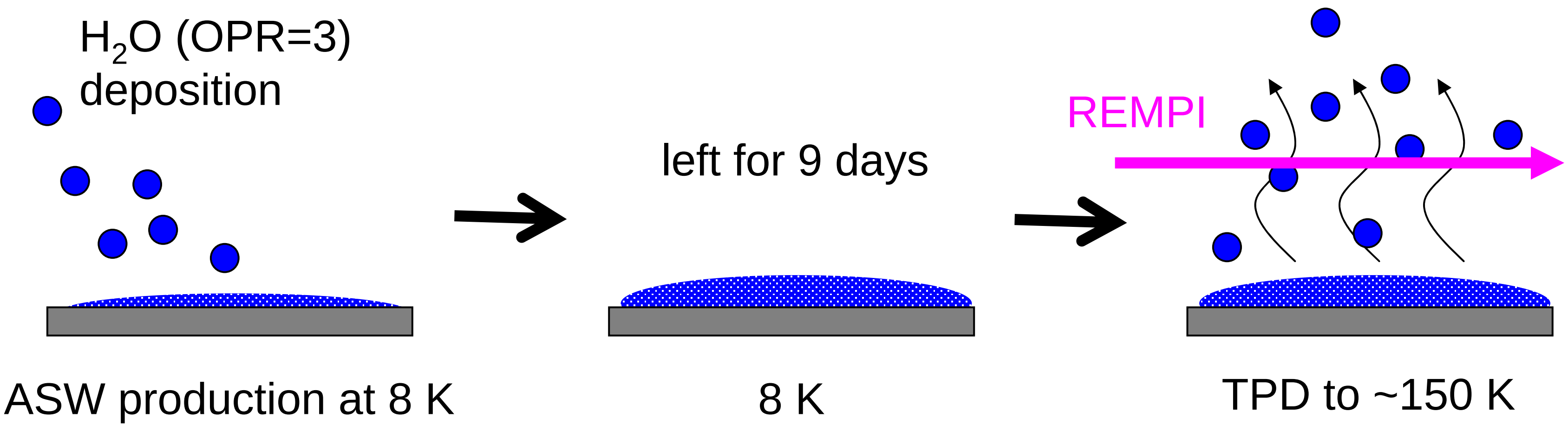
Hama *et al.* ApJL (2012)

- the OPR measurements of photodesorbed H_2O from ices formed at ~10 K

Hama *et al. Science* (2016)

Thermal desorbed: four types of samples

Sample1: Vapor-deposited ASW



OPR measurement

H_2O (OPR=3) deposition

REMPI

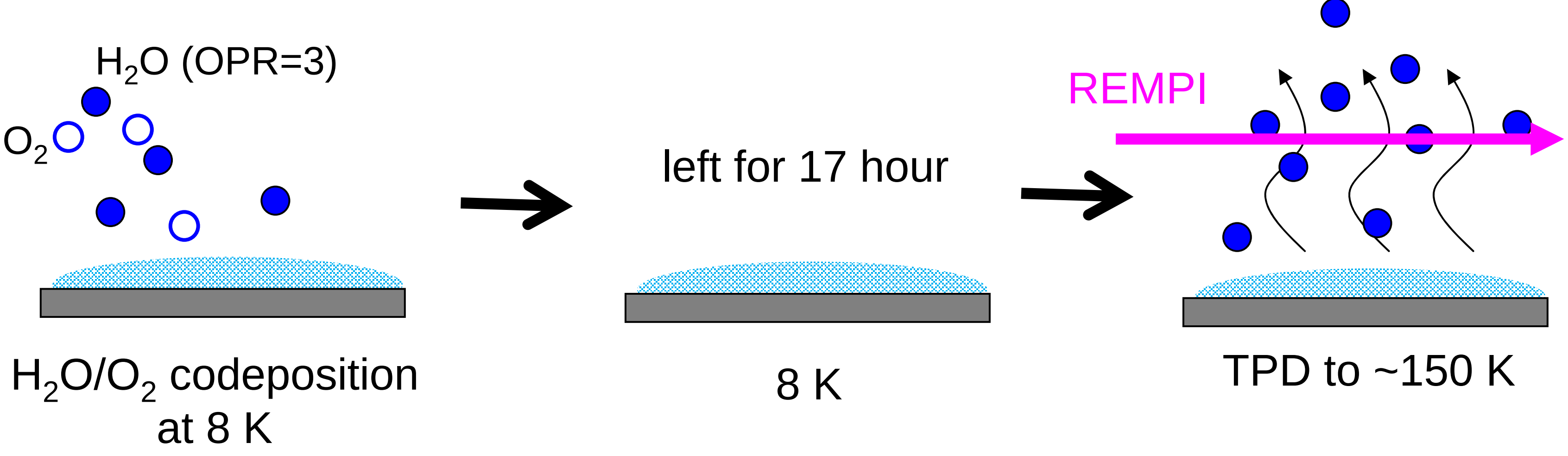
left for 9 days

ASW production at 8 K

8 K

TPD to ~150 K

Sample2: H_2O/O_2~1 mixed ASW



OPR measurement

H_2O (OPR=3)

O_2

REMPI

left for 17 hour

H_2O/O_2 codeposition at 8 K

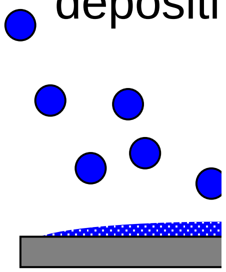
8 K

TPD to ~150 K

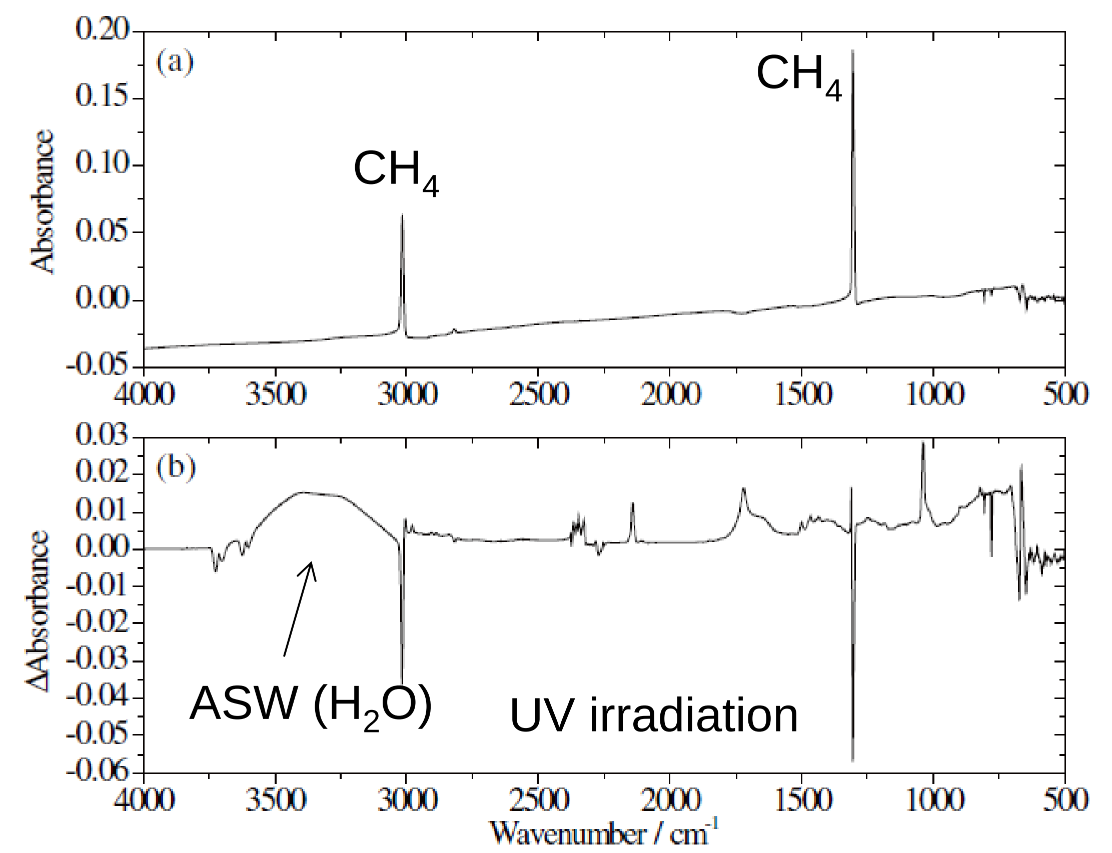
Thermal desorbed: four types of samples

Sample 3: Ph

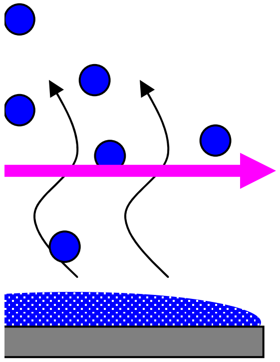
H_2O (OH
depositi



ASW produ



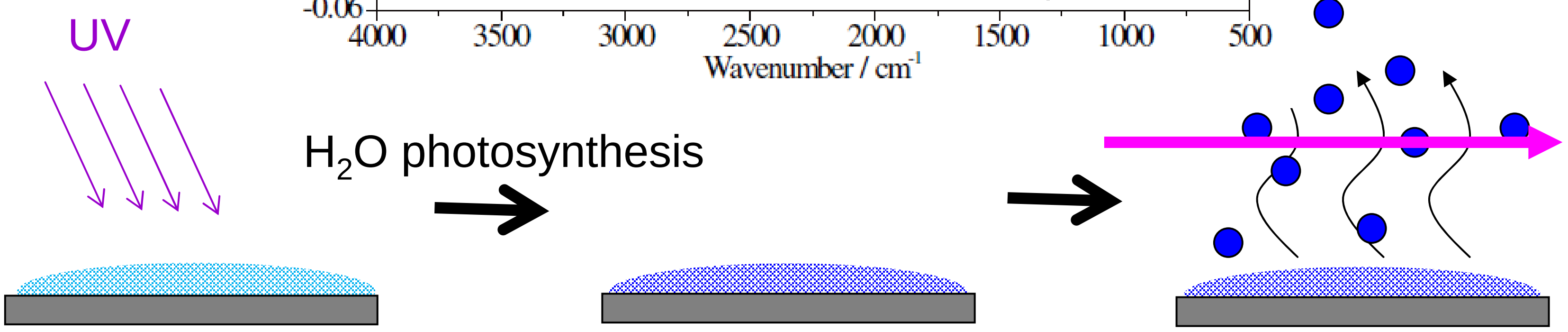
asurement



to ~150 K

Sample 4: Ph

asurement



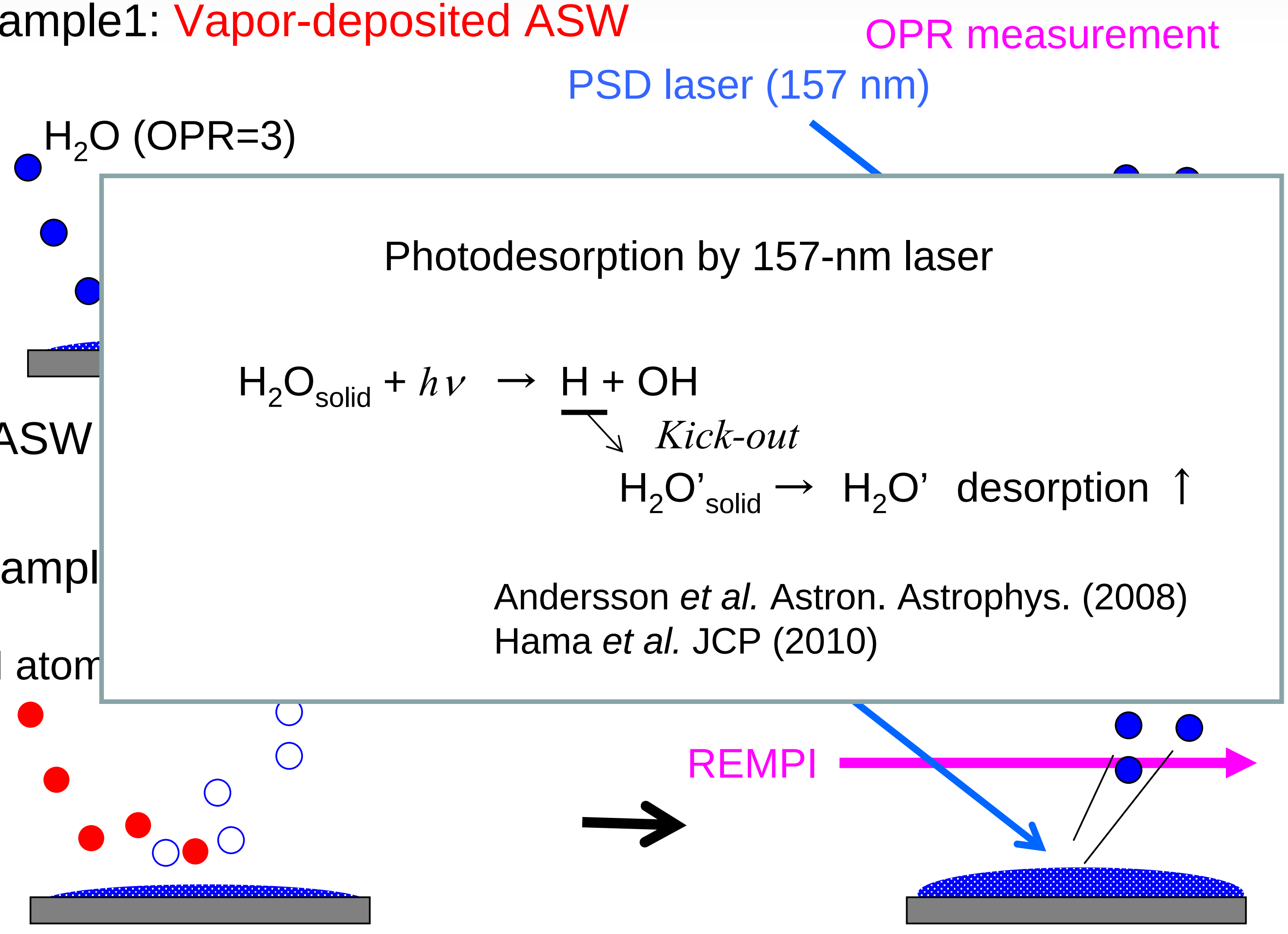
CH_4, O_2 solid mixture
at 8 K

ASW at 8 K

TPD to ~150 K

Photodesorbed at 10 K: two types of samples

Sample1: Vapor-deposited ASW



Photodesorption by 157-nm laser

$$H_2O_{solid} + h\nu \rightarrow \underline{H} + OH$$

Kick-out

$$H_2O'_{solid} \rightarrow H_2O' \text{ desorption} \uparrow$$

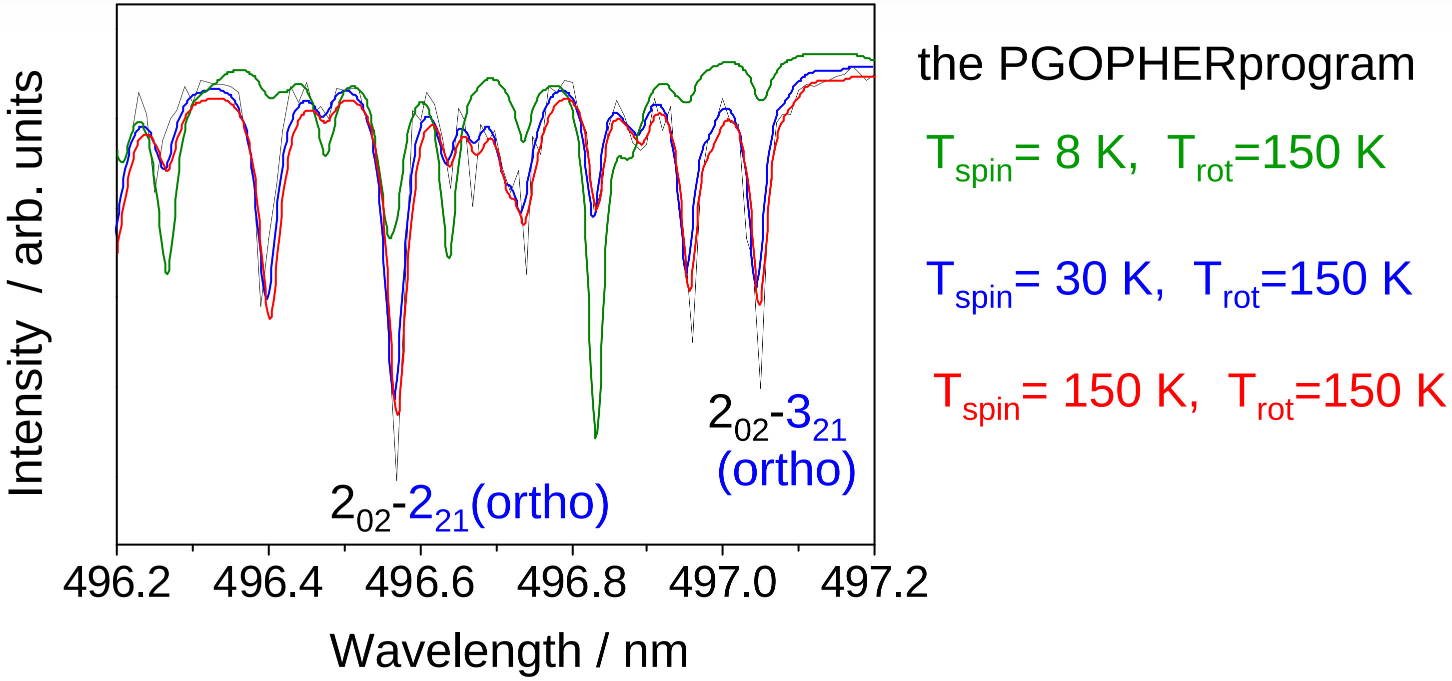
Andersson *et al.* Astron. Astrophys. (2008)
Hama *et al.* JCP (2010)

ASW production at 10 K

at 10 K

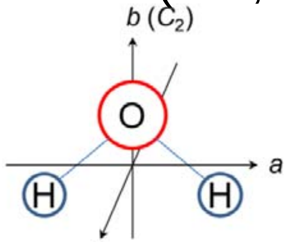
REMPI spectrum for thermal desorbed H_2O + Calculation

spectrum was obtained during TPD at ~150 K



REMPI (2+1) transition in H_2O C (v=0,0,0) ←← X (v=0,0,0) state

rotational state : $J_{Ka, Kc}$ $Ka + Kc$ =odd (ortho)
=even (para)



Spin temperature > 30 K (~high temperature limit) ≠ 8, 10 K

The same results were obtained for all samples incl photodsorbed ones

Results for H_2O

- OPR of thermal desorbed H_2O from ASW is ~3 for all samples.
- OPR of photodesorbed H_2O from ASW at 10 K is ~3 for all samples.

Why?

The rotation of H_2O is locked in ice and thus, energy difference between ortho and para is negligible (~10^{-12} K).

→ H_2O is not necessary to stay in para state even at very low temps.
Microscopically, O ↔ P conversion occurs very quickly (10^{-5}-10^{-4} s).

Statistically, OPR becomes 3! (macroscopically, no OP conversion)

cf. H_2O in Ar matrix where H_2O can rotate → OP conversion occurs!

The low OPRs observed toward star-forming regions and comets require gas phase processes.

For the comets, desorption with jet from nuclei may produce the low OPR.

Summary

- The OPR of H_2 varies rapidly on ice, sensitively depending on the ice temperature

  Steep increase of OP conversion at lower temperature can be explained by two phonon Raman process.

→ In molecular clouds, the OPR of H_2 at desorption into the gas phase depends on when it is released and temperature of dust.

- The OPR of H_2O both thermally-desorbed and photodesorbed at 10 K is statistical value of **3**, independent from ice formation process.

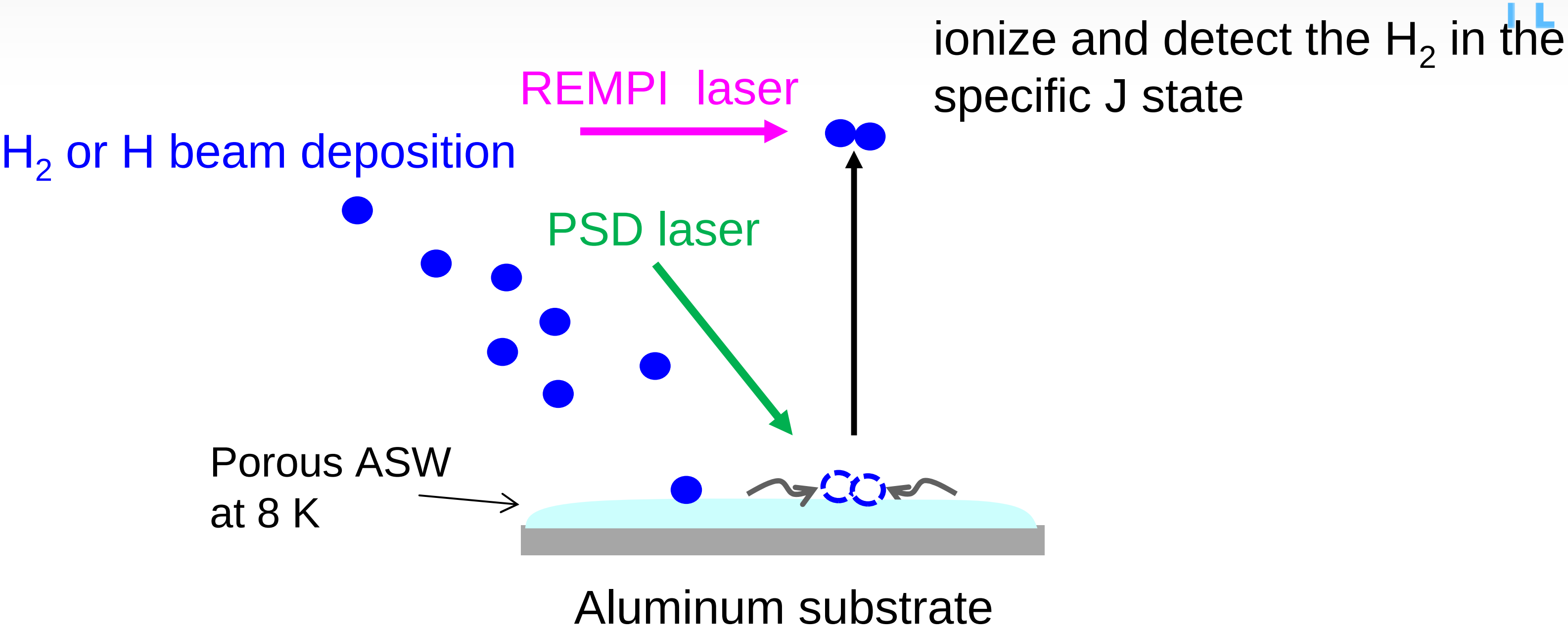
→ Gas phase processes should be considered to produce lower OPRs.

- What makes differences between H_2 and H_2O case

H_2 rotatable on ice (ΔE_{op} significant) ↔ H_2O rotation locked in ice (ΔE_{op} negligible)

Rotation is important! CH_4, NH_3 ??

Procedure

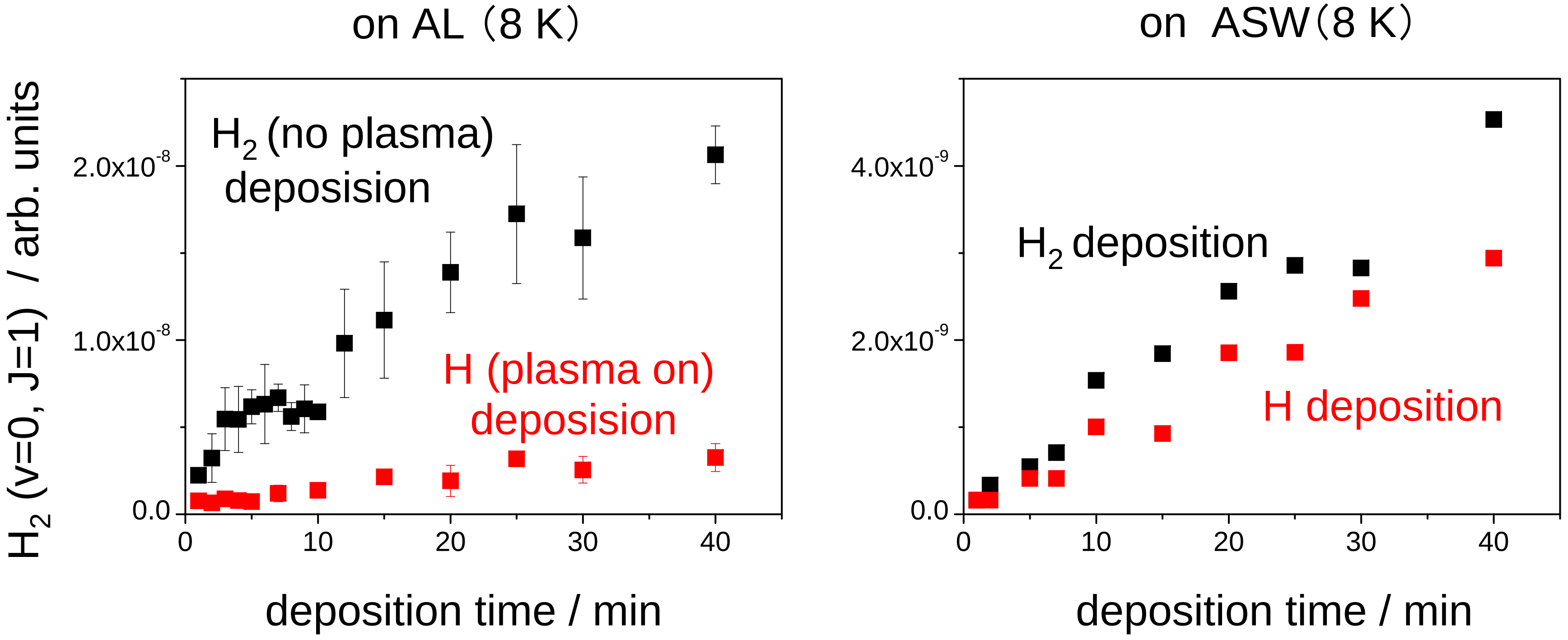


H_2 formed is rotationally-resolved by PSD + REMPI methods
during H_2 or H atom deposition

REMPI: Resonance Enhanced Multi-Photon Ionization

Evidence of H_2 recombination on ASW

Photodesorbed H_2 from ASW for H_2 or H deposition through the beam line with microwave on and off



↓

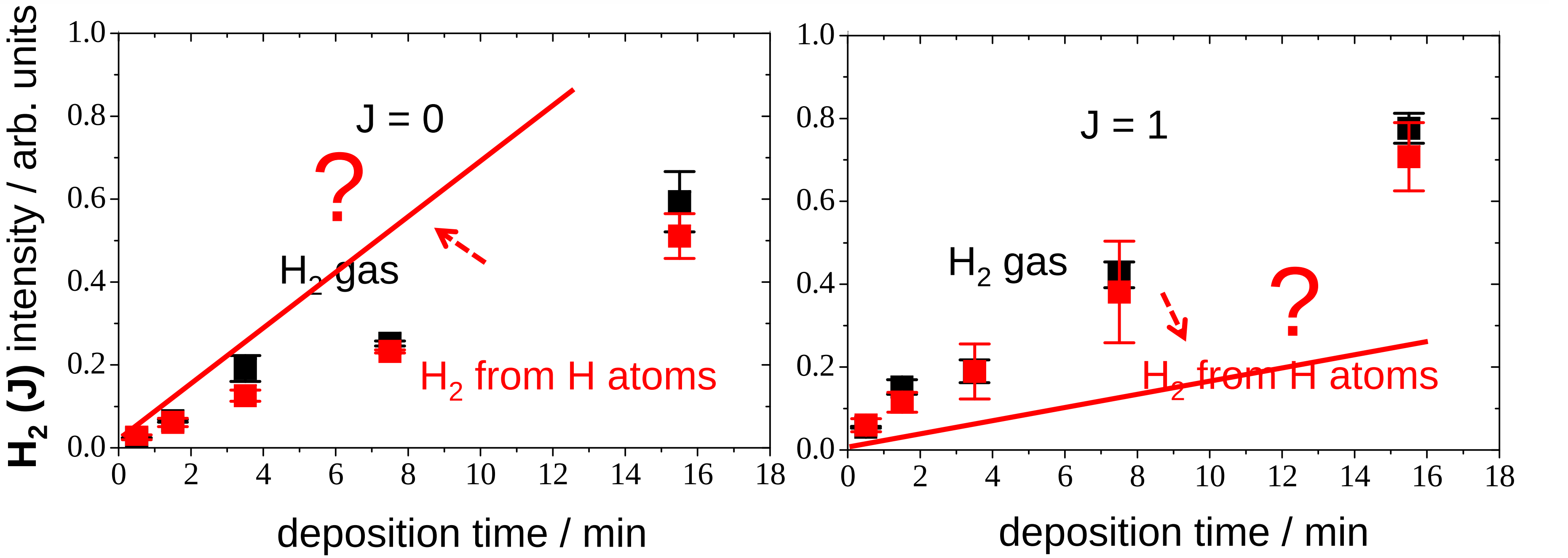
Atomic beam includes little H_2 !

↓

H_2 recombines and retrapped on ASW !

OPR of nascent H_2 on ASW at 8 K

by comparing between H_2 (OPR=3) gas and H atom deposition on ASW

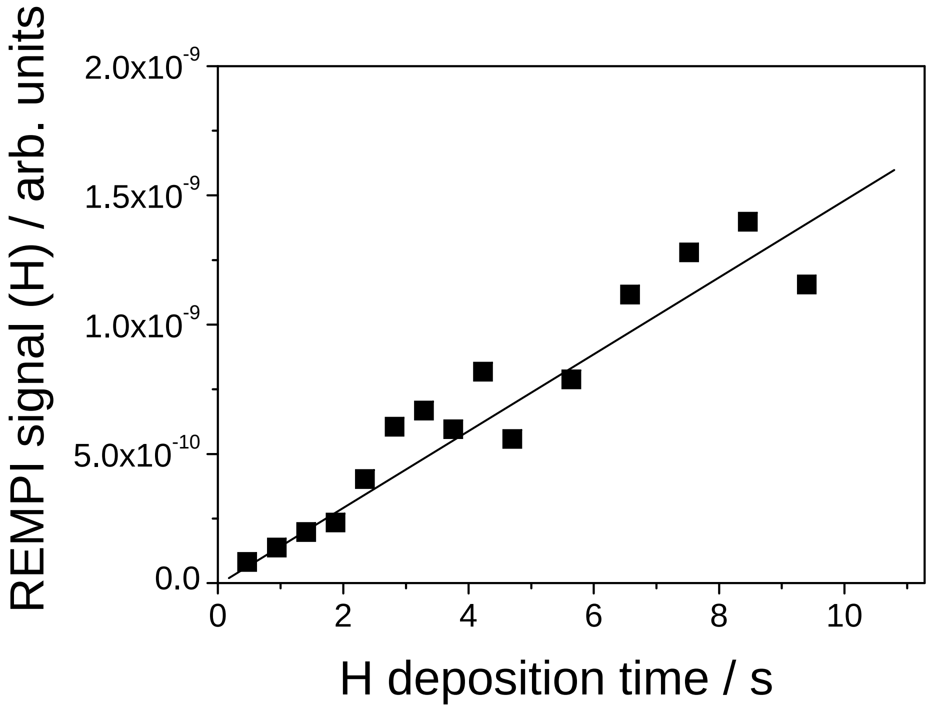


H_2 (J = 0, 1) intensities: H_2 gas deposition = H atom deposition

OPR on ASW : H_2 gas deposition = nascent H_2 molecule !

i.e.   OPR of nascent H_2 molecules ~ 3 (high temperature limit)

Increase of H atom on ASW with continuous deposition at 8 K



Signal intensity of H atom increases linearly.

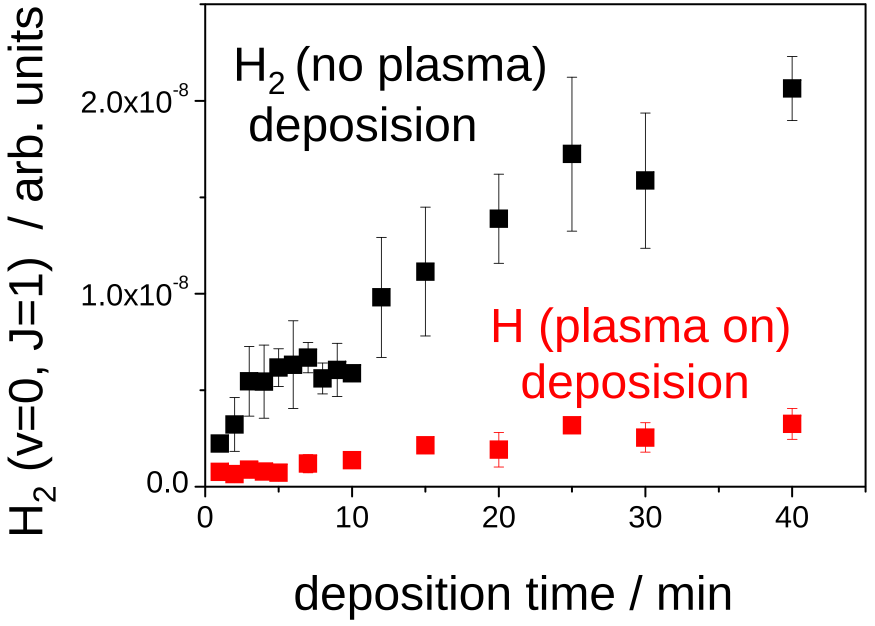
||

Signal intensity ∝ surface number density of H atom on ASW

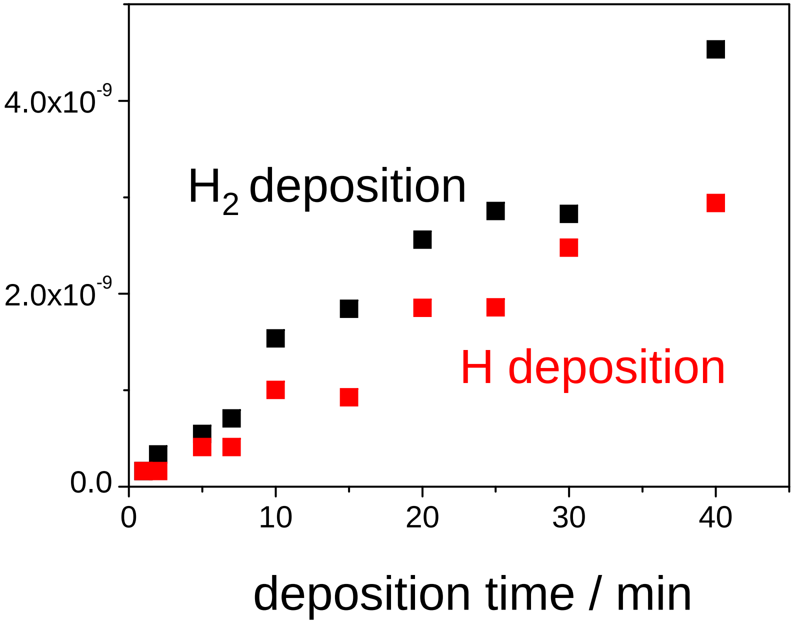
Evidence of H_2 recombination on ASW

H_2 and H deposited through the beam line with microwave on and off

on AL（8 K）



on ASW（8 K）



↓

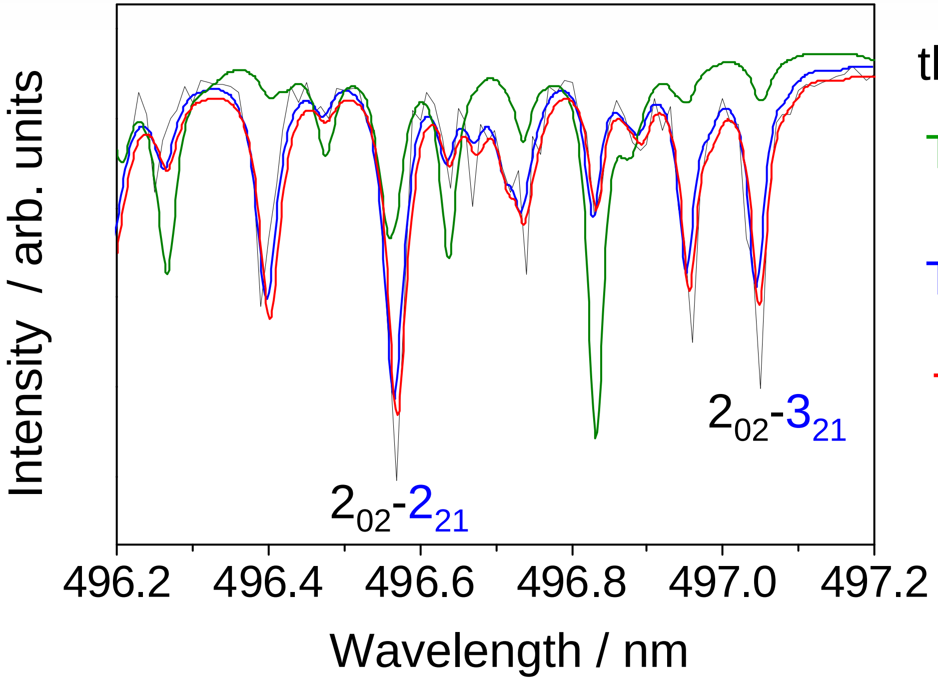
Atomic beam includes little H_2 !
Dissociation fraction ~80%

↓

Most of H atoms recombine
and retrapped as H_2 on ASW !

REMPI spectrum for H_2O after 9 days + Calculation

spectrum was obtained during TPD at ~150 K



the PGOPHERprogram

T_{spin}= 8 K, T_{rot}=150 K

T_{spin}= 30 K, T_{rot}=150 K

T_{spin}= 150 K, T_{rot}=150 K

REMPI (2+1) transition in H_2O C (v=0,0,0) ←← X (v=0,0,0) state

rotational state : $J_{Ka, Kc}$ *Ka* + *Kc* =odd (ortho)
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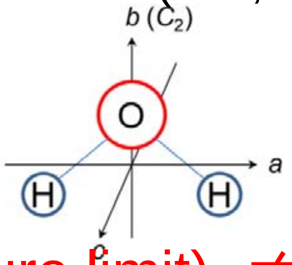
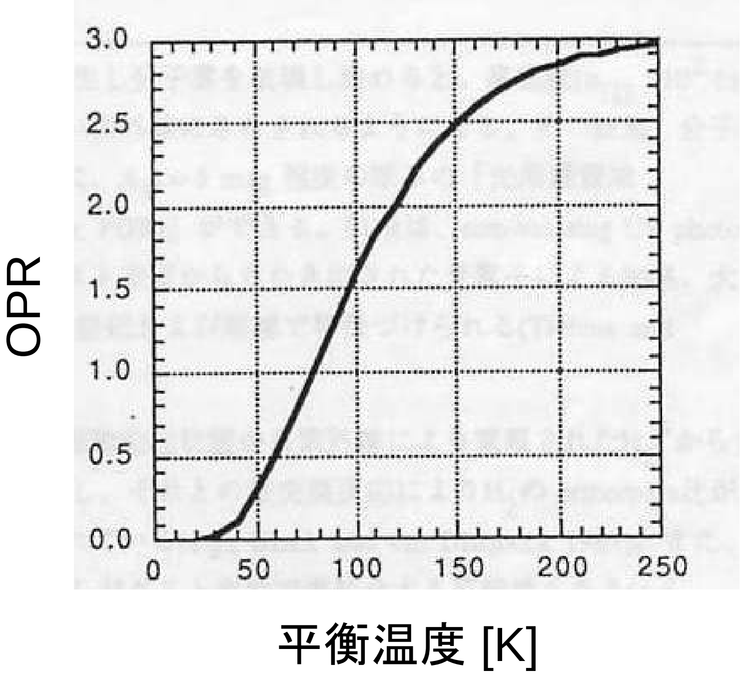


Spin temperature > 30 K (~high temperature limit) ≠ 8 K

The same results were obtained for all samples

水素分子，水分子のOPR

水素分子



水分子

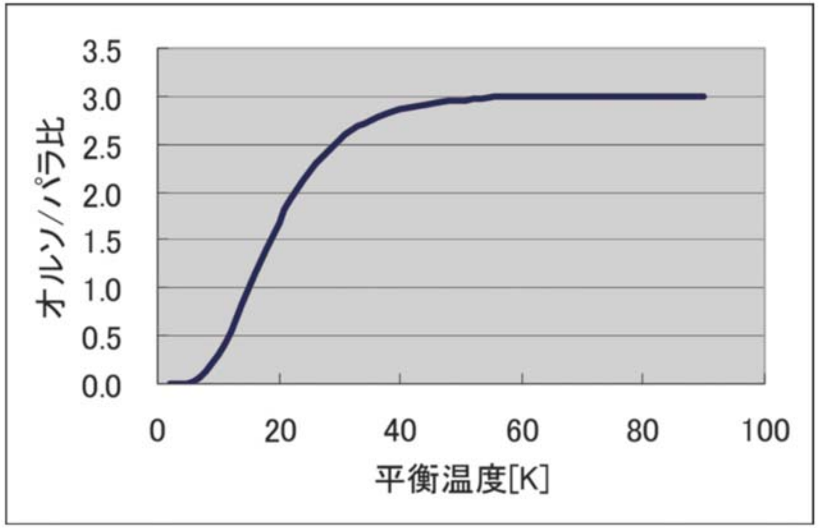
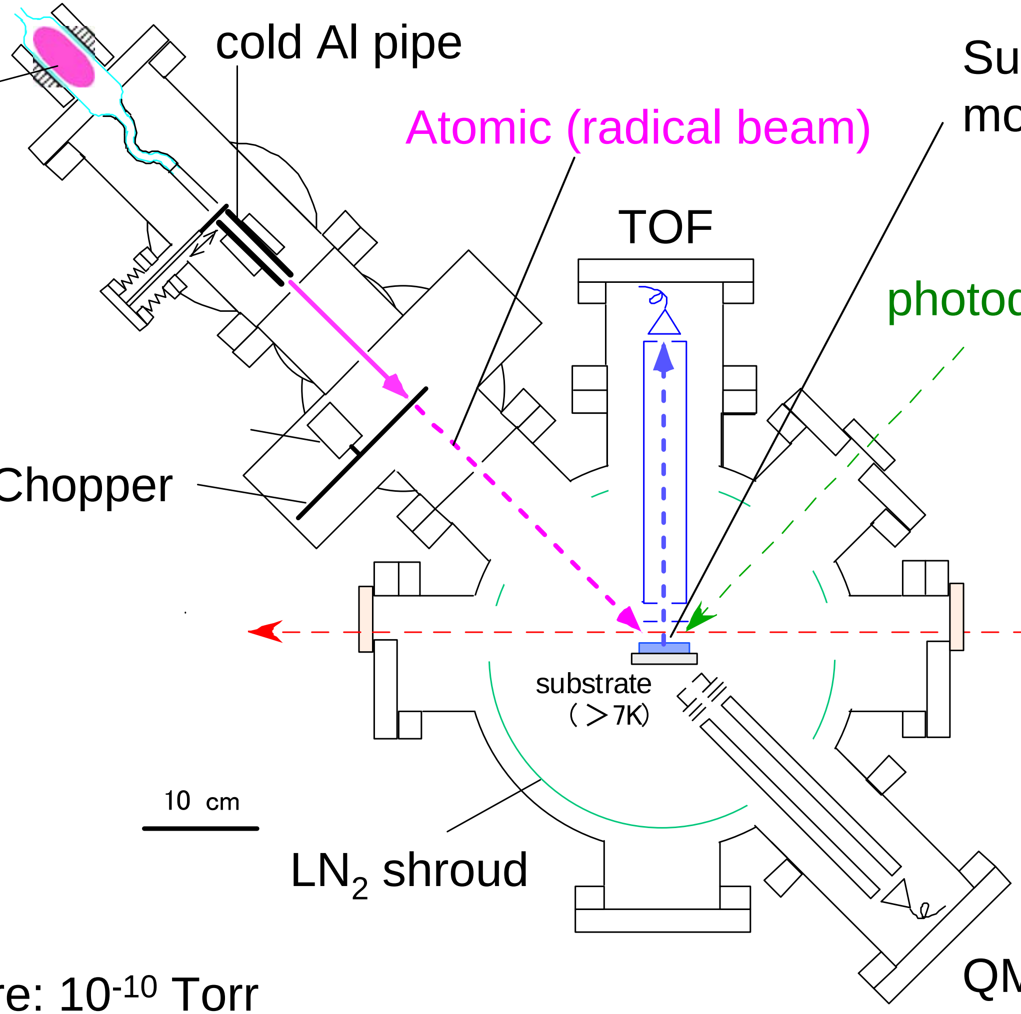


図２：平衡温度とオルソ／パラ比の関係
平衡温度（つまり，原子核スピン温度）が上がるに従って統計重率比３に近づき，50 K 以上になると，ほぼ３となっている．そのため，オルソ／パラ比を温度プローブとして用いることが出来る範囲はおよそ 50 K 以下ということになる．

河北, 小林　低温科学, 66: 89-95 (2008)より

Cross section of RASCAL

Microwave-type atomic (radical) source



Plasma

cold Al pipe

Atomic (radical beam)

Surface species can be monitored by FTIR

TOF

photodesorption laser

Chopper

Laser for REMPI

substrate (>7K)

10 cm

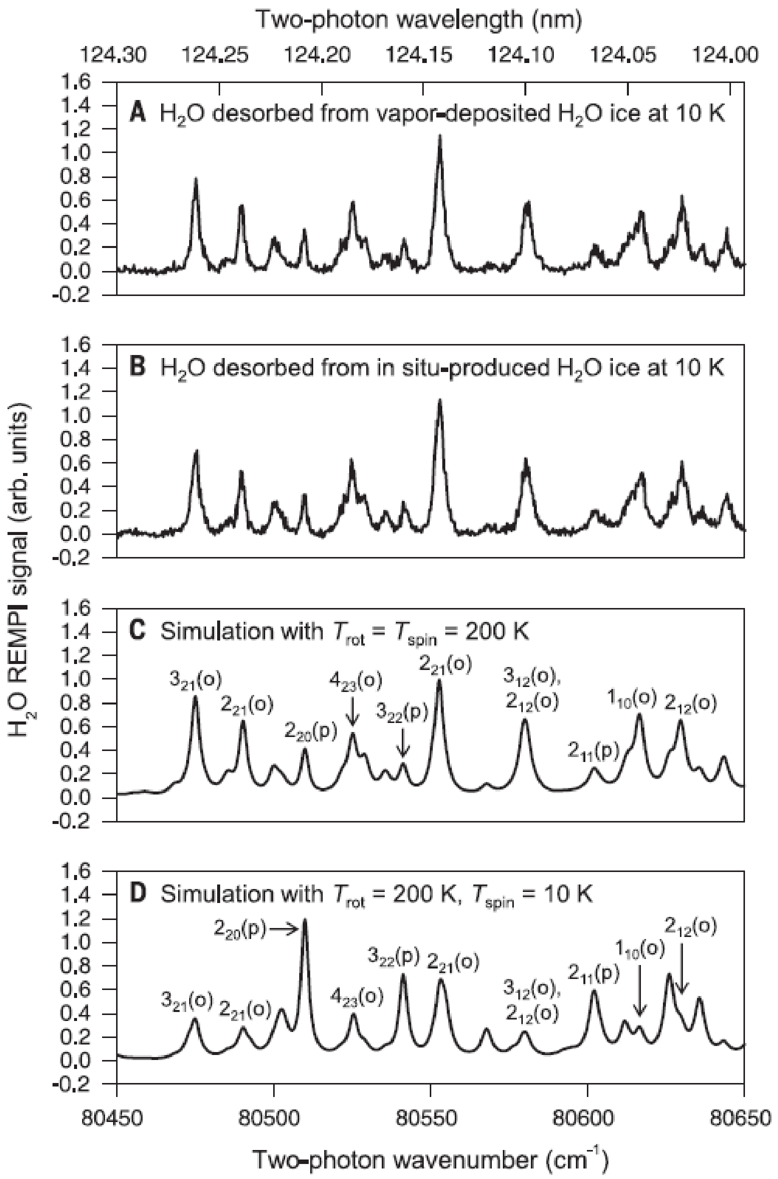
LN_2 shroud

QMS

Base pressure: 10^{-10} Torr

Kinetic temp. of atoms: 100 K

REMPI signal from photodesorbed water from ice at 10 K



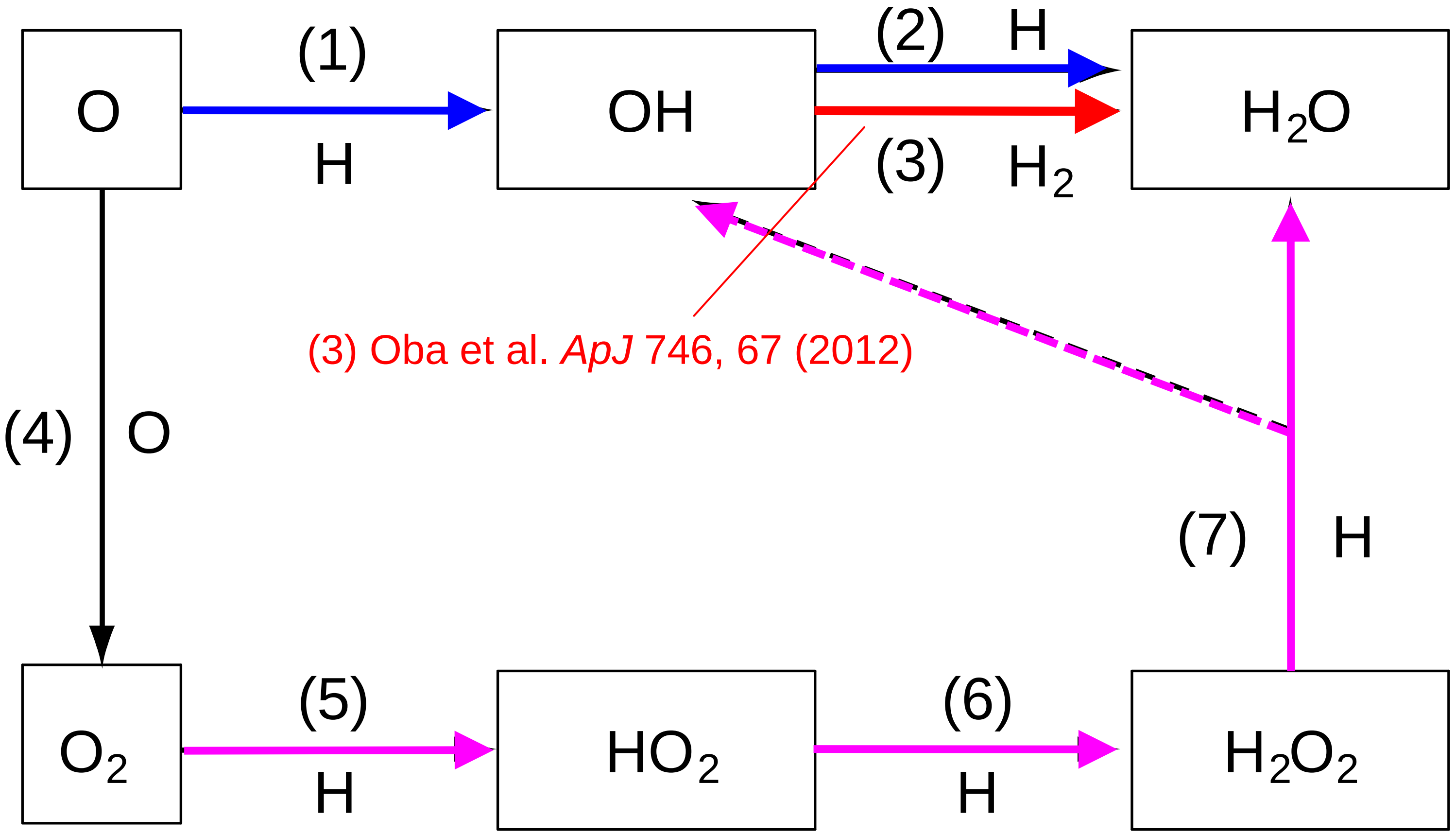
Vapor deposited ice

Ice from O_2-hydrogenation

simulation

Water ice formation on dust grains

(1)+(2): Dulieu et al. *AA* 512 A30 (2010); Jing et al. *ApJ* 741 L9 (2011)



O

(1)

H

OH

(2) H

(3) H_2

H_2O

(4) O

(3) Oba et al. *ApJ* 746, 67 (2012)

(7) H

O_2

(5)

H

HO_2

(6)

H

H_2O_2

(5)+(6)+(7): e.g. Miyauchi *CPL* 456, 27 (2008)+; Ioppolo et al. *ApJ* 686, 1474 (2008)+.

can be a dominant route in MC (Cuppen & Herbst 2007)

Energies of photodesorbed H_2O from ASW

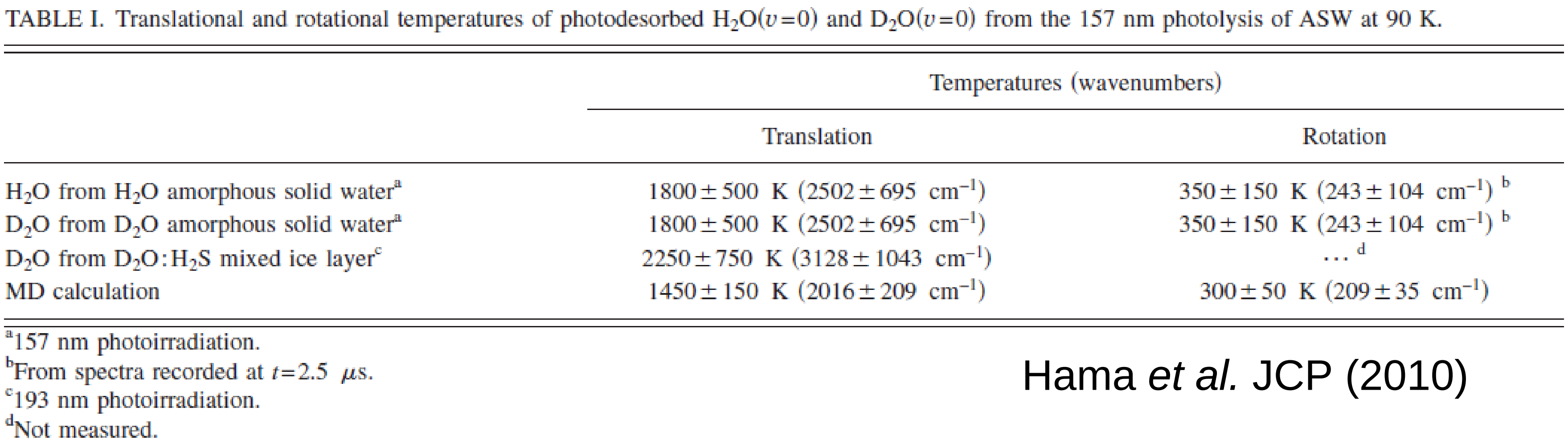


TABLE I. Translational and rotational temperatures of photodesorbed $H_2O(v=0)$ and $D_2O(v=0)$ from the 157 nm photolysis of ASW at 90 K.

	Temperatures (wavenumbers)	
	Translation	Rotation
H_2O from H_2O amorphous solid water[a]	1800 ± 500 K (2502 ± 695 cm^{-1})	350 ± 150 K (243 ± 104 cm^{-1}) [b]
D_2O from D_2O amorphous solid water[a]	1800 ± 500 K (2502 ± 695 cm^{-1})	350 ± 150 K (243 ± 104 cm^{-1}) [b]
D_2O from $D_2O:H_2S$ mixed ice layer[c]	2250 ± 750 K (3128 ± 1043 cm^{-1})	… [d]
MD calculation	1450 ± 150 K (2016 ± 209 cm^{-1})	300 ± 50 K (209 ± 35 cm^{-1})

[a] 157 nm photoirradiation.

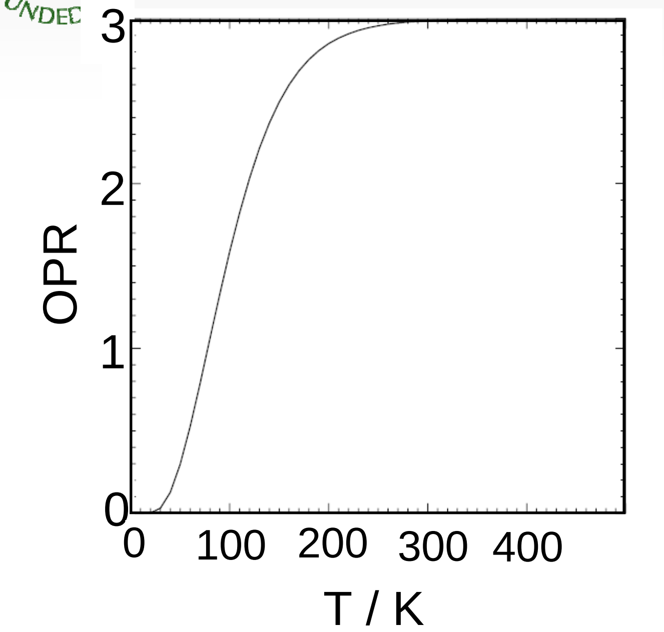
[b] From spectra recorded at $t=2.5$ μs.

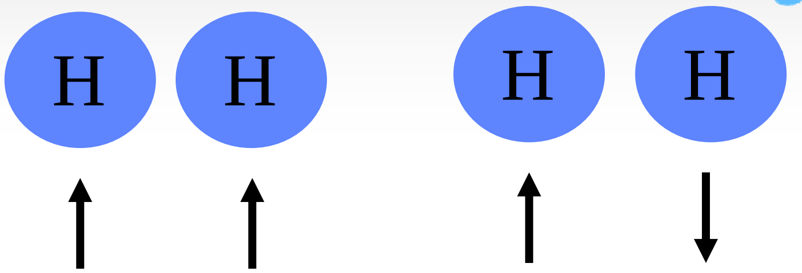
[c] 193 nm photoirradiation.

[d] Not measured.

Hama *et al.* JCP (2010)

OPR of H_2





Total spin	I=1 (ortho)	I=0 (para)
Spin multiplicity	3	1
Rotation	J=1, 3, 5, …	J=0, 2, 6, …

$$\mathrm{OPR} = N_{\mathrm{ortho}} / N_{\mathrm{para}} = \frac{\sum_{v,J=odd} g_I (2J+1)\exp(-E_{v,J}/kT)}{\sum_{v,J=even} g_I (2J+1)\exp(-E_{v,J}/kT)}$$

OPR at high temperature limit = 3 (e.g. 0.01 @30K)

The lowest $\Delta E_{o\text{-}p}$ ~ 170 K ⟶ The OPR of H_2 significantly affects chemistry in molecular clouds

$$\text{e.g. } H_3^+(p) + HD \longrightarrow \underline{H_2D^+}(p) + H_2(p) + 230\ \mathrm{K}$$

Important species for deuterium enrichment in molecules

Requirements for OP conversion

1. Energy difference exists between ortho and para states

→ Rotation required

2. State mixing between ortho and para states induced by perturbation

*e.g. intra-(or inter-)*molecular nuclear magnetic dipole-dipole interaction

Lowest $\Delta E_{\text{o-p}}$ in gas phase: ~ 34 K for H_2O ($J_{ka,\,Kc}$: $0_{00};1_{01}$)

easily mixed

~ 170 K for H_2 (v=0, J=0;1)

$\Delta E_{\text{o-p}} \searrow$ because of rotation hindered in solid

For example, OP conversion rate~ 30 min for H_2O in an Ar matrix at 20 K

(Abouaf–Marguin *et al.* 2007, 2009)

3. Energy release (relaxation) after OP conversion

Energy dissipation by phonons in solid → Significant temp dependence of the conversion rate