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Intermolecular Vibrations of the Water Trimer, a Matrix Isolation Study

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Infrared spectra from 25 to 4000 cm^{-1} have been recorded of water (H$_2$O, D$_2$O and H$_2^{18}$O) matrix isolated in neon, argon, and krypton matrices. Intermolecular absorption bands of different isotopologues of the water trimer and tetramer have been assigned from concentration dependencies and diffusion behavior, using the well-known mid-infrared trimer and tetramer absorption bands as measures of the trimer and tetramer concentrations. The results are compared to ab initio calculations.

Introduction

Water clusters have been the subject of a large number of experimental and theoretical studies. The simplest cluster, the water dimer was first observed in a nitrogen matrix by Pimentel and co-workers.[1] Later matrix studies established that it has a linear hydrogen bond with one of the water molecules acting as hydrogen bond donor and the other as hydrogen bond acceptor.[2−5] Dyke and co-workers[6] used microwave spectroscopy on molecular beams to obtain the structure of the dimer. Since then, numerous microwave and far-infrared experiments on water dimers in molecular beams have mapped out the tunneling path ways between the 8 different potential energy minima of the dimer.[7,8] The intramolecular fundamentals of gaseous water dimers have been measured by different methods.[9,10] The upper intermolecular fundamentals of the water dimer have so far not been observed in the gas phase. We have recently measured them for water dimers in solid neon.[11]

Early ab initio calculations found that the water trimer has a cyclic structure with each water molecule acting both as hydrogen bond donor and hydrogen bond acceptor. The free hydrogens of two of the molecules point to one side of the OOO-plane and that of the third water molecule to the other side. A matrix isolation study of different partially deuterated trimers showed that the three water molecules in the trimer are equivalent, suggesting a rapid tunneling between the six equivalent minima resulting from flipping of the hydrogens from one side of the OOO-plane to the other.[12] Far-infrared spectroscopy measurements by Saykally and co-workers have shown that the torsion tunneling is indeed rapid and that in addition bifurcation tunneling, exchanging free and bound hydrogens occurs but on a slower time scale.[13,14] Wales has shown that the torsion spectrum of the trimer can be understood from a simple model.[15,16] Keutsch et al. have summarized the experimental and theoretical studies of the water trimer.[17] In this paper, we present a matrix isolation infrared spectroscopic study of the water trimer in noble gas matrices with particular emphasis on the far-infrared spectrum, using our newly developed technique to prepare thick matrixes.[11]

Experimental Section

The cryostat used in this work is a small immersion helium cryostat, (IHC-3) from the Estonian Academy of Sciences (Dr. Ants Lômus), modified for matrix work. The cryostat can operate from approximately 2.5 to 300 K. The matrix is deposited on a gold plated OFHC copper mirror. To allow the study of thick matrices, a three 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 allows us to keep the temperature of the mirror constant within less than 0.1 K from 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 (for Kr matrices, we used liquid oxygen) 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 slided 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 parahydrogen 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 (Ne), 17 (argon), or 20 K (krypton). The deposition speed was kept constant by adjustment of the matrix gas flow to keep the temperature constant. Approximately 100 mbar of matrix gas from a 10 l volume was deposited in approximately 1 h. For neon matrices, this corresponds to approximately 1 mm thick matrices.

Spectra were recorded with a Bruker HR120 FTIR spectrometer at 0.1 and 1 cm^{-1} resolution in the mid-infrared region and at 1 cm^{-1} resolution below 650 cm^{-1}. A Ge/KBr beam splitter and an MCT detector operating above 650 cm^{-1} (Judson) was used in the mid-infrared region and a specially coated Mylar beam splitter and a helium cooled Si bolometer (Infrared Laboratories) with cut off filters at 700 cm^{-1} (Used for the CsI region) and at 350 cm^{-1} (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^{-1}, with the

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TABLE 1: (H₂O)₃ Bands in Noble Gas Matrices (cm⁻¹)

Ne	Ar	Kr	assignment
3725	3699.3	3690	free OH str
3529.6	3514.6	3514	bound OH str
3518	3527	3522	shoulder on bound OH str
1608.2	1601.7	1599.7	HOH bending
569.4	550.3	544.8	shear libration see text
578			shoulder on previous band
458.3		439.4	comb. band, see text
434.8	423.2	419.0	comb. band, see text
414.1	400.9	396.9	comb. band, see text
386.8	373	369.7	comb. band, see text
353.0	343.4	339.9	comb. band, see text
310.8	304.4	300.3	*c*-axis libration see text
280	271.0	270.7	
170.2	153.2	150.5	H-bond stretch
151.0	146.3	143.8	H-bond stretch

**TABLE 2: (D₂O)₃ Bands in Noble Gas Matrices (cm⁻¹)**

Ne	Ar	Kr	assignment
2759.1			
2754.2	2736.4	2733	free OD str
2751			
2584.7	2579.0	2576.9	bound OD str
1186.2	1182	1181	DOD bending
428	406	404	shear libration, see text
356			combination band
325.6	313		combination band
318.5			combination band
289.0	279		combination band
272			combination band
227.1	222	204	*c*-axis libration
163.6	146.8	143.3	D-bond stretch
123			
122.7	120.2	115	

normally used, coated Mylar beam splitter, spectra down to 20 cm⁻¹ were obtained. The globar source was used for spectra in the CsI region and the Hg source for spectra in the TPX region. Spectra were recorded at temperatures from 2.8 (Ne) or 4.2 K (argon and krypton) up to 10 (Ne), 30 (argon), or 40 K (krypton). With neon, attempts to go higher lead to an immediate loss of the matrix.

Water was doubly distilled and degassed and D₂O (Norsk hydro 99.5%D) was degassed. In one experiment in each matrix, H₂¹⁸O (Isotech Normalized 95.7 atom % ¹⁸O) was used. In a few experiments in neon, we used a D₂O and a H₂O 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. Argon (L'Air Liquide 99.9995%) and krypton (Air Products 99.995%) were used as received. Apart from traces of carbon dioxide and water, no infrared absorption was observed in the pure noble gas matrices.

Assignment

The mid-infrared spectrum of the water trimer in argon and krypton matrices is summarized in ref 18. The bound OH stretches of (H₂O)₃ and (H₂¹⁸O)₃ in neon matrices are given in ref 19. The remaining intramolecular bands of (H₂O)₃ and the corresponding bands of (D₂O)₃ are identified by comparisons with argon and krypton spectra, concentration dependency studies, and controlled diffusion experiments. The intramolecular fundamentals of (H₂O)₃ are given in Table 1 and the corresponding bands of (D₂O)₃ are given in Table 2. Figure 1 shows the upper part of the far-infrared spectrum of H₂O and of D₂O in neon matrices. Figure 2 shows the upper part of the far-infrared spectrum of H₂O in krypton, argon, and neon matrices.
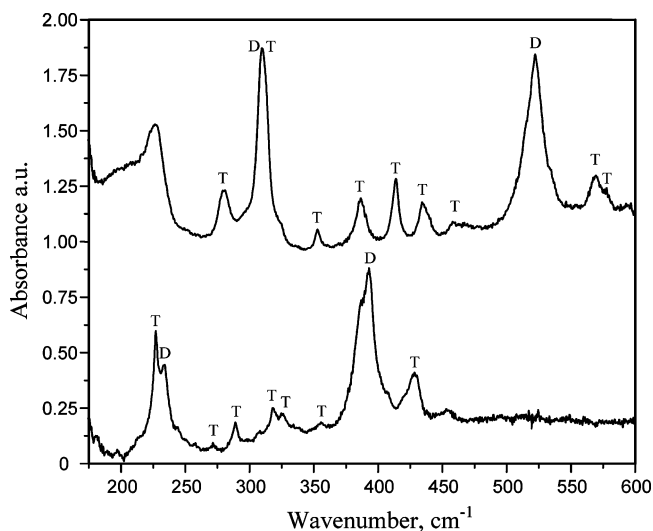
Figure 1. Far-infrared spectrum (180−600 cm⁻¹ region) of H₂O (upper, Ne:H₂O = 500) and D₂O (lower, Ne:D₂O = 356) in solid neon at 2.8 K. Key: D, dimer; T, trimer.
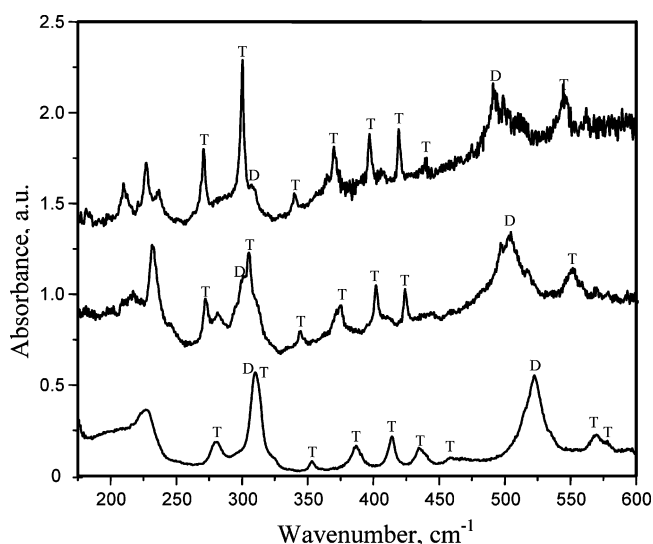
Figure 2. Far-infrared spectrum (180−600 cm⁻¹ region) of H₂O in solid neon (2.8 K, bottom), argon (4.2 K, middle), and krypton (4.5 K, top). Key: D, dimer; T, trimer.

The baseline in the far-infrared in neon matrix experiments is a straight line. It is therefore easy to measure intensities even of weak and broad bands. Concentration dependency studies and comparisons with the intensity of a given band with the intensity of the bound OH stretch in the mid-infrared makes it possible to assign the bands in the far-infrared spectrum to monomer, dimer, trimer, and tetramers of water. The assignments can then be checked in controlled diffusion experiments, where the matrix is warmed to above 8 K for some time and then cooled back to 4 or 2.8 K. Under these conditions the tetramer bands increase by a large factor, trimer bands by a factor on the order of 2 and dimer bands by small amounts. The precise values of the increases in each experiment are obtained from the bound OH stretches of the respective species.

Argon and krypton matrices were more scattering and the baselines in the far-infrared were curved. However, since there is a clear correspondence between bands in neon and in argon and krypton, we had no difficulties in assigning also the argon and krypton spectra. The assignment of (H₂O)₃ is collected in Table 1 and of (D₂O)₃ is collected in Table 2. The tetramer assignment is collected in Tables 3 and 4.

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TABLE 3: $(H_2O)_4$ Bands in Noble Gas Matrices (cm^{-1})

Ne	Ar	Kr	assignment
3718.5	3694.8		free OH stretch
3716.5			free OH stretch
3382.0	3372.5	3368	bound OH stretch
669.2	655	650	shear libration
222.1	216		H-bond stretch
215.9	207	210	H-bond stretch

TABLE 4: $(D_2O)_4$ Bands in Noble Gas Matrices (cm^{-1})

Ne	Ar	Kr	assignment
2745	2733	2726	free OD stretch
2494.1	2487.4	2486.5	bound OD stretch
515			shear libration
498			
213	209.3		D-bond stretch
	200.4		
	199.6		

TABLE 5: Calculated Structural Parameters for $(H_2O)_3$ (Å and deg; See Text) (OH_1 is the Bound OH and OH_2 the Free OH)

	MP2	MP2+zero point
$R(OH_1)$	0.967	0.967
$R(OH_2)$	0.956	0.956
$R(OO)$	2.796	2.836
$\alpha(HOH)$	106.50	106.50
$\alpha(OHO)$	143.12	144.14

Computational Details

To facilitate the interpretation of the experimental spectrum, a series of quantum chemical calculations were performed with the Gaussian program system.[20] All results reported here were obtained at the MP2-level of approximation and a 6-311+G^{2d,2p} basis set was used. In order that the calculated results should be comparable with the experimentally observed spectrum, it is important that a proper geometry is chosen for the calculation of the spectrum. In this work, we have followed the procedure suggested previously by us.[21] In practice, this means that we first performed a full geometry optimization of the $(H_2O)_3$ ring system assuming it to have C_{3h}-symmetry. In a second step we froze the intramolecular degrees of freedom in the water molecules and optimized a new structure, again assuming C_{3h}-symmetry, by minimizing the sum of the MP2 energy for the system and the zero-point vibrational energy. This lead to a structure where the O−O distances are slightly longer than in the optimized MP2 structure. The relevant geometry parameters for the two structures are given in Table 5. It should be noted that the chosen procedure results in a set of imaginary frequencies. These frequencies corresponds to vibrational modes that moves one or more of the free hydrogens out of the molecular plane. Basically no information is lost by this procedure since for the real system the true potential for these degrees of freedom corresponds to double well potentials which cannot be handled in an harmonic approximation. The calculated vibrational frequencies for the MP2 and MP2 plus zero-point vibration energy of $(H_2O)_3$ and for the MP2 plus zero-point vibration energy of $(D_2O)_3$ are given together with the experimentally measured spectra in Tables 6 and 7. In addition we have also studied the water tetramer, but with a somewhat smaller basis set MP2 6-311+G^{1d,1p}. The calculated frequencies of $(H_2O)_4$ are given in Table 8. For comparison we present data calculated for a free H_2O molecule (6-311+G^{2d,2p}) in Table 9 together with experimental frequencies for the same system.

TABLE 6: Calculated and Measured Frequencies for $(H_2O)_3$ $(cm^{-1})^a$

MP2	trimer shift	MP2+ zero point	trimer shift	Ne	trimer shift	sym
3963.4(179)	42.5	3964.0(174)	43.1	3725	13	E+
3962.1(0)		3962.9(0)				A+
3758.8(350)	−162.1	3762.3(302)	−158.6	3529.6	−182.8	E+
3724.2(0)		3732.9(0)				A+
1691.8(0)		1682.0(0)				A+
1662.9(110)	2.7	1660.0(110)	−0.2	1608.2	12.8	E+
592.2(135)		579.6(141)		569.4		A−
580.7(0)		557.7(0)				A+
433.4(0)		434.6(0)				E−
348.2(209)		334.4(203)		310.8		E+
215.6(0)		189.2(0)				A+
179.2(14)		159.8(14)		170.2		E+
				151.0		

^{a} Calculated intensities in km/mol are given in parentheses. Stretch shifts are calculated from the average of the symmetric and antisymmetric OH stretches of H_2O.

TABLE 7: Calculated and Measured $(D_2O)_3$ Frequencies $(cm^{-1})^a$

MP2+ zero point	trimer shift	Ne	trimer shift	sym
2898.0(130)	48.4	2759.1	25.7	E+
		2754.2		
		2751		
2896.9(0)				A+
2719.1(138)	−130.5	2584.7	−148.7	E+
2700.4(0)				A+
1227.3(0)				A+
1214.1(61)	−1.2	1186.2	7.3	E+
416.4(86)		428		A−
411.2(0)				A+
310.9(0)				E−
243.9(92)		227.1		E+
179.5(0)				A+
149.7(18)		163.6		E+
		123		
		122.7		

^{a} Calculated intensities in km/mol are given in parentheses. Calculated monomer frequencies 2916.6, 2782.6, 1215.3 cm^{-1}; experimental monomer frequencies 2790.0, 2676.8, 1178.9 cm^{-1}. The stretch shifts are calculated from the average of the monomer stretches.

Discussion

Both ab initio calculations and spectroscopic results show that the water trimer is cyclic.[17] Ab initio calculations give a cyclic equilibrium structure with each water molecule acting both as hydrogen bond donor and as hydrogen bond acceptor. Two of the free hydrogens are found above the oxygen atom plane and one below. The symmetry of the rigid trimer is therefore C_1, and there are six equivalent minima. The torsion barrier of the free water trimer is low, however, and in the first approximation, the trimer spectrum has to be classified according to a group with six elements, isomorphic with C_{3h}[15,16] (Table 10). The exchange between free and hydrogen bonded hydrogens (bifurcation tunneling) is fast enough to be observable in high-resolution gas-phase experiments and these spectra are classified according to a group with 48 elements.[15] It seems reasonable to expect that the flipping of the free hydrogens is rapid also in noble gas matrices. Studies of matrix isolated trimers with mixed H and D content indicate that the three water molecules are equivalent[12] suggesting that this is indeed true. The line width in matrices is on the order of 1 cm^{-1}, bifurcation tunneling may therefore be ignored except possibly for states involving c-axis librations of the trimer components. We therefore expect that the spectra of matrix isolated water trimer

TABLE 8: Measured and Calculated Frequencies for $(H_2O)_4$ $(cm^{-1})^a$

MP2	tetramer shift	MP2 + zero point	tetramer shift	Ne	tetramer shift	S_4 sym
3977.7(0)		4067.6(0)				A
3976.4(114)	33.2	4066.7(101)	123.6	3718.5	6.1	E
3975.0(120)		4066.0(111)		3716.5		B
3648.5(9)		3660.1(17)				B
3609.7(1285)	−333.4	3627.4(1126)	−315.8	3382.0	−330	E
3522.9(0)		3555.9(0)				A
1690.0(0)		1688.1(0)				A
1669.3(58)		1660.5(62)				E
1660.8(97)	32.5	1648.6(85)	20.3			B
1002.9(0)		951.8(0)				A
824.5(234)		796.6(215)		690		E
788.4(268)		767.8(286)		669.2		B
451.5(39)		366.6(74)				E
416.1(24)		334.0(33)				B
405.1(0)		321.2(0)				A
270.6(0)		226.0(0)				A
246.8(0.4)		182.0(0)				B
236.6(169)		211.2(46)		222.1		E
				215.9		

^{a} Calculated monomer frequencies with the basis set used for the tetramer: 4002.6, 3883.7, 1628.3 cm^{-1}.

TABLE 9: Calculated and Measured Water Monomer Frequencies. (cm^{-1})

	MP2	gas phase	Ne	Ar	Kr
asym str	3981.0	3755.8	3759.5	3734.1	3724.1
sym str	3860.8	3656.7	3665.4	3638.4	3628.8
bend	1660.2	1594.6	1595.4	1588.7	1586.8

TABLE 10: Character Table for the Symmetry Group of $(H_2O)_3$ with a Low Torsion Barrier^a

			"C_{3h}"			
E	"C_3"	$("C_3")^2$	"σ_h"	"S_3"	$("S_3")^2$	
1	1	1	1	1	1	A^+
1	1	1	−1	−1	−1	A^-, z
1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4	E^+, x, y
1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2	E^+
1	ϵ^2	ϵ^4	−1	$-\epsilon^2$	$-\epsilon^4$	E^-
1	ϵ^4	ϵ^2	−1	$-\epsilon^4$	$-\epsilon^2$	E^-

^{a} $\epsilon = \exp(i\pi/3)$.

can be classified according to C_{3h}, with the possible exception of the bands from the *c*-axis libration of water where the upper states are expected to be close to the bifurcation exchange barrier. We note here that the water molecules of the electronic energy minimum of ab initio calculations are all inequivalent. Therefore, all fundamentals are infrared active.[22] The splittings for some groups of frequencies are relatively large and should give observable splittings in the spectra in contrast to our observations. In order for an ab initio calculation to give qualitatively correct vibration data, the effective symmetry of the trimer has to be taken into account.

The water trimer has 21 vibrational degrees of freedom. Nine of these correspond to intramolecular vibrations. Each molecule has a free OH stretch, a bound OH stretch and a bending vibration. The three types of vibration are rather well separated and in each group, the vibrations can be combined into one A^+ and two E^+ vibrations (Table 10). The A^+ vibrations are inactive and the E^+ vibrations are IR active. We therefore expect one trimer band in each of the three regions as is observed (Tables 6 and 7).

The 12 intermolecular degrees of freedom may be divided into three torsions around the bound OH bonds, three stretches of the center of mass distances, three *c*-axis librations, and three librations around the free OH bonds (shear librations). Both the shear vibrations and the *c*-axis librations deform the hydrogen bonds, their force constants are therefore expected to be similar. Only the hydrogen of the hydrogen bond moves in a shear vibration while both hydrogens move equally in a *c*-axis libration. The shear librations are therefore expected to have frequencies approximately 1.4 times higher than the *c*-axis librations. Calculations and matrix isolation experiments have shown that these two types of librations are present in many different binary water complexes, including cyclic complexes,[21] we therefore expect these librations to be present also in the water trimer. Both the stretches and the *c*-axis librations can be combined into one A^+ and two degenerate E^+ components. The shear librations combine into one infrared active A^- and two degenerate infrared inactive E^- librations. One therefore expects one infrared active fundamental band for each of the librations and one for the center of mass stretches. The intermolecular stretching band is expected to be weak with most of its intensity coming from an admixture of librations. The two libration bands are expected to be intense, since they get their intensities from librations of the molecular dipole moments. The pure torsion absorptions are expected to fall in a region, where the water monomer absorption is too strong to allow observation of the trimer bands.

For $(H_2O)_3$ in neon, we observe strong bands at 569.0 and at 309.5 cm^{-1} (Figure 1) which do not shift in $H_2^{18}O$ experiments but shift to 428.5 and 227.3 cm^{-1} with $(D_2O)_3$ (Figure 1). These bands are assigned to the shear and *c*-axis libration bands respectively of the trimer. The corresponding bands are observed in argon and krypton (Figure 2 and Tables 1 and 2). The very small ^{16}O to ^{18}O shifts and the size of the H to D shifts show that only hydrogens are moving. The positions of the two bands are found in the same ranges as the corresponding water libration bands found in several water complexes with water as hydrogen bond donor.[21] The ratio between the shear and the *c*-axis libration is larger than expected from the simple considerations above. We note that the shear vibrations interact to form one nondegenerate, infrared active fundamental and a doubly degenerate inactive pair, while the *c*-axis librations form one nondegenerate, infrared inactive vibration and an infrared active degenerate pair (see Tables 6 and 7). Calculations given in Tables 6 and 7 indicate that the two non degenerate vibrations have the highest frequencies in the two groups and find quite large splittings both for shear and *c*-axis librations.
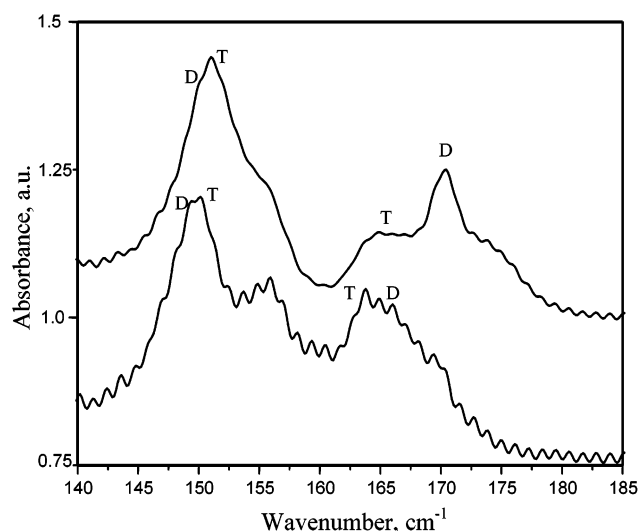
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Figure 3. Far-infrared spectrum (140–185 cm^{-1} region) of H_2O^{16} (top) and H_2O^{18} (bottom) in solid neon at 2.8 K. Key: D, dimer; T, trimer.

Between the two strong bands, assigned to the shear and *c*-axis librations, there are four weaker but distinct bands (Figures 1 and 2). We suggest that they are due to combinations between torsions and *c*-axis librations. The potential functions of the *c*-axis librations are expected to vary strongly with the torsion angles. We may therefore expect to see combined torsion and libration transitions. For the *c*-axis librations, the E$^+$ libration may combine with the first excited torsion state (E$^-$) to form an E$^-$ state and two A$^-$ states, transitions to the A$^-$ states are symmetry allowed. It is difficult to say anything about the splitting of the two A$^-$ states without a picture of the torsion involved. The A$^+$ excited libration state can combine with the second excited torsion state (E$^+$) to form an E$^+$ state, with an allowed transition from the ground state. The position of this state above the pure *c*-axis libration excited state is to a large extent determined by the A to E splitting of the *c*-axis libration, which is calculated to be 223 cm^{-1}. Also the E$^+$ libration states can combine with the second excited torsion state to form two A$^+$ states and an E$^+$ state. The transition to the E$^+$ state is infrared allowed. The distance from the pure *c*-axis libration band is a torsion transition in the *c*-axis libration excited state, which is not identical to a ground-state torsion transition. Since *c*-axis libration is a motion in the direction of bifurcation tunneling the combination bands may be doubled by bifurcation tunneling. We observe corresponding bands in the interval between the *c*-axis libration band at 227 cm^{-1} (Ne) and the shear libration at 428 cm^{-1} (Ne) for $(D_2O)_3$ but there is no simple relation between these bands and the bands of $(H_2O)_3$. This seems reasonable since the distances from the pure libration band depend on the unknown torsion potential of the *c*-axis libration state.

There is a clear $(H_2O)_3$ band at 280 cm^{-1} in solid neon, with corresponding bands in argon and krypton. The ^{16}O to ^{18}O shift is on the order of 2 cm^{-1}. It may be due to a combination between a hydrogen bond stretch and a torsion. We note that $(H_2O)_2$ has a band at 226 cm^{-1} which also cannot be assigned to a fundamental vibration. No corresponding D_2O bands have been observed.

In the region between 140 and 175 cm^{-1} (see Tables 2 and 3 and Figure 3) pairs of bands are found which shift significantly in $H_2^{18}O$ experiments. There are corresponding bands in the D_2O experiments. We believe that these bands contain significant contributions from the hydrogen bond stretches.

We observe a few bands of the water tetramers $(H_2O)_4$ and $(D_2O)_4$. These are given in Tables 3 and 4. The hydrogen bonds of the tetramer are expected to be significantly stronger than those of the trimer, since the hydrogen bond angles are less deformed from the ideal, linear hydrogen bonds. This is reflected in the significantly lower bound OH stretches of tetramer compared to the trimer. It is also reflected in the significantly higher hydrogen bond shear fundamental of the tetramer (669 cm^{-1}, Ne) compared to the trimer (559 cm^{-1}, Ne). For the tetramer we observe a band at 222 cm^{-1}, which has a 11 cm^{-1} redshift in $(H_2^{18}O)_4$. We believe that this is a hydrogen bond stretch of the tetramer, indicating that the hydrogen bond stretch increases by approximately 60 cm^{-1} between the trimer and the tetramer.

We note that our ab initio calculations give very good predictions for the shear and *c*-axis librations. It is also interesting to note the calculations predict that the *c*-axis libration is more intense than the shear libration in the trimer, while for the tetramer the shear libration is calculated to be quite intense while the *c*-axis libration is calculated to be weak. We observe that the shear libration of the trimer is slightly weaker than the *c*-axis libration as expected from the calculations. We have no difficulties in observing the shear libration of the tetramer, but see no trace of the *c*-axis libration.

The widths of the intermolecular trimer bands change rapidly with temperature. Even the drop from 10 to 4.5 K sharpens the bands significantly. Their widths also vary significantly between different bands. The shear vibrations are approximately 10 cm^{-1} wide (full width at half-maximum), and the *c*-axis librations of the trimer are overlapped with the corresponding dimer band, but the resulting band is significantly narrower than the shear band. The low-frequency stretching bands in Ar and Kr are less than 2 cm^{-1} wide. For all bands, the bands in Ne matrix are twice to three times wider than the bands in Ar or Kr. The bands in Kr are somewhat sharper than the Ar bands. The mass of a water molecule is almost the same as the mass of a neon atom but much smaller than the masses of Ar and Kr. Impulsive energy transfer from an excited intermolecular vibration to the matrix is therefore expected to be fastest in Ne and slowest in Kr.

We have noted, in particular in experiments in parahydrogen that the shape of the trimer bound OH stretch changes with the water concentration.[22] The limiting structures of the torsion motions have dipole moments on the order of 1 D. The presence of a polar molecule close to a trimer may therefore lock the torsion in one of the limiting structures, which is expected to shift the bound OH stretch slightly. A similar phenomenon has been observed for hydrogen peroxide in matrixes.[23]

Conclusion

Binary water complexes with water as proton donor have two high-frequency intermolecular vibrations, a libration around the free OH bond of water (highest) and a *c*-axis libration of water. The remaining fundamentals have significantly lower frequencies.[21] This frequency distribution is present also in the water trimer, but here the interactions between the water librations produce larger shifts than the splittings between the two types of libration.

The observed intramolecular and upper intermolecular vibrations reflect the effective C_{3h} symmetry of the trimer. Ab initio calculations of fundamental frequencies for one of the ab initio minima give frequencies with an intensity pattern which differs significantly from what is observed, while calculations for a C_{3h} structure reproduce the experimentally observed pattern.

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