

## Electronic Supplementary Information

# VUV Photochemistry and Nuclear Spin Conversion of Water and Water-Orthohydrogen Complexes in Parahydrogen Crystals at 4 K

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## I. Water transition wavenumbers and their spectral line intensities.

Label <sup>a</sup>	Species <sup>b</sup>	Vib. mode	Rotational assignment <sup>c</sup> $J_{K_a K_c}$ or $j_k$	Wavenumber ( $\text{cm}^{-1}$ )	Spectral line Intensity <sup>d</sup> ( $\text{km mol}^{-1}$ )
–	$\text{oD}_2\text{O}$	$\nu_2$ bending	$1_{11} \leftarrow 0_{00}$	1197.70	37.090
P(1) <sup>D2O</sup>	$\text{pD}_2\text{O}$	$\nu_3$ stretching	$0_{00} \leftarrow 1_{01}$	2765.96	5.384
G1	$\text{pD}_2\text{O}-\text{oH}_2$	$\nu_3$ stretching	$0_0 \leftarrow 1_1$	2769.30	5.384 <sup>e</sup>
G2	$\text{pD}_2\text{O}-(\text{oH}_2)_2$	$\nu_3$ stretching	$0_0 \leftarrow 1_1$	2771.19	5.384 <sup>e</sup>
F3	$\text{oD}_2\text{O}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	2781.17	
F2	$\text{oD}_2\text{O}-(\text{oH}_2)_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	2782.59	30.863 <sup>e</sup>
F2'	$\text{oD}_2\text{O}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	2783.42	
F1	$\text{oD}_2\text{O}-\text{oH}_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	2785.18	30.863 <sup>e</sup>
F1'	$\text{oD}_2\text{O}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	2786.07	
R(0) <sup>D2O</sup>	$\text{oD}_2\text{O}$	$\nu_3$ stretching	$1_{01} \leftarrow 0_{00}$	2789.40	30.863
R(1) <sup>D2O</sup>	$\text{pD}_2\text{O}$	$\nu_3$ stretching	$2_{02} \leftarrow 1_{01}$	2800 <sup>f</sup>	
–	HDO	$\nu_2$ bending	$1_{01} \leftarrow 0_{00}$	1416.94	22.196
E4	$\text{HDO}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3699.04	
E3	$\text{HDO}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3700.69	
E2	$\text{HDO}-(\text{oH}_2)_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3702.55	
E2'	$\text{HDO}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3703.02	
E1	$\text{HDO}-\text{oH}_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3705.46	19.944
E1'	$\text{HDO}-(\text{oH}_2)_n$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3705.89	
T1	HDO-H	$\nu_3$ stretching		3708.89	
R(0) <sup>HDO</sup>	HDO	$\nu_3$ stretching	$1_{01} \leftarrow 0_{00}$	3710.24	19.944
–	$\text{pH}_2\text{O}$	$\nu_2$ bending	$1_{11} \leftarrow 0_{00}$	1631.60	68.226
P(1) <sup>H2O</sup>	<i>ortho</i> - $\text{H}_2\text{O}$	$\nu_3$ stretching	$0_{00} \leftarrow 1_{01}$	3719.79	17.397
D3	$\text{oH}_2\text{O}-(\text{oH}_2)_2$	$\nu_3$ stretching	$0_0 \leftarrow 1_1$	3724.45	17.397 <sup>e</sup>
D1	$\text{oH}_2\text{O}-\text{oH}_2$	$\nu_3$ stretching	$0_0 \leftarrow 1_1$	3725.43	17.397 <sup>e</sup>
D2	$\text{oH}_2\text{O}-(\text{oH}_2)_2$	$\nu_3$ stretching	$0_0 \leftarrow 1_1$	3728.30	17.397 <sup>e</sup>
C3	$\text{pH}_2\text{O}-(\text{oH}_2)_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3754.42	48.611 <sup>e</sup>
C1	$\text{pH}_2\text{O}-\text{oH}_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3758.44	48.611 <sup>e</sup>
S1	$\text{pH}_2\text{O}-\text{H}$	$\nu_3$ stretching		3764.21	
R(0) <sup>H2O</sup>	$\text{pH}_2\text{O}$	$\nu_3$ stretching	$1_{01} \leftarrow 0_{00}$	3765.47	48.611
C2	$\text{pH}_2\text{O}-\text{oH}_2$	$\nu_3$ stretching	$1_1 \leftarrow 0_0$	3773.41	48.611 <sup>e</sup>
R(1) <sup>H2O</sup>	$\text{oH}_2\text{O}$	$\nu_3$ stretching	$2_{02} \leftarrow 1_{01}$	3787.23	

<sup>a</sup> Labels used in Fig. 2 in the main text.

<sup>b</sup> The assignment of the number of  $\text{oH}_2$  in  $(\text{water})(\text{oH}_2)_n$  complexes is tentative.

<sup>c</sup> Most of the assignments are based on Refs. S1 and S2. The quantum number  $J_{K_a K_c}$  is for an isolated water molecule with a standard asymmetric rotor notation. The quantum number  $j_k$  is for  $(\text{water})(\text{oH}_2)$  complexes with  $j$  and  $k$  corresponds to the rotational angular momentum of water and its projection onto the axis of the complex.

<sup>d</sup> Spectral line intensities are calculated from the Einstein- $A$  coefficient obtained from the HITRAN web page (Ref. S3. The original publication is found in Ref. S4.). In order to convert the coefficient  $A_{ij}$  ( $\text{s}^{-1}$ ) to the spectral line intensities  $S_{ij}$  ( $\text{km mol}^{-1}$ ) at  $T = 0$  K, we used the following equation

$$S_{ij} = \frac{A_{ij}}{8\pi c \nu_{ij}^2} \frac{g'}{g''},$$

where  $c = 3 \times 10^{10}$  (cm s<sup>-1</sup>) is the speed of light,  $\nu_{ij}$  (cm<sup>-1</sup>) is the transition wavenumber in the gas phase, and  $g'$  and  $g''$  are the statistical weights in the upper and lower state, respectively. Similar values can be also obtained in Ref. S5 using  $T = 4$  K and  $P = 10^{-5}$  atm. As mentioned in the main text, an additional correction due to the dielectric properties of the matrix host is also included, which increases the spectral line intensities by 6.0% in the solid (Ref. S6).

<sup>e</sup> These intensities are assumed to be the same as that without *o*H<sub>2</sub> clustering.

<sup>f</sup> A broad line.

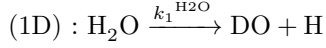
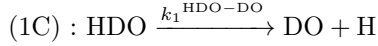
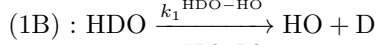
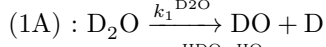
## References

- S1 M. E. Fajardo, S. Tam and M. E. DeRose, *J. Mol. Struct.*, 2004, **695-696**, 111 - 127.
- S2 K. A. Kufeld, W. R. Wonderly, L. O. Paulson, S. C. Kettwich and D. T. Anderson, *J. Phys. Chem. Lett.*, 2012, **3**, 342 - 347.
- S3 <https://hitran.org/lbl>
- S4 I Gordon et al., *J. Quant. Spectrosc. Rad. Trans.*, 2017, **203**, 3 - 69.
- S5 Y. Babikov, I. Gordon, S. Mikhailenko, L. Rothman and S. Tashkun, HITRAN on the Web, <https://hitran.iao.ru>.
- S6 T. Wakabayashi, T. Momose and M. E. Fajardo, *J. Chem Phys.* 2019, **151**, 234301.

## II. Reaction schemes used in the simulation.

In order to simulate the concentration changes, we have considered the following reactions and solved the coupled reaction rate equations numerically. For simplicity, we ignored the nuclear spin conversion and the conservation of nuclear spin in the reactions. We assumed that the nuclear spin conversion is faster than our experimental timescale, such that all water molecules were assumed to be in their lowest energy nuclear spin state (*i.e.*  $p\text{H}_2\text{O}$  and  $o\text{D}_2\text{O}$ ).

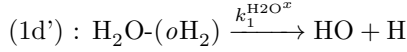
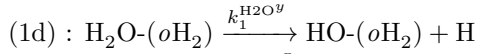
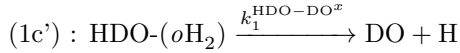
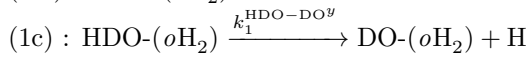
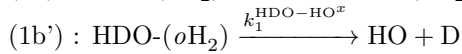
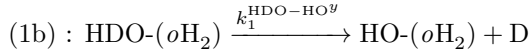
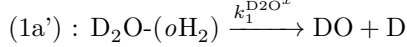
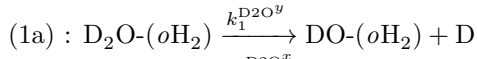
(1) Photodissociation reactions



Here, the isotope dependence on the photodissociation rates is given by

$$k_1^{\text{D}_2\text{O}} = 1.163 \times k_1^{\text{H}_2\text{O}}, \quad k_1^{\text{HDO}-\text{HO}} = 1.054 \times k_1^{\text{H}_2\text{O}} \times 0.8, \quad \text{and} \quad k_1^{\text{HDO}-\text{DO}} = 1.054 \times k_1^{\text{H}_2\text{O}} \times 0.2$$

(taken from Ref. S7). The multiplication factors of 0.8 and 0.2 for  $k_1^{\text{HDO}-\text{HO}}$  and  $k_1^{\text{HDO}-\text{DO}}$ , respectively, represent the branching ratio of the dissociation of HDO.



Here,

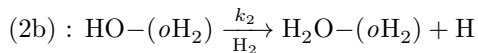
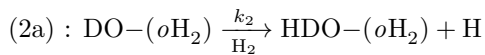
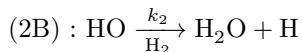
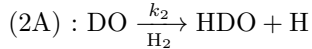
$$k_1^{\text{D}_2\text{O}^x} = k_1^{\text{D}_2\text{O}} \times r, \quad k_1^{\text{D}_2\text{O}^y} = k_1^{\text{D}_2\text{O}} \times (1 - r),$$

$$k_1^{\text{H}_2\text{O}^x} = k_1^{\text{H}_2\text{O}} \times r, \quad k_1^{\text{H}_2\text{O}^y} = k_1^{\text{H}_2\text{O}} \times (1 - r),$$

$$\text{and } k_1^{\text{HDO}^x} = k_1^{\text{HDO}} \times r, \quad k_1^{\text{HDO}^y} = k_1^{\text{HDO}} \times (1 - r),$$

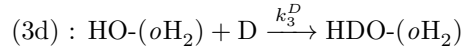
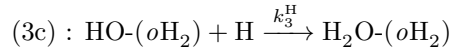
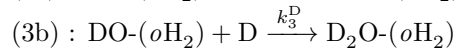
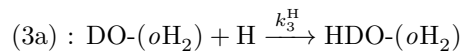
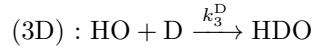
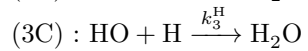
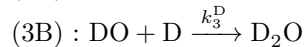
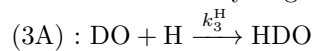
where  $r$  is the branching ratio for the  $o\text{H}_2$  conversion upon photodissociation.

(2) Reactions with surrounding  $\text{H}_2$  molecules



Here, the reaction rate  $k_2$  is assumed to be the same for all isotopes. Also, for simplicity, it was assumed that no  $o\text{H}_2$  conversion occurs by the reactions of (2a) and (2b).

(3) Reactions with a hydrogen atom



Here,  $k_3^{\text{D}} = 0.5 \times k_3^{\text{H}}$ . The reaction rate  $k_3$  is assumed to be the same for all the isotopes. The difference between  $k_3^{\text{D}}$  and  $k_3^{\text{H}}$  originates in the difference in the tunneling rate between H and D atoms (see the main text in Sec. 3.4). Also, for simplicity, it was assumed that no  $o\text{H}_2$  conversion occurs by the reactions of (3a), (3b), (3c), and (3d).

S7 N. Shafer, S. Satyapal and R. Bersohn, *The Journal of Chemical Physics*, 1989, **90**, 6807-6808.

### III. Simulated concentration changes with various parameters.

The dependence of different rate constant values on the concentration changes are show below. Here, we changed the values of  $k_1^{\text{H}_2\text{O}}$ ,  $k_2$ ,  $k_3^{\text{H}}$ , and  $r$  given in the above reaction schemes. The isotope dependences are fixed to those listed in the above Sec. II. The initial concentration of each species used in the simulation is listed in the table below.

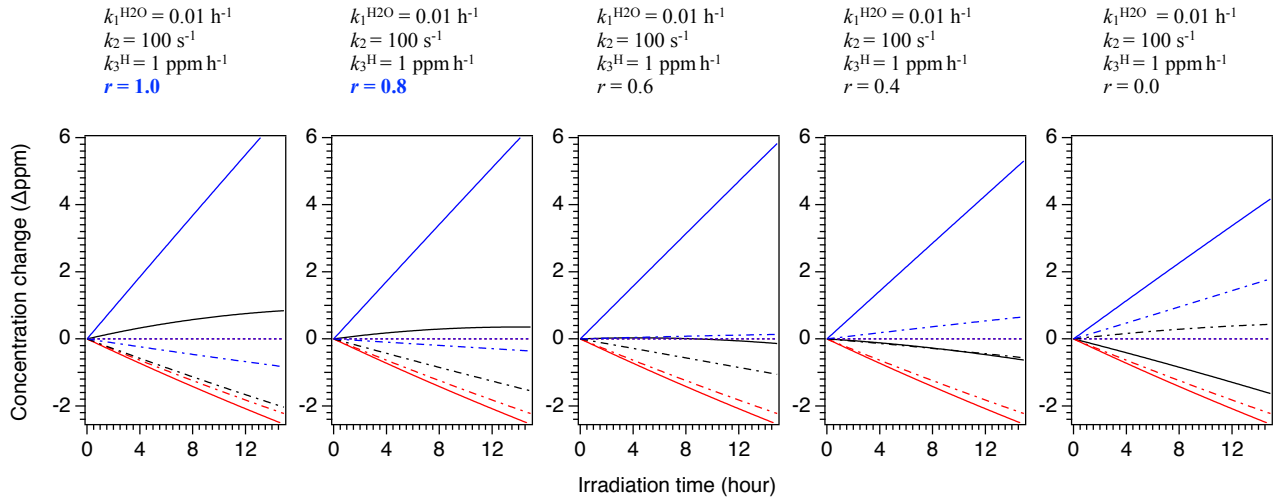
Species	Initial concentration ppm	Species	Initial concentration ppm
$o\text{D}_2\text{O}$	16	$o\text{D}_2\text{O}-(o\text{H}_2)$	14
$p\text{D}_2\text{O}$	0	$p\text{D}_2\text{O}-(o\text{H}_2)$	0
HDO	34	HDO- $(o\text{H}_2)$	14
$p\text{H}_2\text{O}$	10	$p\text{H}_2\text{O}-(o\text{H}_2)$	6
$o\text{H}_2\text{O}$	0	$o\text{H}_2\text{O}-(o\text{H}_2)$	0
HO	0	HO- $(o\text{H}_2)$	0
DO	0	DO- $(o\text{H}_2)$	0
H	0		
D	0		

#### Graph legends

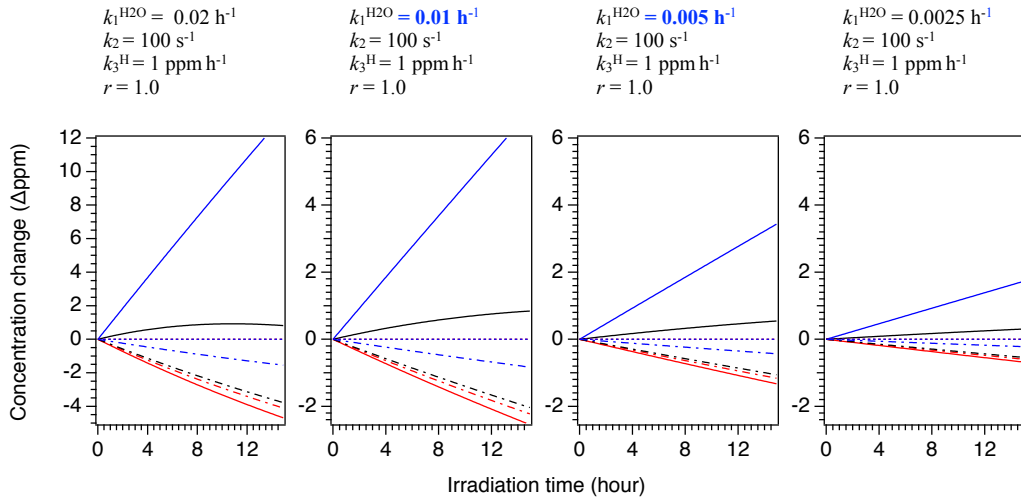
- $o\text{D}_2\text{O}$
- HDO
- $p\text{H}_2\text{O}$
- ..... OD
- ..... OH
- $o\text{D}_2\text{O}-o\text{H}_2$
- HDO- $o\text{H}_2$
- $p\text{H}_2\text{O}-o\text{H}_2$

Parameter values that reproduce the observed concentration changes are marked in bold blue in the following figures.

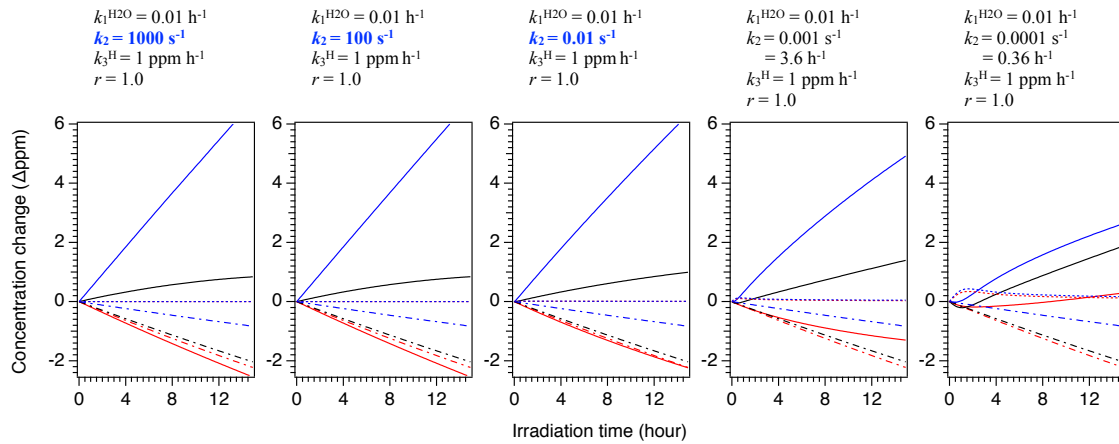
**IIIa.  $r$  dependence.** The acceptable range is  $1.0 \geq r \gtrsim 0.8$ .



**IIIb.  $k_1^{\text{H}_2\text{O}}$  dependence.** The acceptable range is  $0.01 \text{ h}^{-1} \gtrsim k_1^{\text{H}_2\text{O}} \gtrsim 0.005 \text{ h}^{-1}$ .



IIIc.  $k_2$  dependence. The acceptable range is  $k_2 \gtrsim 0.01 \text{ s}^{-1}$ .



IIIId.  $k_3^{\text{H}}$  dependence. The acceptable range is  $10 \text{ ppm s}^{-1} \gtrsim k_3^{\text{H}}$ .

