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# ADVERTISEMENT



# On the structure of the water trimer. A matrix isolation study

Anders Engdahl and Bengt Nelander

Division of Thermochemistry, Chemical Center, University of Lund, Box 124, S-221 00 Lund, Sweden

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The infrared spectra of several isotopomers of the water trimer have been studied in argon and krypton matrices. The results show that the trimer is cyclic, with three equivalent water molecules.

## INTRODUCTION

The water dimer has been the subject of many investigations using matrix isolation techniques,<sup>1-11</sup> molecular beam spectroscopy,<sup>12-15</sup> *ab initio* quantum mechanical calculations,<sup>16-20</sup> and other techniques.<sup>21-23</sup> The gas phase data and the *ab initio* calculations show that a free water dimer has an open, linear structure with one water molecule acting as a proton donor and the other as a proton acceptor. The interpretation of the matrix data has been the subject of some controversy, but now the linear structure has been established for the noble gas,<sup>6</sup> deuterium,<sup>8</sup> and nitrogen matrices.<sup>2,7</sup>

The water trimer has been studied far less than the water dimer. Ab initio calculations<sup>24</sup> and semiempirical potential calculations<sup>25,26</sup> favor a cyclic trimer structure, with almost equivalent components. Molecular beam deflection data of Dyke and Muenther<sup>27</sup> show that the trimer has a small dipole moment, in contrast to the dimer. It therefore seems likely that the free water trimer is cyclic. Bentwood *et al.*<sup>9</sup> argue, on the basis of spectral data for  $(H_2O)_3$ , that the trimer has an open, linear structure in solid argon. Since extensive isotope data were necessary to establish the structure of the matrix-isolated dimer, we have carried out a study of all H-and D-containing trimers in argon and krypton matrices. Our data give clear evidence of a cyclic trimer structure formed from three effectively equivalent water molecules.

## **EXPERIMENTAL**

The cryostat used was based on an Air Products Displex CS208 refrigeration system.

Argon-water mixtures were prepared by standard manometric techniques and deposited on a combined CsI sapphire window kept at 17 (argon) or 20 K (krypton). The deposition rate was 9 mmol/h. The deposition setup allows two separate gas streams to enter the cryostat simultaneously. In some experiments, one side of the deposition system was treated with  $D_2O(g)$ , while the other side was free from deuterium. In this way we could carry out experiments with  $H_2O$  and  $D_2O$  with only small amounts of HDO in the matrix.

Water was doubly distilled and degassed,  $D_2O$  (99.5% D) was degassed. Equilibrium mixtures of  $H_2O$  and  $D_2O$  were used to obtain HDO. Argon (L'Air Liquid 99.9995%) was passed through a glass spiral immersed in  $O_2(1)$  before use. Krypton (Air Products 99.995%) was used as received.

Infrared spectra were run on a Bruker 113v FTIR instrument at  $0.5 \text{ cm}^{-1}$  resolution.

# NOMENCLATURE

In the water dimer and trimer, the intramolecular vibrations of the water molecules involved are only slightly shifted from their unperturbed positions. Therefore, in order to simplify the notation, the *i*th fundamental of A in a dimer or trimer with B, or B and C, will be denoted as  $v_i$  (A·B) or  $v_i$ [A·(B·C)]. H or D bonding for HDO will be indicated as  $v_3$ (DOH·aq) or  $v_1$ (HOD·aq), respectively. aq represents any isotopomer of water.

## ASSIGNMENT

Table I summarizes previous assignments of water trimer absorption bands. We observe the same HDO and  $D_2O$  bands as reported in Ref. 6 and agree with their assignment to trimeric aggregates of water. For H<sub>2</sub>O, we do not observe the 1632 and 1620  $\text{cm}^{-1}$  bands of Ref. 9. In our experiments they would be hidden in the wings of the strong  $1_{11} \leftarrow 0_{00}$  rotational component of monomeric water. It is true that this peak broadens as the water concentration increases, but it also broadens when other impurities are added to the matrix. We therefore believe that the broadening is due, at least in part, to so-called Stark broadening, induced by the electric fields from, for instance, water dimers and nonrotating water monomers. We agree with the previous assignment of the 3516, 3527 cm<sup>-1</sup> band to  $(H_2O)_3$ , but we do not observe the 3612, 3624.2, and 3695  $cm^{-1}$  bands. Judging from published spectra, the latter seem to appear only at water concentration higher than 1:100, while the 3516, 3527, and 1602.3  $\text{cm}^{-1}$  bands are easy to observe at water concentrations around 1:150. We do occasionally observe a band at 3702  $\text{cm}^{-1}$ , but then it is clearly due to an HDO impurity in the matrix. Published spectra indicate that there is a genuine H<sub>2</sub>O absorption here at very high water

TABLE I. Water trimer assignments from the literature.

	H <sub>2</sub> O	HDO	$D_2O$
<i>v</i> <sub>3</sub>	3702.5 <sup>a,b</sup>	<u> </u>	2738ª
	3695 <sup>b</sup>		
ν <sub>1</sub>	3624.2*		
	3612 <sup>6</sup>		
	3525ª.b		2579.5
	3517 <sup>a,b</sup>		
<i>v</i> <sub>2</sub>	1632 <sup>6</sup>		
	1620 <sup>b</sup>		
	1602.3 <sup>a,b</sup>	1389.2ª	1182.7*

\* Reference 6.
<sup>b</sup> Reference 9.

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concentrations, but again this absorption is absent at concentrations where a significant amount of trimer is formed and therefore has to be due to aggregates larger than the trimer. We have observed that the water dimer band  $v_3(\text{HOH}\cdot\text{OH}_2)$  at 3708.2 cm<sup>-1</sup> gets a satellite band at 3707.2 cm<sup>-1</sup> at concentrations where the other  $(\text{H}_2\text{O})_3$ bands appear. We assign this band to  $v_3[\text{HOH}\cdot(aq_2)]$ .

The only band previously assigned to an HDO-containing trimer is a bending vibration at 1389.2 cm<sup>-1</sup>. The lack of assigned HDO-trimer bands is probably due to the fact that it is difficult to vary the HDO concentration while keeping the H/D ratio constant. We have tried instead to vary the water isotopomer composition, keeping an approximately constant total water concentration. From these experiments we conclude that the bands on the high wave number side of the 2576.5 cm<sup>-1</sup> (D<sub>2</sub>O)<sub>3</sub> band are due to trimers of water containing HDO. The bands appear at the same total water concentrations as the (D<sub>2</sub>O)<sub>3</sub> band and their relative intensities are related to the relative concentrations of HDO, H<sub>2</sub>O, and D<sub>2</sub>O.

No trimer H-bonding OH absorption is observed unless  $H_2O$  is present in the matrix in a significant concentration, while trimer bands appear in the D-bonding OD region as soon as HDO is present. We therefore believe that HDO in the trimer forms only D bonds, as one may expect from the observation that only D bonding occurs in a water dimer containing at least one D atom. At temperatures above 20 K H-bonding HDO in equilibrium with D-bonding HDO has been observed in solid krypton.<sup>28</sup>

The trimer spectra, in the bonding OH and OD stretching regions, in argon and krypton matrices are closely similar and there is a shift of less than  $3 \text{ cm}^{-1}$  between corresponding bands in the two matrices. The discussion below refers to the krypton matrix, but an identical argument can be given for the argon matrix.

Figure 1 shows the trimer bands in the OH and OD stretching regions obtained from experiments with predominantly  $H_2O$  and HDO in krypton. It is seen from the upper left-hand panel that the 2584.8 cm<sup>-1</sup> peak dominates at low



FIG. 2. The bound OD-stretching region at 0.1 cm<sup>-1</sup> resolution. Ar/ HDO = 154; 25.8 mmol of Ar deposited 10 K (cm<sup>-1</sup>, absorbance).

HDO/H<sub>2</sub>O ratios. It is therefore assigned to  $v_1[\text{HOD} \cdot (\text{H}_2\text{O})_2]$ . Note that the middle panels of Fig. 1 show  $v_1(\text{HOD} \cdot aq)$  and the three peaks in the two lower panels are due to (from left to right)  $v_1(\text{HOD} \cdot \text{OD}_2)$ ,  $v_1(\text{HOD} \cdot \text{OHD})$ , and  $v_1(\text{HOD} \cdot \text{OH}_2)$ . The relative intensities of these three peaks are a measure of the relative D<sub>2</sub>O, HDO, and H<sub>2</sub>O concentrations. Note that in the upper panel,  $v_1(\text{HOD} \cdot \text{OD}_2)$  is too weak to be observable and  $v_1(\text{HOD} \cdot \text{OH}_2)$  is visible only as a shoulder on the  $v_1(\text{HOD} \cdot \text{OH}_2)$  band.

For H<sub>2</sub>O, it is clear that the 3514.2 cm<sup>-1</sup> band (Fig. 1) is due to  $v_1$  [HOH  $\cdot$  (H<sub>2</sub>O)<sub>2</sub>]. When the HDO/H<sub>2</sub>O ratio increases, the 3500.9 band increases and in the lower right-hand panel of Fig. 1, where HDO dominates, it is the stron-



FIG. 1.  $H_2O$  and HDO containing trimers. Upper panels  $Kr/H_2O = 129$ ; 31 mmol of Kr deposited (HDO is present as an impurity from the deposition system). Middle panels Kr/HDO = 141; 41 mmol of Kr deposited. Lower panels Kr/HDO = 125; 30 mmol of Kr deposited (a second  $H_2O$   $D_2O$  mixture was used here). Left-hand panels; the bound OD-stretching region of the trimer (11K). Middle panels; the  $v_1$ (HOD aq) region 20 K. Right-hand panels; the bound OHstretching region (11 K) (cm<sup>-1</sup>, absorbance).

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FIG. 3. D<sub>2</sub>O containing trimers. Upper panels:  $Kr/D_2O = 129$ ; 30 mmol of Kr Middle deposited. panels: Kr/  $H_2O = 123$ ,  $Kr/D_2O = 191$ ; 30 mmol of Kr deposited. Lower panels: Kr/  $D_2O = 216$ , Kr/HDO = 210; 31 mmol of Kr deposited. Left-hand panels: the bound OD-stretching region (11 K). Middle panels: the  $v_1(\text{DOD} \cdot aq)$  (left) and  $v_1(\text{HOD} \cdot aq)$  (right) bands (20 K). Right-hand panels: the bound OHstretching region (11 K) (cm<sup>-1</sup>, absorbance).

gest band. This band is therefore assigned to  $v_1$ [HOH·(HDO)<sub>2</sub>]. Note that the 3500.9 cm<sup>-1</sup> band is absent in the upper right-hand panel of Fig. 1. The band to the left of the main peak is at 3487 cm<sup>-1</sup> and is assigned to  $v_1$ [HOH·(H<sub>2</sub>O·HDO)], as will be discussed further below.

If the assignments given above are correct, it seems natural to assign the high wave number component of the three bands in the middle and lower left-hand panels of Fig. 1 to  $v_1$ [HOD·(HDO)<sub>2</sub>]. The shape of this peak depends on the HDO concentration and the position of the maximum shifts towards lower wave numbers when the HDO/H<sub>2</sub>O ratio increases. It therefore seems clear that it has at least two components. In an experiment in an argon matrix, we were able to resolve it into peaks by using  $0.1 \text{ cm}^{-1}$  resolution (see Fig. 2). From the concentration dependency of the shape of the band, it is clear that the low wave number component of the doublet in Fig. 2 is due to  $v_1$  [HOD · (HDO)<sub>2</sub>]. The concentration dependency of the band makes it clear that the high wave number component of the doublet, together with the weaker band at 2574.3 cm<sup>-1</sup>, is due to  $v_1$ [HOD·  $(H_2O \cdot HDO)$ ]. The low wave number component of the doublet is  $v_1$  [HOD · (HDO)<sub>2</sub>].

The band at 3514.2 cm<sup>-1</sup> shifts towards lower wave numbers when HDO is introduced in the matrix. At the same time a weak band appears at 3487 cm<sup>-1</sup>. The similarities between the OH and OD regions are striking, and it seems clear that  $v_1$ [HOH·(H<sub>2</sub>O·HDO)] has two components, one at 3487 cm<sup>-1</sup> and the other just below the  $v_1$ [HOH·(H<sub>2</sub>O)<sub>2</sub>] band. The position of this component given in Table I is the maximum of the band at high HDO/ H<sub>2</sub>O ratios.

The  $D_2O$  trimer has a single band at 2576.5 cm<sup>-1</sup> (Fig. 3 upper panels). As can be seen from the upper middle panel of the figure, there is some HDO in the matrix. It is responsible for the absorption to the right of the main peak in the upper left-hand panel. Note that the  $D_2O$  band is broader than the HDO bands (compare Figs. 1 and 2). This makes it harder to separate bands due to different  $D_2O$ -containing trimers.

Figure 3, middle panels, shows spectra from an experiment with mostly  $H_2O$  and  $D_2O$  in the matrix. The center panel shows both the  $v_1(\text{DOD} \cdot aq)$  and  $v_1(\text{HOD} \cdot aq)$ bands and gives an indication of the relative concentrations. Note that  $v_1$  (DOD·OHD) and  $v_1$  (HOD·OHD) are visible only as shoulders on the H<sub>2</sub>O peaks. The sharper bands, on the high wave number side of  $v_1$  [DOD  $\cdot$  (D<sub>2</sub>O)<sub>2</sub>], are due to HDO-containing species and are disregarded for the moment. On the low wave number side of the  $(D_2O)_3$  band, bands due to H<sub>2</sub>O and D<sub>2</sub>O containing trimers appear at 2555.9 and 2570.1 cm<sup>-1</sup>. The  $(D_2O)_3$  band shifts slightly towards higher wave numbers when H<sub>2</sub>O is present, similar to the  $(HDO)_3$  band. We use the analogy with the  $v_1(\text{HOH} \cdot aq_2)$  and  $v_1(\text{HOD} \cdot aq_2)$  regions and assign the 2570.1 cm<sup>-1</sup> band to  $v_1[DOD \cdot (H_2O)_2]$  and the peaks at 2555.9  $\text{cm}^{-1}$  and at 2578.2  $\text{cm}^{-1}$  to  $v_1$ [DOD · (H<sub>2</sub>O · D<sub>2</sub>O)]. The position of the latter peak is taken from experiments with large H<sub>2</sub>O/D<sub>2</sub>O ratios. The  $v_1$ [HOH·(D<sub>2</sub>O)<sub>2</sub>] and  $v_1$ [HOH·(H<sub>2</sub>O·D<sub>2</sub>O)] bands are close to their HDO counterparts.

The lower panels of Fig. 3 show spectra from an attempt to study D<sub>2</sub>O and HDO containing trimers. Unfortunately, it is difficult to lower the H<sub>2</sub>O concentration until it is insignificant and at the same time have a reasonable concentration of HDO. The lower middle panel gives an idea of the H<sub>2</sub>O concentration. The broad peak in the lower lefthand panel is due to an overlap between  $v_1[DOD(D_2O)_2]$ and  $v_1[DOD(HDO \cdot D_2O)]$ . The peak with a shoulder on the high wave number side of the broad peak is due to  $v_1[HOD \cdot (D_2O)_2]$  and the shoulder to  $v_1$ [HOD·(HDO·D<sub>2</sub>O)]. The high wave number peak is a second component of  $v_1[HOD(HDO \cdot D_2O)]$ . The small peaks on the lower wave number side are  $v_1$ [DOD·(H<sub>2</sub>O·HDO)],  $v_1$ [DOD·(H<sub>2</sub>O·D<sub>2</sub>O)], and  $v_1$ [DOD · (D<sub>2</sub>O · HDO)], from high to low wave numbers, respectively. The peak in the lower right-hand panel has contributions from  $v_1$ [HOH·(D<sub>2</sub>O)<sub>2</sub>],  $v_1$ [HOH·(HDO)<sub>2</sub>], and  $v_1$  [HOH · (HDO · D<sub>2</sub>O)]. Table II summarizes the assignments.

TABLE II. Observed and calculated band positions for water trimers.

				Calc.	
Funda- mental	Trimer	Kr	Ar	Position	Relative intensity
$\overline{v_1}$	(H <sub>2</sub> O) <sub>3</sub>	3514.2	3516	3516.3	
-	$(D_2O)_3$	2576.5	2578.5	2579.3	3
	(HDO) <sub>3</sub>	2592.5	2594.3	2595.2	3
	$(H_2O)_2D_2O$	3513.3	3515	3514.5	1.5
		3486.7	3489	3490.7	0.5
		2570.1	2572.2	2570.7	1
	$H_2O(D_2O)_2$	3497.3	3498	3501.3	1
		2578.2	2579.8	2580.9	1.5
		2555.9	2557.5	2557.8	0.5
	$(H_2O)_2HDO$	3513.1		3515.5	1.5
		3487		3491.8	0.5
		2584.8	2586.6	2586.5	1
	$H_2O(HDO)_2$	3500.9	3502	3503.3	1
	-	2593.5	2595.5	2595.7	1.5
		2574.3	2576.0	2576.6	0.5
	$(D_2O)_2HDO$	2587.9	2590.4	2590.4	1.45
		2577.8		2580.3	1.50
		2549.5		2551.1	0.06
	$D_2O(HDO)_2$	2591.7	2593.0	2594.3	1.50
		2585.5	2586.0	2587.6	1.40
		2555.8(?)		2557.7	0.10
	$H_2O \cdot HDO \cdot D_2O$			3501.3	1
				2591.7	1.39
		2562.4	2564.3	2564.8	0.59
				3503.3	1
			2587.9	2589.6	1.43
		2562.4	2564.3	2564.9	0.55
<i>v</i> <sub>2</sub>	$H_2O(H_2O)_2$ $H_2O(HDO)_2$		1602.3		
	$H_0(D_0)$	1599.6	1601.3		
	HDO(aq)	1387.3	1389		
	$D_{\alpha}O(aa)_{\alpha}$		1183.4		
Va	$H_{2}O(aq)_{2}$		3707.2		
- 3	$D_2O(aq)_2$	2732	2737.8		

### CALCULATIONS

In order to check the assignment of the trimer bands given above, it seems useful to carry out a GF calculation<sup>29</sup> for the water trimer. As discussed below, the trimer spectra in the  $v_1(\text{HOH} \cdot aq_2)$  and  $v_1(\text{HOD} \cdot aq_2)$  regions suggest that the trimer is formed from three equivalent water molecules. The equation to be solved has then the following structure:

$$\begin{pmatrix} G_{1} & 0 & 0 & G_{1e} \\ 0 & G_{2} & 0 & G_{2e} \\ 0 & 0 & G_{3} & G_{3e} \\ G_{e1} & G_{e2} & G_{e3} & G_{e} \end{pmatrix} \begin{pmatrix} F_{1} & F_{12} & F_{12} & F_{1e} \\ F_{21} & F_{1} & F_{12} & F_{1e} \\ F_{21} & F_{21} & F_{1} & F_{1e} \\ F_{e1} & F_{e1} & F_{e1} & F_{e} \end{pmatrix} L$$

$$= \lambda L.$$

$$(1)$$

Here  $G_1$ ,  $G_2$ , and  $G_3$  are the G matrices for the intramolecular coordinates of the three trimer-forming water molecules and  $F_1$  is the corresponding F matrix.  $F_{12}$  is a  $3 \times 3$  matrix of coupling constants between the intramolecular degrees of freedom.  $G_e$  and  $F_e$  are the  $12 \times 12$  G and F matrices for the intermolecular degrees of freedom and  $G_{1e}$  and  $F_{1e}$  the interintra molecular coupling matrices. Very little is known about the intermolecular vibrations of the water trimer and we are therefore forced to try to estimate their effect on the intramolecular vibration spectrum. By choosing as intermolecular coordinates combinations of rigid rotations about the centers of gravity and rigid translations of the centers of gravity of the trimer components, we can eliminate  $G_{1e}$ ,  $G_{2e}$ , and  $G_{3e}$ . This choice of coordinates introduces a slight isotope dependency into the  $F_{1e}$  and  $F_e$  matrices, since the centers of gravity have slightly different positions in the molecular frames of H<sub>2</sub>O, HDO, and D<sub>2</sub>O. This mass dependence should not seriously influence the estimate made below. We now write Eq. (1) as

$$\begin{pmatrix} G_i & 0\\ 0 & G_e \end{pmatrix} \begin{pmatrix} F_i & F_{ie}\\ F_{ei} & F_e \end{pmatrix} \begin{pmatrix} L_i\\ L_e \end{pmatrix} = \lambda \begin{pmatrix} L_i\\ L_e \end{pmatrix}.$$
 (2)

Since we are interested only in the intramolecular fundamentals we solve for  $L_e$ :

$$L_e = (E\lambda - G_e F_e)^{-1} G_e F_{ei} L_i$$
(3)

and get

$$G_i \left[ F_i + F_{ie} \left( E\lambda - G_e F_e \right)^{-1} G_e F_{ei} \right] L_i = \lambda L_i.$$
(4)

The intramolecular fundamentals are therefore obtained from an equation with an F matrix, which is the sum of the original F matrix and a term depending on the intermolecular fundamentals, which is inversely proportional to the difference between the inter- and intramolecular fundamentals. Note that we may choose the intermolecular coordinates such that  $G_e F_e$  is diagonal, with  $(2\pi c v_{en})^2$  as diag- $(v_{e1} - v_{e12})$  are the intermolecular onal elements fundamentals). Consider the coupling between an intramolecular stretching vibration of one molecule and an intermolecular coordinate, which is mainly a rotation of the same molecule. For H<sub>2</sub>O,  $\lambda \sim (2\pi c \cdot 3500)^2$  and the largest eigenvalue of  $G_{e}F_{e}$  is likely to be smaller than  $(2\pi c \cdot 600)^{2}$ . We now assume that V has the form

$$V = \frac{1}{2}f(r - r_0)^2 + F_{ie}(r - r_0)\cdot\theta + \cdots,$$

where  $(r - r_0)$  and  $\theta$  are the intra- and intermolecular coordinates under consideration.

The equilibrium r for a given  $\theta$  is given by

$$=r_0-\frac{F_{ie}}{f}\cdot\theta.$$

As a reasonable estimate, let  $r - r_0 = 0.01 \cdot r_0$  for  $\theta = 1$ . The OH distance changes 0.004 Å from free H<sub>2</sub>O to the hydrogen bonding OH of the donor in the dimer.<sup>30</sup> The corresponding correction term of Eq. (4) is then approximately given by

$$\frac{F_{ie}^2(1/I)}{\lambda}$$

r

(1/I) is an approximation to the  $G_e$  matrix element for a rotational coordinate. With  $\lambda \sim (f/m_{\rm H})$  and  $I \sim 2m_{\rm H} r_0^2$ we get

$$\frac{(f \cdot 0.01 r_0)^2 \cdot (1/2m_{\rm H} r_0^2)}{(f/m_{\rm H})} \sim f \cdot 5 \times 10^{-5}.$$

The effect of the intermolecular vibrations on the intramolecular vibrations is therefore likely to be small and we use the approximation

$$G_i F_i L_i = \lambda L_i \tag{5}$$

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and treat  $F_i$  as an isotope independent matrix. By multiplying both sides of the equation with  $G_i^{-1/2}$  we get

$$G_{i}^{1/2} F_{i} G_{i}^{1/2} L_{i}' = L_{i}',$$
  
where  $L_{i}' = G_{i}^{-1/2} L_{i}$ :  
$$G_{i}^{1/2} F_{i} G_{i}^{1/2}$$
$$= \begin{pmatrix} G_{1}^{1/2} F_{1} G_{1}^{1/2} & G_{1}^{1/2} F_{12} G_{2}^{1/2} & G_{1}^{1/2} F_{12} G_{3}^{1/2} \\ G_{2}^{1/2} F_{21} G_{1}^{1/2} & G_{2}^{1/2} F_{1} G_{2}^{1/2} & G_{2}^{1/2} F_{12} G_{3}^{1/2} \\ G_{3}^{1/2} F_{21} G_{1}^{1/2} & G_{3}^{1/2} F_{21} G_{2}^{1/2} & G_{3}^{1/2} F_{1} G_{3}^{1/2} \end{pmatrix}.$$

By a proper choice of coordinates, we may diagonalize the blocks on the diagonal:

$$G_n^{1/2}F_1G_n^{1/2} = \begin{pmatrix} \lambda_1^{(n)} & 0 & 0 \\ 0 & \lambda_2^{(n)} & 0 \\ 0 & 0 & \lambda_3^{(n)} \end{pmatrix}.$$

We now need an estimate of the effects of the couplings between the intramolecular fundamentals in different molecules. Consider the interaction between  $\lambda_p^{(n)}$  and  $\lambda_q^{(m)}$  where  $n \neq m$ . If no other interactions were present, we would have to solve

$$\begin{vmatrix} \lambda_p^{(n)} - \epsilon f_{12} \\ f_{21} & \lambda_q^{(m)} - \epsilon \end{vmatrix} = 0$$
  
for  $\lambda_p^{(n)} = \lambda_q^{(m)}$ ,

$$\epsilon = \lambda_p^{(n)} \pm \sqrt{f_{12}f_{21}},$$

and

$$\nu = \frac{1}{2\pi c} \sqrt{\epsilon} \approx \frac{1}{2\pi c} \sqrt{\lambda_p^{(n)}} \left( 1 \pm \frac{1}{2} \frac{\sqrt{f_{12} f_{21}}}{\lambda_p^{(n)}} \right)$$

The wave number split is given by

$$\frac{1}{2\pi c}\sqrt{\frac{f_{12}f_{21}}{\lambda_p^{(n)}}}.$$

If  $\lambda_p^{(n)} \neq \lambda_q^{(m)}$  we use a second order treatment and get

$$\epsilon = \lambda_p^{(n)} + \frac{f_{12}f_{21}}{\lambda_p^{(n)} - \lambda_q^{(m)}}$$

(and a corresponding result for  $\lambda_{a}^{(m)}$ ) and

$$v \approx \frac{1}{2\pi c} \sqrt{\lambda_{p}^{(n)}} \left( 1 + \frac{f_{12}f_{21}}{2\lambda_{p}^{(n)}(\lambda_{p}^{(n)} - \lambda_{q}^{(m)})} \right).$$

If the assignment given above is correct, we get for  $(1/2\pi c)\sqrt{\lambda} = 3500 \,\mathrm{cm}^{-1}$ , a  $25 \,\mathrm{cm}^{-1}$  split between two coupled initially degenerate fundamentals. Thus,

$$\sqrt{f_{12}f_{21}} \cdot \left(\frac{1}{2\pi c}\right)^2 \sim 3500 \cdot 25$$

The nondegenerate intramolecular fundamentals differ by more than  $100 \text{ cm}^{-1}$ . Therefore,

$$\frac{f_{12}f_{21}}{2\lambda_{p}^{(n)}(\lambda_{p}^{(n)}-\lambda_{q}^{(m)})} \leq 4 \times 10^{-4}$$

and the couplings between nondegenerate intramolecular vibrations in different molecules are expected to give shifts less than  $1 \text{ cm}^{-1}$ .

 $v_1(\text{DOD}\cdot\text{OH}_2)$  and  $v_1(\text{DOD}\cdot\text{OHD})$  differ from

 $v_1(\text{DOD}\cdot\text{OD}_2)$  by 2.0 and 1.2 cm<sup>-1</sup>, respectively. It is not clear if these splits are due to harmonic or to higher potential terms.<sup>7</sup>

In the following, we neglect the couplings between the nondegenerate intramolecular fundamentals. Calculations were therefore carried out for the following model:

(1) Only the three OH, OD stretching fundamentals involved in the hydrogen bonding are considered.

(2) HDO engages only in D bonding.

(3) Each oscillator has an unperturbed position  $\epsilon_{\rm H}$ ,  $\epsilon_{\rm X}$ , or  $\epsilon_{\rm D}$  for H<sub>2</sub>O, HDO, or D<sub>2</sub>O, respectively.

(4) Two oscillators interact with an interaction matrix element  $\vartheta_{\rm HH}$ ,  $\vartheta_{\rm HX}$ ,  $\vartheta_{\rm DD}$ ,  $\vartheta_{\rm DX}$ , and  $\vartheta_{\rm XX}$ , depending on the nature of the two oscillators.

(5) An oscillator is shifted  $\delta_{\rm H}$ ,  $\delta_{\rm X}$ , or  $\delta_{\rm D}$  when it binds to H<sub>2</sub>O, HDO, or D<sub>2</sub>O, respectively. (Compare the splittings in the dimer bands. Middle panels in Figs. 1 and 3.) (6) The dipole derivative of an OH, OD oscillator is assumed to be collinear with the bond and has the same value for HDO and D<sub>2</sub>O. (This affects only the intensity estimates.)

As an example, the hydrogen bond stretching fundamen-



FIG. 4. The two possible isomers of a cyclic  $H_2O \cdot HDO \cdot D_2O$  trimer.

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tals of  $(H_2O)_2$ ·HDO are the eigenvalues of

The calculations were carried out with the following parameters, which were chosen to fit the argon data:

$$\begin{aligned} \epsilon_{\rm H} &= 3504, \quad \epsilon_{\rm X} = 2586.8, \quad \epsilon_{\rm D} = 2571.0, \\ \vartheta_{\rm HH} &= \vartheta_{\rm HX} = \vartheta_{\rm HD} = -12, \\ \vartheta_{\rm DD} &= -11.3, \quad \vartheta_{\rm XX} = -9.4, \quad \vartheta_{\rm XD} = -10.4, \\ \delta_{\rm H} &= 0, \quad \delta_{\rm X} = 1, \quad \delta_{\rm D} = 3. \end{aligned}$$

Figure 4 illustrates the two possible isomers of  $H_2O \cdot HDO \cdot D_2O$ . The calculated spectra are given in Table II.

## DISCUSSION

The observation of a single sharp bonding OD stretching fundamental for the HDO  $(H_2O)_2$  trimer is clearly compatible with a cyclic trimer structure with equivalent components. For an open, linear trimer, one would expect two different bound OD-stretching fundamentals, corresponding to the two inequivalent deuterium donor molecules. Note that HDO has been found to act as a D donor rather than as an H donor in all complexes studied so far.  ${}^{6,7,28,31-37}$  For the (HDO)<sub>2</sub>·H<sub>2</sub>O trimer, the cyclic model predicts two bound OD-stretching fundamentals, with positions approximately symmetrical around the  $v_1$ [HDO·(H<sub>2</sub>O)<sub>2</sub>] band. For the open trimer, one expects two pairs of peaks, corresponding to the pairs

H H H  $HOD \cdot OD \cdot OH_2, HOD \cdot O-H \cdot OHD$ 

and

# H H H $HOD \cdot O-D \cdot OH_2$ , $HOH \cdot OD \cdot OHD$ .

The absorbing molecule is underlined. The prediction from the cyclic model agrees with the observed spectra while too many peaks are predicted for the open structure. There remains the possibility that, because of the greater stability of the D bond compared to an H bond, only one each of the possible isomers of the open HDO  $(H_2O)_2$  and  $(HDO)_2 \cdot H_2O$  trimers are formed. However, it is next to impossible to understand why an open, linear (HDO)<sub>3</sub> has only one bound IR-active OD stretch. For the cyclic model, one expects only a simple bound OD stretch for  $(HDO)_3$ , since this trimer is effectively  $C_3$  symmetric and therefore has an IR inactive  $A_1$  symmetric OD fundamental and a doubly degenerate IR-active OD fundamental. The OH and OD stretching fundamentals of  $(H_2O)_n \cdot (D_2O)_{3-n}$  and the bound OH stretches of  $(H_2O)_n \cdot (HDO)_{3-n}$  show exactly the same patterns as the bound OD stretches of  $(H_2O)_n \cdot (HDO)_{3-n}$ . For the  $(HDO)_n \cdot (D_2O)_{3-n}$  and  $H_2O \cdot HDO \cdot D_2O$  trimers, the predictions from a cyclic model will depend on the strength of the interactions between the bound OD-stretching fundamentals in HDO and D<sub>2</sub>O, and therefore have to be tested through calculations.

In solid argon, but not in krypton,  $v_1[\text{HOH} \cdot (\text{H}_2\text{O})_2]$ has a shoulder at 3527 cm<sup>-1</sup>. One also observes a shoulder on the high wave number side of  $v_1[\text{DOD} \cdot (\text{D}_2\text{O})_2]$ , but this shoulder is due to  $v_1[\text{HOD}(\text{D}_2\text{O})_2]$ . For  $(\text{H}_2\text{O})_3$ , there seem to be two possibilities open: either the shoulder is due to a trace of open trimer, trapped so that it cannot rearrange to the cyclic form, or it may be due to a combination between  $v_1[\text{HOH} \cdot (\text{H}_2\text{O})_2]$  and some intermolecular vibration of  $(\text{H}_2\text{O})_3$ . Since the band is observed for  $(\text{H}_2\text{O})_3$  only, we are unable to choose between these possibilities.

For the free OH and OD stretching fundamentals and for the bending fundamentals, the cyclic model predicts similar splitting patterns as for the bound stretching fundamentals. The interactions are expected to be much weaker and it does not seem unreasonable that, for instance, the free OD stretching fundamentals of all  $(D_2O)_n \cdot (H_2O)_{3-n}$  trimers overlap. The observation of only one trimer band in the bending regions of  $D_2O$ , HDO, and  $H_2O$  and in the (free) OD- and OH- stretch regions of  $D_2O$  and  $H_2O$  therefore does not contradict a cyclic trimer structure. The trimer free OH-stretching fundamental of HDO has not been observed. It is expected in a region which is rather crowded and is probably hidden under a monomer HDO band.

Bentwood *et al.*<sup>9</sup> argue that the small shift towards higher wave number of the  $(H_2O)_3$  band at 1602 cm<sup>-1</sup> suggests that it is due to a proton accepting water molecule in an open trimer. The monomer fundamental is at 1589 cm<sup>-1</sup>. In fact, the shifts towards higher wave numbers of  $v_2(H_2O \cdot A)$  so far observed are all less than 4 cm<sup>-1</sup>; for the strong  $H_2O \cdot SO_3$  complex the bend is shifted towards lower wave numbers.<sup>38</sup> On the other hand, for the weak HOH  $\cdot C_2H_4$  complex,<sup>31</sup> where water acts as a proton donor, the HOH bend is observed at 1594.7 cm<sup>-1</sup>, while for the water dimer  $v_2(HOH \cdot OH_2)$  is observed at 1610.6 cm<sup>-1</sup>. Considering that the hydrogen bonds of a cyclic trimer are bent, the 1602.3 cm<sup>-1</sup> band seems to be in a perfectly reasonable position for a cyclic trimer.

The important feature of the model used for the calculations of the trimer spectrum is the interaction between the bound stretches in molecules of the same kind. Only an OD and an OH interaction parameter are necessary to predict the general shapes of the trimer spectra. The interactions between OH and OD vibrations are insignificant and could very well be ignored. In the dimer spectrum, the positions of, for instance,  $v_1(\text{HOD} \cdot \text{OD}_2)$ ,  $v_1(\text{HOD} \cdot \text{OHD})$ , and  $v_1(\text{HOD} \cdot \text{OH}_2)$  differ; the  $\delta$  parameters were added to the model since there should be similar shifts in trimers. The  $\delta$ parameters of the model are small and, while they improve the numerical agreement between calculated and observed band positions, they have no influence on the general patterns of the calculated spectra.

If we assume for the moment that the interaction between two bound OH oscillators in  $(H_2O)_3$  is mainly dipole-dipole interaction, we may estimate its magnitude from intensity data for the water dimer:

$$\vartheta = \frac{|\langle 1|\mu|0\rangle|^2}{R^3} \left[ \mathbf{e}_1 \mathbf{e}_2 - 3(\mathbf{e}_1 \mathbf{e}_r)(\mathbf{e}_2 \mathbf{e}_r) \right].$$

Here  $e_1$  and  $e_2$  are unit vectors pointing in the directions of

the transition dipole moments of the two interacting OH stretches. e, is a unit vector pointing from the center of one of the OH oscillators towards the center of the other. R is the distance between the oscillators and  $|\langle 0|\mu|1\rangle|$  is the transition dipole moment for a bound OH-stretching fundamental. For simplicity we assume that the three OH bonds of H<sub>2</sub>O engaged in hydrogen bonding sit at the vertices of an equilateral triangle, forming 120° angles with each other. The O…O distance of the water dimer is 2.98 Å<sup>12</sup> and we therefore assume R to be 3 Å. Zilles and Person<sup>39</sup> have estimated the intensity of  $\nu_1(\text{HOH}\cdot\text{OH}_2)$  to 182.2 km/mol. From this figure we can estimate  $|\langle 0|\mu|1\rangle|^2 = 2.4 \times 10^{-38}$  esu<sup>2</sup> cm<sup>2</sup> and therefore  $\vartheta_{\text{HH}} = -15$  cm<sup>-1</sup>. The observed interaction parameters are thus of the expected order of magnitude.

The intensity predictions from the cyclic model may be summarized as follows: a symmetric trimer has one intense band. For the  $H_2O(HDO)_2$  trimer, the model predicts two bound OD stretches with the high wave number component twice as intense as the low wave number component (compare Fig. 2). Similar predictions are made for the OH stretches of  $(H_2O)_2 \cdot HDO$  and  $(H_2O)_2 \cdot D_2O$  and for the OD stretches of  $H_2O \cdot (D_2O)_2$ . For trimers containing both HDO and  $D_2O$ , the situation is intermediate between that of a symmetric trimer  $[(D_2O)_3 \text{ or } (HDO)_3]$  and a trimer formed from, say,  $D_2O$  and  $H_2O$ . For instance, the lowest wave number component of  $\nu_1[DOD \cdot (D_2O \cdot HDO)]$  is weakly allowed, as can be seen in Fig. 3.

Both the peak positions and the intensity predictions calculated for the cyclic model agree with the observed spectra and we therefore conclude that the water trimer in argon and krypton matrices has a cyclic structure and that its three water molecules are equivalent.

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