Nuclear-spin dynamics of interstellar water ice

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HOKKAIDO UNIVERSITY ILTS

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the Auditorium of the University Pierre et Marie Curie, Paris, France.

Nuclear-spin isomers of H_2O (oxygen hydride)

Like H_2, ortho (I = 1, triplet) and para (I = 0, singlet) H_2O.

Proton is a fermion with a nuclear spin angular momentum of I = 1/2.

The Pauli principle:

(1) Ortho-H_2O and para-H_2O must exist in different rotational states.

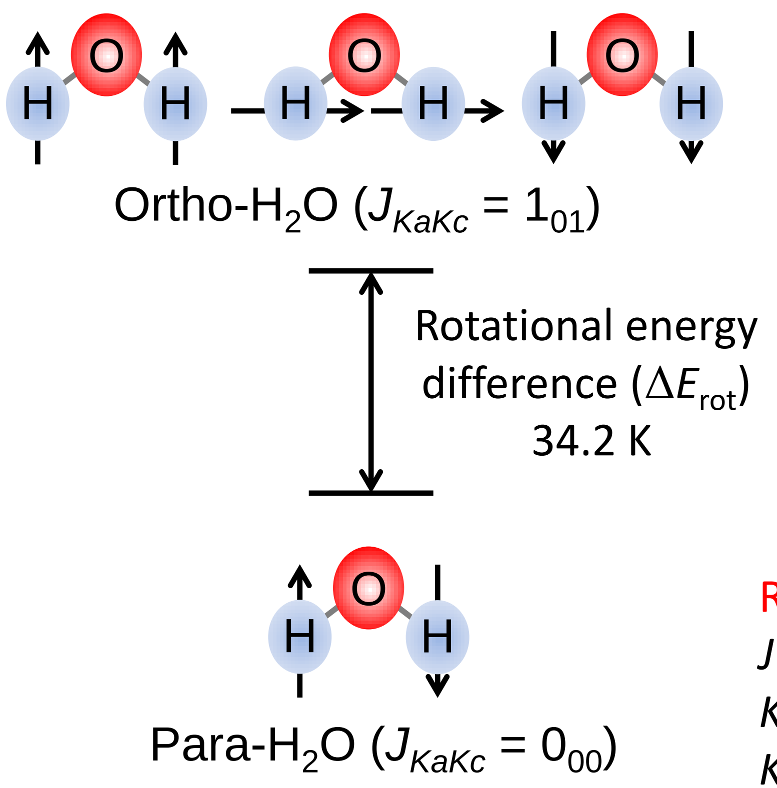
In the electronic and vibrational ground state H_2O $X\,^1A_1(v=0, J_{Ka,\,Kc})$,

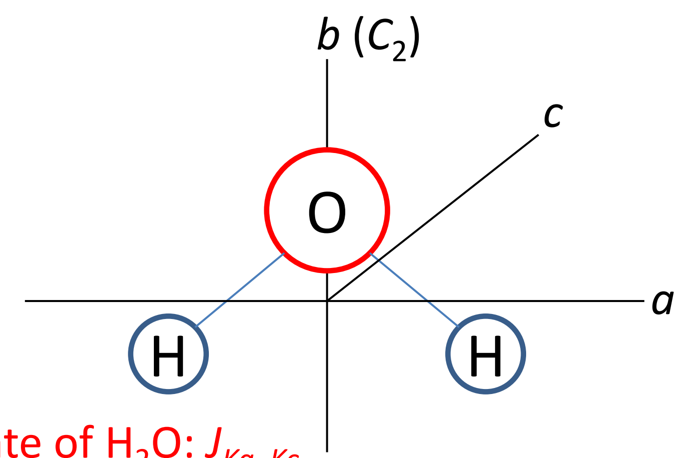
Orhto-H_2O → $K_a + K_c$ = odd ($J_{Ka,\,Kc}$ = 1_{01})　　Para-H_2O → $K_a + K_c$ = even ($J_{Ka,\,Kc}$ = 0_{00})

(2) Nuclear spin conversion is very slow in the gas phase by radiation or nonreactive collisions.

Miani and Tennyson, JCP, 2004, 120, 2732.

Cacciani et al., Phys. Rev. A, 2012, 85, 012521.





Rotational state of H_2O: $J_{Ka,\,Kc}$

J: the total rotational angular momentum.

Ka: the projection of J on the molecular a axis.

Kc: the projection of J on the molecular c axis.

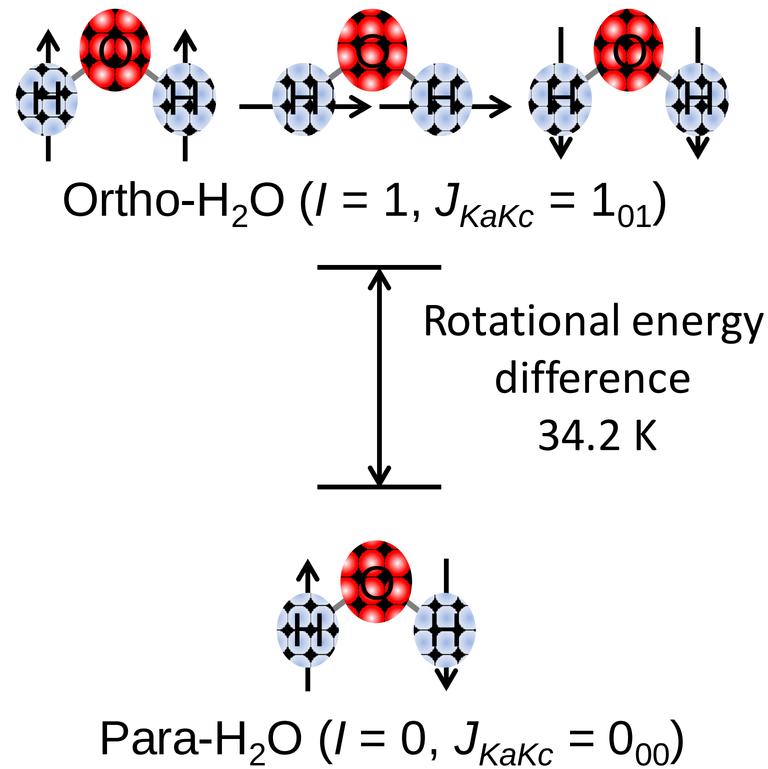
The ortho-to-para ratio (OPR) is related to the spin temperature (T_{spin}), defined at thermodynamic equilibrium.

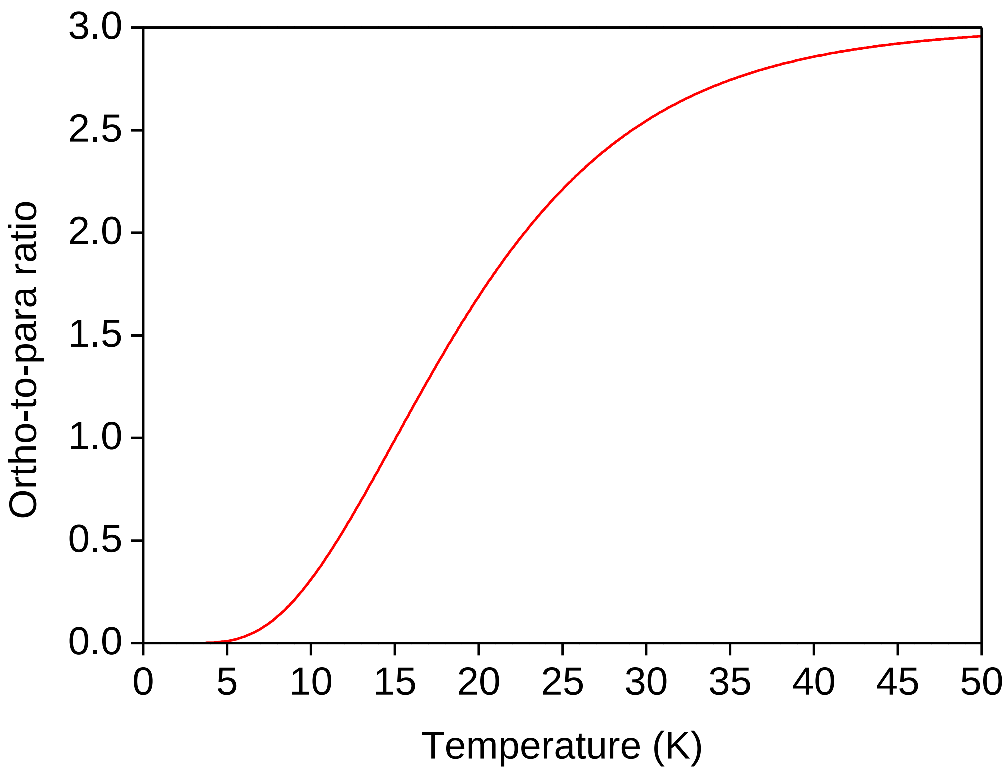
Spin and rotational degeneracy

Rotational energy

$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_{\mathrm{o}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}{\sum(2J+1)\exp\left[\frac{-E_{\mathrm{p}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}$$

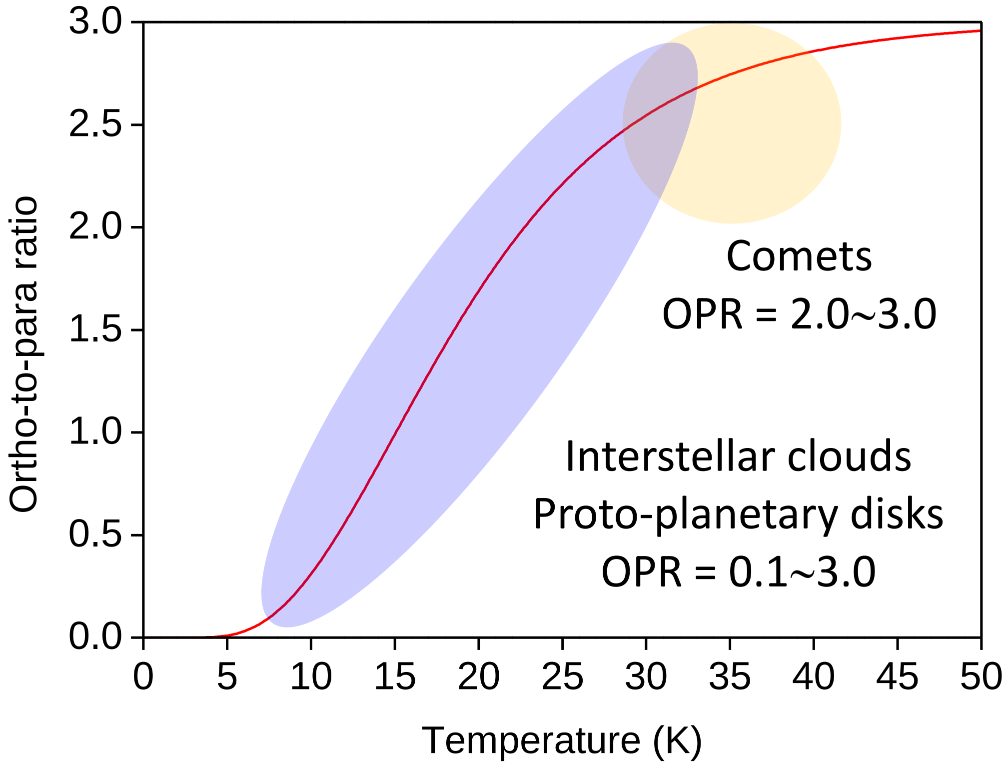
Because of the ΔE_{rot} of 23.8cm^{-1} (34.2 K), para-H_2O ($J_{Ka,\,Kc} = 0_{00}$) is more stable than ortho-H_2O ($J_{Ka,\,Kc} = 1_{01}$) in the gas phase below 50 K .

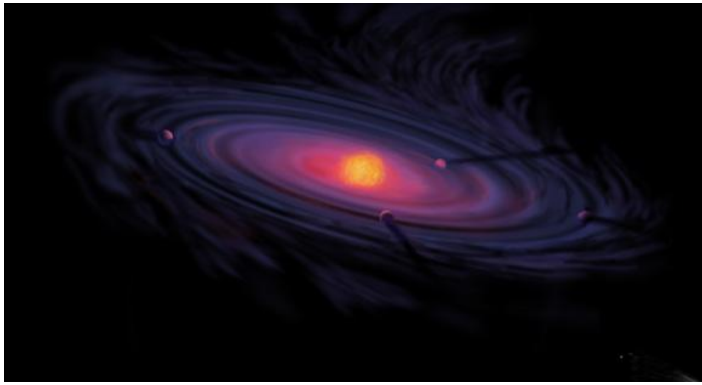




A probe for low-temperature regions?

The anomalous OPRs of gaseous H_2O in space





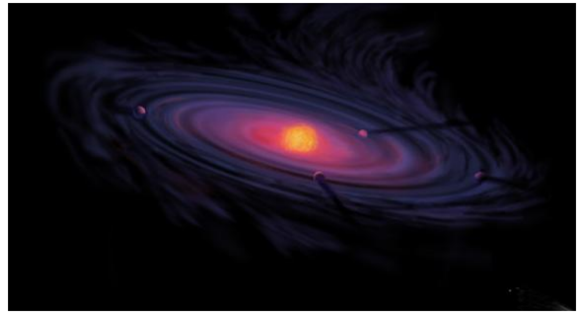
The OPR is a tracer for
the water formation temperature ?

Lis et al.,Astron. Astrophys. 521, L26 (2010) .
Hogerheijde et al., Science 334, 338 (2011).
Choi et al., Astron. Astrophys. 572, L10 (2014).
Willacy et al., Space Sci. Rev. 197, 151 (2015).

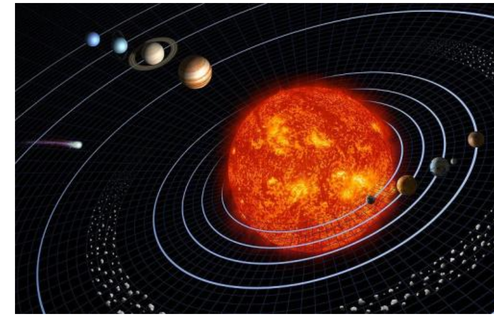
T_{spin} is the cometary ice formation temperature 4.6 billion years ago ?

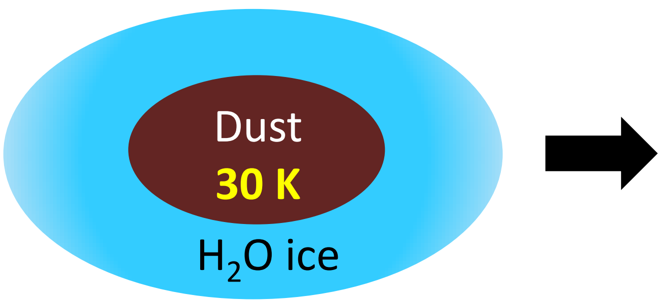
Interstellar clouds

Proto-planetary disks

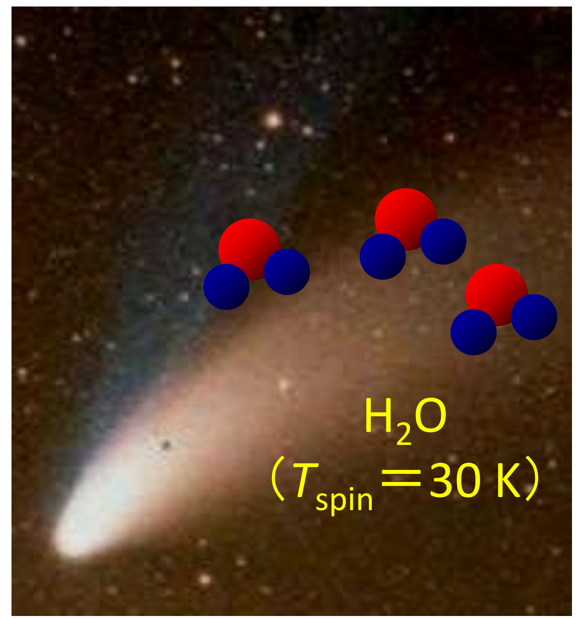


The Solar -system





Comets



Detection of Water Vapor in Halley's Comet
Mumma et al., Science 232, 1523 (1986).

The meaning of the observed T_{spin} remains a topic of continuing debate.

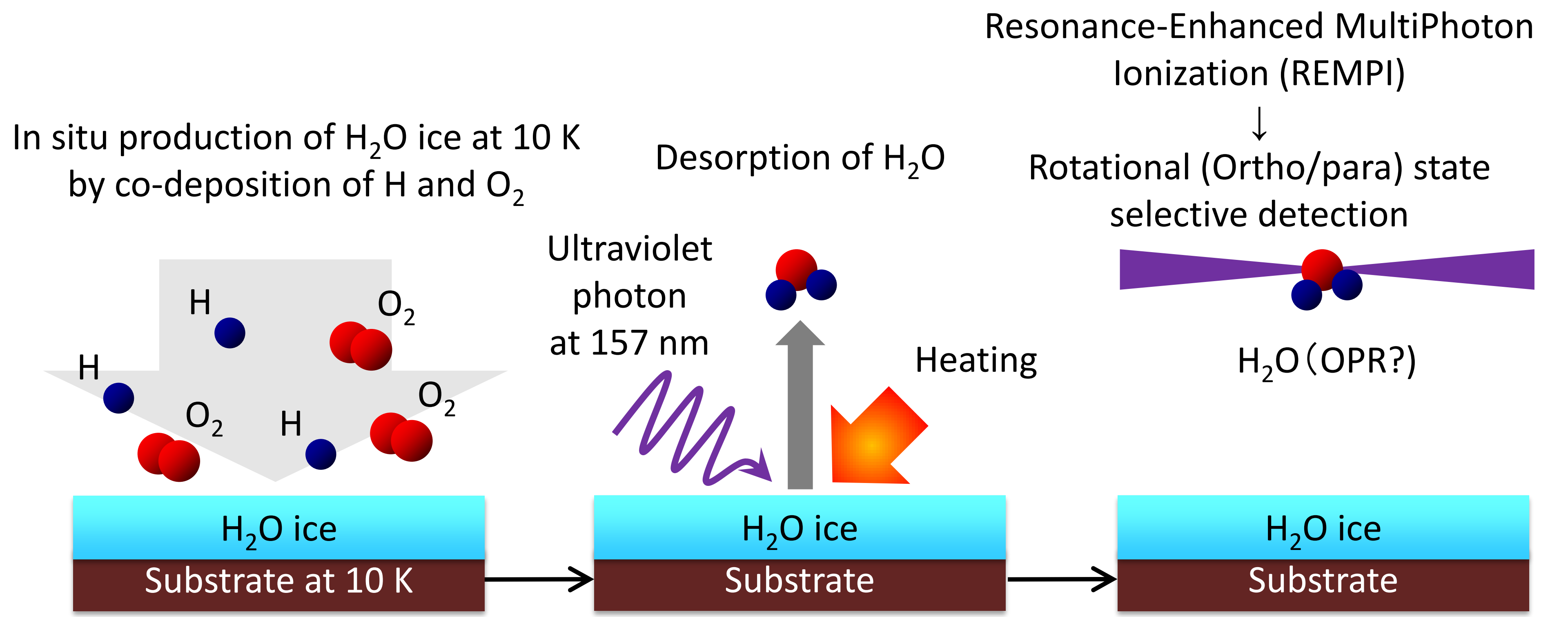
Measurement of the OPR of desorbed H_2O from water ice at 10 K

To test the relation between T_{spin} and the formation temperature,
H_2O ice was produced in situ through the hydrogenation of solid O_2 at 10 K.

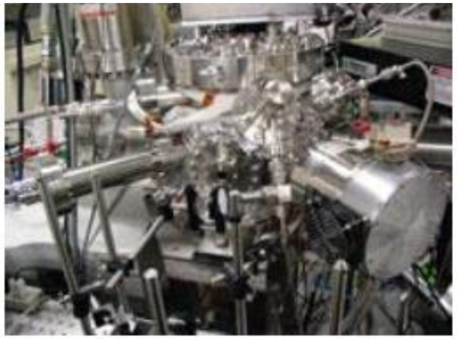
$O_2 + H \rightarrow HO_2,$	(1)
$HO_2 + H \rightarrow H_2O_2,$	(2)
$H_2O_2 + H \rightarrow H_2O + OH,$	(3)
$OH + H \rightarrow H_2O,$	(4)
$OH + H_2 \rightarrow H_2O + H.$	(5)

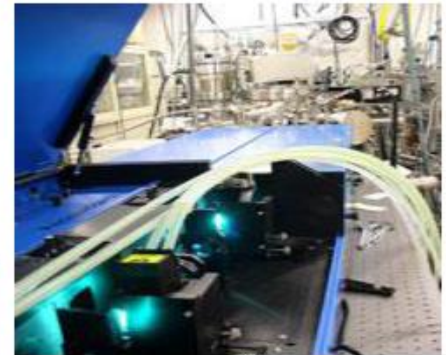
Reactions (3) – (5) are the formation processes of interstellar H_2O ice.

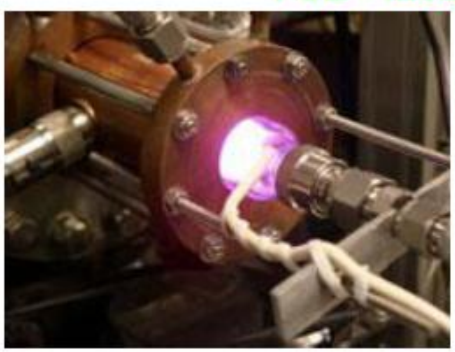
Van Dishoeck, Herbst, and Neufeld, Chem. Rev. 113, 9043 (2013).

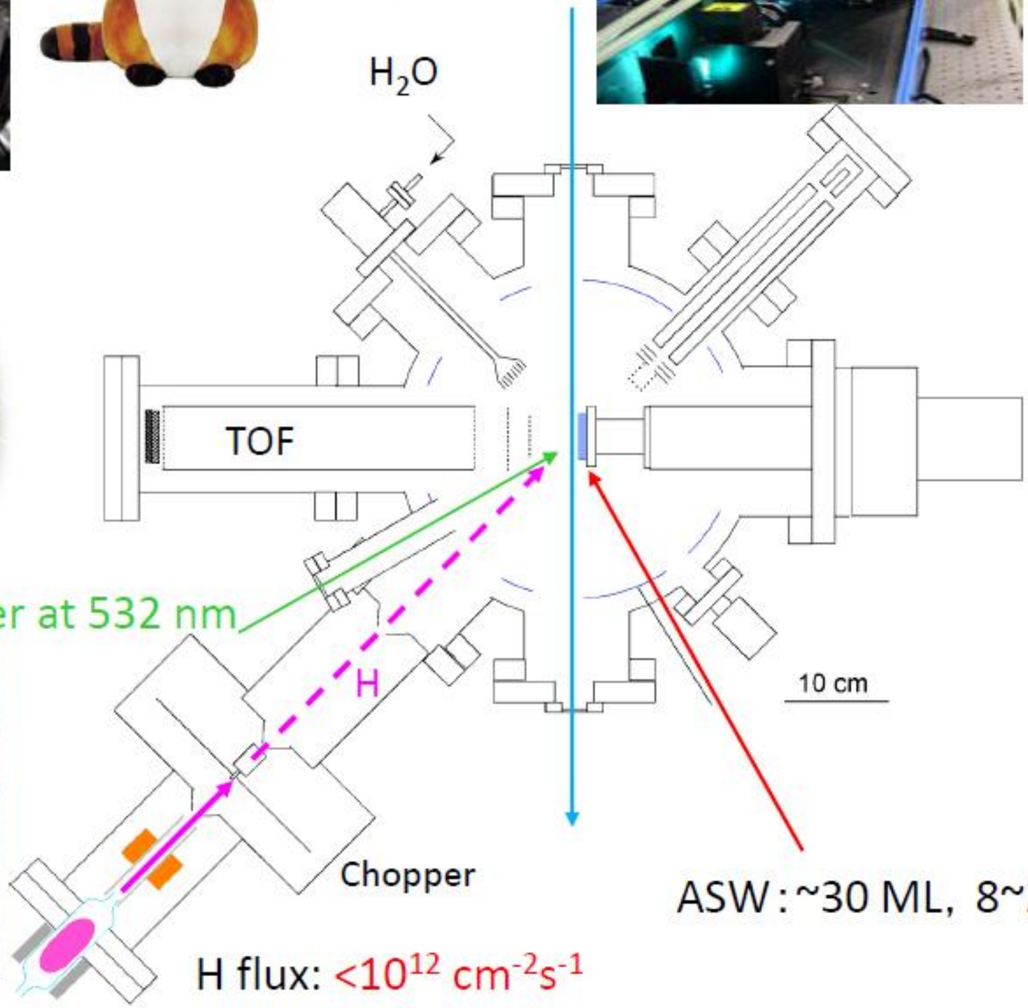


Experiment with RASCAL





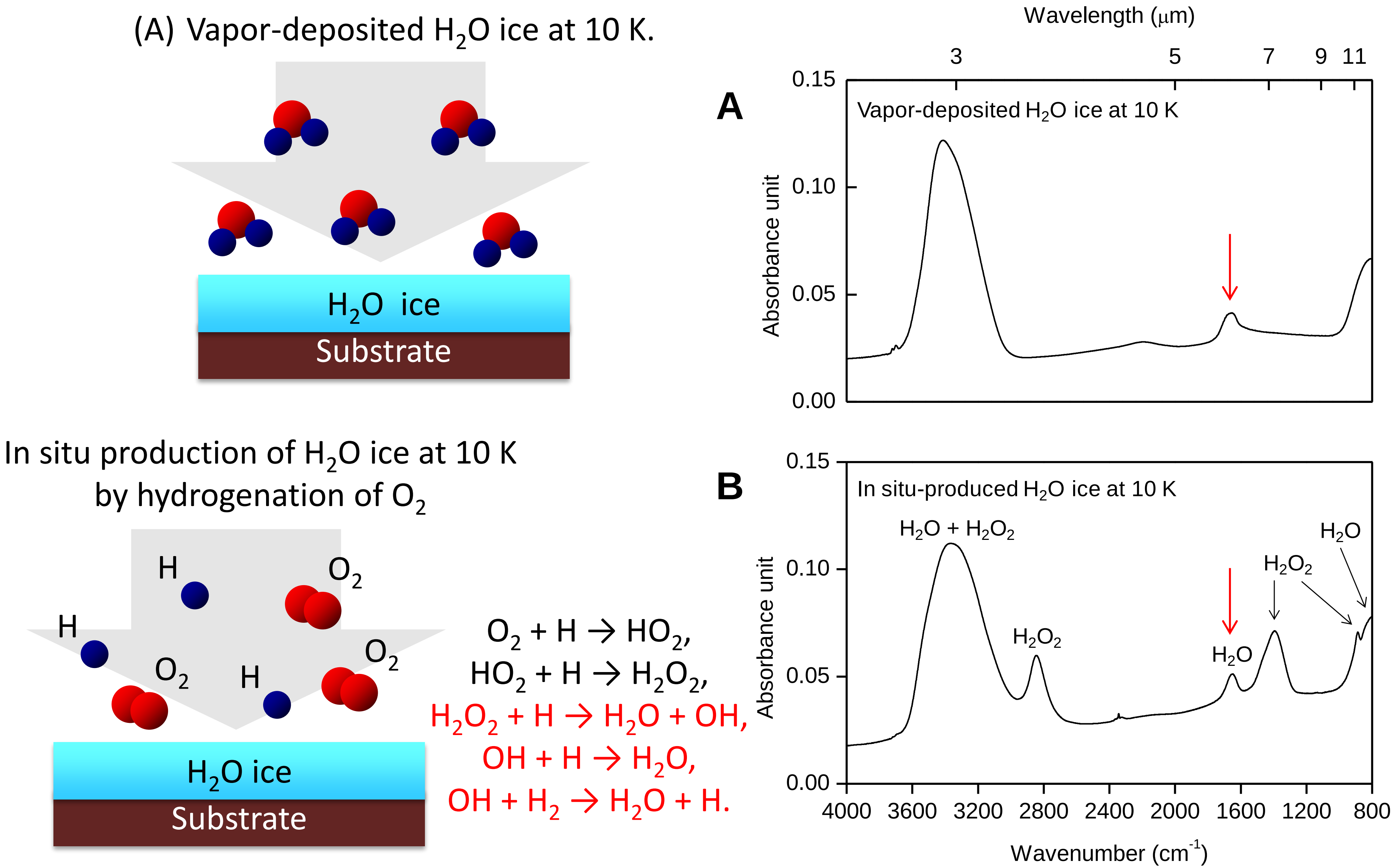




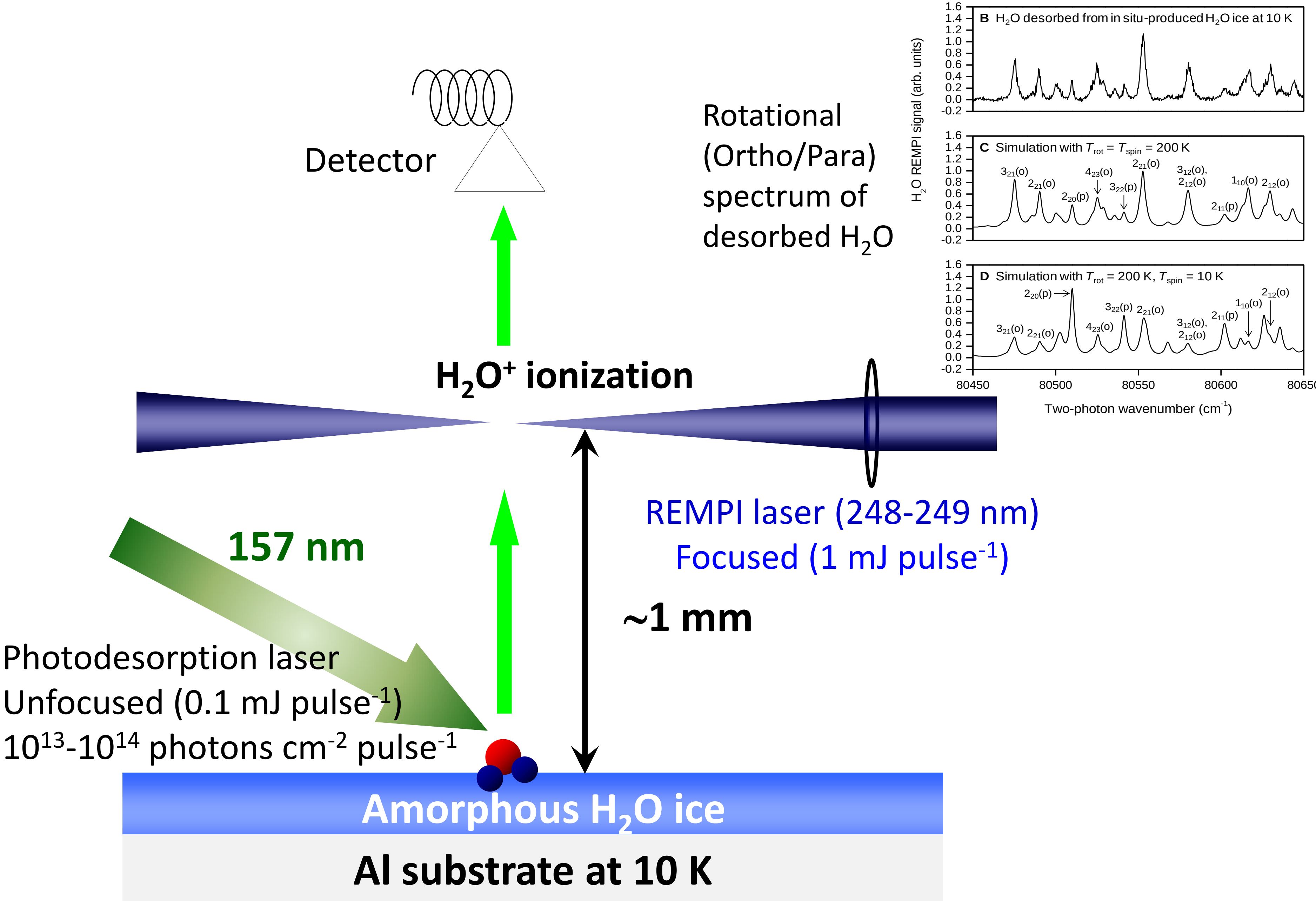
Infrared reflection–absorption spectra at 4000–800 cm^{-1}.

(A) Vapor-deposited H_2O ice at 10 K.

(B) H_2O ice produced in situ by co-deposition of O_2 with atomic H at 10 K for 420 min.

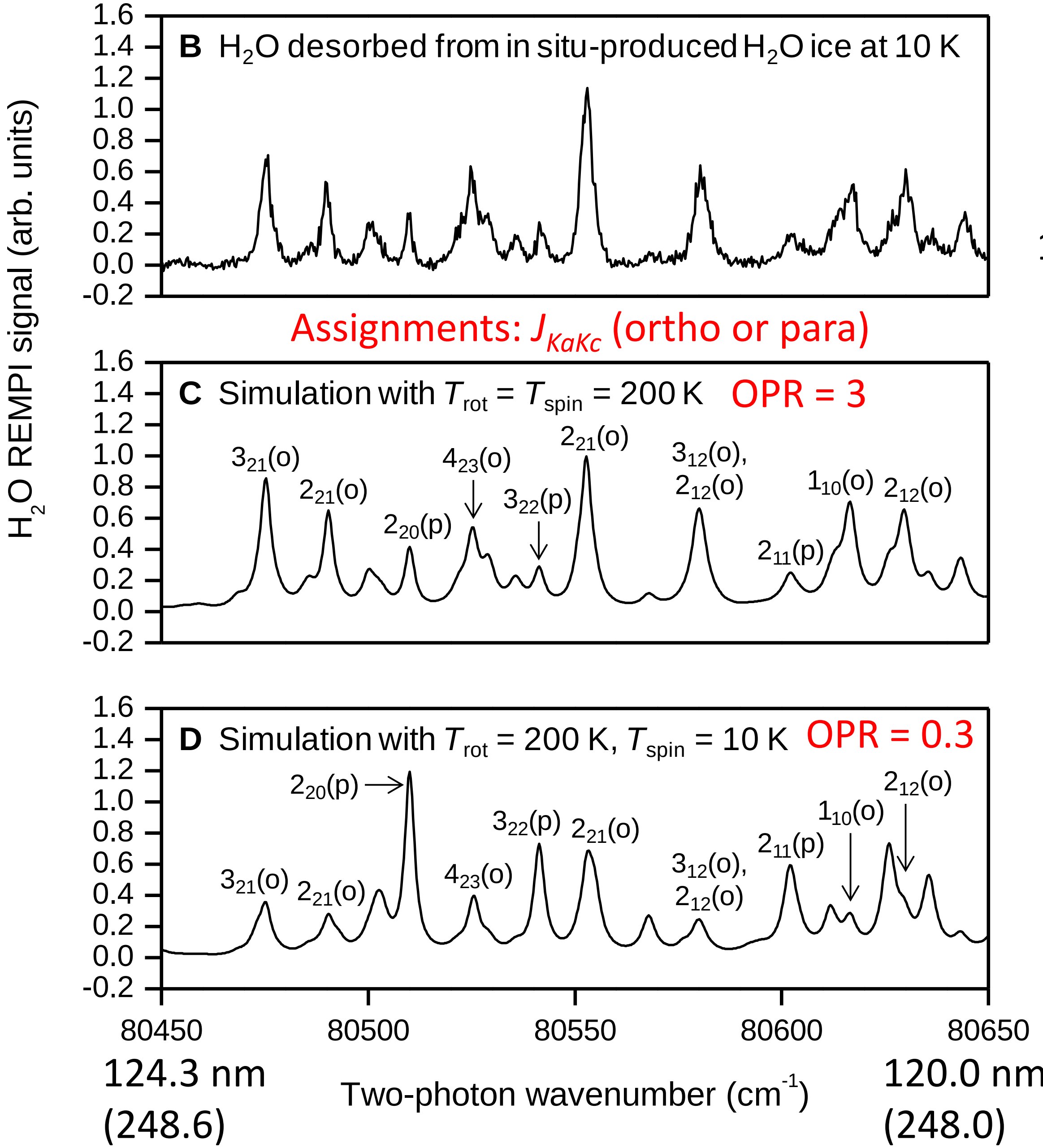


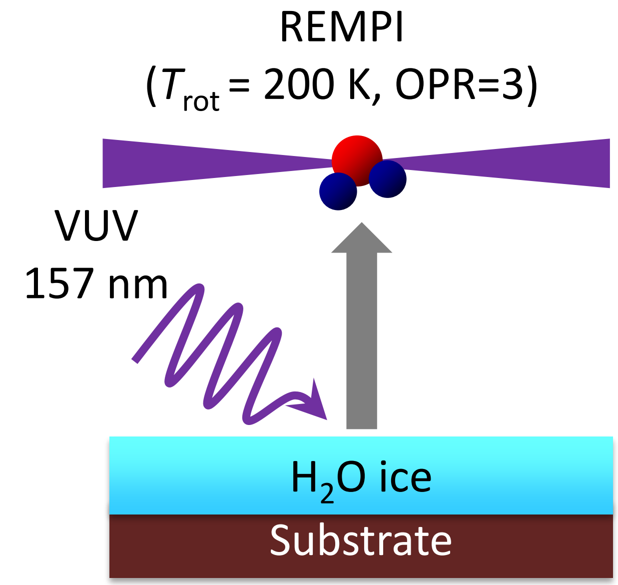
Resonance Enhanced Multi-Photon Ionization (REMPI) spectroscopy



C. M. Western, the PGOPHER program, and the H2OCX.pgo file., University of Bristol.

REMPI rotational spectrum of H_2O photodesorbed from ice at 10 K (interstellar clouds)





Stronger ortho-H_2O lines than para-H_2O lines.

Well-reproduced with OPR = 3.

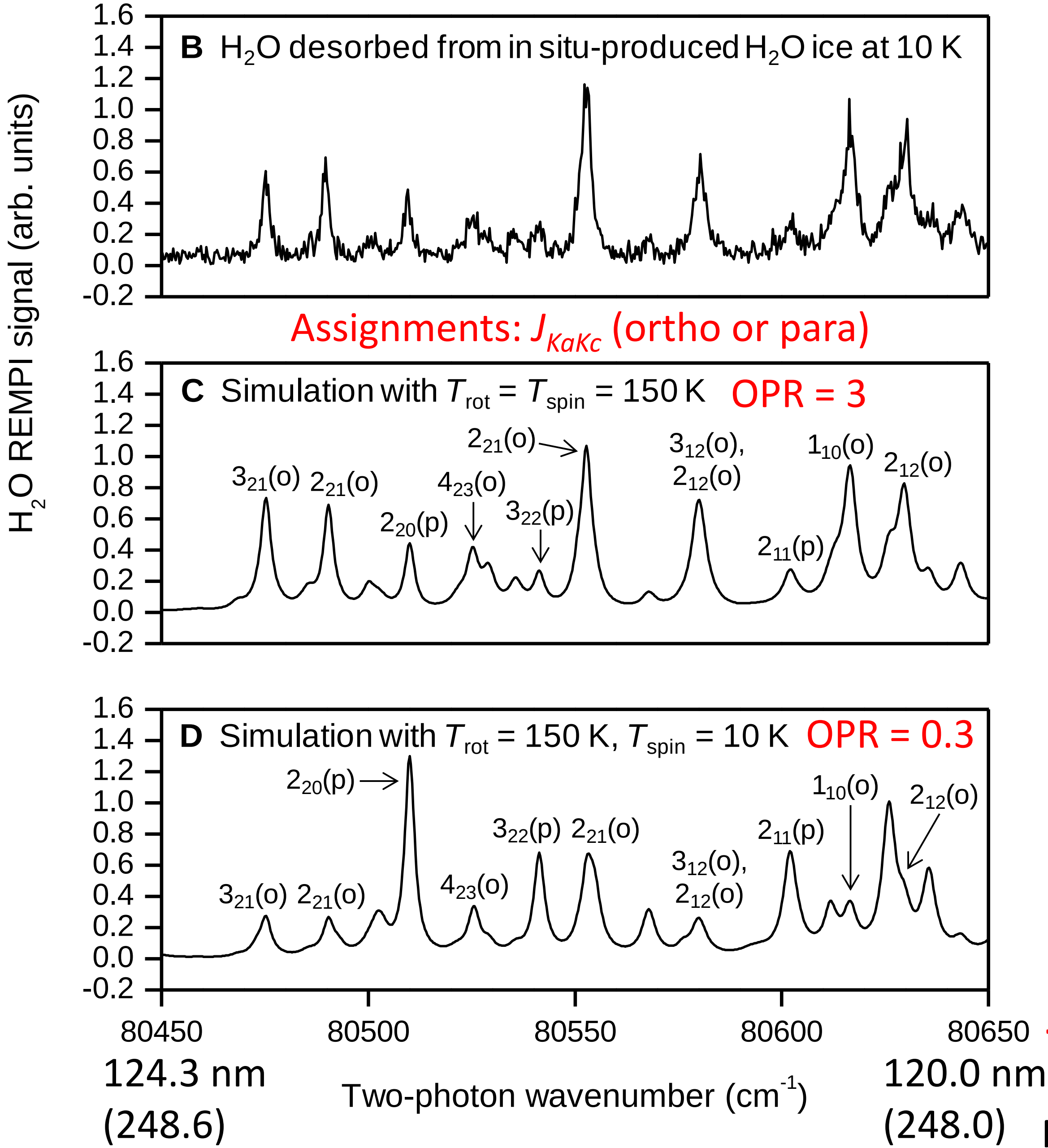
↕

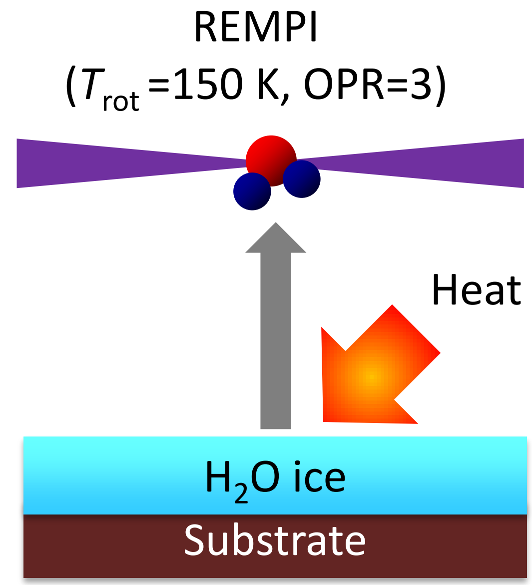
Para-H_2O signals are too strong with OPR = 0.3 (10 K).

The OPR is not related to the ice formation temperature.

Meijer et al., JCP 85, 6914 (1986).

REMPI rotational spectrum of H_2O thermally desorbed from ice at 150 K (comet coma)





Stronger ortho-H_2O lines than para-H_2O lines.

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↕

Para-H_2O signals are too strong with OPR = 0.3 (10 K).

The OPR is not related to the ice formation temperature.

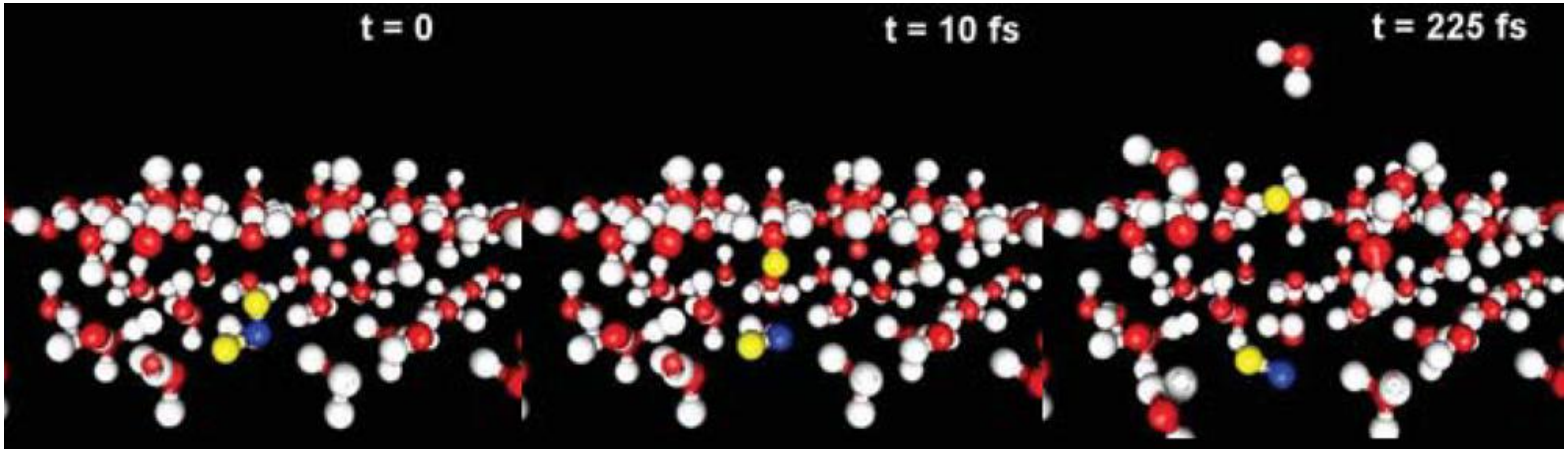
Meijer et al., JCP 85, 6914 (1986).

Photodesorption mechanism

Theory: Andersson, and van Dishoeck, Astron. Astrophys. , 491, 907 (2008).
Experiment (My PhD work): Hama et al., JCP. 132, 164508 (2010).

"kick-out" : An H_2O molecule is desorbed without intramolecular bond dissociation by the momentum transfer from an energetic H atom photodissociated from a neighboring H_2O.

$$H_2O(\text{ice}) + h\nu \rightarrow \text{hot H} + \text{OH},$$
$$\text{hot H} + H_2O(\text{ice}) \rightarrow \text{H} + H_2O$$



The T_{rot} value of 200 K ≈ calculated values for the kick-out mechanism of H_2O (T_{rot} = 300 ± 50 K).

The desorbed H_2O preserves the original OPR of the ice.
Why the statistical value (OPR=3) ?

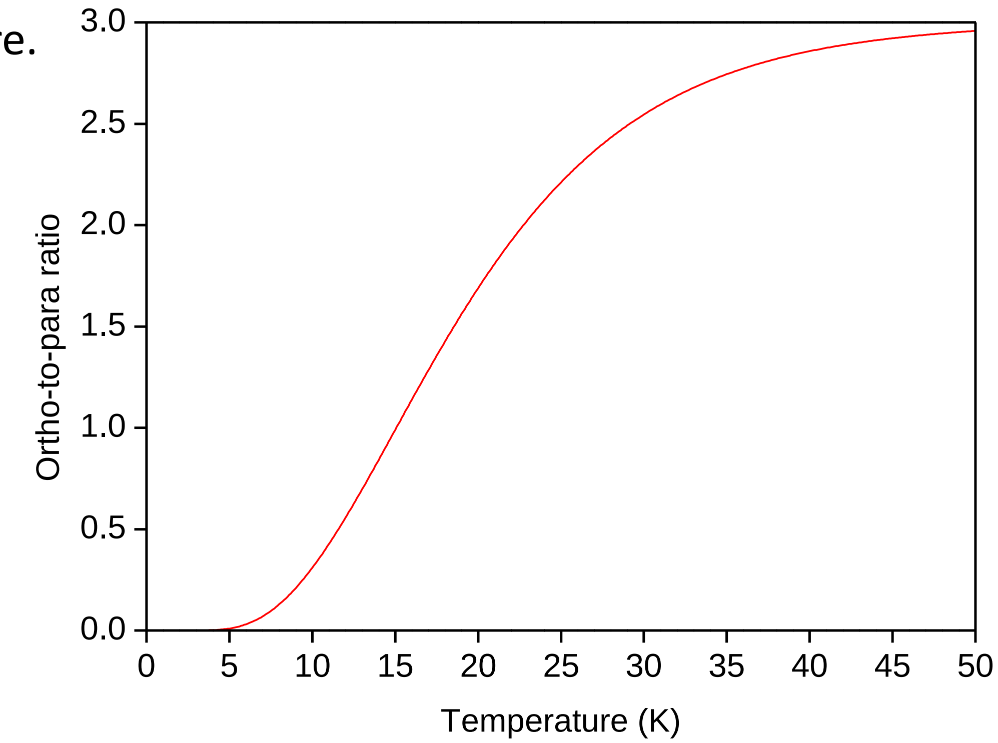
Large difference of rotational state of H_2O between the gas and solid phases.

Check the definition of spin temperature.

Spin and rotational degeneracy

$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_{\mathrm{o}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}{\sum(2J+1)\exp\left[\frac{-E_{\mathrm{p}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}$$

Rotational energy !!

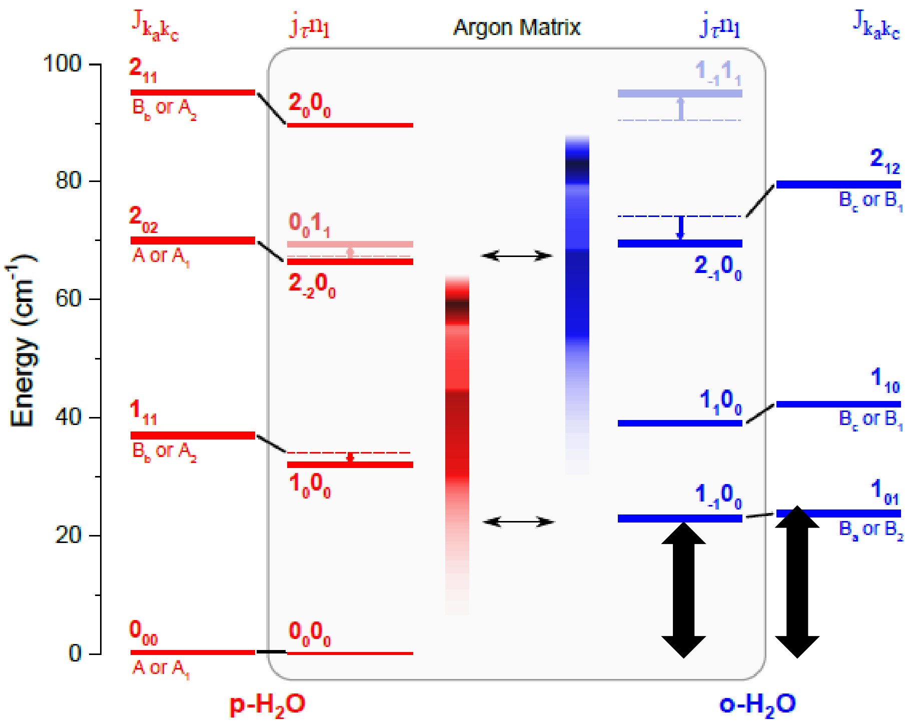


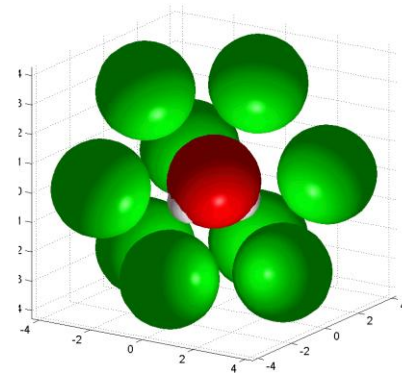
Due to "the rotational energy difference" (ΔE = 23.8 cm^{-1}, 34.2 K),
Para-H_2O (J_{KaKc} = 0_{00}) is more stable than ortho-H_2O (J_{KaKc} = 1_{01}).

However, in rotationally hindered system (i.e., solid), the "rotational" energy difference (ΔE_{rot}) generally becomes small. (perturbation theory)

The T_{spin} curve only applies to H_2O in the gas phase, i.e., when the molecules are free to rotate.

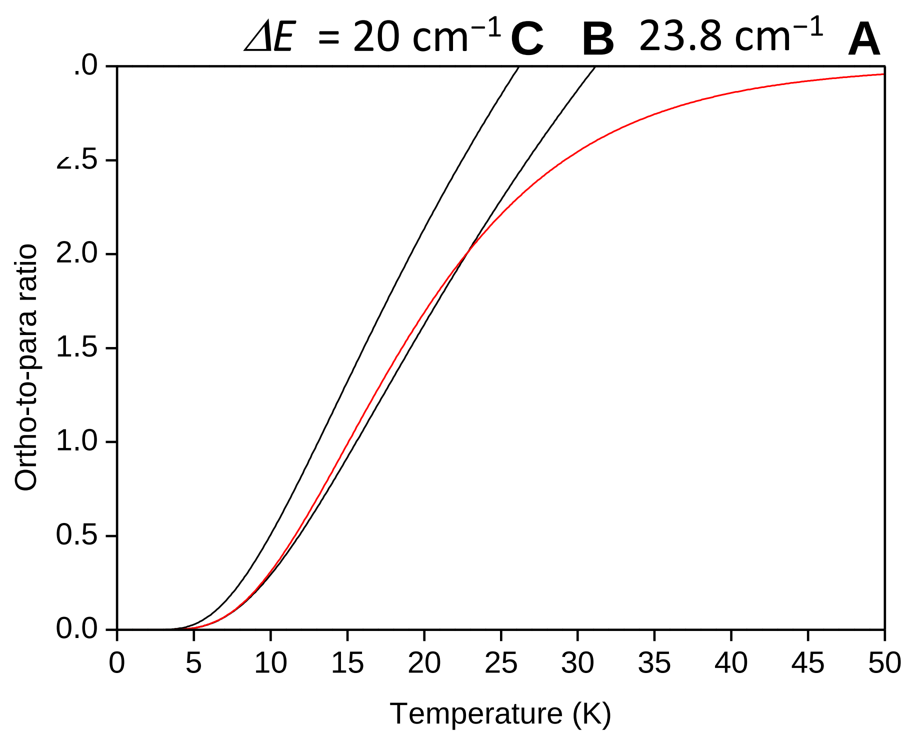
Even in a solid Ar matrix, the ΔE_{rot} becomes small ~20 cm^{-1} (23.8 cm^{-1} in the gas).





Turgeon et al., arXiv:1611.08453 (2016)
Michaut et al., Vib. Spec. 34 83 (2004)

The OPR can reach 3 at low temperature and low ΔE.



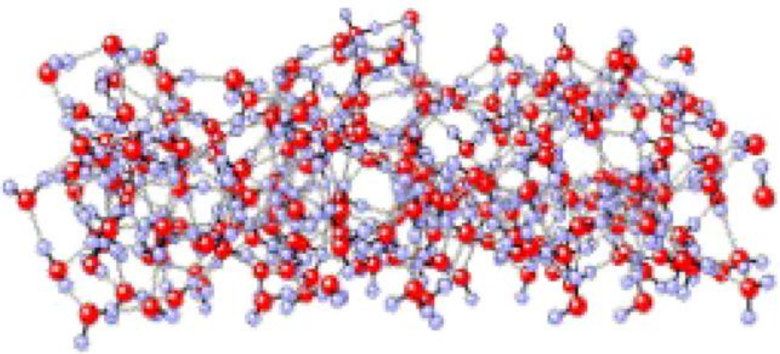
Approximated OPR-T_{spin} curve
(Only considering the lowest rotational states)

$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_o(J_{K_a,K_c})}{k_B T_{spin}}\right]}{\sum(2J+1)\exp\left[\frac{-E_p(J_{K_a,K_c})}{k_B T_{spin}}\right]}$$

$$\approx 9\exp\left(\frac{-\Delta E}{k_B T_{spin}}\right)$$

In ice, H_2O has a high barrier (6700 K) to rotation because of its hydrogen bonds.

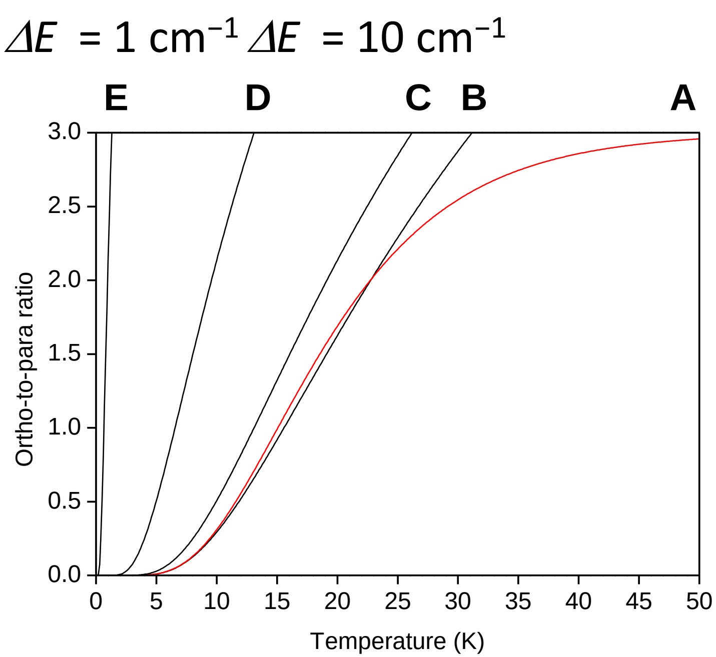
Wittebort et al., J. Am. Chem. Soc. 110, 5668–5671 (1988).

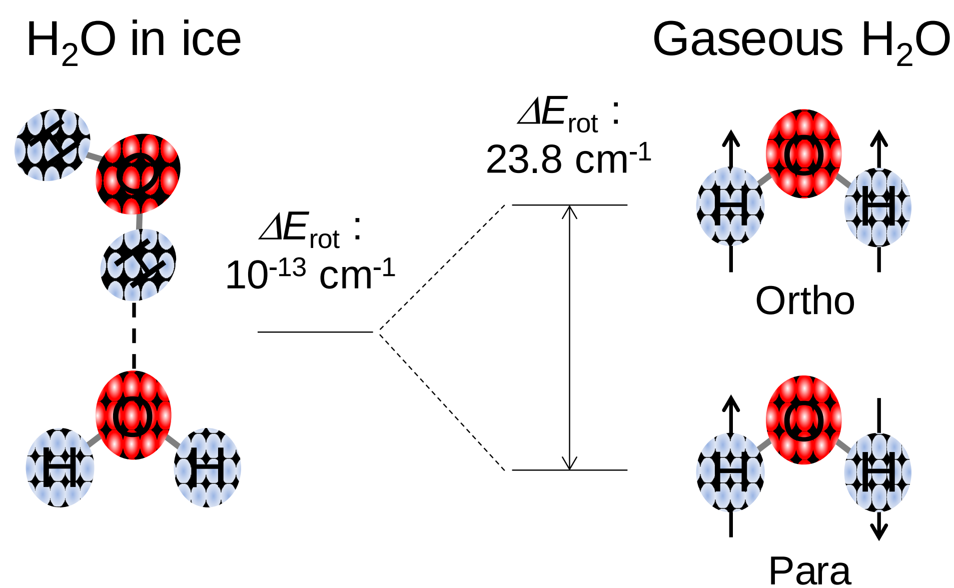


Suter et al., Chem. Phys. 2006, 326, 281

Both ortho- and para-H_2O are no longer free rotors.
→ The same energy level !!
The quenched ΔE value: 3×10^{-13} cm^{-1} (5×10^{-13} K).

Buntkowsky et al., Z. Phys. Chem. 222, 1049 (2008).





At 10 K, the thermodynamic stability of ortho- and para-H_2O should be comparable in ice.

Fast nuclear spin conversion of H_2O occurs in ice

NSC can occur by ortho-para state mixing induced by magnetic perturbation.
(e.g., paramagnetic catalysis, such as O_2)

Fillion et al., EAS Pub. Ser., (2012), 58, 307., Fukutani and Sugimoto, Prog. Surf. Sci., (2013), 88, 279.
Hama, and Watanabe, Chem. Rev. 113, 8783 (2013).

$$\Psi_- \approx \Psi_a + \frac{|\langle a|H^1|b\rangle|}{\Delta E_{ab}}\Psi_b$$

Perturbation theory (in two levels):

Ψ_- , Ψ_+ : Perturbed wave functions

Ψ_a , Ψ_b, : Unperturbed wave functions

$|\langle a|H_1|b\rangle|$: Strength of perturbation

ΔE_{ab} : Energy difference

$$\Psi_+ \approx \Psi_b - \frac{|\langle a|H^1|b\rangle|}{\Delta E_{ab}}\Psi_a$$

When $|\langle a|H_1|b\rangle| \gg \Delta E_{ab}$,
or in a degenerate system, $\Delta E_{ab} = 0$,
each perturbed state is a complete mixture of the two states.

$$\Psi_- = \frac{\Psi_b + \Psi_a}{\sqrt{2}}$$

$$\Psi_+ = \frac{\Psi_b - \Psi_a}{\sqrt{2}}$$

In ice, ortho- and para-states are strongly mixed, because of
(1) Magnetic interactions by protons of H_2O molecules in ice.
(2) Rotational quenching

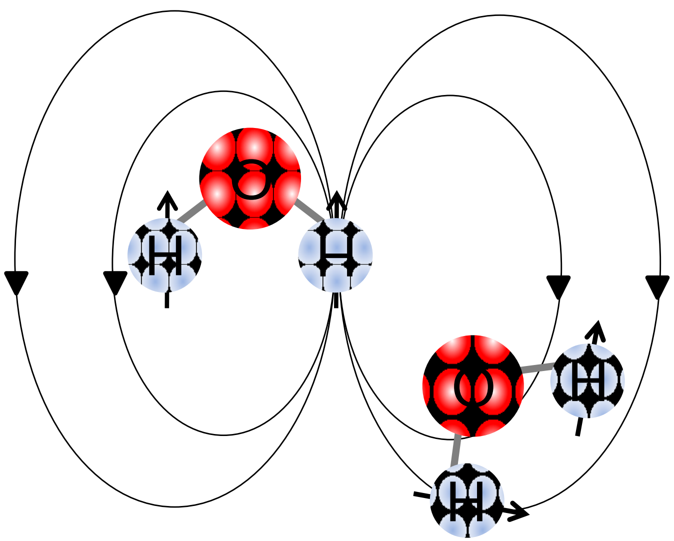
10^{-7} to 10^{-6} cm^{-1} > ΔE_{rot} (10^{-13} cm^{-1})

In ice, each proton feels magnetic fields created by all protons in ice.

Intermolecular proton–proton magnetic dipolar interactions.

10^{-7} to 10^{-6} cm^{-1}

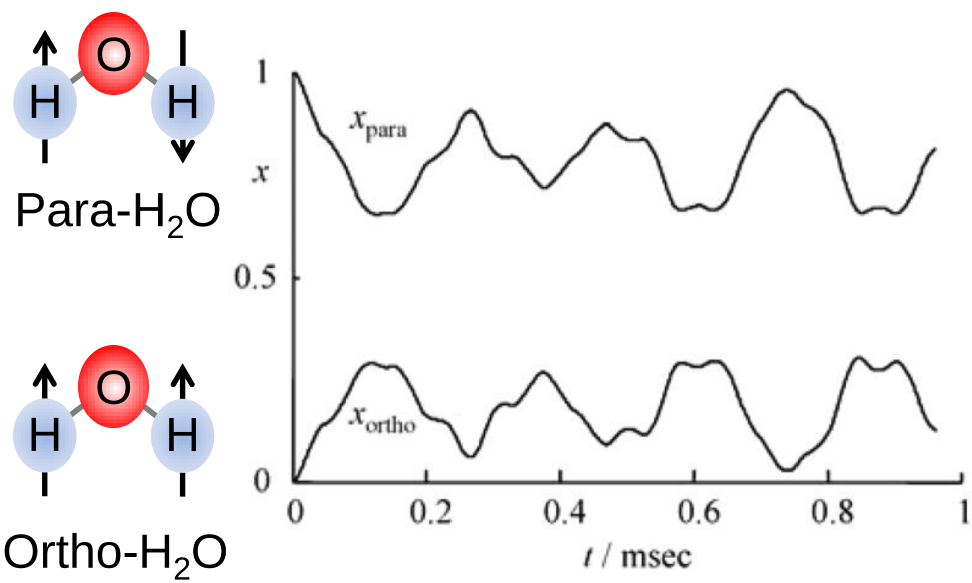
(In terms of NMR, 10^5 to 10^4 Hz)



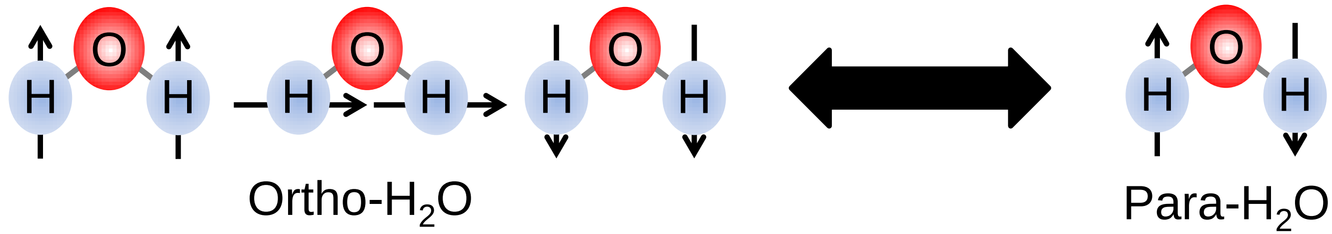
Fast nuclear spin conversion of H_2O in ice.

Limbach et al. 2006, Chem. Phys. Chem., 7, 551.
Buntkowsky et al. 2008, Z. Phys. Chem., 222, 1049.

Time scale: the inverse of the strength of the dipolar interaction, 10^{-5} to 10^{-4} s !!

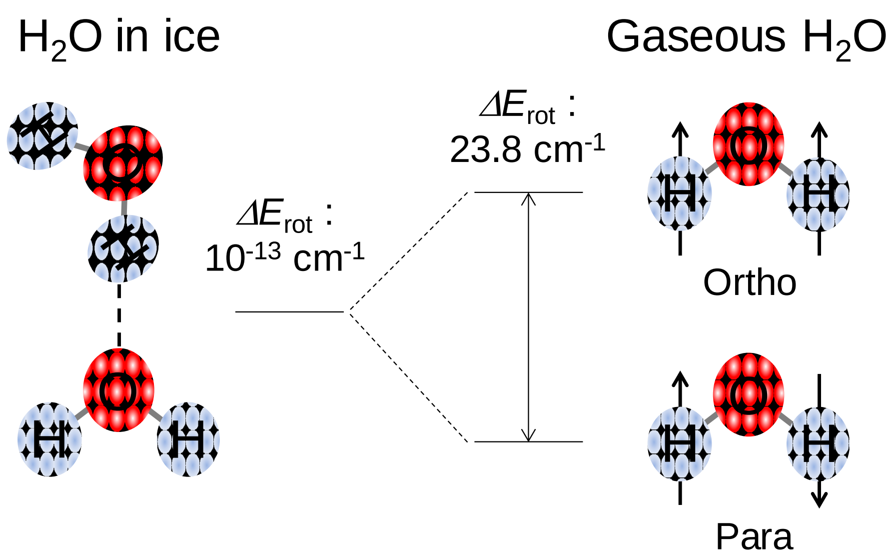


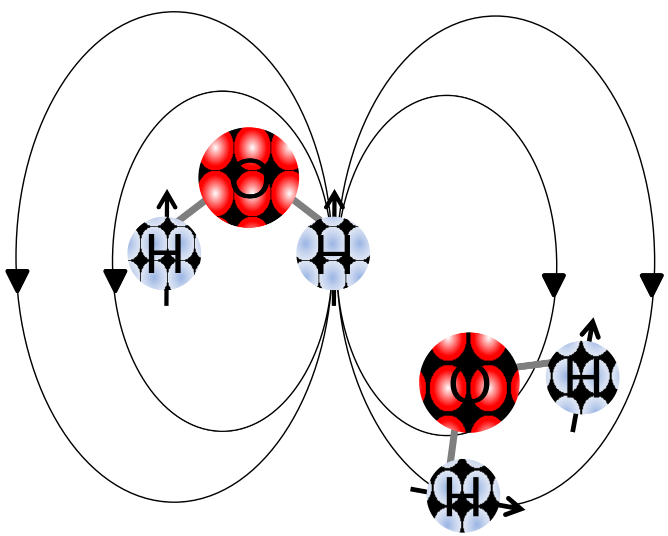
The OPR of H_2O in ice is practically in dynamic equilibrium at the statistical value of 3.



(1) Comparable thermodynamic stability of ortho- and para-H_2O by rotational quenching

(2) Fast continuous ortho-para interconversion





Note: More precisely, the ortho and para states are mixed in ice.

The origin of the anomalous OPRs of interstellar H_2O is still an open question.
The gas-phase chemistry may be important.

(1) The NSC of H_2O via its chemical reaction with ions such as H^+ or H_3O^+.

$$\text{Ortho-}H_2O\ (J_{Ka,\,Kc} = 1_{01}) + H^+ \longrightarrow \text{Para-}H_2O\ (J_{Ka,\,Kc} = 0_{00}) + H^+$$
$$\text{Ortho-}H_2O\ (J_{Ka,\,Kc} = 1_{01}) + H_3O^+ \longrightarrow H_3O^+ + \text{Para-}H_2O\ (J_{Ka,\,Kc} = 0_{00})$$

These two reactions can be endothermic at low temp., because ΔE_{rot} = 34.2 K.
Might lead to para-enrichment of H_2O.

(2) Gas-formation processes.

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$
$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$
$$H_3O^+ + e \rightarrow H_2O + H$$

H_2, H_2O^+, H_3O^+ have nuclear-spin isomers. Nuclear-spin effects should be considered.

However, accurate state-to-state rate coefficients at low temperature are unknown…
Fully quantum mechanical (including nuclear-spin effects) gas-chemistry.

Gas-phase converion: Lique et al., Int. Rev. Phys. Chem. 33, 125 (2014).
Nuclear-spin selection rules: Gerlich et al., Proc. R. Soc. A. 364, 3007 (2006).

Summary

(1) H_2O desorbed from ice at 10 K shows a statistical high-temperature OPR of 3, even when the ice is produced in situ at 10 K.

(2) **Practically, the OPR of H_2O in ice is in dynamic equilibrium at the statistical value.**
Comparable thermodynamic stability of ortho- and para-H_2O by rotational quenching
(Note: only H_2 can rotate on/in solid state)

Fast continuous ortho-para interconversion

(3) Reinterpretation of previous observations is necessary.

(4) Importance of the gas-phase chemistry.
(a) The NSC of H_2O via its reaction with H^+ or H_3O^+.
(b) Gas-formation processes.

Hama, and Watanabe, Chem. Rev. 113, 8783 (2013).
Hama et al., Science 351, 65-67 (2016).

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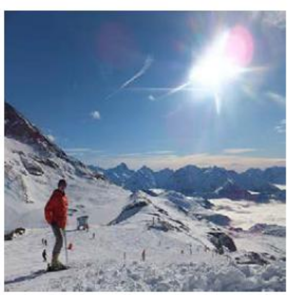

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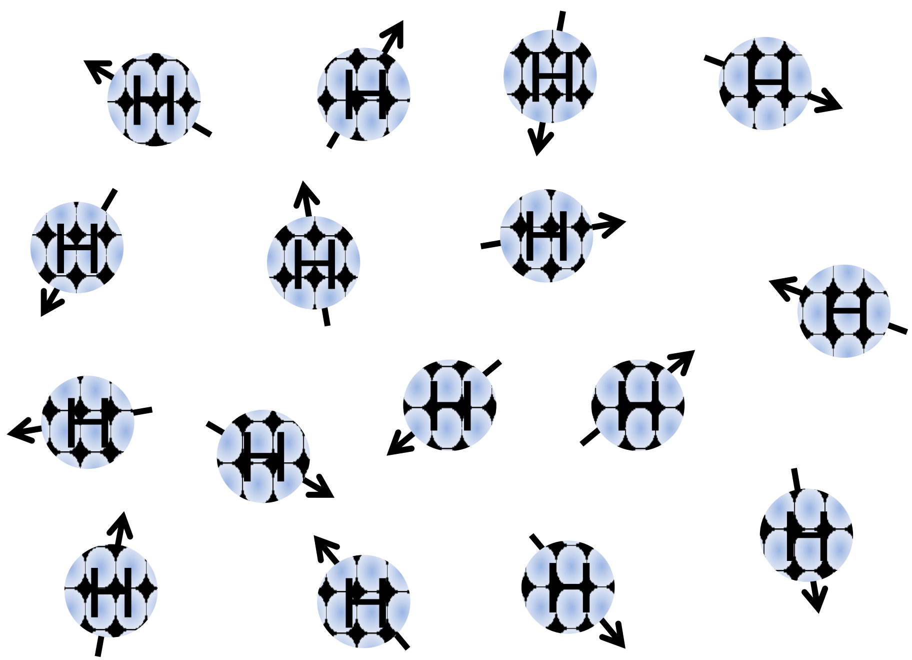
More precisely, the ortho and para states are not
the eigenstates in ice , because they are mixed.
So maybe not very good to use for ice.

However, almost impossible to calculate the spin-state in ice,
accounting for couplings of all protons.

For reference, in NMR, water ice is approximated as
“an ensemble of protons” for the use of density matrix,
rather than ortho-para mixed state.



Levitt, Spin Dynamics: 2nd Edition, Wiley.

Other photodesorption mechanisms

(1) Barrier-less recombination of H and OH on the ice surface,
A vibrationally excited H_2O molecule: H + OH → H_2O ($v > 0$). ↔ H_2O($v=0$) for kick out

H_2O ($v > 0$) is hard to detect with REMPI.
However, recombination photodesorption involves H–OH bond breaking and reformation, which would lead the OPR of the H_2O to be the statistical value of 3.

The OPR = 3 has been confirmed for H_2 formed by recombining H atoms on the ice surface, (H + H → H_2), which is the same spin system as H_2O because the two protons are coupled.

(2) Repulsive interaction of an electronically excited H_2O with its neighbors,
It also does not involve bond dissociation of the desorbed H_2O like the kick-out.

(3) Other chemical desorption processes using the excess energy of photodissociation (e.g., OH′ + H_2O → HOH′ + OH, H′ + H_2O → H′OH + H) have not been positively identified.

Even if other photochemical processes do contribute to the desorption, it is still true that the OPR of photodesorbed H_2O is non-thermal, and does not reflect the low surface temperature.

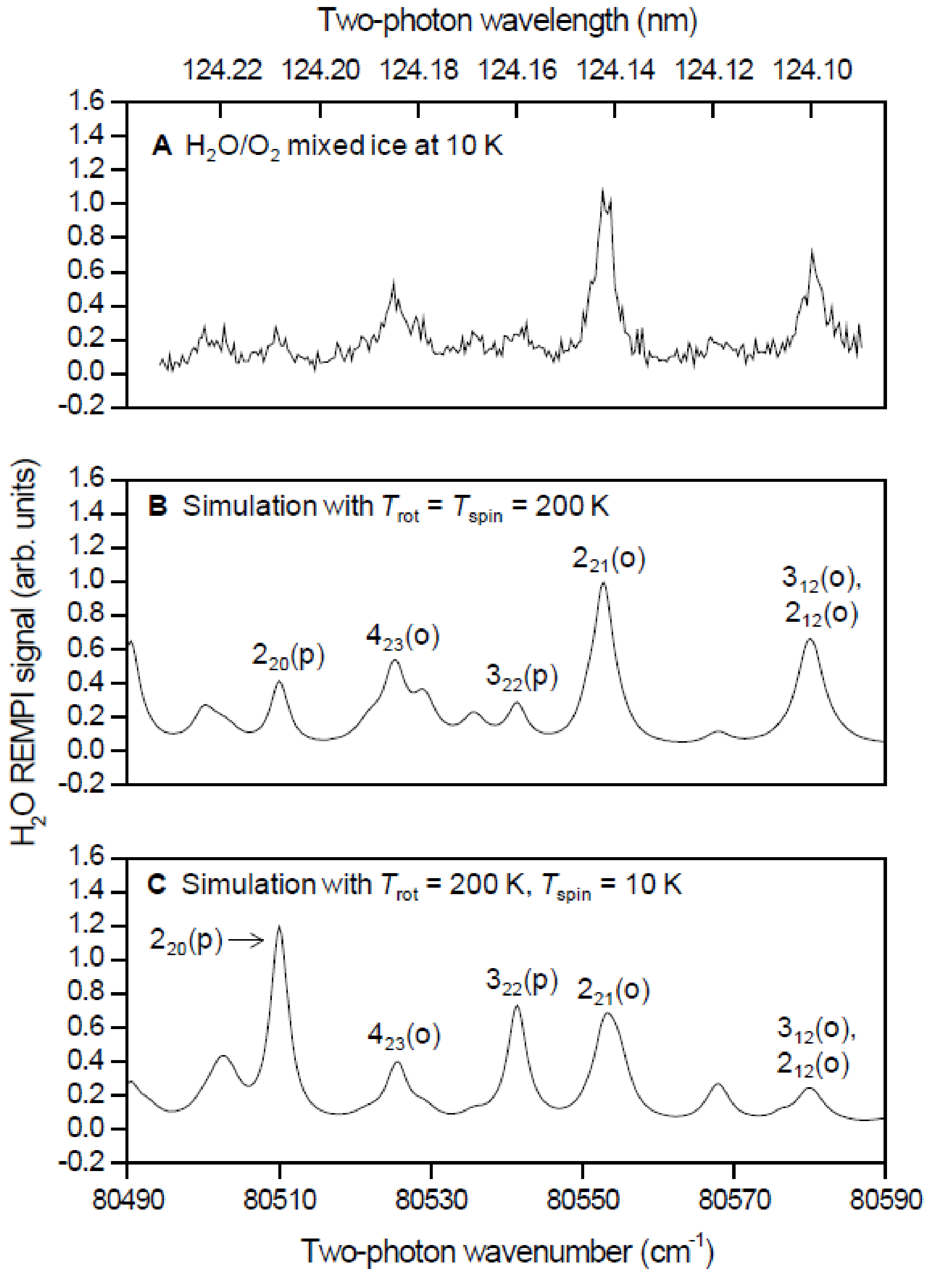
Paramagnetic catalytic effects on the NSC of H_2O during photodesorption.

REMPI spectra of photodesorbed H2O from H2O/O2 (1:1) mixed ice at 10 K.

Stronger ortho-H2O lines than para-H2O lines.

Reproduced by the simulation with Trot = Tspin = 200 K.

Although the electron magnetic moment is about −658 times larger than the proton magnetic moment, the timescale for photodesorption (femto-s) is much shorter than that for NSC through magnetic interactions (micro-sec).



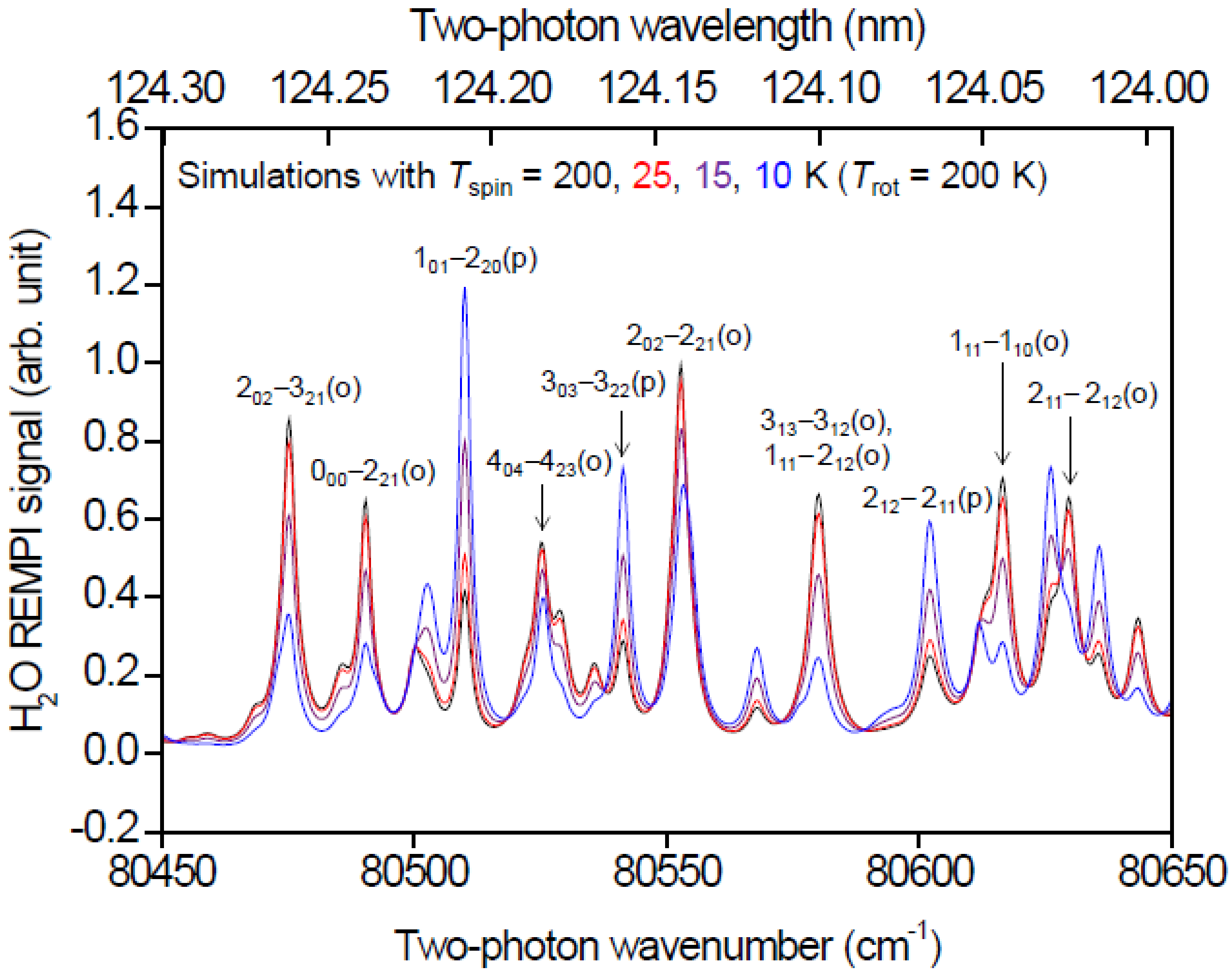
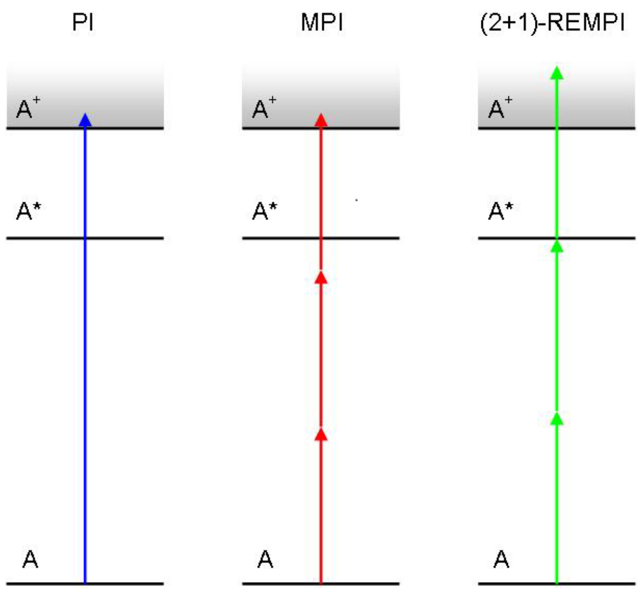


Fig. S3: REMPI spectral simulations. T_{spin} = 200 (black), 25 (red), 15 (purple), and 10 (blue) K. T_{rot} is fixed at 200 K. T_{spin} and T_{rot} represent nuclear spin and rotational temperatures, respectively. Indications ($J'_{Ka',Kc'} - J_{Ka,Kc}$) are rotational assignments of the $\widetilde{C}\ {}^1B_1(v = 0) - \widetilde{X}\ {}^1A_1\ (v = 0)$ transition in H_2O, where "o" and "p" denote ortho and para, respectively.

Resonance Enhanced Multi-Photon Ionization (REMPI) spectroscopy

Ordinary photoionization techniques cannot distinguish ortho/para H_2O (m/z = 18)

One photon ionization   Multiphoton ionization   2+1 REMPI



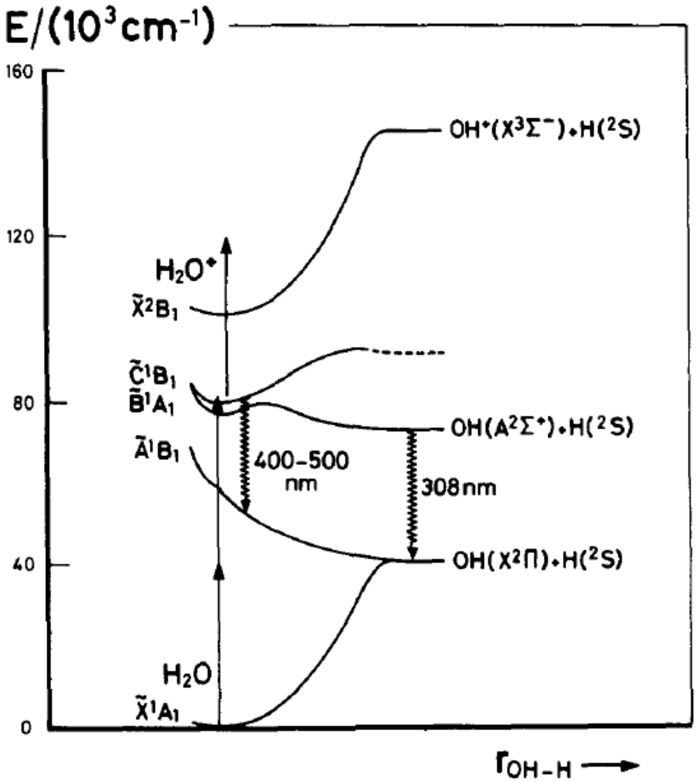


FIG. 1. Correlation diagram showing the processes involved (after Ref. 16).

In 2+1 REMPI of H_2O, 2-photon absorption excites population from the ground $X\ ^1A_1$ (v=0, $J_{Ka,Kc}$) state to the intermediate $C\ ^1B_1$(v'=0, $J'_{Ka',Kc'}$) state.

The absorption of one further photon transfers population into the ionization continuum.

Since the REMPI transition is rotationally (i.e., OPR) resolved, we can get the rotational and spin temperature of desorbed H_2O.

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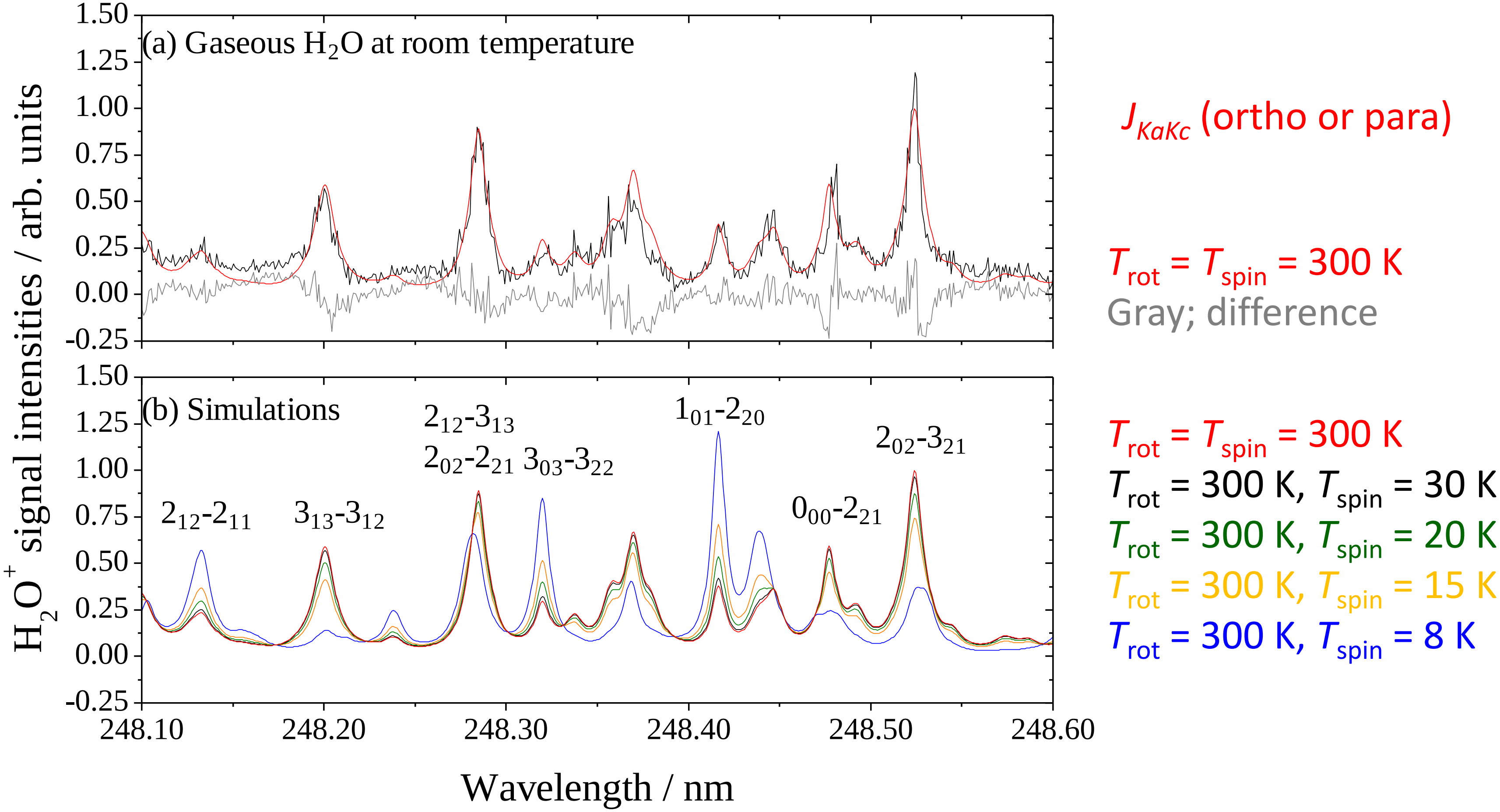
G. Meijer, J. J. ter Meulen, P. Andresen, and A. Bath, The Journal of Chemical Physics 85, 6914 (1986).

2+1 REMPI spectrum of H_2O via the $C\ ^1B_1(v=0) \leftarrow X\ ^1A_1\ (v=0)$ transition. ($J'_{Ka',Kc'} \leftarrow J_{Ka,Kc}$) are rotational assignments.



T_{rot} and T_{trans} are different.

↓

Not in thermodynamic equilibrium.

↓

No local heating (non-equilibrium process)

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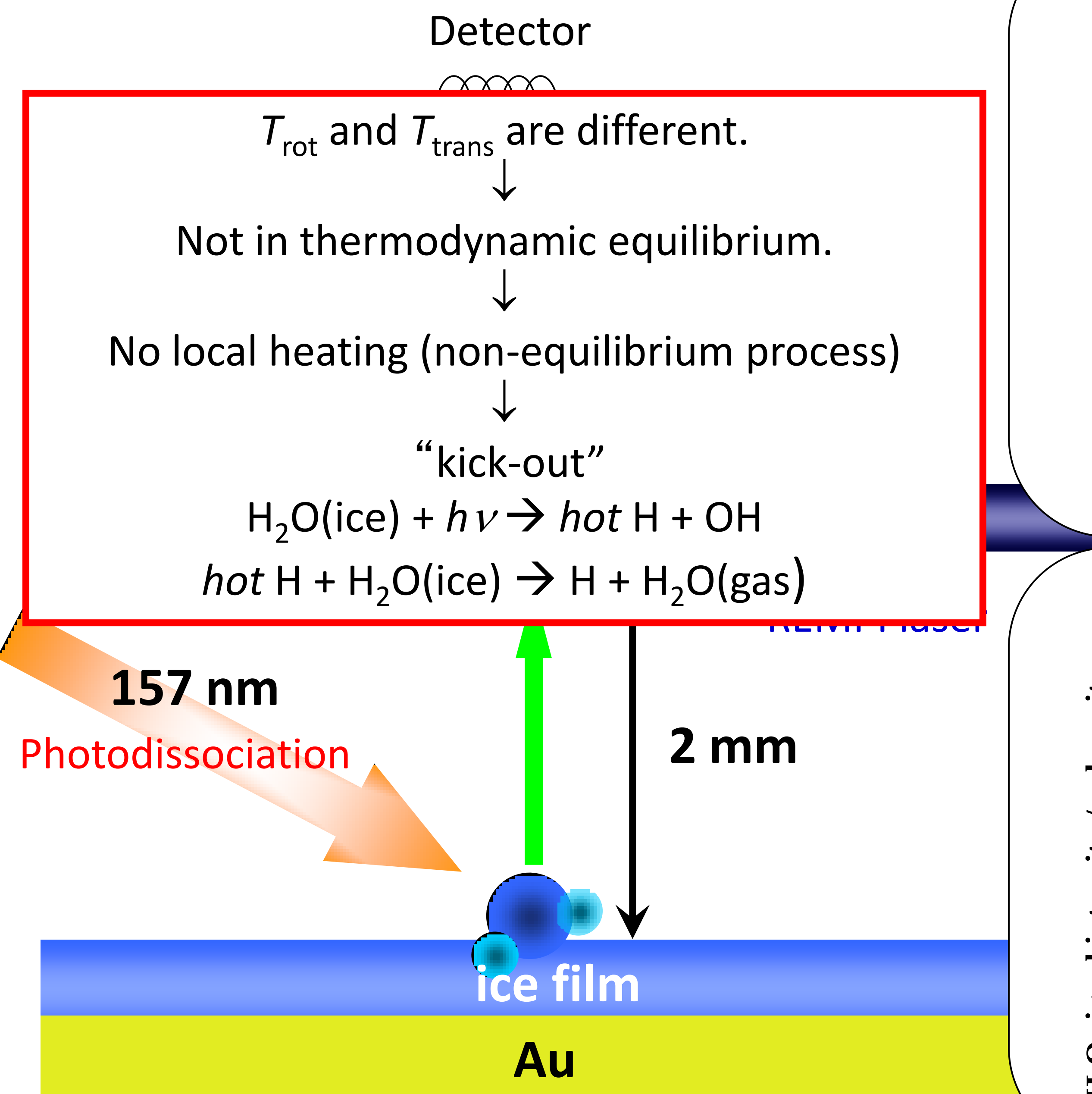
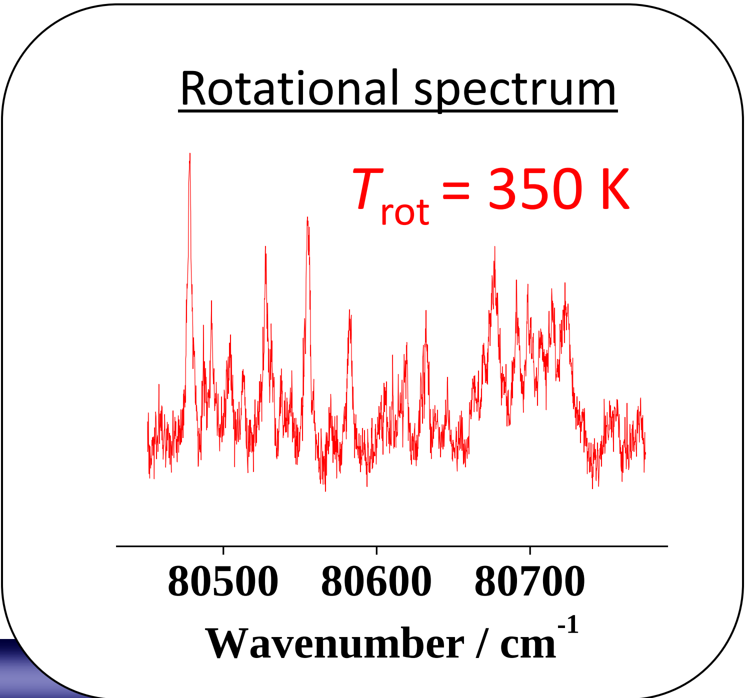
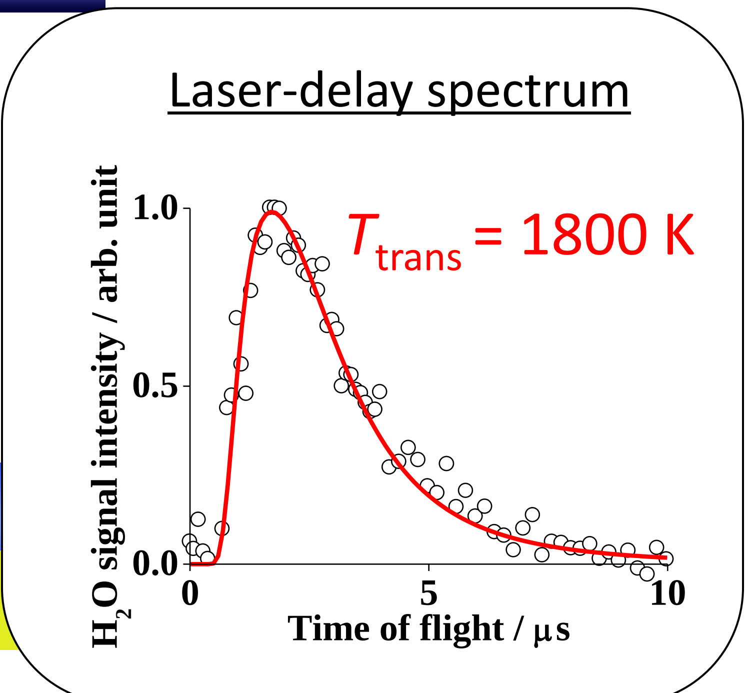
"kick-out"

H_2O(ice) + $h\nu$ → *hot* H + OH

hot H + H_2O(ice) → H + H_2O(gas)







Andersson and van Dishoeck, A. & A. **491**, 907 (2008).

“kick-out”： D_2O detection from $D_2O + H_2S$ mixed ice.

H_2S(ice) + 193 nm → hot H + SH
hot H + D_2O(ice) → H + D_2O(gas) !!

No D_2O following 193 nm irradiation of water ice.