Supplementary Information for

Toward elimination of discrepancies between theory and experiment:
Rotational-vibrational spectrum of water in solid noble gas matrices

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This PDF file includes:

Supplementary text
Table S1

Supplementary Information Text

Assignment of Water Monomers in Argon and Neon MI-IR Spectra.

Argon matrix
H_2O v_3 $(B2)$: We do not observe the non-rotating (NR) transition ((1),(2): 3735 cm^{-1}), yet we see a broad N_2 induced band at 3731.1 cm^{-1}. Directly observed rotational-vibrational (RV) transitions are the $2_{02} \leftarrow 1_{01}$ at 3776.9 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 3757.2 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ at 3711.8 cm^{-1}. v_1 $(A1)$: We do not observe the NR transition ((1),(2): 3638 cm^{-1}), yet we see a broad N_2 induced band at 3640.1 cm^{-1}. One directly observed RV transition is $1_{11} \leftarrow 0_{00}$ at 3670.6 cm^{-1}. v_2 $(A1)$: We observe the NR transition at 1589.9 cm^{-1} together with the N_2 induced band at 1600.0 cm^{-1}. Directly observed RV transitions are the $2_{12} \leftarrow 1_{01}$ at 1636.9 cm^{-1}, the $1_{11} \leftarrow 0_{00}$ at 1624.0 cm^{-1} and the $1_{10} \leftarrow 1_{01}$ at 1608.1 cm^{-1}.
HDO v_3 (A'): We do not observe the NR transition ((3): 3685.7 cm^{-1}). In the 1:250 experiments, there is a signal at 3690.6 cm^{-1}, which can be assigned as N_2 induced ((3): 3689.7 cm^{-1}), yet also as the RV $1_{10} \leftarrow 1_{11}$ ((3): 3689 cm^{-1}). Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 3713.5 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 3702.6 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ at 3673.0 cm^{-1}. v_1 (A'): We observe the NR transition at 2707.9 cm^{-1} in the 1:500 and 1:250 experiments. Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 2738.1 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 2724.4 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ at 2694.2 cm^{-1}. v_2 (A'): We observe the NR transition at 1398.6 cm^{-1}. Directly observed RV transitions are $1_{11} \leftarrow 0_{00}$ at 1427.7 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 1414.0 and the $0_{00} \leftarrow 1_{01}$ transition at 1383.4 cm^{-1}.
D_2O v_3 $(B2)$: We observe the NR transition at 2771.2 cm^{-1}. Directly observed RV transitions are the $2_{02} \leftarrow 1_{01}$ at 2793.9 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 2783.0 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ transition at 2759.3 cm^{-1}. v_1 $(A1)$: We observe the NR transition at 2659.5 cm^{-1}. One directly observed RV transitions is the $1_{11} \leftarrow 0_{00}$ at 2677.8 cm^{-1}. v_2 $(A1)$: We observe the NR transition at 1174.7 cm^{-1}. Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 1195.1 cm^{-1} and the $1_{10} \leftarrow 1_{01}$ at 1185.9 cm^{-1}.

Neon matrix
H_2O v_3 $(B2)$: We do not observe the NR transition ((4): 3759.5 cm^{-1}). Directly observed RV transitions are the $2_{02} \leftarrow 1_{01}$ at 3801.5 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ at 3784.0 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ transition at 3736.5 cm^{-1}. v_1 $(A1)$: We observe the NR transition at 3660.3 cm^{-1}. Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 3697.4 cm^{-1} and the $1_{10} \leftarrow 1_{01}$ at 3681.2 cm^{-1}.
v_2 $(A1)$: We do not observe the NR transition ((4),(5): 1595 cm^{-1}). Directly observed RV transitions are the $2_{12} \leftarrow 1_{01}$ at 1650.2 cm^{-1}, the $1_{11} \leftarrow 0_{00}$ at 1630.9 cm^{-1}, the $1_{10} \leftarrow 1_{01}$ at 1614.5 cm^{-1} and tentatively the $1_{01} \leftarrow 1_{10}$ at 1580.0 cm^{-1}.
HDO v_3 (A'): We observe the NR transition at 3699.6 cm^{-1} (corresponding to (5) at 3699.0 cm^{-1}) and at 3713.9 cm^{-1} (corresponding to (4) at 3713.8 cm^{-1}). This is in disagreement with literature. In analogy to the argon spectrum, the signal at 3718.9 cm^{-1} is tentatively assigned as N_2 induced (in (5) assigned as $1_{10} \leftarrow 1_{01}$). Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 3740.1 cm^{-1} (in (5) assigned as $2_{12} \leftarrow 1_{01}$) and the $1_{01} \leftarrow 0_{00}$ at 3729.6 cm^{-1} (in (5) assigned as $1_{11} \leftarrow 0_{00}$). v_1 (A'): We do not observe the NR transition ((5): 2722.9 cm^{-1}). Directly observed RV transitions are the $1_{01} \leftarrow 0_{00}$ at 2742.8 cm^{-1} and the $0_{00} \leftarrow 1_{01}$ at 2713.0 cm^{-1}. v_2 (A'): We observe the NR transition at 1403.7 cm^{-1}. Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ transition at 1433.3 cm^{-1}, the $1_{01} \leftarrow 0_{00}$ transition at 1419.4

cm^{-1}[1] and the $0_{00} \leftarrow 1_{01}$ transition at 1389.9 cm^{-1}. Furthermore, there is an unassigned transition at 1421.7 cm^{-1}.

D$_2$O v_3 (B2): We do not observe the NR transition ((4): 2790.0 cm^{-1}). Directly observed RV transition are the $1_{01} \leftarrow 0_{00}$ at 2802.2 cm^{-1}, and tentatively the $0_{00} \leftarrow 1_{01}$ at 2778.7 cm^{-1}. **v_1 (A1):** We observe a weak signal of the NR transition ((5): 2672.7 cm^{-1}) in the three layer experiment. One directly observed RV transition is the $1_{11} \leftarrow 0_{00}$ at 2696.3 cm^{-1}. **v_2 (A1):** We do not observe the NR transition ((5): 1178.7 cm^{-1}). Directly observed RV transitions are the $1_{11} \leftarrow 0_{00}$ at 1199.4 cm^{-1} and the $1_{10} \leftarrow 1_{01}$ at 1190.4 cm^{-1}. A weak signal indicates the $1_{01} \leftarrow 1_{10}$ at 1170.8 cm^{-1}.

Assignment of Water Dimers in Argon and Neon MI-IR spectra.

The experiments in here focus on the study of the water monomer and are not performed to identify dimers. Still, water dimers are observed in the matrix and ruled out to not interfere with the monomer assignment. Preliminary VSCF calculations are performed and listed together with the experimental observation in Table S1. We identify some bands pertaining to water dimers, as inferred from comparison with literature experiments (1)(5). Monomers within hydrogen-bridged water oligomers can be distinguished as proton acceptor (PA) and proton donor (PD) species, where the corresponding vibs of PA and PD are shifted compared to the isolated monomer species (6). In Ar matrices, vibs of PD and PA in the water dimer isotopomers (H_2O, HDO and D_2O) are well characterized in literature and summed up by Engdahl et al. (1). In Ne matrices, the vibs of PA and PD in the water dimer were previously studied considering H_2O (7), H_2O and D_2O (8), or H_2O, HDO and D_2O (5). When compared to literature and preliminary VSCF calculations of the water dimer, we find 8 PD bands and 3 PA bands in Ar matrix, whereas in Ne matrix we find 9 PD bands and 4 PA bands. Some of the here assigned PD bands of HDO in Ne matrix were not mentioned in previous studies. The assignments of water dimers are listed in the Supporting Information (see Tab. S1).

We are planning further experiments and calculations in order to study whether a combination of MI-IR and VSCF/VCI will help to add knowledge to the water dimer.

Table S1. Directly observed vibration transitions of water dimers.

Table S1: Directly observed vibration transitions of water dimers. Vibration transitions of water dimers build from the isotopomers $H_2^{16}O$, $HD^{16}O$ and $D_2^{16}O$ in argon and neon matrices at 6 K.
Each cell contains the v_3, v_1, v_2 fundamentals in descending order.
Green = new assigned, as similar to Argon matrix.
VCI(SDTQ) on a 3-mode PES with localized (local=3) normal-modes at CCSD(T)-F12/VTZ-F12 level of theory.
[f] Ref. (1) [g] Ref. (3) [h] Ref. (5) [i] Ref. (8) [k] (2)

Vibration of the Proton Donor (PD)

PA \ PD		Argon			Neon			VSCF / VCI		
		H_2O	HDO	D_2O	H_2O	HDO	D_2O	H_2O	HDO	D_2O
H_2O	v_3	**3707.8**	**3693.6**	**2746.5**	**3734.2**			3682.6 / 3703.1		
	v_1	*3573.6*[f]	**2638.6**	**2615.8**	**3591.1**	2646.6	2628.5	3529.9 / 3624.5		
	v_2	*1610.6*[f]	*1397.9*[f]	**1189.5**	*1616.4*[i]			1641.8 / 1683.9		
HDO	v_3			*2745.7*[f]						
	v_1		**2636.3**	**2614.6**		2645.9	2627.7			
	v_2					1402.0				
D_2O	v_3			*2745,1*[f]			**2763.4**			
	v_1		*2635.4*[f]	*2613.9*[f]			**2626.2**			
	v_2						*1192.2*[i]			

Vibration of the Proton Acceptor (PA)

PD \ PA		Argon			Neon			VSCF / VCI		
		H_2O	HDO	D_2O	H_2O	HDO	D_2O	H_2O	HDO	D_2O
H_2O	v_3	*3737.8 / 3715.7*[k]			*3763.4*[i]			3723,9 / 3744.2		
	v_1	*3633.1*[k]			*3674.0 / 3672.1*[i]			3671,6 / 3647.5		
	v_2	**1593.4**			**1599.6**			1599.3 / 1636.9		
HDO	v_3		*3679.9*[f]	*2764.7*[f]						
	v_1	*3632.5*[f]	*2704.5*[f]	*2653.9*[f]						
	v_2		**1402.7**	**1176.9**		1408.3				
D_2O	v_3		*3679.9*[f]	*2764.7*[f]			**2785.3**			
	v_1	*3632.5*[f]	*2704.5*[f]	*2653.9*[f]			*2676.8 / 2676.4*[i]			
	v_2		**1402.7**	**1176.9**			**1181.8**			

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