

## Water Dimer in Solid Neon. Far-Infrared Spectrum

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Infrared spectra of water and deuterated water isolated in neon matrices have been recorded between 20 and 5000  $\text{cm}^{-1}$ . The water concentration has been varied between very low concentrations with only monomers present up to concentrations where pentamers and possibly hexamers are present in significant amounts. The concentration dependencies of the observed absorption bands have been used to assign the dimer spectrum. The matrices studied were on the order of 1 mm thick, which has made it simpler to vary concentrations in a manner which discriminates between higher aggregates. It has also made it possible to avoid the baseline problems which appear when the matrices are only slightly thicker than the wavelengths in the far-infrared part of the spectrum.

### Introduction

The water dimer is formed from a hydrogen bond acceptor and a hydrogen bond donor, with an almost linear bond from the donor to the acceptor. The structure was established by microwave investigations of Dyke et al.<sup>1</sup> However, the structure is far from rigid, the acceptor hydrogens can change places, the donor and acceptor molecule can change roles, and the bonded donor hydrogen can change place with the free donor hydrogen. All exchanges which keep the covalent bonds intact are possible; the symmetry group of the water dimer has the order 16.<sup>2</sup> The interchange pathways have been elucidated by combinations of theoretical investigations and microwave-terahertz spectroscopy.<sup>3,4</sup> The intermolecular vibration spectrum below approximately 150  $\text{cm}^{-1}$  has been measured by Saykally and co-workers,<sup>4–7</sup> and potential energy functions which are in approximate agreement with the observed spectra have been constructed.<sup>6,8,9</sup> After some initial difficulties connected with the tendency of molecular beam sources to form surprisingly large concentrations of water trimers, the intramolecular vibration spectrum of the free water dimer has been assigned.<sup>10–12</sup>

Early *ab initio* calculations have already predicted a linear water dimer, formed from a hydrogen bond acceptor and a hydrogen bond donor.<sup>13</sup> Present-day high-level calculations give a very accurate description of the minimum energy configuration and of the barriers to the different interchange mechanisms. The intermolecular vibration fundamentals in the small-amplitude limit can be obtained from the calculations with a reasonable effort. However, the amplitudes of the intermolecular vibrations are far from small, and the calculated frequencies of the lower fundamentals are not in agreement with the experimental spectrum.

Pimentel and co-workers used water to study the isolation properties of matrices, and obtained the first spectroscopic observation of the intramolecular vibration spectrum of the dimer.<sup>14</sup> The low resolving power of the infrared spectrometers of the 1950s prevented them from observing the shifted fundamentals of the acceptor. They therefore assumed that the dimer has a center of symmetry. When infrared spectrometers

with higher resolving powers became available in the 1970s, this difficulty was rapidly cleared up and the linear structure was established.<sup>15–17</sup> The only study of the intermolecular part of the water dimer spectrum is a preliminary study by Bentwood et al.,<sup>18</sup> which gives results for  $\text{H}_2\text{O}$ – $\text{HOH}$  in nitrogen and argon matrices. No previous study of the far-infrared spectrum of the water dimer in a neon matrix has been published.

### Experimental Section

The cryostat used in this work is a small immersion helium cryostat (IHC-3) from the Estonian Academy of Sciences (Dr. Ants Lõmus), modified for matrix work. The cryostat can operate from approximately 2.3 to 300 K. The matrix is deposited on a gold-plated OFHC copper mirror. To allow the study of thick matrices, a 3 mm deep, 10 mm diameter cavity with a flat bottom is drilled in the center of the mirror. The mirror temperature is measured with a Lake Shore silicon diode. Home-built electronics allow us to keep the temperature of the mirror constant within less than 0.1 K of a desired temperature. The outer shroud has a valve through which the depositions are performed. To decrease the heat load on the cryostat, the matrix gas is precooled with liquid nitrogen before entering the cryostat. The water is deposited from a separate volume, kept at 0 °C with ice–water, through a needle valve and a separate stainless steel tube parallel to the inlet tube for matrix gas. Before deposition, the valve on the shroud is opened and the deposition tubes are slid into the cryostat to a point approximately 10 mm from the cavity in the mirror. After deposition, the deposition tubes are withdrawn and the valve is closed. The cryostat has been used to study almost 3 mm thick para hydrogen matrices with no particular difficulties. The lower part of the outer shroud of the cryostat can rotate relative to the inner part. It has a CsI and a TPX window in addition to the deposition valve. It is therefore possible to record spectra over the entire infrared region.

The matrices were deposited at 3.6 K. The deposition speed was kept constant by adjustment of the matrix gas flow to keep the temperature constant. Approximately 100 mbar of Ne from a 10 L volume was deposited in approximately 1 h. The same deposition geometry was used for para hydrogen experiments. In these experiments we could use absorption bands of para

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**TABLE 1: Mid-Infrared Spectral Data of H<sub>2</sub>O–HOH (cm<sup>-1</sup>)**

3890	H <sub>2</sub> O–HOH combination band (3590.4 + 309.5)
3763.4	$\nu_3$ (H <sub>2</sub> O–HOH), decreases reversibly with <i>T</i>
3733.66	$\nu_3$ (HOH–OH <sub>2</sub> )
3674.0	$\nu_1$ (H <sub>2</sub> O–HOH)
3672.1	$\nu_1$ (H <sub>2</sub> O–HOH)
3660.6	$\nu_1$ (H <sub>2</sub> O–HOH)
3590.4	$\nu_1$ (HOH–OH <sub>2</sub> )
1909.8	(H <sub>2</sub> O) <sub>2</sub> (309.5 + 1616.4)
1884.2	(H <sub>2</sub> O) <sub>2</sub> (309.5 + 1599.2)
1767.5	(H <sub>2</sub> O) <sub>2</sub> (1616.4 + 150.8)
1725.0	(H <sub>2</sub> O) <sub>2</sub> (1599.2 + 122.2)
1711.2	(H <sub>2</sub> O) <sub>2</sub> (1616.4 + 92.2)
1616.4	$\nu_2$ (HOH–OH <sub>2</sub> )
1599.19	$\nu_2$ (H <sub>2</sub> O–HOH)

**TABLE 2: Mid-Infrared Spectral Data of D<sub>2</sub>O–DOD (cm<sup>-1</sup>)**

2785.0	$\nu_3$ (D <sub>2</sub> O–DOD), decreases reversibly with <i>T</i>
2762.6	$\nu_3$ (DOD–OD <sub>2</sub> )
2672.7	$\nu_1$ (D <sub>2</sub> O–DOD)
2676.4	$\nu_1$ (D <sub>2</sub> O–DOD)
2676.8	$\nu_1$ (D <sub>2</sub> O–DOD)
2625.9	$\nu_1$ (DOD–OD <sub>2</sub> )
1192.2	$\nu_2$ (DOD–OD <sub>2</sub> )
1181.56	$\nu_2$ (D <sub>2</sub> O–DOD)

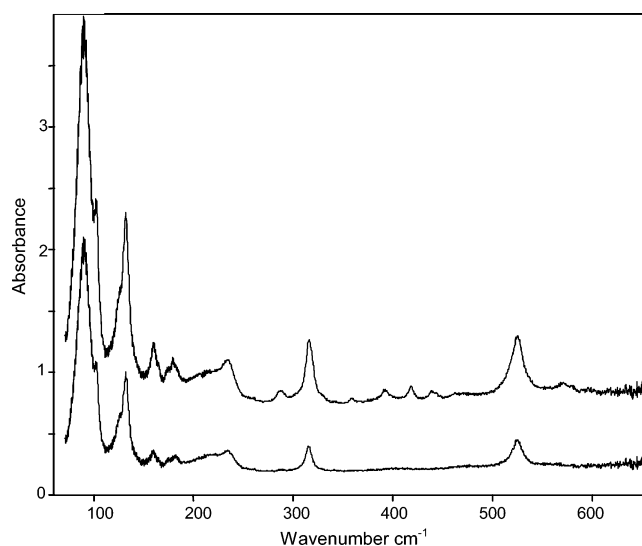
hydrogen to estimate the matrix thickness.<sup>19</sup> Using data for solid neon and for solid para hydrogen, we can estimate the matrix thickness from the amount of neon deposited. The neon matrix thickness was 0.95 mm in the present experiments. Crude estimates of the water concentration can then be obtained from the integrated intensities of water monomer bands.

Spectra were recorded with a Bruker HR120 FTIR spectrometer at 0.1 and 1 cm<sup>-1</sup> resolution in the mid-infrared spectrum and at 1 cm<sup>-1</sup> resolution below 650 cm<sup>-1</sup>. A globar source was used for most of the spectrum; a Hg lamp was used below 200 cm<sup>-1</sup>. A Ge/KBr beam splitter and an MCT detector operating above 650 cm<sup>-1</sup> (Judson) were used in the mid-infrared region and a specially coated Mylar beam splitter and a helium-cooled Si bolometer (Infrared Laboratories) with cutoff filters at 700 cm<sup>-1</sup> (used for the CsI region) and at 350 cm<sup>-1</sup> (used for the TPX region) in the far-infrared region. In a few experiments, a 75 μm Mylar beam splitter was used to obtain spectra down to 10 cm<sup>-1</sup>; with the normally used, coated beam splitter, spectra down to 20 cm<sup>-1</sup> were obtained. Spectra were recorded at temperatures from 2.8 to 10 K. Attempts to go higher lead to an immediate loss of the matrix.

Water was doubly distilled and degassed, and D<sub>2</sub>O (Norsk hydro, 99.5% D) was degassed. In one experiment, H<sub>2</sub><sup>18</sup>O was used. In a few experiments, we used a D<sub>2</sub>O and a H<sub>2</sub>O volume simultaneously, with separate needle valves. In this way we could study HDO-containing matrices. Ne (L'Air Liquide, 99.5%) was used as received. Apart from traces of carbon dioxide and water, no infrared absorption was observed in an almost 1 mm thick pure neon matrix.

### Assignment

The mid-infrared spectrum of water in solid neon has been studied by Forney et al.<sup>20</sup> Our spectra are in very good agreement with their observations both for the monomer and for the dimer. They were not able to observe the antisymmetric stretch of the acceptor of the dimer. We observed a component of this band at 3763.4 cm<sup>-1</sup>. It is easy to observe below 4 K but decreases rapidly when the temperature increases. The observations of the corresponding band of D<sub>2</sub>O suggest that there is more than one component. Unfortunately, the band is



**Figure 1.** Far-infrared spectrum of H<sub>2</sub>O in solid neon at 2.8 K (Ne/H<sub>2</sub>O = 650). The upper curve is the original spectrum, and the lower curve gives the spectrum when the trimer absorption has been subtracted. The strong band at 79.4 cm<sup>-1</sup> is a monomer band.

surrounded by intense water monomer absorptions, which may easily hide the relatively weak dimer absorption. The assignment of the mid-infrared spectrum of the water dimer is collected in Tables 1 and 2.

The intensities of the bands of a given species vary in the same way with concentration. The mid-infrared spectrum and the far-infrared spectrum are recorded of the same sample, and we have used the well-assigned mid-infrared spectrum to assign the far-infrared bands. When the matrix is warmed to above approximately 8 K, irreversible changes due to diffusion are observed. It is generally observed that bands due to the tetramer increase by a factor larger than 3, while trimer bands increase by a factor in the range 1.5–2 and dimer bands show small increases. The changes in a particular experiment are obtained from the mid-infrared spectrum. The diffusion behavior has been used to confirm the assignment in the far-infrared region.

The use of very thick matrices (close to 1 mm) has made the problems with irreproducible baselines much less than in conventional matrix isolation spectroscopy, where the matrix thickness is comparable to the far-infrared wavelengths. The assignment of the two highest far-infrared bands of the H<sub>2</sub>O experiments and of the corresponding bands in the D<sub>2</sub>O experiments is straightforward. There is a slight problem since the second highest band has a concentration dependency which is intermediate between those of the dimer and the trimer at higher concentrations. Its intensity also increases more than those of dimer bands when the matrix is warmed, but not as much as those of trimer bands. However, it is present and rather strong also in experiments where practically no trimer is present (Figure 1). In D<sub>2</sub>O experiments the corresponding band is split into two components (Figure 2), one of which increases significantly in diffusion experiments. In this case, there is no doubt that the band which increases irreversibly at 9 K is due to the trimer and the other band is due to the dimer. We are convinced that the dimer and trimer bands almost coincide in the H<sub>2</sub>O case. This idea is supported by the observation that the band shifts slightly less than 1 cm<sup>-1</sup> to higher frequencies at high water concentrations and in diffusion experiments.

A very broad band is observed at 226 cm<sup>-1</sup>. When the temperature is increased from 3 K, it decreases reversibly in intensity and obtains a low wavenumber satellite at 196 cm<sup>-1</sup>.

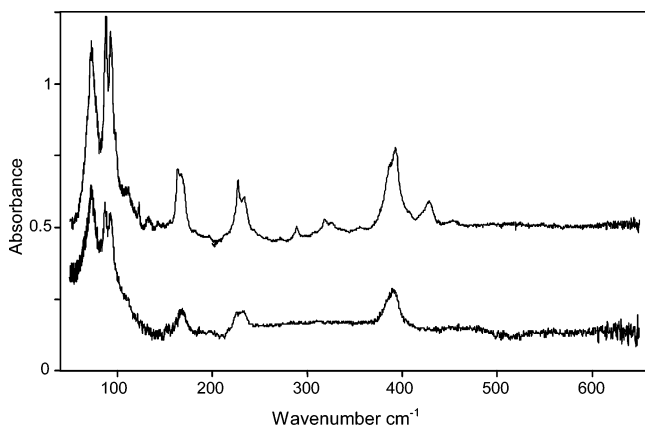
TABLE 3: Intermolecular Fundamentals ( $\text{cm}^{-1}$ )

H <sub>2</sub> O–H OH								
Ne <sup>a</sup>	Ne <sup>a</sup> [(H <sub>2</sub> <sup>18</sup> O) <sub>2</sub> ]	B <sup>b</sup> (N <sub>2</sub> )	B <sup>b</sup> (Ar)	POA <sup>c</sup>	D <sup>d</sup>	calcd <sup>e</sup>	gas <sup>f</sup>	assignment <sup>g</sup>
522.4	521.7	520		548.0	645			OPS
309.5	308.8	320	290	301.3	354			IPS
226	226	243						
173	165			137.3	186	165.64 <sup>h</sup>		S
						134.37		(DT) <sup>2</sup>
150.6	149.7	155	147	177.1	145	132.43		AT
122.2	122.2				157	113.39	107.93	AW
92	92				140	118.26		DT

D <sub>2</sub> O–D OD				aq–DO H				
Ne <sup>a</sup>	POA <sup>c</sup>	calcd <sup>e</sup>	gas <sup>f</sup>	assignment <sup>g</sup>	D <sub>2</sub> O–D OH		H <sub>2</sub> O–D OH	
					Ne <sup>a</sup>	POA <sup>c</sup>	Ne <sup>a</sup>	POA <sup>c</sup>
388	394.0			OPS	393 <sup>i</sup>	394.0	415	410.2
233.5	218.9			IPS	257.6	249.0	257.6	245.7
167.3	126.7	146.82		S	170	142.9		145.5
		123.07	104.24	(DT) <sup>2</sup>				
98		92.04	92.91	AT				
93.3		91.58	82.64	AW				
87.8		67.35	75.38	DT				

<sup>a</sup> This work. <sup>b</sup> Reference 18. <sup>c</sup> Reference 23. <sup>d</sup> Reference 25. <sup>e</sup> References 8 and 9. <sup>f</sup> References 6 and 7. <sup>g</sup> See refs 9 and 23. OPS = out of plane shear, IPS = in plane shear, S = stretch, DT = donor torsion, AT = acceptor twist, and AW = acceptor wag. <sup>h</sup> Average value of all tunneling components. <sup>i</sup> Shifts to 402  $\text{cm}^{-1}$  in HDO–DOH.



**Figure 2.** Far-infrared spectrum of D<sub>2</sub>O in solid neon at 2.8 K (Ne/D<sub>2</sub>O = 360). The upper curve is the original spectrum, and the lower curve gives the spectrum after the trimer absorption has been subtracted. The band at 72.8  $\text{cm}^{-1}$  is the monomer D<sub>2</sub>O band, corresponding to the 79.4  $\text{cm}^{-1}$  band of H<sub>2</sub>O.

With all isotopologues, we observe a band near 170  $\text{cm}^{-1}$  which seems to be mass sensitive; the shifts between different dimers are of the order of magnitude expected for a hydrogen bond stretch. Unfortunately, the band is broad and for H<sub>2</sub>O–HOH and for H<sub>2</sub><sup>18</sup>O–H<sup>18</sup>OH disturbed by a nearby trimer peak. It is therefore not possible to give precise isotope shifts, but the fact that a band is present here for all isotopologues we have studied suggests that the band is due to the hydrogen bond stretch.

There is a strong dimer band at 122.2  $\text{cm}^{-1}$  and a weaker dimer band at 150.6  $\text{cm}^{-1}$ ; the second band is overlapped by a trimer band at higher water concentrations. There is a weak dimer band at 92  $\text{cm}^{-1}$ , on the high-wavenumber side of the water monomer band at 79.4  $\text{cm}^{-1}$ , which decreases reversibly with temperature. Finally there is a weak band at 105.1  $\text{cm}^{-1}$  which is seen at temperatures higher than 2.8 K. Its intensity increases reversibly with temperature, and its activation energy appears to be between 6 and 9  $\text{cm}^{-1}$ .

The assignment of the mid-infrared spectrum of H<sub>2</sub>O–HOH is given in Table 1 and the mid-infrared spectrum of D<sub>2</sub>O–

DOD in Table 2. The complete assignment of the far-infrared spectrum of the water dimer, including the D<sub>2</sub>O–DOD dimer and some data on HDO-containing dimers, is collected in Table 3. The bands due to HDO-containing dimers are taken from experiments with predominantly H<sub>2</sub>O or D<sub>2</sub>O, where we know from the mid-infrared spectra that HDO is present as a D donor. Dimer spectra of H<sub>2</sub>O–HOH and of D<sub>2</sub>O–DOD are given in Figures 1 and 2.

As was already observed by Bentwood et al.,<sup>18</sup> a number of combination bands between the two intramolecular bending modes of the water dimer and its intermolecular fundamentals are observed in the 1700–2000  $\text{cm}^{-1}$  region; they are given in Table 1.

## Discussion

It has been known for a long time that at the low temperatures used in matrix isolation experiments the water dimer prefers to form D bonds to H bonds.<sup>16,17</sup> This is due to a difference in zero-point vibration energy between isomers with H and D bonds. A detailed analysis of the intra- and intermolecular fundamentals of different isotopologues of the water dimer showed that the main contribution to this energy difference comes from the out of plane shear vibration of the donor molecule.<sup>21–23</sup> In this vibration, the motion is almost entirely confined to the H (D) atom of the hydrogen bond, which moves orthogonal to the bond. Experimentally the zero-point vibration energy difference was found to be approximately 50  $\text{cm}^{-1}$  for several different isotopologues of the water dimer,<sup>22</sup> indicating that the frequency of the out of plane shear vibration is not far from 500  $\text{cm}^{-1}$  in H<sub>2</sub>O–HOH. In the measurements presented here we find the highest observed intermolecular band of H<sub>2</sub>O–HOH at 522.4  $\text{cm}^{-1}$ , and of D<sub>2</sub>O–DOD at 388  $\text{cm}^{-1}$ . The ratio, 1.33, is clearly of the right order of magnitude for a pure hydrogen motion. For a harmonic vibration the ratio is expected to be 1.41, but anharmonicity makes it smaller. We assign this band to the out of plane shear vibration of the hydrogen bond donor. The next highest intermolecular band of H<sub>2</sub>O–HOH is found at 309.5  $\text{cm}^{-1}$ . In D<sub>2</sub>O experiments it shifts to 233.5  $\text{cm}^{-1}$ ; the ratio H/D is 1.32 in this case. This band is assigned to the

in plane shear vibration of the hydrogen bond donor. When significant concentrations of HDO are present, we observe new bands at  $402\text{ cm}^{-1}$  (broad) and at  $257.6\text{ cm}^{-1}$ . In experiments with  $\text{D}_2\text{O}$ , contaminated by a relatively small amount of HDO, the first band shifts to  $393\text{ cm}^{-1}$ , and in experiments where  $\text{H}_2\text{O}$  dominates, it is found at  $415\text{ cm}^{-1}$ . The  $257.6\text{ cm}^{-1}$  band shifts insignificantly. We assign these bands to the out of plane and in plane shear vibrations of HDO as D bond donor to another water molecule. As expected,<sup>22,23</sup> the out of plane shear vibration of D-bonded HDO ( $\text{H}_2\text{O}$ ,  $415\text{ cm}^{-1}$ ; HDO,  $402\text{ cm}^{-1}$ ;  $\text{D}_2\text{O}$ ,  $393\text{ cm}^{-1}$ ) is close to the corresponding vibration in donor  $\text{D}_2\text{O}$  ( $392.8\text{ cm}^{-1}$ ), while the in plane shear vibration ( $257.6\text{ cm}^{-1}$ ) is intermediate between the corresponding vibrations of  $\text{H}_2\text{O}$  ( $309.5\text{ cm}^{-1}$ ) and  $\text{D}_2\text{O}$  ( $233.8\text{ cm}^{-1}$ ). The out of plane shear fundamentals observed here are in good agreement with the corresponding bands for HDO–DOH ( $412\text{ cm}^{-1}$ ) and for HDO–HOD ( $536\text{ cm}^{-1}$ ) in solid argon, observed by Engdahl and Nelander in a laser irradiation experiment.<sup>24</sup>

The model of Åstrand et al.,<sup>23</sup> which takes cubic anharmonicity into account, works very well for the two upper intermolecular fundamentals. This is illustrated by the comparison with ref 25, which gives harmonic frequencies. The model of Åstrand et al. gives both band positions and H to D shifts, which are close to their experimental values. It fails completely for the lower fundamentals. The theoretical calculations give no indication of the nature of the  $226\text{ cm}^{-1}$  band of  $\text{H}_2\text{O}$ –HOH.

There is a reasonable correspondence between the calculated values of refs 8 and 9 and our observed low-frequency dimer bands (Table 3). Only the calculated and observed gas-phase components from the lower acceptor switching state of the  $\text{H}_2\text{O}$  dimer and  $\text{D}_2\text{O}$  dimer are given in Table 3 since we expect that transitions from the upper component will be absent at our lowest temperature (2.8 K) and appear only at higher matrix temperatures. The only matrix band which does not seem to have a clear correspondence with gas-phase or calculated dimer bands is the  $92\text{ cm}^{-1}$  band. It appears as a weak satellite on the high-frequency side of the monomer band at  $79.4\text{ cm}^{-1}$ , and it is impossible to measure its concentration dependency. It is present already at low concentrations, ruling out its assignment to a water aggregate larger than the dimer. Since its intensity decreases with increasing temperature, we do not think it is due to monomer  $\text{H}_2\text{O}$ .

For  $\text{H}_2\text{O}$ –HOH we observe some bands in the far-infrared, which appear when the matrix is heated. For one such band, at  $105.1\text{ cm}^{-1}$ , we can estimate that the lower state is  $6\text{--}9\text{ cm}^{-1}$  above the ground state. This is reasonably close to the  $11.18\text{ cm}^{-1}$  difference between the upper acceptor switching state and the ground state in the gas phase.<sup>7</sup> The presence of acceptor switching may explain why the  $A''$  intramolecular bands  $\nu_3$ –( $\text{H}_2\text{O}$ –HOH) and  $\nu_3$ ( $\text{D}_2\text{O}$ –DOD) are temperature dependent and more difficult to observe than the other intramolecular bands.

The potential of ref 8 gives good predictions of the vibration–tunneling–rotation transitions observed in molecular beam spectroscopy.<sup>4–7</sup> Our peak positions are reasonably close to the calculated band positions of refs 8 and 9. It therefore seems as if a neon matrix has a relatively minor influence on the intermolecular motions of the water dimer. There is a clear correspondence between the water dimer spectrum observed in this work and the data of Bentwood et al. for nitrogen and argon matrices,<sup>18</sup> indicating that their assignments were correct despite the very large experimental difficulties they had to overcome.

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