Spin dynamics of water ice and the OPR of gaseous water desorbed from ice

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ILTS

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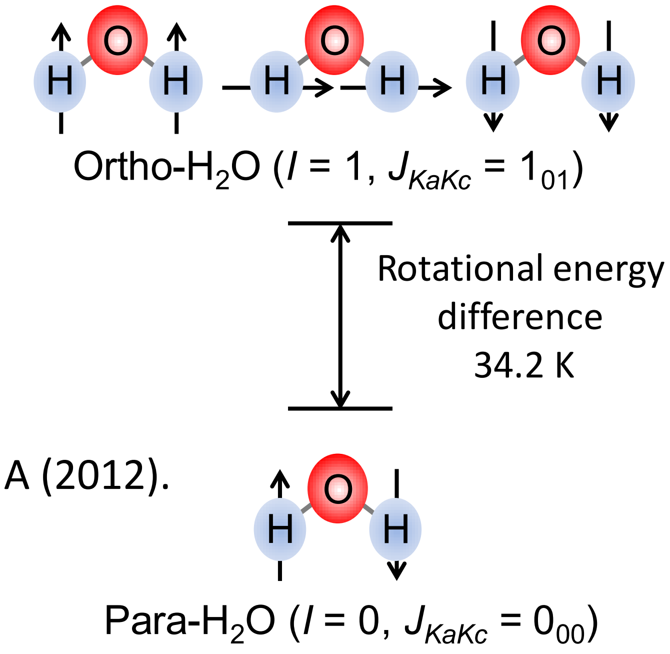
Ortho and para water

(1) Ortho-H_2O and para-H_2O must exist in different rotational states. (Proton is a fermion)



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

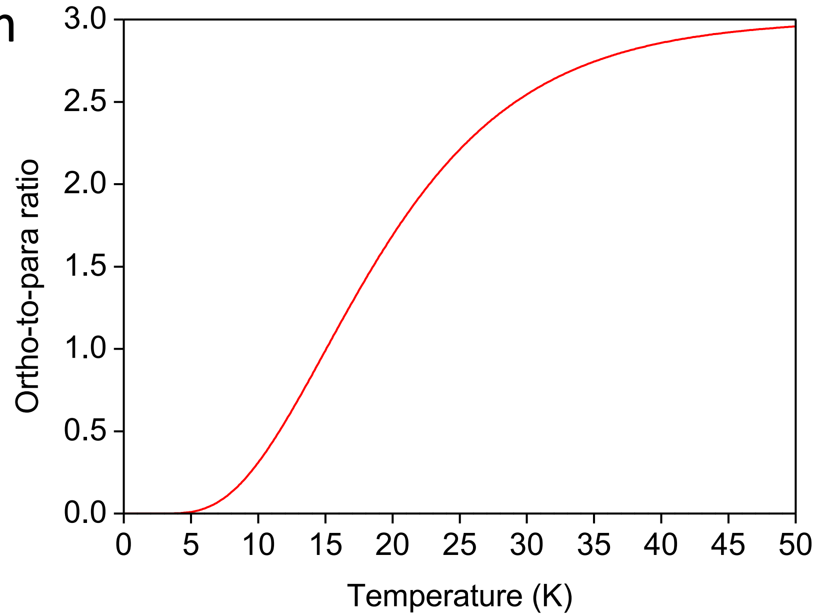
Miani and Tennyson, JCP (2004)., Cacciani et al., Phys. Rev. A (2012).

Spin temperature (T_{spin}): Ortho-to-para ratio (OPR) assuming thermodynamic equilibrium

Spin and rotational degeneracy

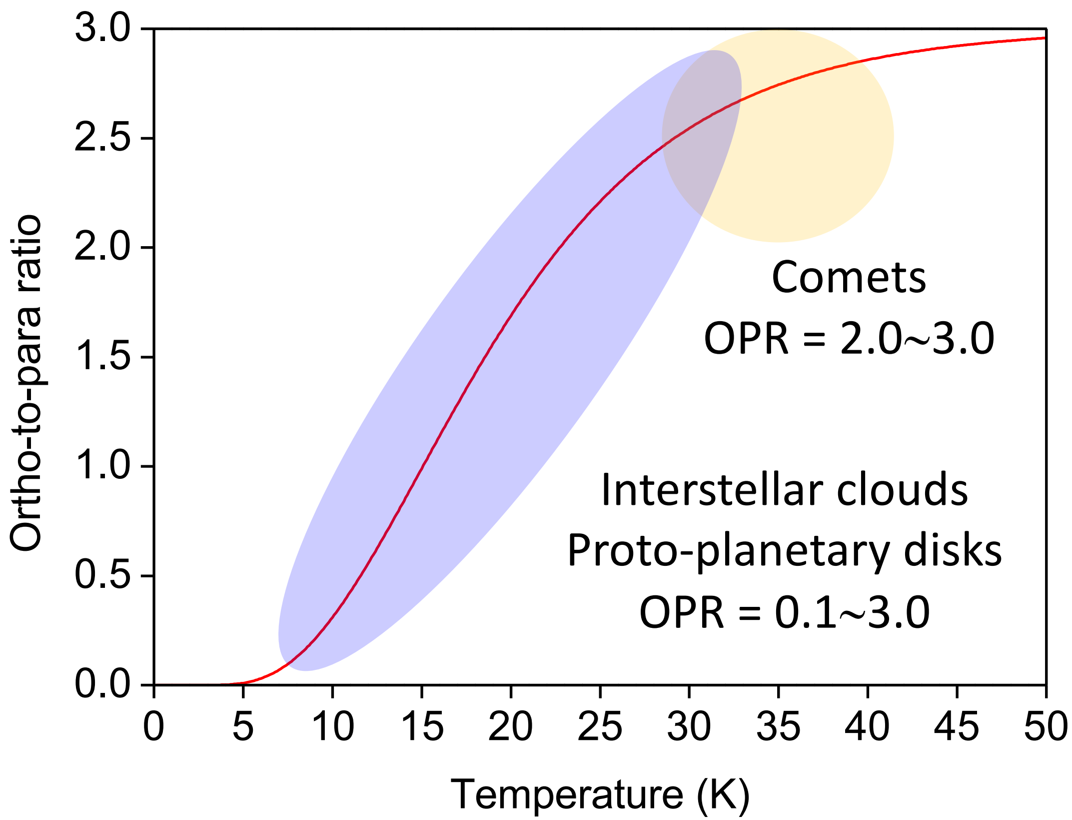
Rotational energy

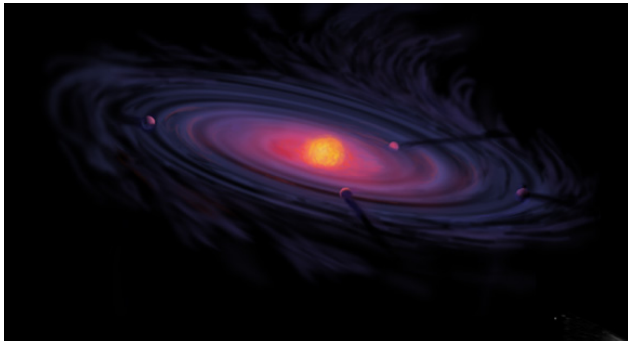
$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_\mathrm{o}(J_{K_a,K_c})}{k_\mathrm{B}T_\mathrm{spin}}\right]}{\sum(2J+1)\exp\left[\frac{-E_\mathrm{p}(J_{K_a,K_c})}{k_\mathrm{B}T_\mathrm{spin}}\right]}$$



Because of ΔE_{rot} (23.8cm^{-1}, 34.2 K), para-H_2O ($J_{Ka,\,Kc}$ = 0_{00}) enrichment below 50 K.

The anomalous OPRs of gaseous H_2O have been observed in space.





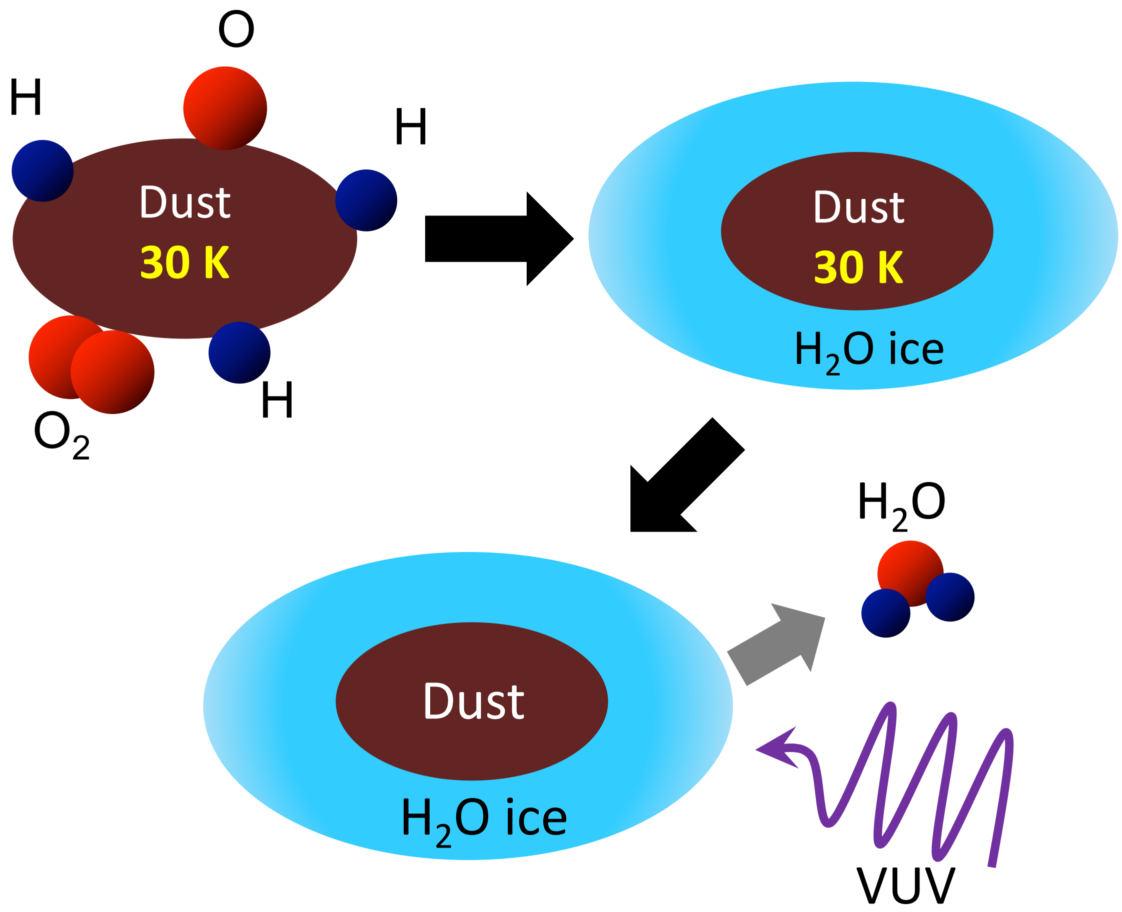
The meaning of the observed T_{spin} remains a topic of continuing debate.

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).

Hypothesis: T_{spin} reflects the formation temperature of ice?

Interstellar clouds / Proto-planetary disks

H_2O ice is formed through dust surface reactions, e.g., H atom addition to O, O_2, and OH.

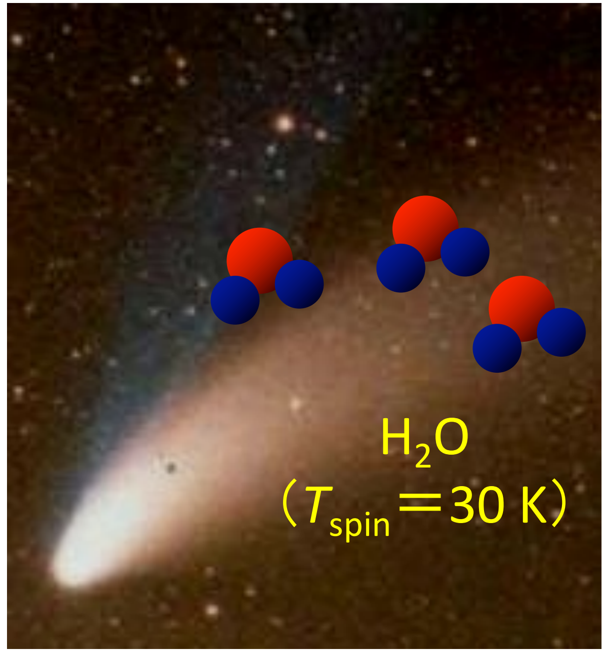


Photodesorption

Ice-covered dust (< 50 K) is too cold for the thermal desorption.

Comets

(Thermal desorption)

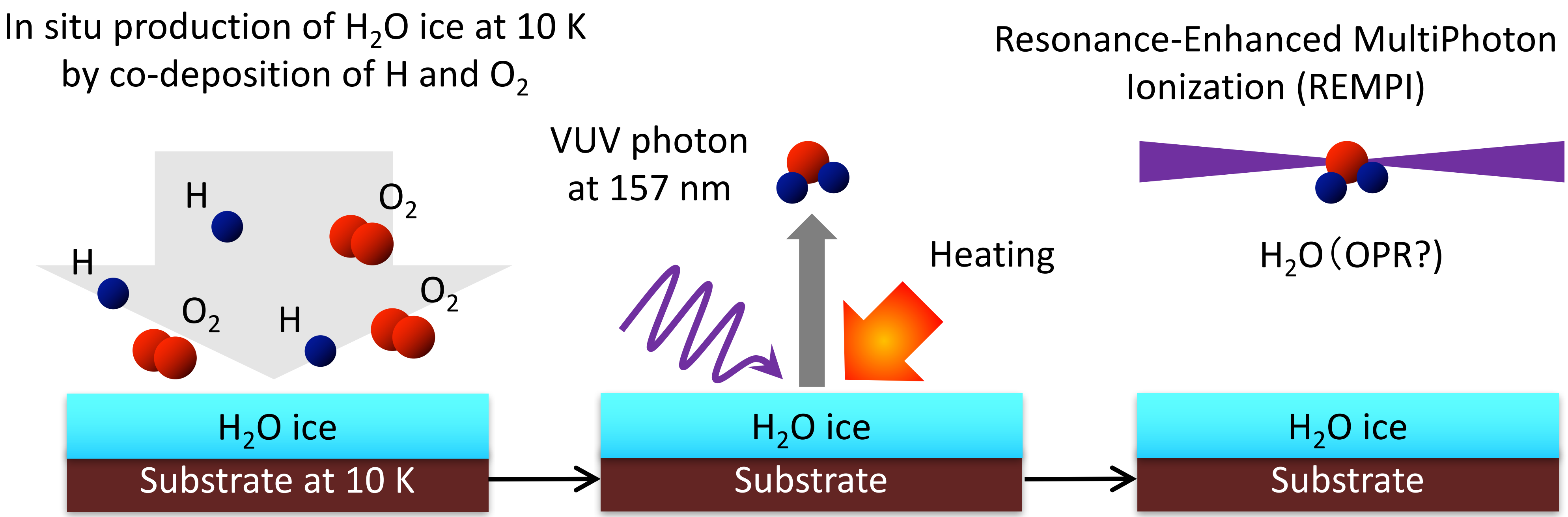


What is the real meaning of the OPR?

↓

Measurements of the OPR of H_2O desorbed from ice.

Test the relation between T_{spin} and the ice 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)

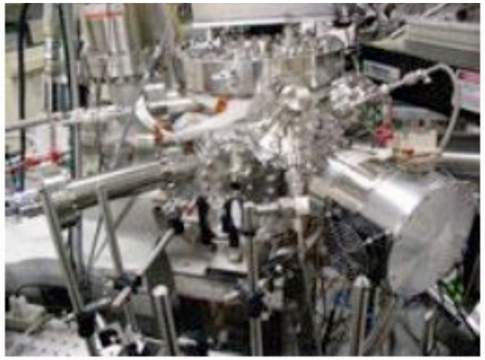
$OH + H \rightarrow H_2O$, (4)

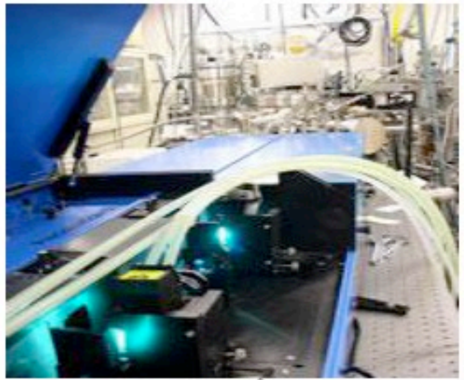
$OH + H_2 \rightarrow H_2O + H$. (5)

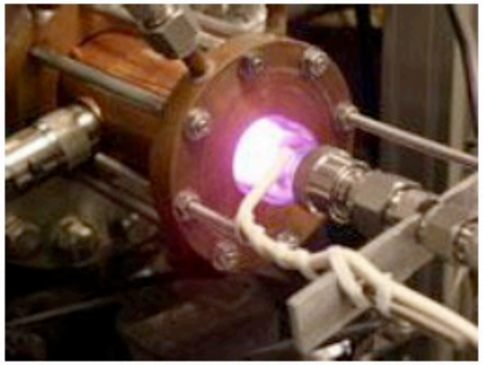
Surface reactions (3) – (5) are the formation processes of interstellar H_2O ice.

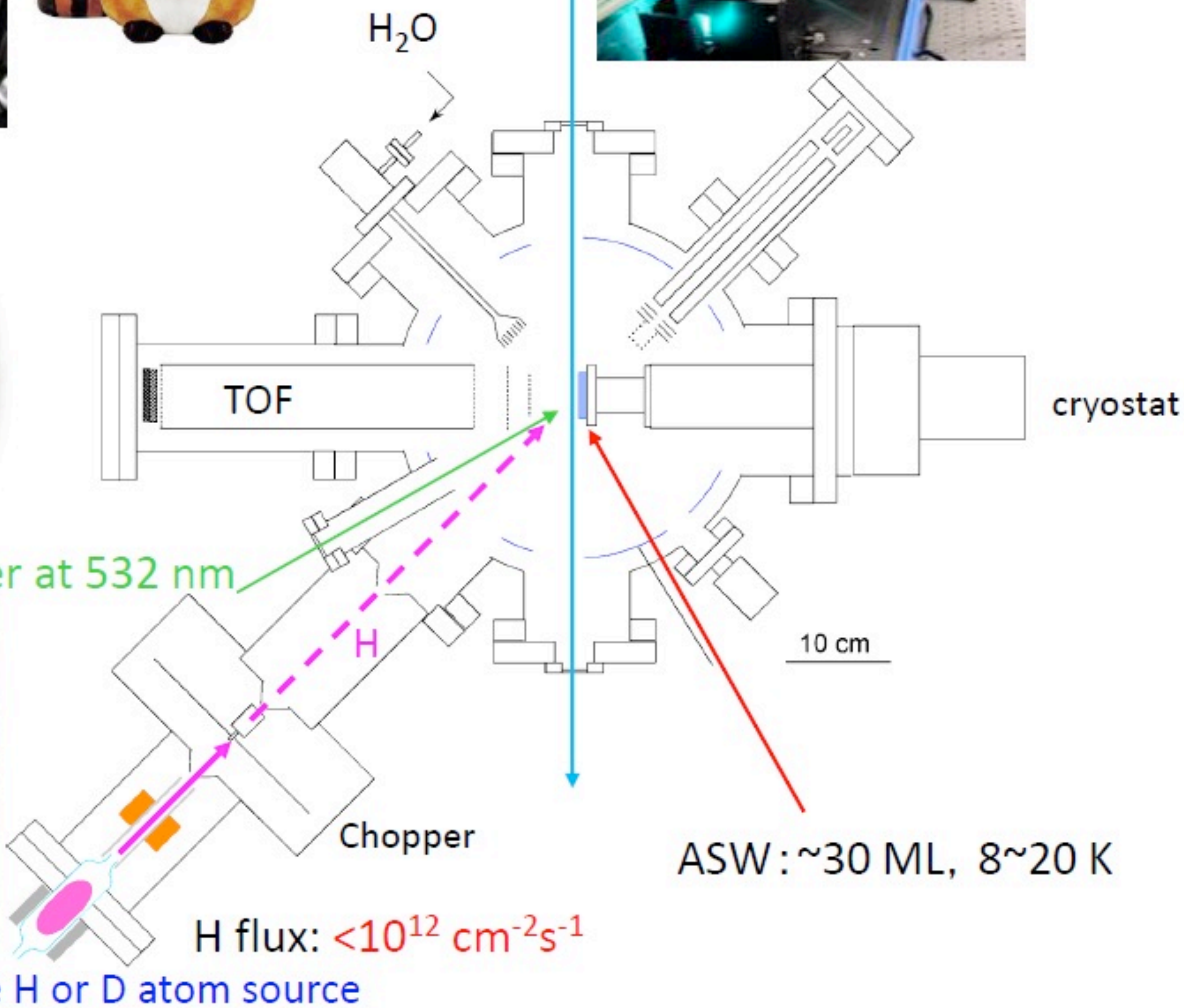
Van Dishoeck, Herbst, and Neufeld, Chem. Rev. 113, 9043 (2013).
Hama, and Watanabe, Chem. Rev. 113, 8783 (2013).

Experiment with RASCAL





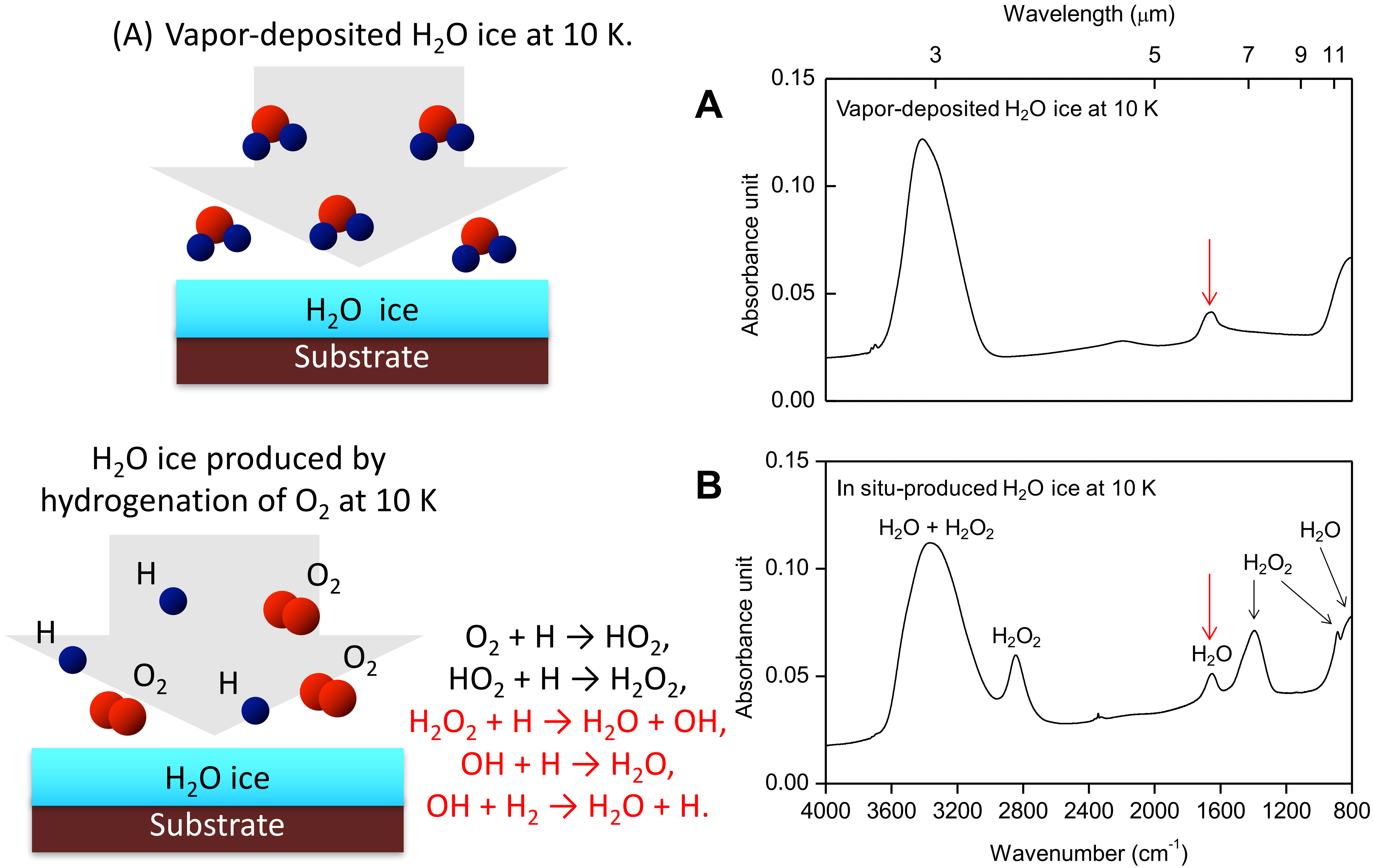


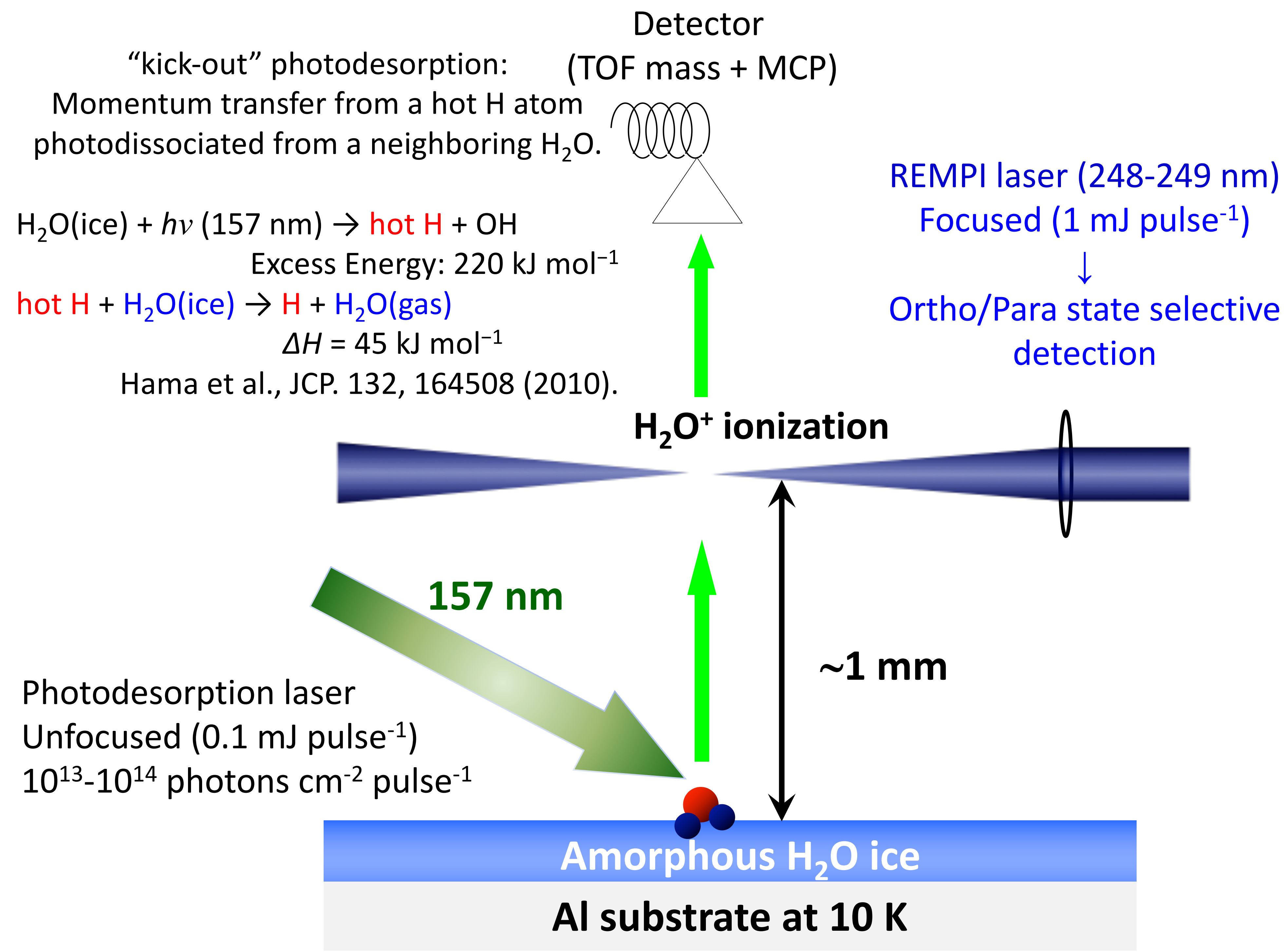


Infrared reflection–absorption spectra at 4000–800 cm^{-1}.

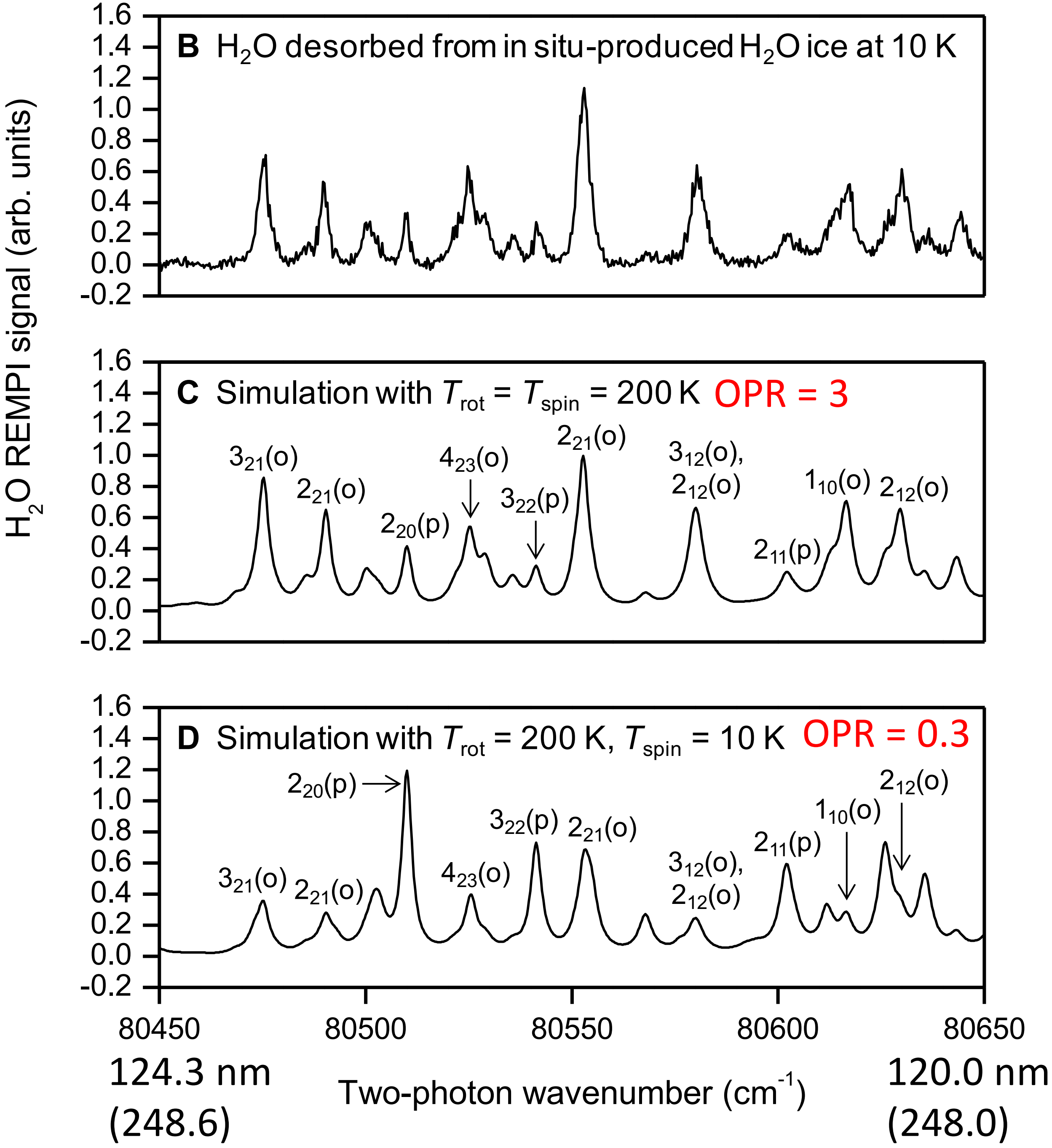
(A) Vapor-deposited H_2O ice at 10 K.

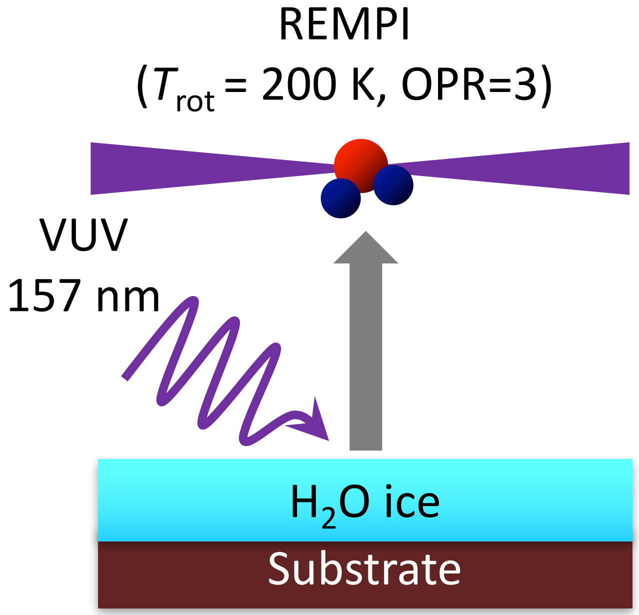
(B) H_2O ice produced by co-deposition of O_2 with atomic H at 10 K for 420 min.




Detector
(TOF mass + MCP)
"kick-out" photodesorption:
Momentum transfer from a hot H atom
photodissociated from a neighboring H_2O.
H_2O(ice) + $h\nu$ (157 nm) → hot H + OH
Excess Energy: 220 kJ mol^{-1}
hot H + H_2O(ice) → H + H_2O(gas)
ΔH = 45 kJ mol^{-1}
Hama et al., JCP. 132, 164508 (2010).
REMPI laser (248-249 nm)
Focused (1 mJ pulse^{-1})
↓
Ortho/Para state selective
detection
H_2O^+ ionization
157 nm
~1 mm
Photodesorption laser
Unfocused (0.1 mJ pulse^{-1})
10^{13}-10^{14} photons cm^{-2} pulse^{-1}
Amorphous H_2O ice
Al substrate at 10 K

REMPI rotational spectrum of H_2O photodesorbed from ice at 10 K





Assignments: J_{KaKc} (ortho or para)

Stronger ortho-H_2O lines than para-H_2O lines.

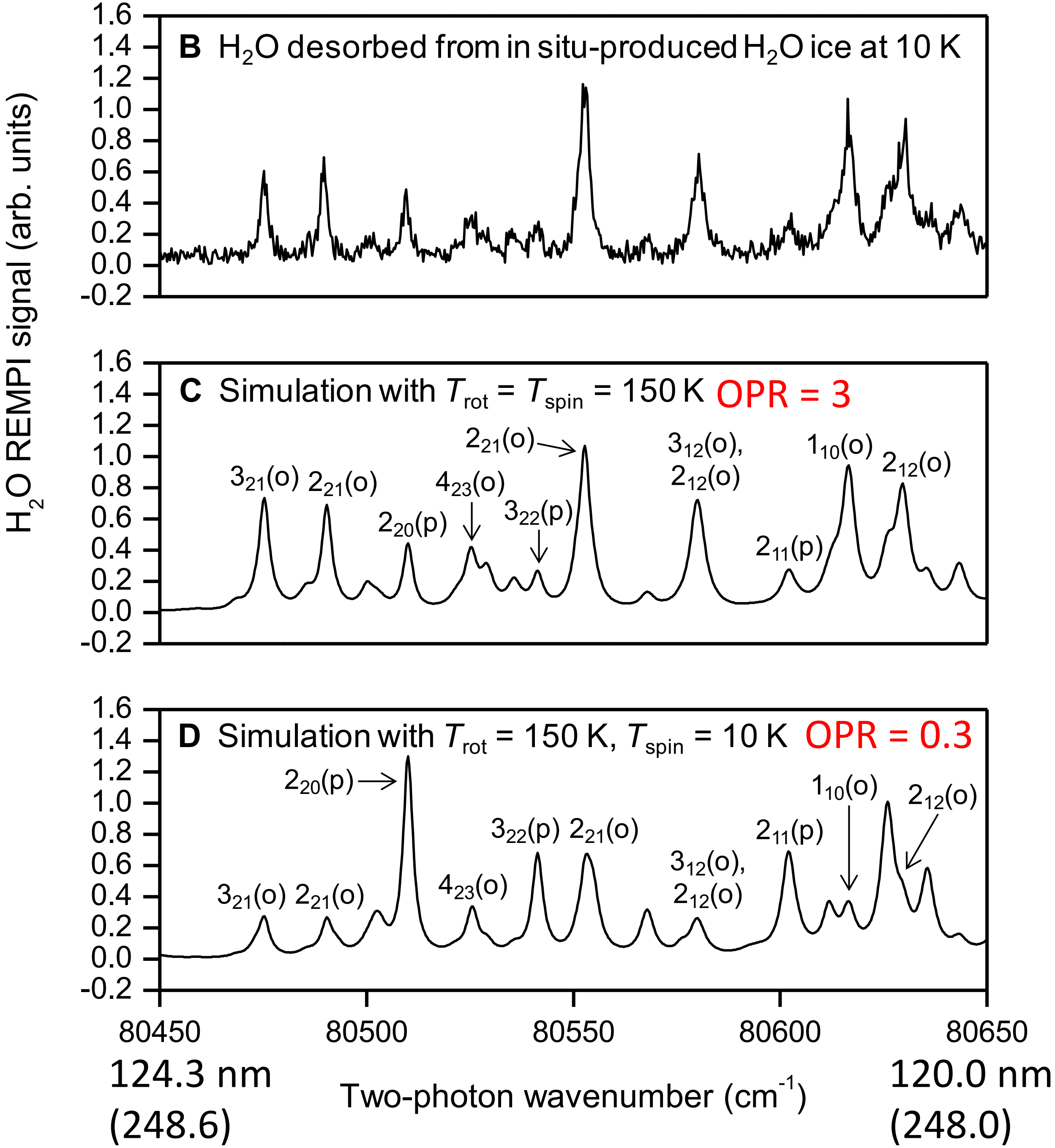
Well-reproduced with OPR = 3.

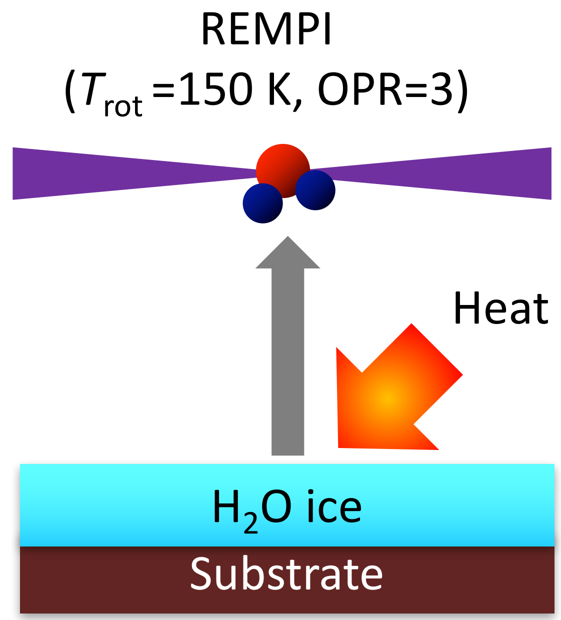
↕

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

The OPR is not related to the ice formation temperature.

REMPI rotational spectrum of H_2O thermally desorbed from ice at 150 K





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.

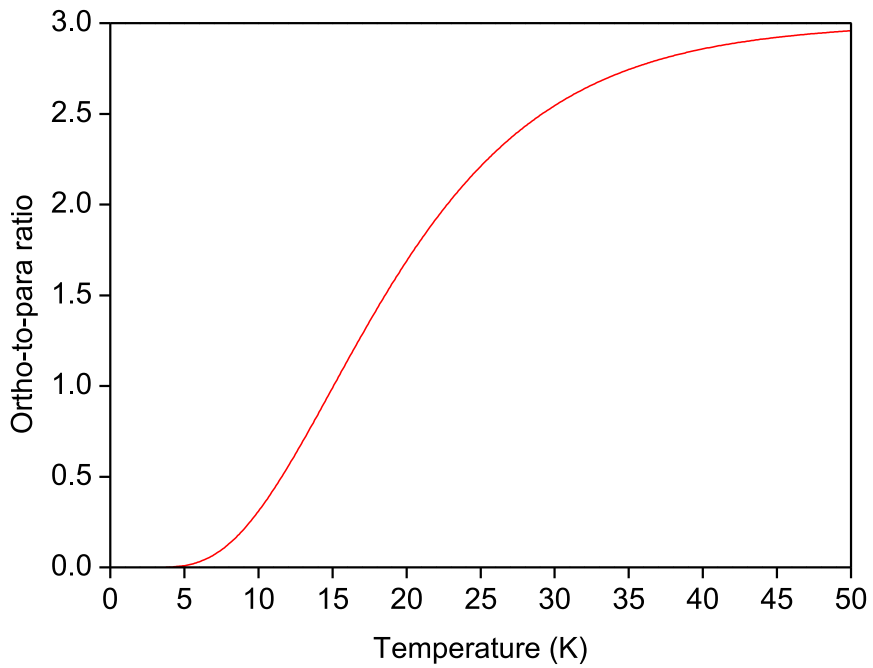
Large difference of “rotational state of H_2O” between the gas and solid phases.

The definition of spin temperature.

Spin and rotational degeneracy

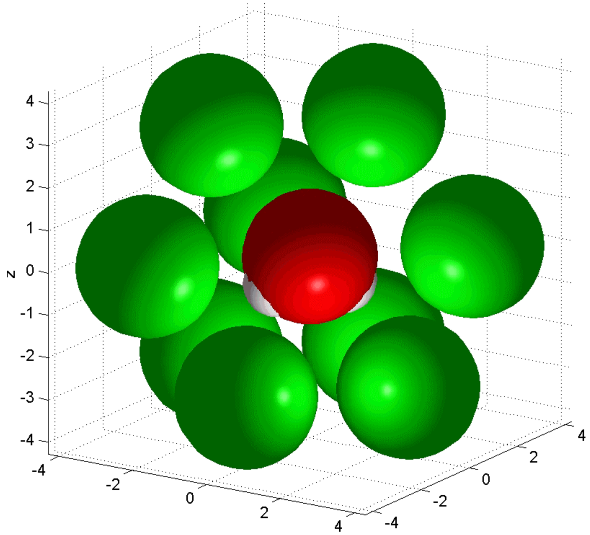
$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_{\mathrm{o}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}{\sum(2J+1)\exp\left[\frac{-E_{\mathrm{p}}(J_{K_a,K_c})}{k_{\mathrm{B}}T_{\mathrm{spin}}}\right]}$$

Rotational energy is important !!
ΔE = 34.2 K.



In rotational-hindered system,
the “rotational” energy difference (ΔE_{rot}) becomes small.

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



Turgeon et al., JPCA, 121 , 1571 (2017).
Michaut et al., Vib. Spec. 34 83 (2004).

OPR-T_{spin} curves in rotational hindered systems

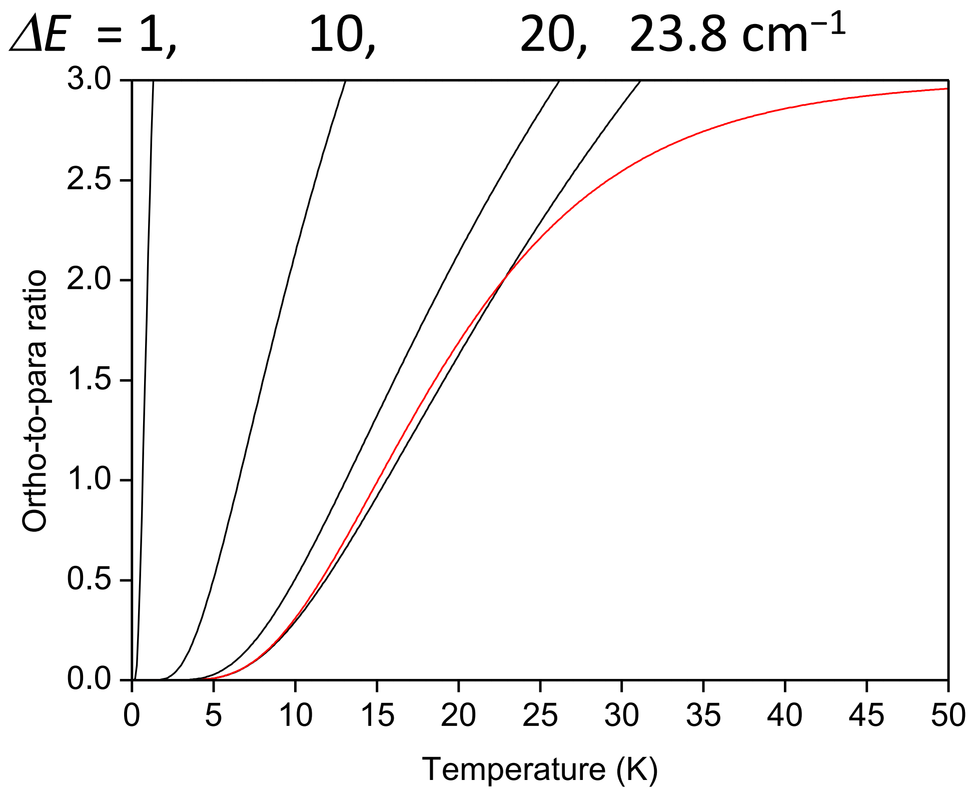
Approximated (crude) OPR-T_{spin} curve;

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

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

Only consider the lowest two rotational levels.
(since we cannot know all rotational levels.)

Rotationally hindered ⟷ Free rotation

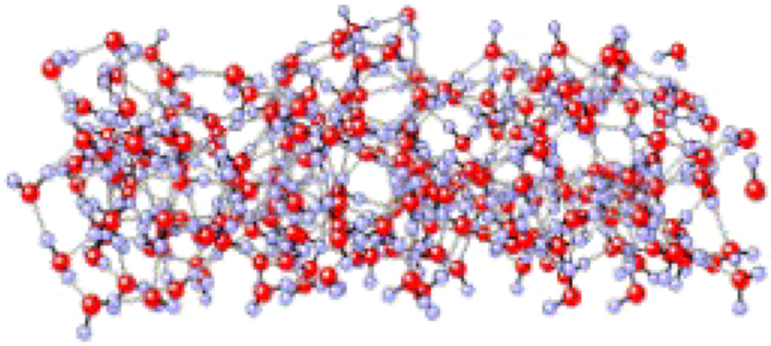


As the ΔE value decreased, the OPR reaches 3 at low temperature.
→ The energies of ortho-, and para-H_2O become comparable.

The T_{spin} curve only applies to H_2O in the gas phase (free rotors).

In ice, H_2O has a high barrier (6700 K) to rotation, because of hydrogen-bond network.

Wittebort et al., JACS. 110, 5668 (1988).



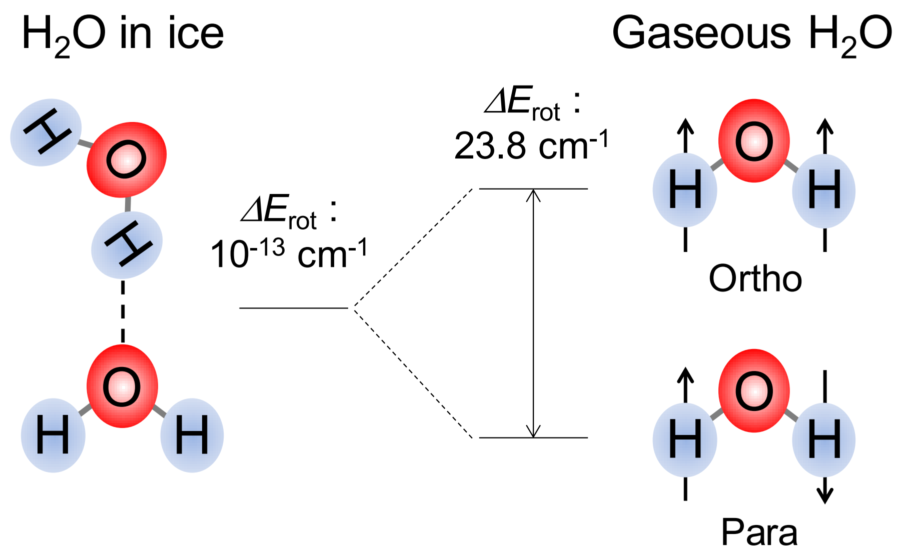
Both ortho- and para-H_2O are no longer free rotors.

The quenched ΔE value: 10^{-13} cm^{-1} (10^{-13} K)

(The same energy level !!)

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

Ortho- and para-H_2O are energetically comparable at 10 K in strongly rotational-hindered systems (ice).



Nuclear spin conversion of H_2O

NSC: ortho-para state mixing by magnetic perturbation (e.g., paramagnetic O_2).

Proton has a magnetic moment (10^{-26} J T^{-1})

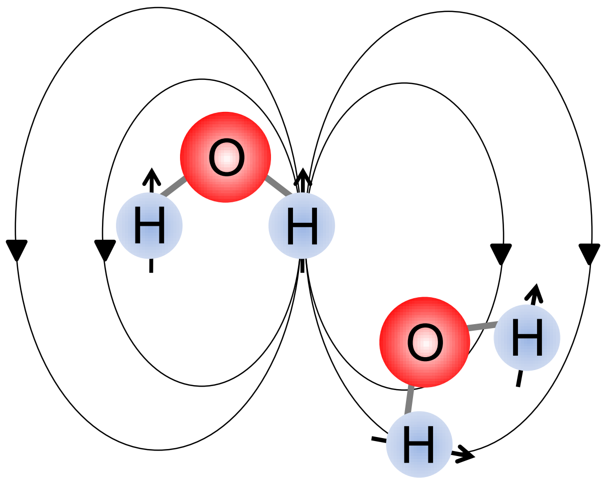
Intermolecular proton–proton dipolar interaction can induce NSC.

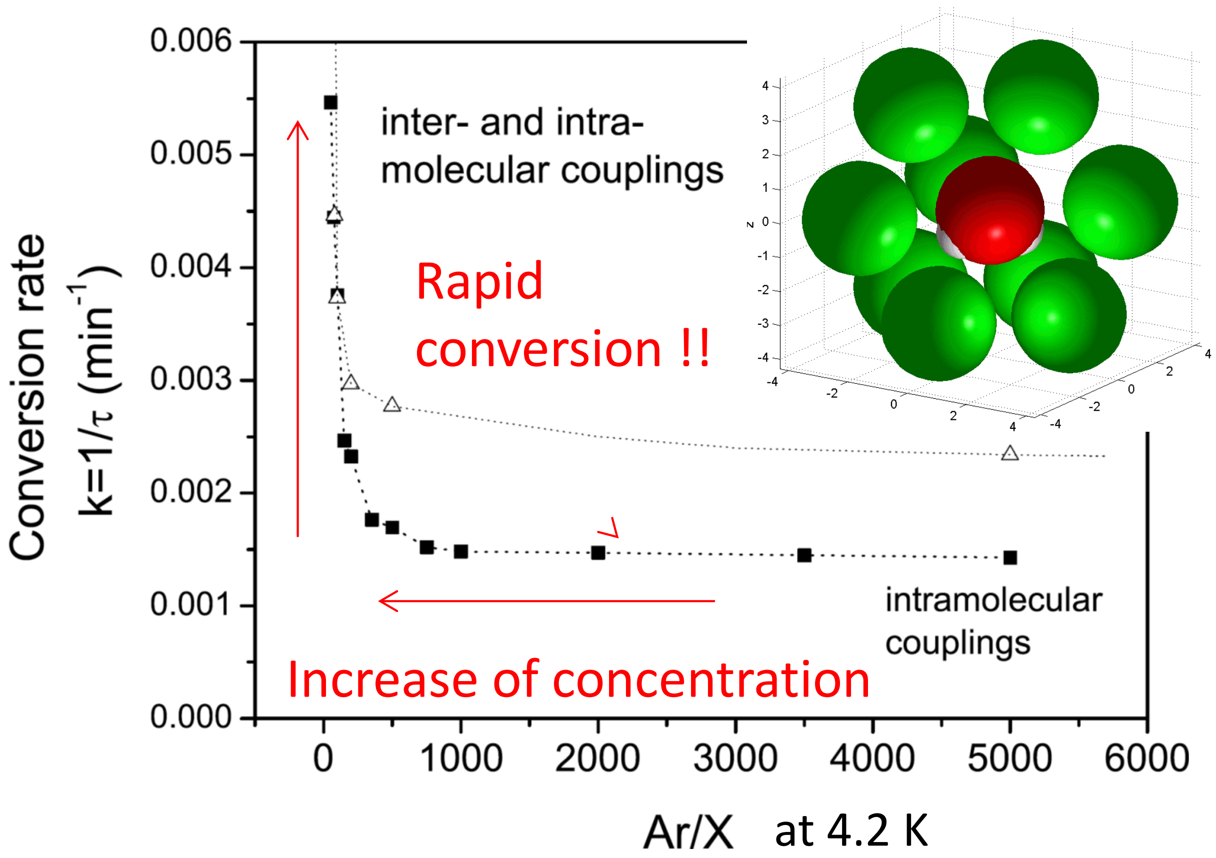
NSC of water (■) and methane (△) in an Ar matrix:

Enhanced by intermolecular proton-proton dipolar interaction.

10^{-7} to 10^{-6} cm^{-1} (10^{-30} J)

(In terms of NMR, 10 kHz)





Fillion et al., EAS Pub. Ser., (2012)., Fukutani and Sugimoto, Prog. Surf. Sci., (2013).

As a result of rotational quenching, fast nuclear spin conversion of H_2O can occur in ice

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

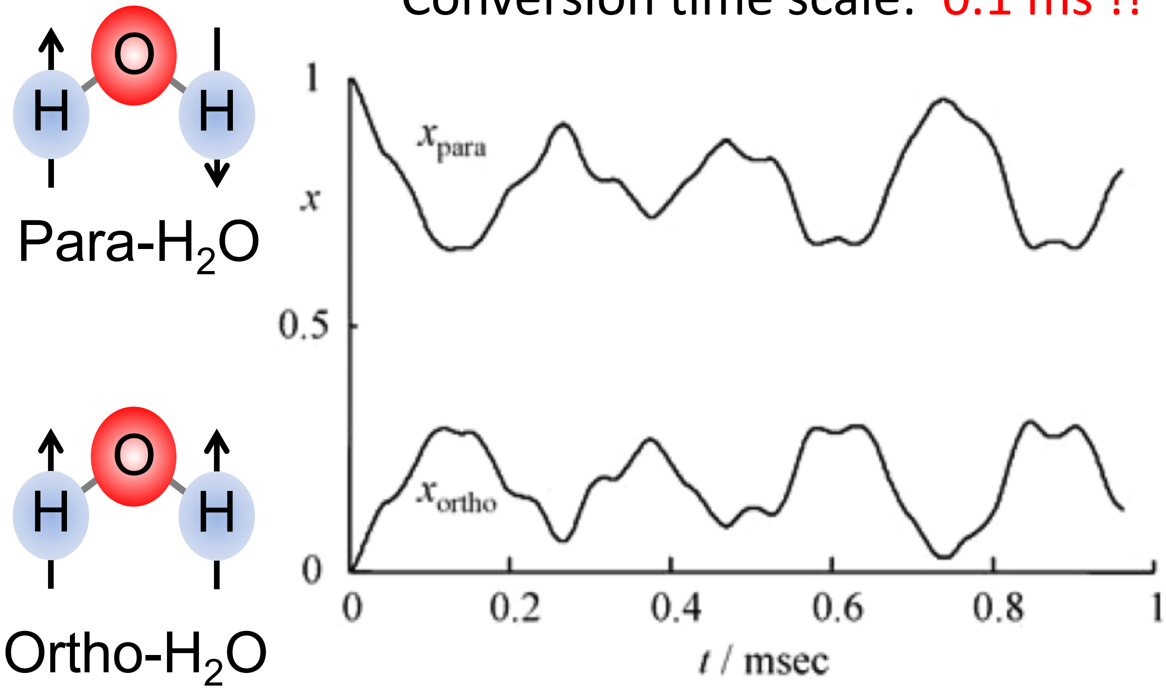
↓

Ortho- and para-states are strongly mixed:

Intermolecular proton magnetic interaction >> rotational energy difference (ΔE_{rot}).

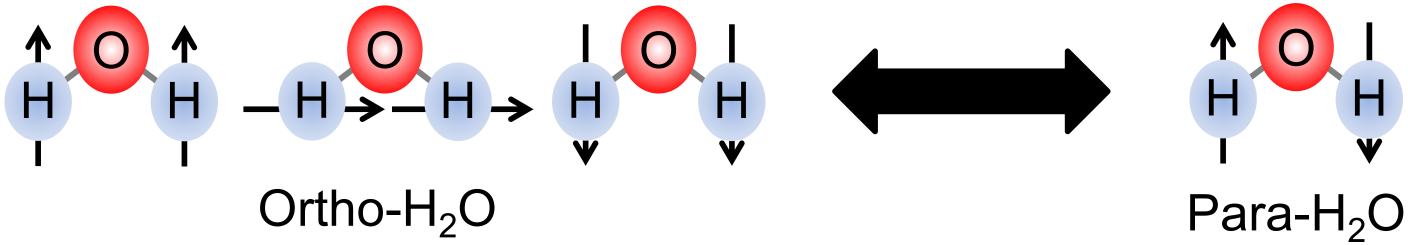
10^{-7} to 10^{-6} cm^{-1} >> 10^{-13} cm^{-1}

Conversion time scale: 0.1 ms !!

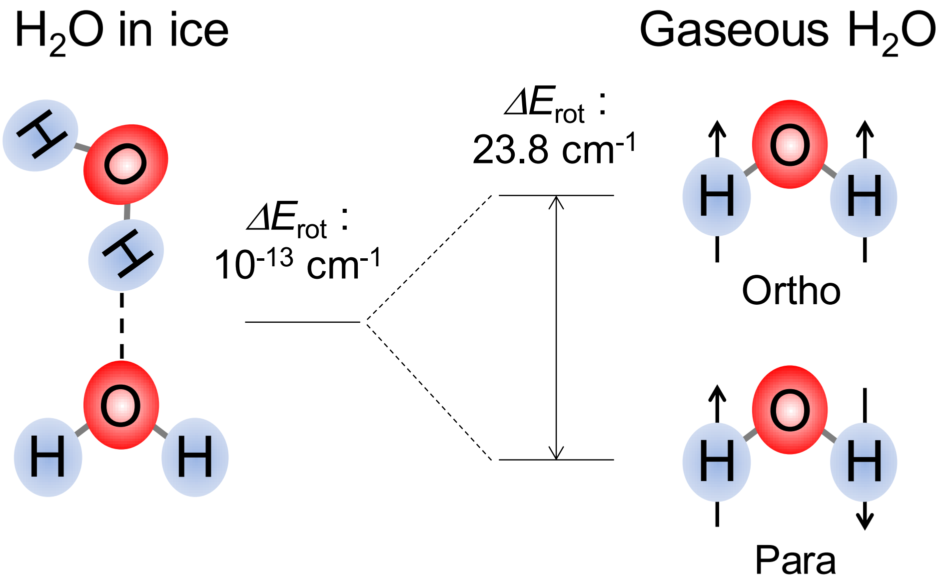


Limbach et al. 2006, Chem. Phys. Chem., 7, 551.
Buntkowsky et al. 2008, Z. Phys. Chem., 222, 1049.

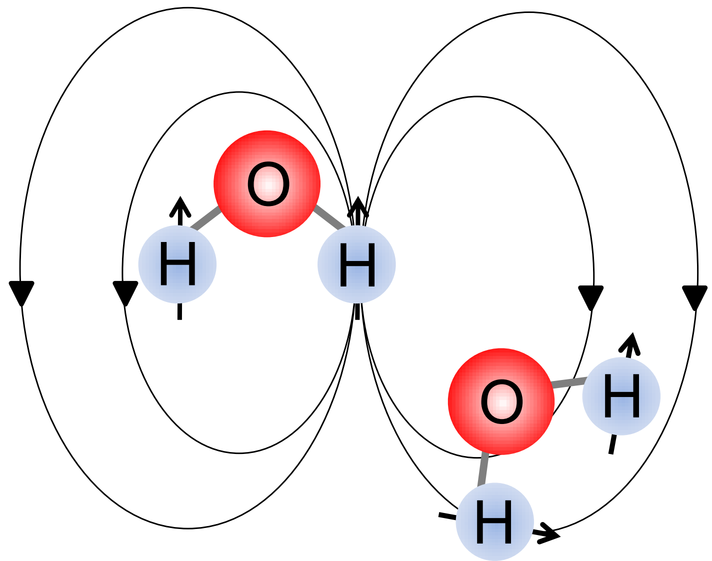
The OPR of H_2O in ice is in dynamic equilibrium at the statistical value of 3.
(The spin state of H_2O is superposition of ortho- and para-H_2O)



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



(2) Fast continuous ortho-para interconversion



The origin of the anomalous OPRs of interstellar H_2O is still an open question.
Nuclear-spin effects in gas-chemistry are key.

(1) NSC via ion-molecule reactions, e.g., 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.

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

Since H_2 can be para-enriched in interstellar clouds,
the H_2O products might be also para-enriched.

H_2O^+, H_3O^+ have also nuclear-spin isomers.
Nuclear-spin effects should be considered.
Accurate state-to-state rate coefficients at low temperature are unknown…

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 OPR of 3, even when the ice is produced in situ at 10 K.

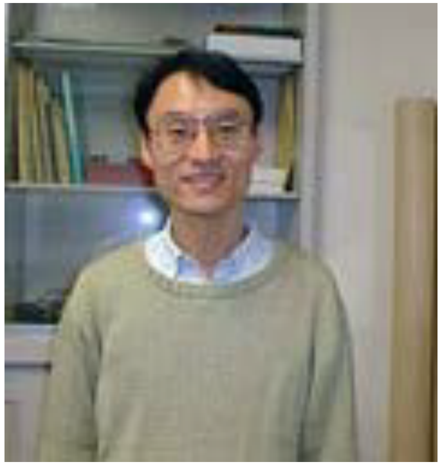
(2) Reinterpretation of previous observations is necessary.

(3) Importance of the gas-phase chemistry.

(a) NSC via ion-molecule reactions, e.g., H^+ or H_3O^+.

(b) Gas-formation processes.

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



Financial supports:
JSPS (grant 24224012), MEXT (grant 25108002).

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Another explanation for nuclear spin state of H_2O in ice: NMR

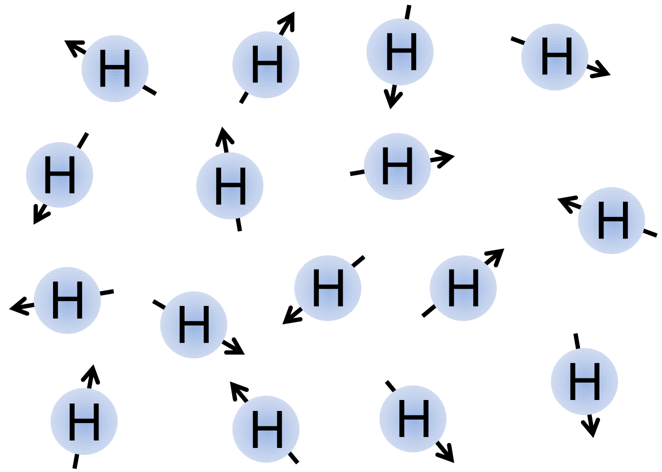
Water ice: a diamagnetic insulator (No macroscopic nuclear magnetization).

↓

The direction of the proton spin angular momentum is distributed uniformly in ice.
(No net magnetic moment).

Each proton feels
magnetic fields created by all protons in ice, while
Proton-proton dipolar interactions << thermal energy

10^{-30} J (10 kHz) << 10^{-22} J (10 K)

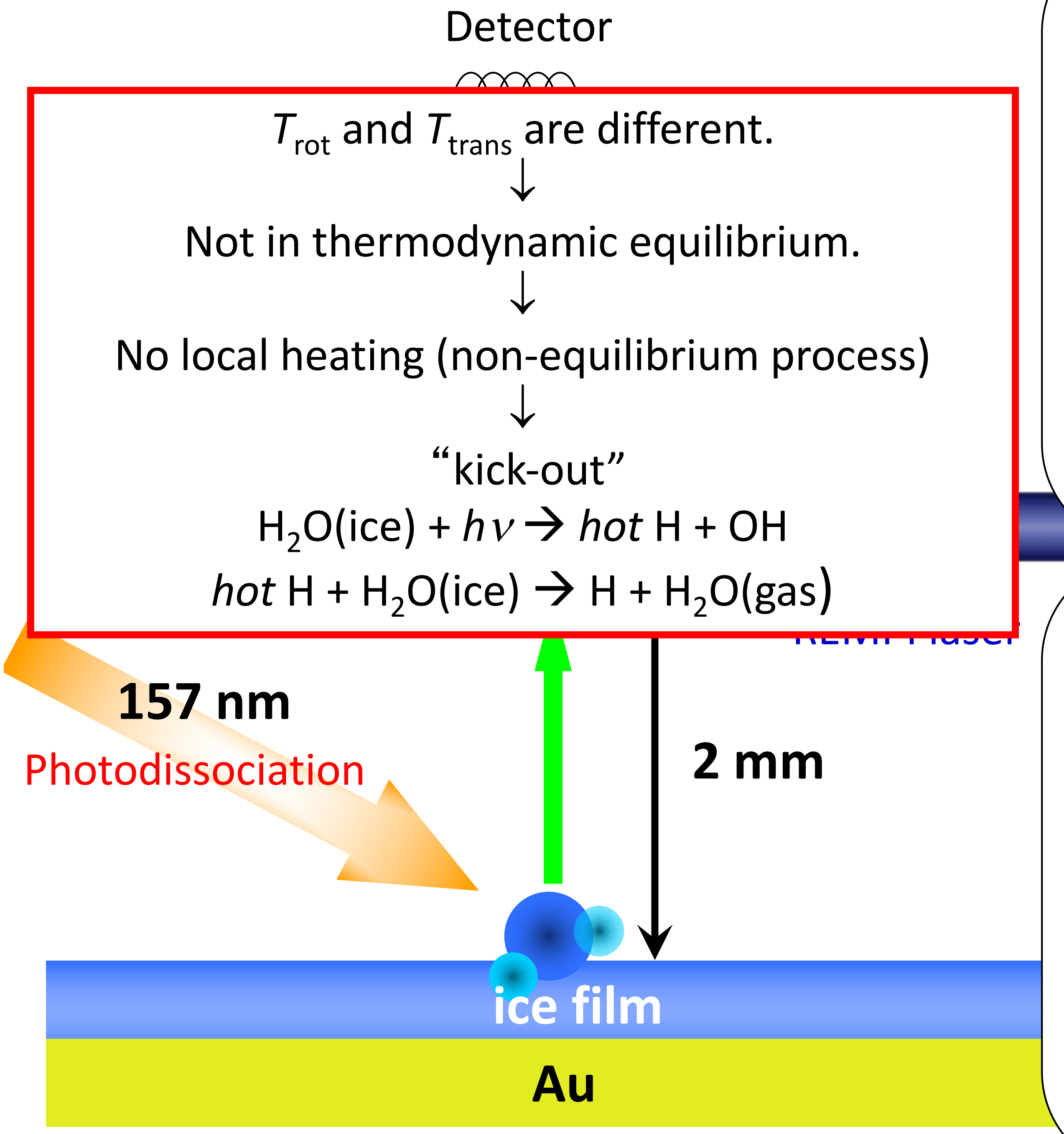


When an H_2O molecule is desorbed from the ice into the gas phase,
it is restored as “a coupled homonuclear spin-1/2 pair”, ortho (I=1), or Para (I=0).

↓

Since the desorbed H_2O molecules have sufficient energy,
(> 34.2 K, ΔE_{rot} in the gas phase),
the OPR can be statistical.

Abragam: Principles of Nuclear Magnetism (1961).
Levitt: Spin Dynamics: Basics of Nuclear Magnetic Resonance (2008).



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

↓

Not in thermodynamic equilibrium.

↓

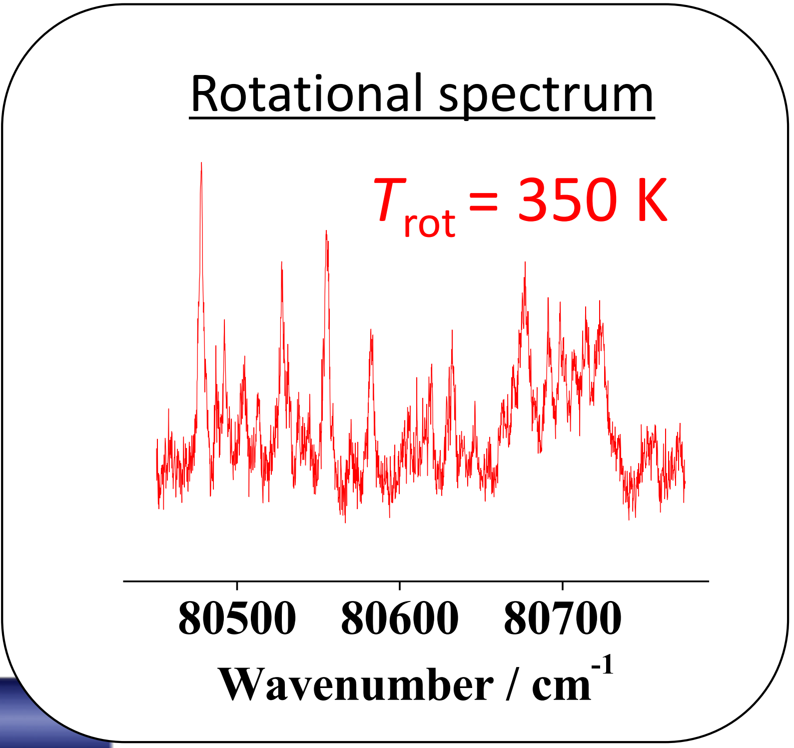
No local heating (non-equilibrium process)

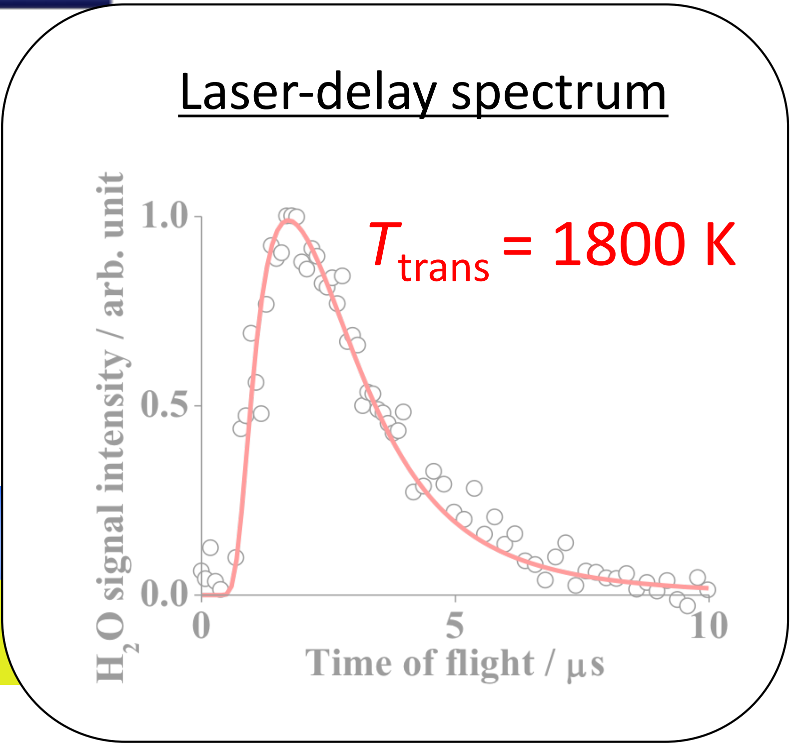
↓

"kick-out"

H_2O(ice) + $h\nu$ → *hot* H + OH

hot H + H_2O(ice) → H + H_2O(gas)



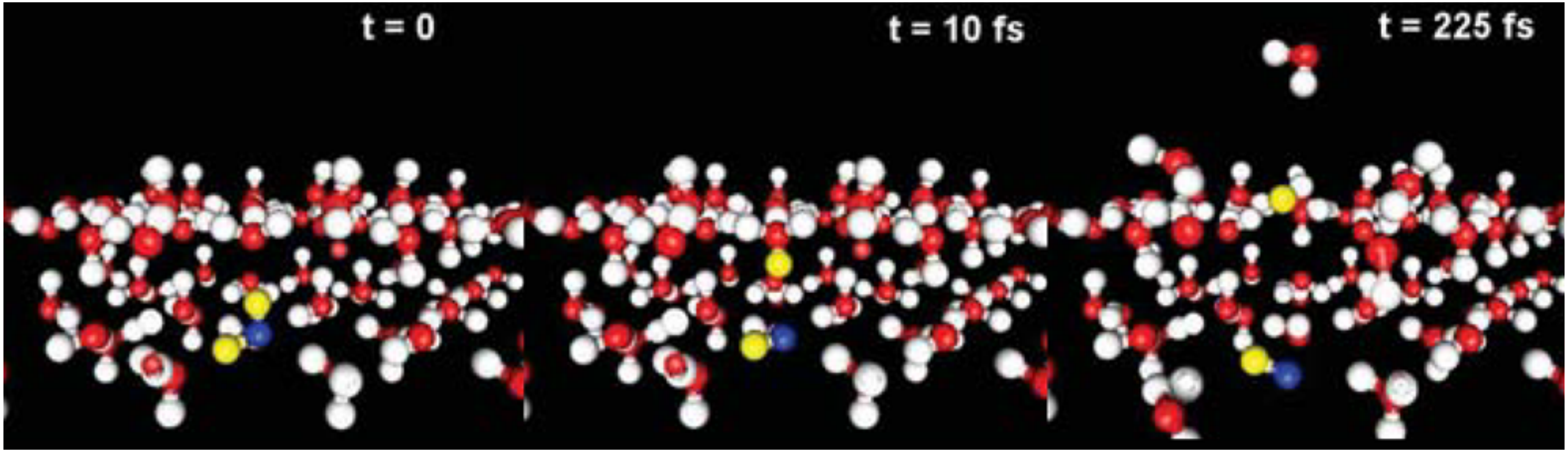


Andersson and van Dishoeck, A. & A. **491**, 907 (2008).

Photodesorption mechanism

"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.

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

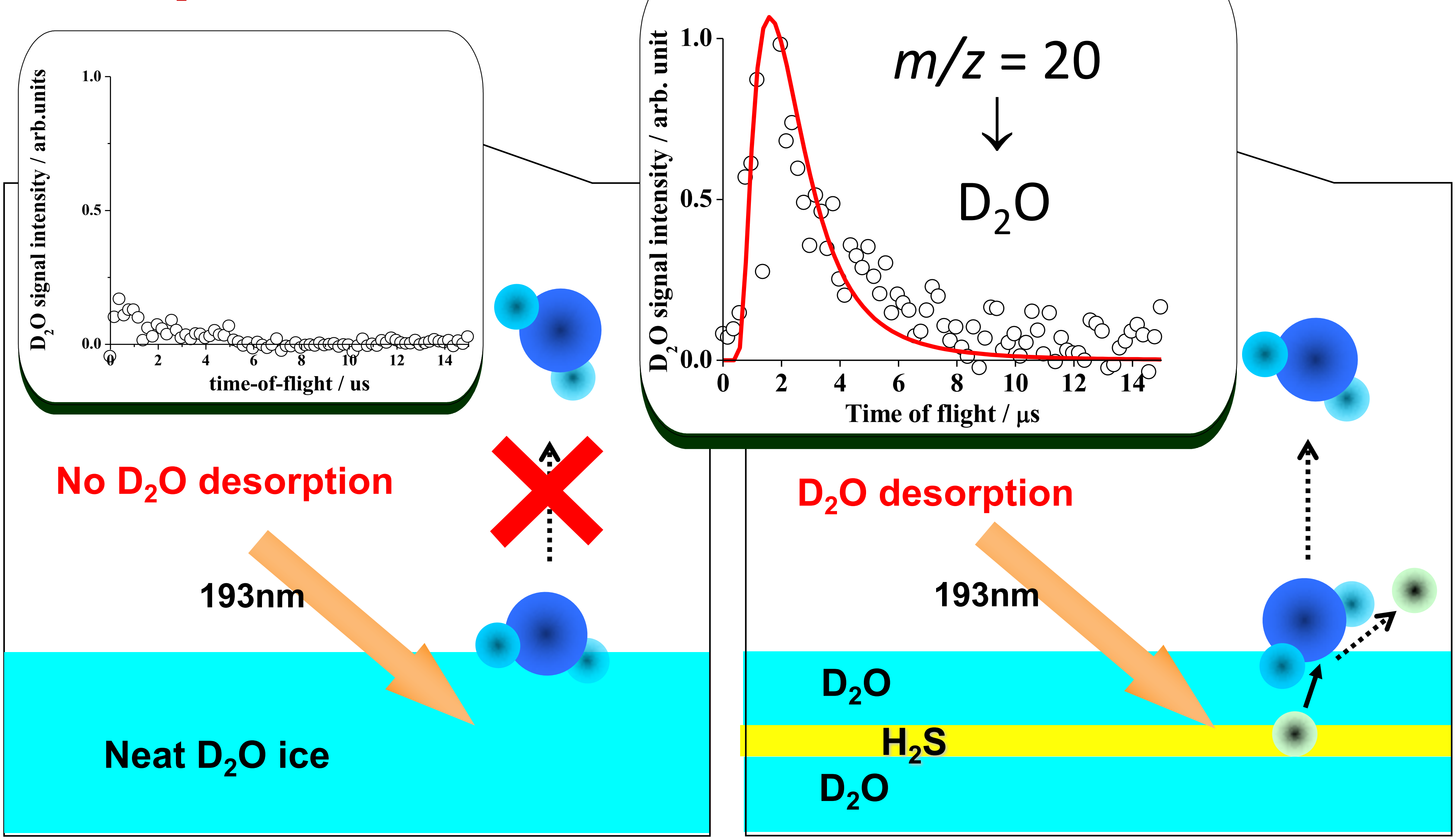


Andersson, and van Dishoeck, Astron. Astrophys. , 491, 907 (2008).

kick-out: D_2O desorption from "D_2O + H_2S layered ice" by 193 nm irradiation.

No D_2O following 193 nm irradiation of pure D_2O ice (no absorption).

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

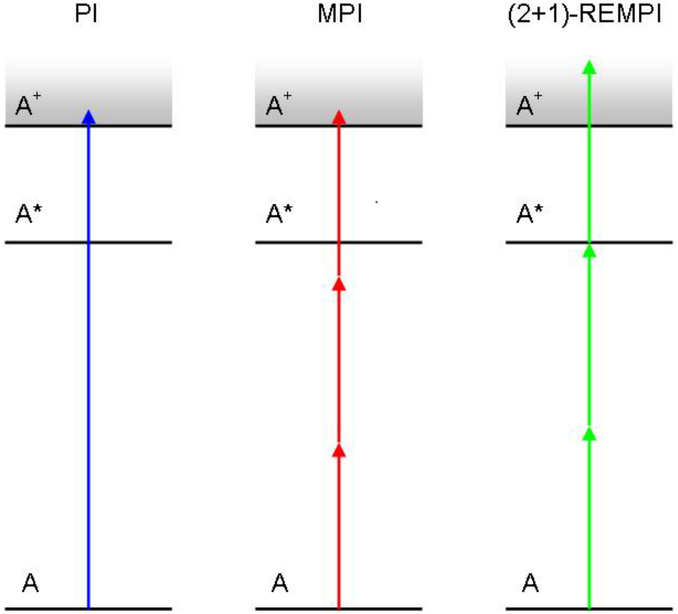


Experiment (My PhD work): Hama et al., JCP. 132, 164508 (2010).

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



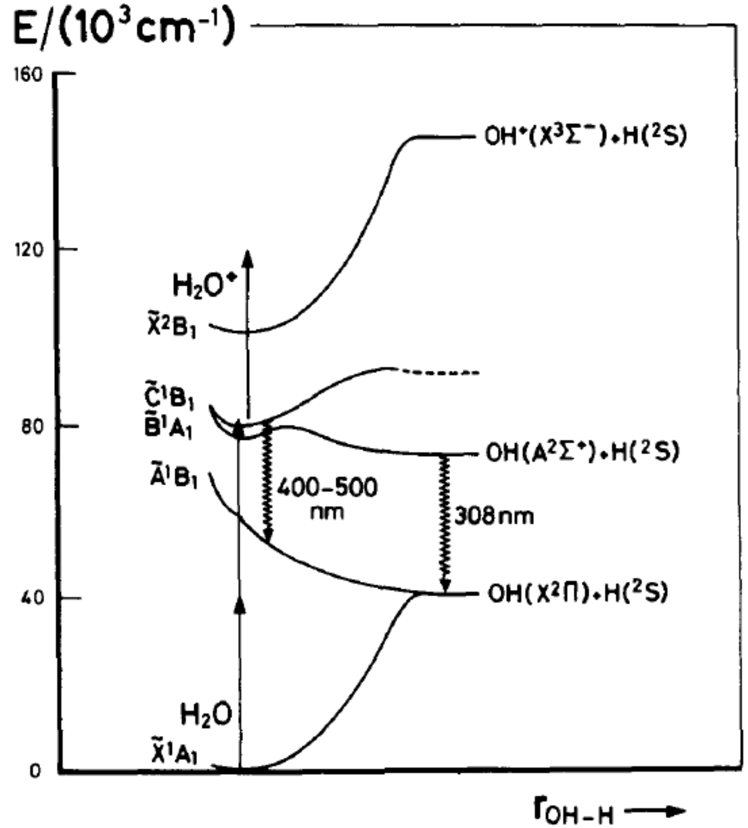


FIG. 1. Correlation diagram showing the processes involved (after Ref. 16).

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.

Physical Chemistry Research Lab Course A TU Braunschweig, Institute of Physical and Theoretical Chemistry SS 2014

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

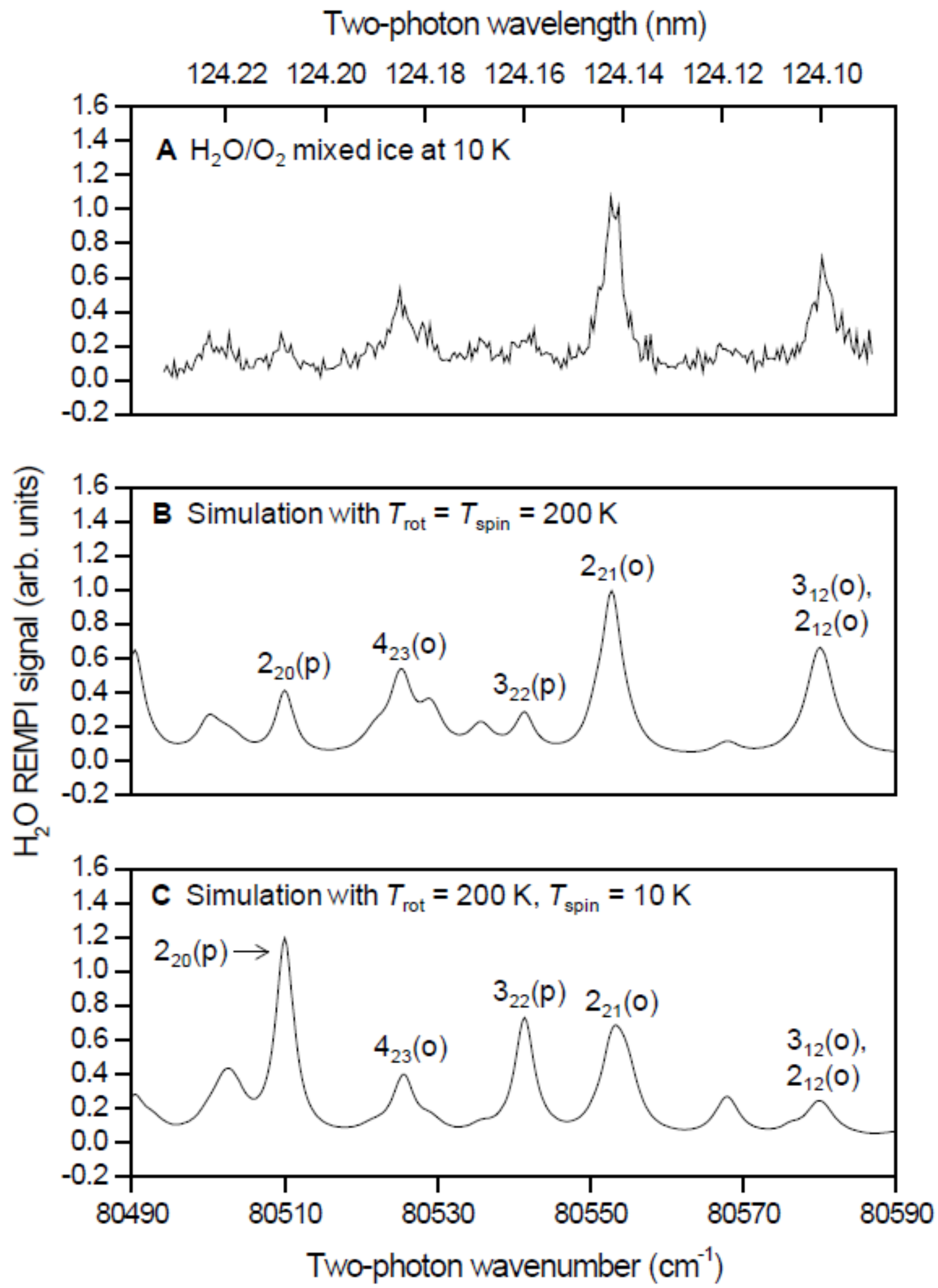
Paramagnetic catalytic effects on the NSC of H_2O during photodesorption.

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).



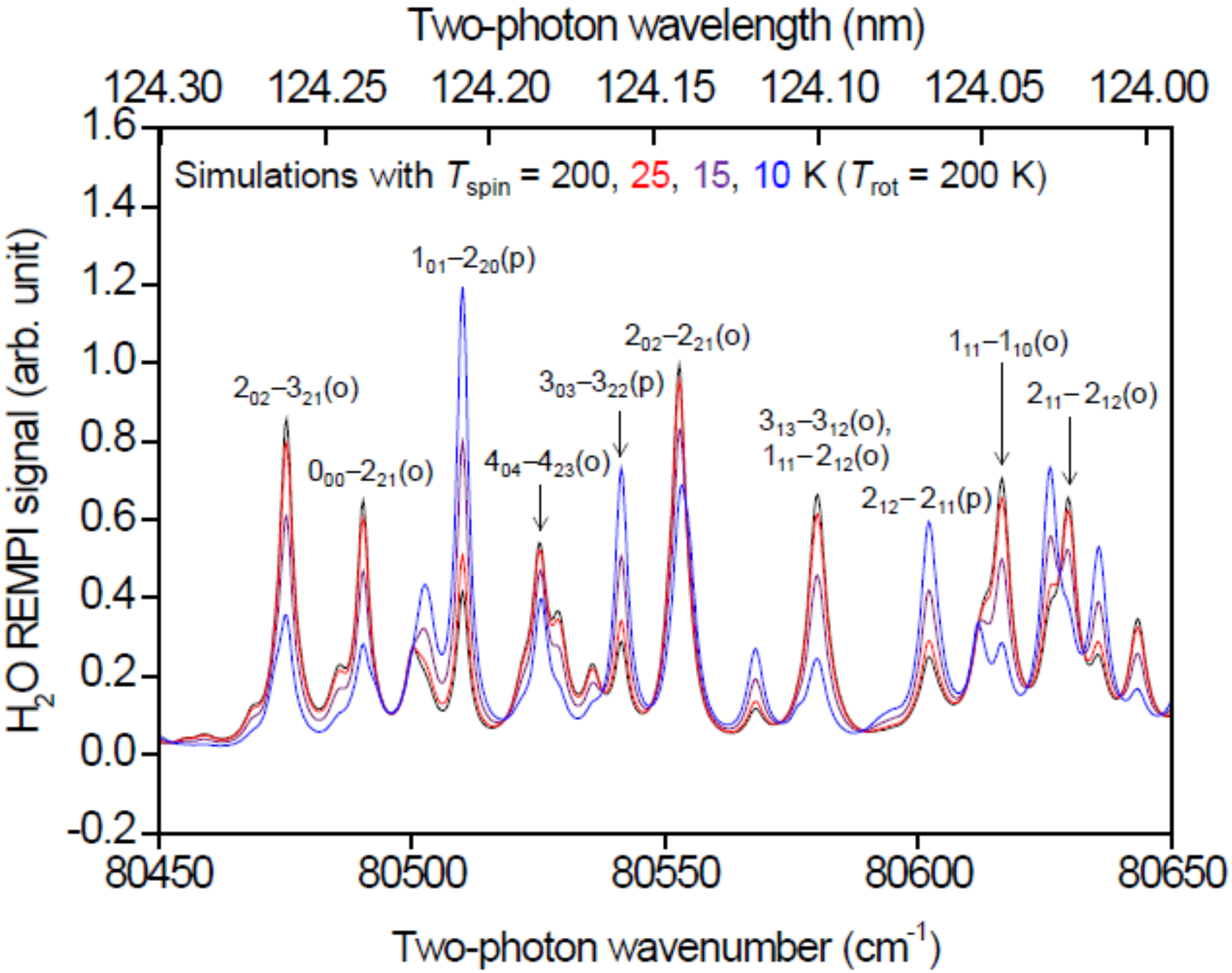
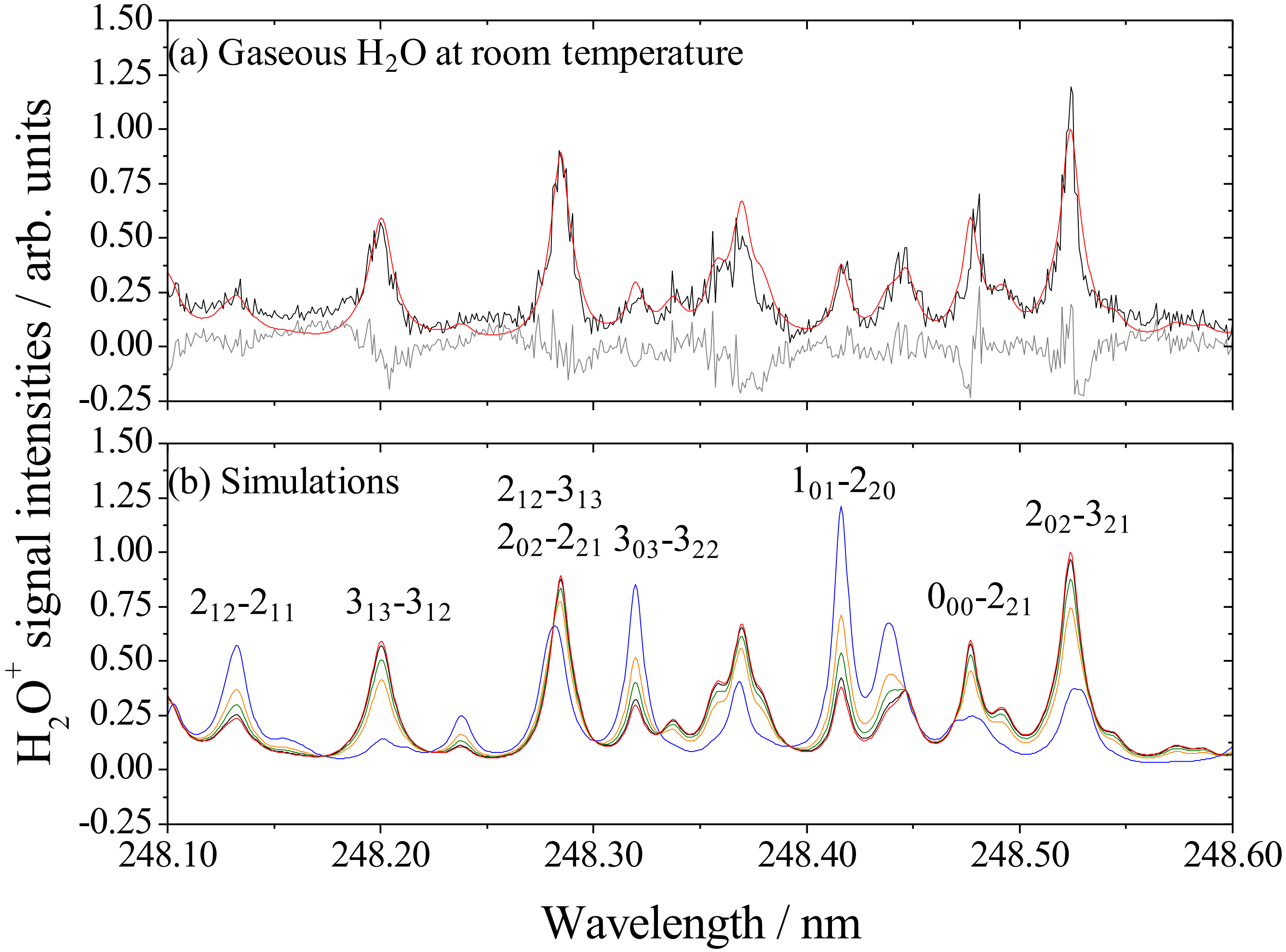


Fig. S3: REMPI spectral simulations. T_{spin} = 200 (black), 25 (red), 15 (purple), and 10 (blue) K. T_{rot} is fixed at 200 K. T_{spin} and T_{rot} represent nuclear spin and rotational temperatures, respectively. Indications ($J'_{Ka',Kc'} - J_{Ka,Kc}$) are rotational assignments of the $\tilde{C}\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

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.



J_{KaKc} (ortho or para)

$T_{rot} = T_{spin}$ = 300 K
Gray; difference

$T_{rot} = T_{spin}$ = 300 K
T_{rot} = 300 K, T_{spin} = 30 K
T_{rot} = 300 K, T_{spin} = 20 K
T_{rot} = 300 K, T_{spin} = 15 K
T_{rot} = 300 K, T_{spin} = 8 K