

Studies of Intermolecular Interactions by Matrix Isolation Vibrational Spectroscopy

Self-association of Water

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The mid- and far-infrared spectra of water in argon and nitrogen matrices have been reinvestigated. The water molecule rotates in an argon matrix, but in a nitrogen matrix two low-frequency bands are attributed to libration of the water monomer about its *A* and *C* rotational axes. Combinations of these modes with the stretching and bending modes of the water monomer were observed. A detailed concentration-dependence study enabled bands to be attributed to dimer, trimer, and tetramer or higher multimers. The dimer and trimer were both found to have open chain structures, whereas tetramer or higher multimer species appear to be predominantly cyclic. Intermolecular modes, observed for dimer and trimer in the far-infrared spectra, are tentatively assigned.

INTRODUCTION

The infrared spectrum of water trapped in low-temperature matrices has been the subject of many investigations. A practical reason for this is that water is a likely impurity in any matrix isolation experiment, so that it is important to be aware of its spectral behavior. The rotation and nuclear spin conversion of water in noble gas matrices have been studied in detail (1–7); in nitrogen (8–13) and deuterium (14) matrices rotation does not occur. The structures of the water dimer and other small multimers are of interest as a starting point for understanding the structure and dynamics of liquid water. After many years of controversy, there is now a consensus that the dimer has an open-chain structure. Dyke *et al.* (15) have shown that the dimer is open chain in the gas phase using molecular beam–electric resonance spectroscopy. A similar structure has been predicted by most recent *ab initio* and semiempirical quantum mechanical calculations (e.g., Ref. (16)). In the earliest matrix study, Van Thiel *et al.* (8) found only two dimer bands in the OH stretching region and one in the bending region of water in a nitrogen matrix, suggesting a cyclic structure. Later studies of water in a nitrogen matrix (11, 13), using higher resolution, found additional dimer bands close to the monomer frequencies, which is consistent with an open-chain structure. A recent exhaustive study of the water dimer in argon matrices (17) led to similar conclusions. However Huang and Cornut (18) suggested that both open-chain and cyclic dimers were present in argon and nitrogen matrices.

Although the intramolecular vibrational modes of water in the dimer are well established, the position with regard to intermolecular modes of the dimer is

much less satisfactory. Far-infrared matrix studies at comparatively high concentrations (9, 19, 20) gave contradictory results. A band at 218 cm^{-1} for water in a nitrogen matrix has been assigned (9) to libration of the monomer, which should be absent in an argon matrix (where the monomer rotates). However, Mann *et al.* (19) reported spectra of water in both argon and nitrogen matrices dominated by a broad band centered near this frequency. Clearly further work is needed to disentangle the bands due to monomer, dimer, and higher multimers in the low-frequency region.

Little information is available for trimer or higher multimers. Theoretical calculations suggest that a cyclic trimer, with three hydrogen bonds, is more stable than an open-chain trimer with two hydrogen bonds (16). An electric deflection observation (21) of a very small permanent electric dipole for the trimer also points to a cyclic structure. A number of bands in argon and nitrogen matrices have been tentatively assigned to trimer and tetramer (8, 17), but no conclusions were drawn as to the structures of these species. The purpose of the present work was to obtain further information on the small multimers of water from a reexamination of the near- and far-infrared spectra in low-temperature matrices.

EXPERIMENTAL DETAILS

Distilled water was degassed under vacuum prior to use. High-purity argon and nitrogen matrix gases were each passed through a liquid-nitrogen trap before use. The water and matrix gases were mixed, in the desired proportions (between 1 in 100 and 1 in 1000), in a vacuum line using standard manometric procedures. The mixture was sprayed at a rate of 4 to 10 mmole hr^{-1} onto a cold window maintained at ca. 20 K using a CTI Cryodyne Model 21, controlled by an Oxford Instruments digital temperature controller. For the region 4000 to 200 cm^{-1} , cesium iodide outer and cold windows were used, but for the far-infrared region a silicon cold window and polyethylene outer windows were used. Spectra were recorded on a Perkin-Elmer 180 spectrometer, calibrated using standard gases.

RESULTS

Infrared spectra were recorded in the intramolecular stretching and bending regions of water in argon matrices over a wide range of concentrations. In the stretching region at a matrix to absorber (M/A) ratio of 1000, the spectrum was dominated by the complex vibration-rotation pattern of the monomer together with a band at 3574 cm^{-1} due to dimer. As the concentration was increased to M/A 600, the four bands due to dimer could be readily identified (Fig. 1). Note that the dimer band at 3726 cm^{-1} is superimposed on a Q -branch vibration-rotation line of the monomer. Raising the concentration further led to two groups of bands successively increasing in intensity (Fig. 2). The first group, at ca. 3700, 3612, and 3516 cm^{-1} , grew relative to dimer over the concentration range M/A 1000 to 300. The second group, with prominent features at ca. 3374, 3327, and 3212 cm^{-1} , grew relative to the first group of bands over the concentration range M/A 600 to 300. It would seem reasonable to assign the first group of bands to a trimer species and the second group of bands to multimers of unspecified size, but larger than trimer.

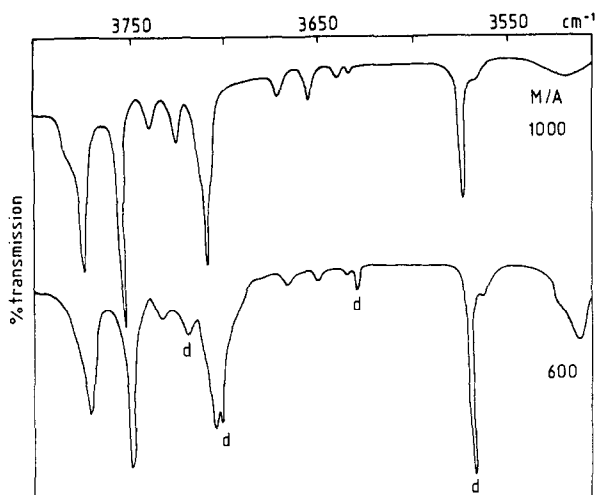


FIG. 1. Stretching region of H₂O in argon matrices at low concentrations (d indicates a dimer band).

The bending region showed similar changes (Fig. 3). Again the monomer spectrum is complex due to the vibration-rotation structure, but the two dimer bands could be readily identified at 1611 and 1593 cm⁻¹. A band at 1602 cm⁻¹ grew in parallel with the bands in the stretching region assigned to a trimer species, while overlapping absorptions around 1620 cm⁻¹ appeared to be due to higher multimer as well as trimer species.

The infrared spectrum of water in an argon matrix doped with 1% nitrogen was dominated by monomer bands at the band center positions (ca. 3733, 3638, and 1590 cm⁻¹), the vibration-rotation lines being almost entirely suppressed.

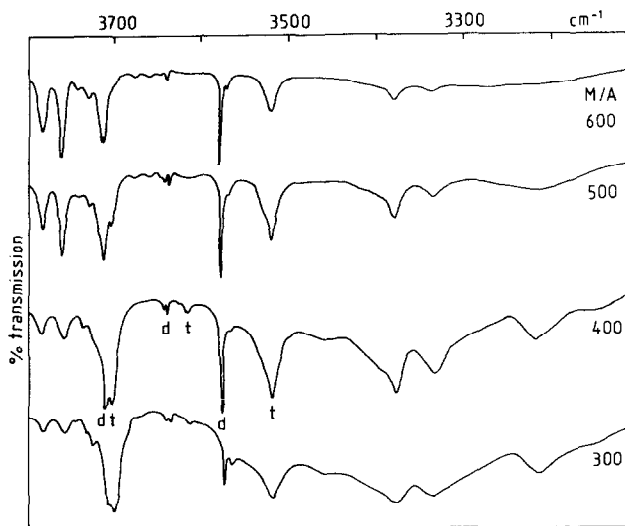


FIG. 2. Stretching region of H₂O in argon matrices at higher concentrations (d indicates a dimer band, t a trimer band).

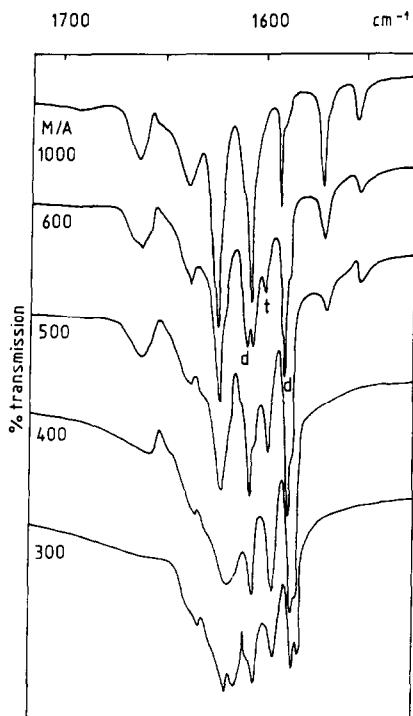


FIG. 3. Bending region of H_2O in argon matrices over a range of concentrations (d indicates a dimer band, t a trimer band).

The spectra of water in argon matrices published by Mann *et al.* (19) showed these features, suggesting that their matrices contained nitrogen as impurity. The dimer band, at 3574 cm^{-1} in an undoped argon matrix, was shifted to 3566 cm^{-1} (a weak feature can be seen at this wavenumber in the low-concentration spectra in Fig. 1).

The low-frequency region of water in argon matrices showed only very weak absorptions at ca. 290 and 147 cm^{-1} , and a broad band at ca. 650 cm^{-1} at higher concentrations. In a nitrogen matrix at $M/A\ 300$, the far-infrared spectrum was dominated by relatively sharp bands at 218 and 145 cm^{-1} , with high-frequency shoulders which became more prominent as the concentration was increased (Fig. 4). A number of bands between 700 and 200 cm^{-1} , due to different species, have been noted by previous workers (9, 20), but the bands below 200 cm^{-1} had not previously been reported. This region of the spectrum of water in an argon matrix doped with 1% nitrogen was rather similar to that in a nitrogen matrix, thus explaining the anomalous results of Mann *et al.* (19).

The infrared spectrum in the intramolecular stretching and bending regions of water in a nitrogen matrix, and its concentration dependence, is generally similar to that found in argon matrices, with the exception that the monomer spectrum is much simpler in a nitrogen matrix since rotation does not occur. Examination of a thick matrix of water in nitrogen at $M/A\ 200$ (Fig. 5) showed the presence of

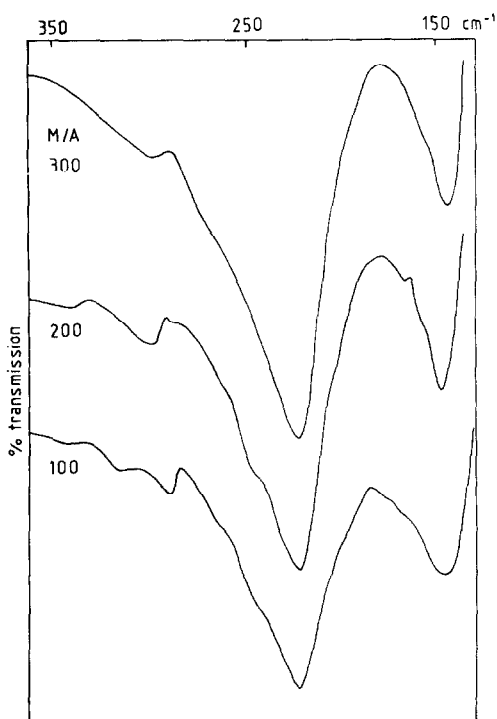


FIG. 4. Far-infrared spectra of H₂O in nitrogen matrices over a range of concentrations.

weak bands at ca. 3956 ($\nu_3 + 218$), 3874 ($\nu_3 + 145$), 1822 ($\nu_2 + 218$), and 1744 ($\nu_2 + 145$) cm⁻¹.

The bands observed for water in argon and nitrogen matrices, together with their assignments, are listed in Table I. Literature data for D₂O and HDO, assigned on a basis similar to that of the H₂O frequencies, are collected in Tables II and III.

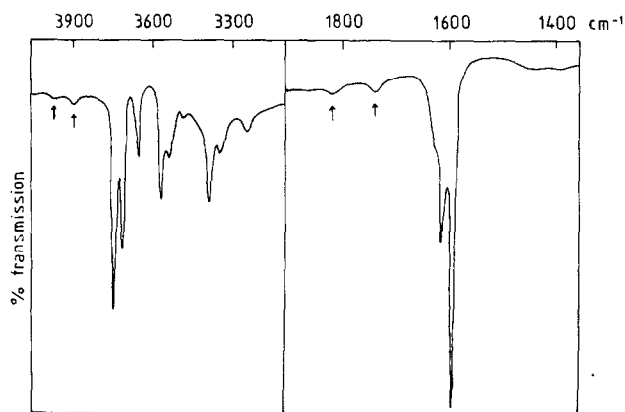


FIG. 5. Stretching and bending regions of H₂O in a thick nitrogen matrix at M/A 200; the combination bands are arrowed.

TABLE I

Bands Observed (cm^{-1}) in the Infrared Spectra of H_2O in Argon and Nitrogen Matrices

Species	Assignment	Ar	N_2^a
monomer	$\nu_3 + 218$	-	3956
monomer	$\nu_3 + 145$	-	3874
monomer	ν_3	3733 ^b	3727
dimer	ν_3 acceptor	3726	3715
dimer	ν_3 donor	3709	3699
trimer	ν_3 donor	3700	3688
trimer	ν_3 donor	3695 (sh)	
multimer		3690	
monomer	ν_1	3638 ^b	3635
dimer	ν_1 acceptor	3634	3627
trimer	ν_1 acceptor	3612	
dimer	ν_1 donor	3574	3550
$(\text{H}_2\text{O})_2 \cdot \text{N}_2$	ν_1 donor	3566	-
multimer		3565	
multimer		~ 3540	
trimer	ν_1 donor	3528 (sh)	
trimer	ν_1 donor	3516	3510
multimer		~ 3500	
multimer		~ 3445	3435
multimer		~ 3415	
multimer		~ 3390	
multimer		3374	3355
multimer		3327	3320
multimer		~ 3320	
multimer		3212	3220
multimer		3150	
monomer	$\nu_2 + 218$	-	1822
monomer	$\nu_2 + 145$	-	1744
trimer	ν_2 donor	1632	1630
multimer		1626	
trimer	ν_2 donor	1620	
multimer		1615 (sh)	
dimer	ν_2 donor	1611	1619
trimer	ν_2 acceptor	1602	1614
dimer	ν_2 acceptor	1593	1601
monomer	ν_2	1590 ^b	1598
multimer		650	700
multimer			640
dimer	H bond bend		520
trimer	H bond bend		430

TABLE I—Continued

Species	Assignment	Ar	N ₂ ^a
dimer	H bond bend	290	320
trimer	H bond bend		265 (sh)
dimer	H bond bend		243 (sh)
monomer	libration (A axis)	-	218
trimer	H bond stretch		165 (sh)
dimer	H bond stretch	147	155 (sh)
monomer	libration (C axis)	-	145
monomer	rotation ($1_{-1} \rightarrow 2_{-1}$)	47 ^c	-
monomer	rotation ($0_0 \rightarrow 1_0$)	33 ^c	-
monomer	rotation ($1_{-1} \rightarrow 1_{+1}$)	16 ^d	-

a refs. 8, 9, 11, 13, 20 and this work.

b vibration-rotation band centre.

c ref. 4.

d J.A.Cugley and A.D.E.Pullin, Chem. Phys. Letters 19, 203 (1973)

DISCUSSION

Monomer

Redington and Milligan (3) successfully interpreted the infrared spectra of monomeric water in noble gas matrices as arising from water molecules undergoing essentially free rotation. Ayers and Pullin (6) reassigned the ν_1 regions of H₂O and HDO, leading to greater consistency between the band origins in argon and nitrogen matrices. Weak bands, near the band center positions, were assigned to nonrotating monomer, which can arise in two ways: at low concentrations, small traces of nitrogen impurity lead to bands at these positions, whereas at higher concentrations interaction between water molecules not close enough to form a hydrogen bond inhibits rotation and leads to increasing intensity of these bands (Figs. 2 and 3). Detailed examination of the assignments of Redington and Milligan in argon matrices shows that a number of bands, particularly those assigned to nonrotating monomer, are in fact due to dimer (H₂O 1594 cm⁻¹, D₂O 1189 and 1178 cm⁻¹, HDO 3695 and 1403 cm⁻¹). The assignments of Ayers and Pullin (17) for nonrotating monomer in argon matrices are confusing since they apparently do not distinguish clearly between Q-branch lines of rotating monomer and genuinely nonrotating monomer. A revised assignment of all monomer lines for H₂O, D₂O, and HDO in argon matrices is presented in Table IV. For H₂O, the assignments can be fitted best with effective rotational constants slightly smaller than the gas-phase values; for D₂O and HDO there are insufficient data to fix effective rotational constants, so the gas-phase values were used to calculate the line positions. The lines listed as "band center" are due to nonrotating monomer.

TABLE II

Intramolecular Modes (cm^{-1}) Observed for D_2O in Argon and Nitrogen Matrices

Species	Assignment	Ar ^a	N ₂ ^b
monomer	ν_3	2772 ^c	2766
dimer	ν_3 acceptor	2766	2757
multimer		2755	
dimer	ν_3 donor	2746	2738
trimer	ν_3 donor	2738	2724
trimer	ν_3 donor	2733	
monomer	ν_1	2658 ^c	2655
dimer	ν_1 acceptor	2655	2650
dimer	ν_1 donor	2615	2599
multimer		2600	
multimer		2592	
trimer	ν_1 donor	2580	2575
multimer			2525
multimer		2496	
multimer		2488	2475
multimer		2456	2450
multimer			2380
trimer	ν_2 donor	1196	1200
dimer	ν_2 donor	1189	1193
trimer	ν_2 acceptor	1183	1190
dimer	ν_2 acceptor	1178	1181
monomer	ν_2	1176 ^c	1179

a ref. 17.

b refs. 11,13.

c vibration-rotation band centre.

In a nitrogen matrix, rotation does not occur and monomer bands observed in the far-infrared spectrum at 218 and 145 cm^{-1} are clearly due to librational modes of the water molecule. Libration about the *B* axis is infrared inactive; thus the two bands may be assigned to libration about the *A* (218 cm^{-1}) and *C* (145 cm^{-1}) axes. The two bands are rather closer together than would be expected

TABLE III

Intramolecular Modes (cm^{-1}) Observed for HDO in Argon and Nitrogen Matrices

Species	Assignment	Ar ^a	N ₂ ^b
dimer	ν_3 donor (D)	3694	3689
monomer	ν_3	3688 ^c	3682
dimer	ν_3 acceptor	3681	3674 3670
dimer	ν_3 donor (H)		3562
dimer	ν_1 donor (H)		2713
monomer	ν_1	2709 ^c	2706
dimer	ν_1 acceptor	2706	2701 2698
dimer	ν_1 donor (D)	2639	2619
multimer		2596	
multimer		2587	
multimer		2577	
multimer		2510	
multimer		2494	
multimer		2465	
dimer	ν_2 donor (H)		1445
dimer	ν_2 acceptor	1403	1410 1408
monomer	ν_2	1398 ^c	1405
dimer	ν_2 donor (D)	1398	1403
multimer		1389	

a ref. 17.

b refs. 11,13.

c vibration-rotation band centre.

simply from their respective rotational constants, implying that libration about the *C* axis is more restricted than that about the *A* axis. Miyazawa (9) calculated that the relative intensities of the two librations should be ca. 3:1, which is approximately what was observed.

The hydrogen halides (22) and ammonia (23), which rotate in argon matrices, also exhibit librational modes in their far-infrared spectra in nitrogen matrices. Combination bands of the librations and the stretching modes of the hydrogen

TABLE IV
Monomer Rotational Bands (cm^{-1}) Observed for H_2O , D_2O , and HDO in Argon Matrices at 20 K

Assignment	H_2O			D_2O			HDO		
	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2
$1_{-1} \rightarrow 2_{+2}$	{3835} ^a	-	-	{2832}	-	-	{3776}	{2797}	{1486}
$1_0 \rightarrow 2_{+2}$	-	{3730}	$\sim 1690(\text{vw})$	-	{2710}	-	{3762}	..	{1472}
$1_{+1} \rightarrow 2_{+1}$	-	{3721}	1660(w)	-	{2708}	1228(vw)	{3764}	..	{1474}
$1_{-1} \rightarrow 2_{-1}$	-	{3687}	1636(w)	-	{2688}	1204(vw)	{3732}	..	1439(w)
$1_{+1} \rightarrow 2_0$	3785(sh)	-	-	-	-	-	{3722}	{2743}	{1432}
$1_{-1} \rightarrow 2_{-2}$	3776(m)	-	-	2795(w)	-	-	2739(w)
$1_0 \rightarrow 2_{-1}$	{3772}	-	-	-	-	-	{3716(m)}	{2739}	1428(s)
$0_0 \rightarrow 1_0$	-	3672(w)	1624(s)	-	2677(w)	1196(s)
$1_0 \rightarrow 2_{-2}$	-	{3671}	{1623}	-	{2674}	{1192}	{3702}	..	{1412}
$0_0 \rightarrow 1_{-1}$	3756(s)	-	-	2783(s)	-	-	2725(m)
$1_{-1} \rightarrow 1_{+1}$	-	3654(w)	1607(m)	-	{2688}	1186(w)	{3703(s)}	..	1414(s)
$1_0 \rightarrow 1_{+1}$	3738(w)	-	-	{2776}	-	-	3691(w)	{2711}	1400(w)
band centre ^b	3733(w)	3638(vw)	1590(w)	2772(w)	2658(vw)	1176(w)	{3688}	2709(w)	{1398}
$1_{+1} \rightarrow 1_0$	3726(w)	-	-	2766(vw)	-	-	3686(w)	{2707}	{1396}
$1_{+1} \rightarrow 1_{-1}$	-	{3621}	1573(w)	-	{2648}	1166(w)	1383(w)
$1_{-1} \rightarrow 1_0$	3711(m)	-	-	2761(w)	-	-	3674(m)	2695(w)	..
$1_0 \rightarrow 0_0$	-	{3605}	1556(w)	-	{2638}	1155(w)	{3658}	..	1367(w)

a calculated using H_2O : $A=25$, $B=4.5$, $C=8 \text{ cm}^{-1}$ (cf. gas phase $A=27.4$, $B=14.6$, $C=9.5 \text{ cm}^{-1}$); D_2O : $A=15.2$, $B=7.3$, $C=4.9 \text{ cm}^{-1}$ (gas phase); HDO: $A=22.7$, $B=9.1$, $C=6.6 \text{ cm}^{-1}$ (gas phase). Gas phase constants from

W.S. Benedict, N. Gailar and E.K. Plyler, J. Chem. Phys., 24, 1139 (1956).

b non-rotating monomer.

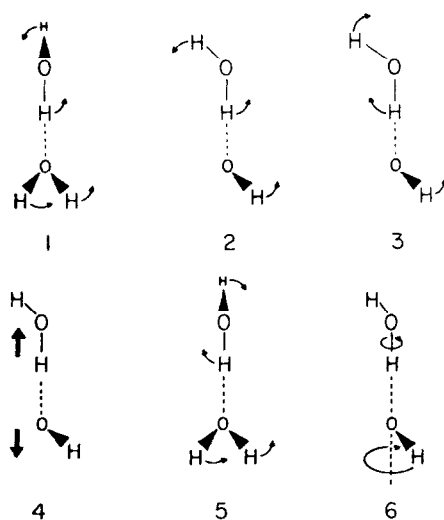


FIG. 6. Intermolecular normal mode vibrations of the open-chain dimer of water. Reprinted with permission from Ref. (25). © by the American Chemical Society.

halides (22) or the bending mode of ammonia (24) have been observed, but no such bands had previously been reported for water in a nitrogen matrix. The observation of these combination bands confirms the assignment of the 218- and 145-cm⁻¹ bands as monomer librational modes.

Dimer

The intramolecular modes of the water dimer in argon and nitrogen matrices are well established, and the present work agrees with previous assignments (11, 13, 17). The number of bands observed (four stretching and two bending)

TABLE V

Comparison of Calculated and Observed Intermolecular Modes of the Open-Chain Dimer of Water

				calculated ^a		N ₂ matrix
				ω	$(\partial\mu/\partial Q)^2$	ν
ν_1	H bond o.p. shear	A''		593	2.41	520
ν_2	H bond i.p. shear	A'		496	2.02	320
ν_3	H bond i.p. bend	A'		189	5.54	243
ν_4	H bond stretch	A'		168	0.35	155
ν_5	H bond o.p. bend	A''		161	0.03	-
ν_6	H bond torsion	A''		98	3.59	-

^a ref. 25.

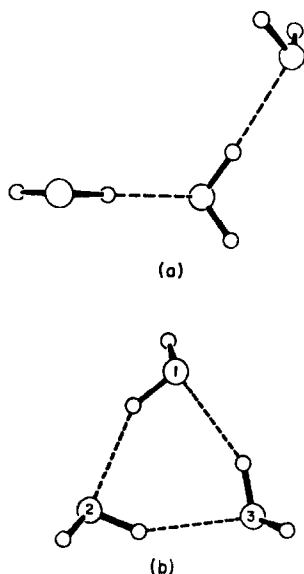


FIG. 7. Structures of open-chain and cyclic trimers of water. Reprinted with permission from Ref. (25). © by the American Chemical Society.

and their frequencies (three close to the monomer band centers and three shifted by hydrogen bonding) are consistent with an open-chain structure; no evidence was found for the existence of a cyclic dimer species.

The intermolecular modes (Fig. 6) in the far-infrared spectrum are poorly defined, thus only a tentative assignment can be made. Dyke *et al.* (15) estimated the hydrogen bond stretching frequency in the gas phase as 150 cm^{-1} , from centrifugal distortion constants. The band in an argon matrix at 147 cm^{-1} , and the shoulder at ca. 155 cm^{-1} on the 145-cm^{-1} monomer band in a nitrogen matrix, may then be assigned to this mode. Three other dimer bands appear, at 520, 320, and 243 cm^{-1} (nitrogen matrix), which may be assigned as hydrogen bond bending modes. Owicki *et al.* (25) calculated frequencies and intensities for the intermolecular modes; they found two relatively high frequency librational modes, with the remaining four modes below 300 cm^{-1} . In a gas-phase study of the $\text{H}_2\text{O} \cdots \text{HF}$ complex, Thomas (26) assigned two librational modes at 696 and 666 cm^{-1} , two at 170 and 145 cm^{-1} , and the hydrogen bond stretching vibration at 180 cm^{-1} . Trapping the water dimer in a matrix will undoubtedly shift the low-frequency librational modes to higher frequency because of the effect of the cage, but Owicki *et al.* calculated that one of these modes will have negligible intensity. Thus the most reasonable assignment of the observed bands is that given in Table V, although the separation of the high-frequency librational modes (520 and 320 cm^{-1}) is rather larger than expected.

Trimer

The bands observed which, from their concentration dependence, are attributable to trimer closely parallel the dimer absorptions, particularly in the intra-

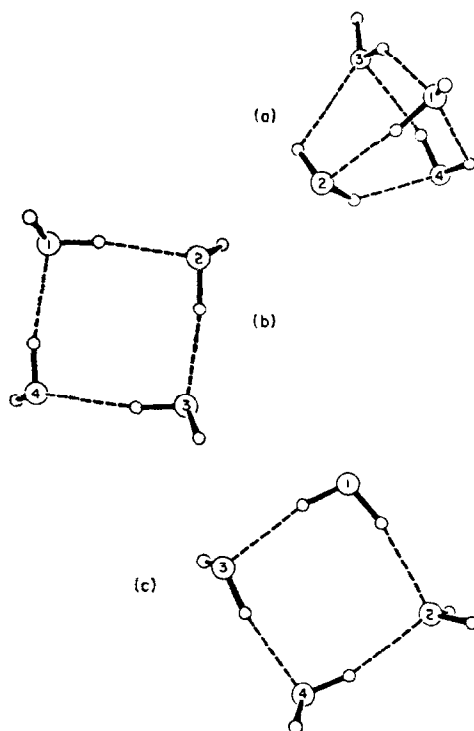


FIG. 8. Possible structures for water tetramers: (a) pyramid, (b) S_4 cyclic, (c) asymmetric cyclic. Reprinted with permission from Ref. (25). © by the American Chemical Society.

molecular region (Table I). An open-chain trimer should give bands due to both proton donor and acceptor water molecules, whereas a cyclic dimer contains only donor/acceptor water molecules (Fig. 7). The bands at 3612 and 1602 cm^{-1} are in the regions expected for acceptor water molecules (i.e., close to the monomer band centers). Thus the structure of the trimer in low-temperature matrices is believed to be open chain. The intermolecular modes observed in the far-infrared spectrum are assigned in a manner analogous to the manner in which those of the dimer are assigned.

Higher Multimers

A complex pattern of absorptions was found in the OH stretching region to frequency lower than that of the bands assigned to dimer and trimer, with a concentration dependence consistent with tetramer or higher multimer species. There was no evidence of bands attributable to open-chain tetramer, i.e., showing a pattern similar to that of the dimer and trimer absorptions. The more prominent bands (3374 , 3327 , and 3212 cm^{-1} in argon) are shifted to frequencies considerably lower than that of trimer; in particular the band at 3212 cm^{-1} must indicate the presence of water molecules acting as double proton donors. Owicki *et al.* (25) calculated the most stable forms of the tetramer to be the pyramid and symmetrical (S_4) cyclic structures (Fig. 8). The pyramid tetramer (and also asymmetric

cyclic tetramers) contains double proton donor water molecules; thus the observed bands would be consistent with such a structure. However, there may be a number of different tetramer structures, and possibly higher multimers, contributing to the spectrum.

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