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Author's Review

Matrix Isolation and Molecular Orbital Studies of Water

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Matrix isolation infrared spectroscopic studies and theoretical calculations on the association of water molecules are reviewed. Evidence is deduced that the dimer and trimer have an open-chain structure whereas higher multimers can also exist in cyclic form.

INTRODUCTION

In the development of molecular science one can roughly distinguish three steps; these are concerned with atoms, molecules, and the association of species. In the first two quantum mechanics provides a sound basis for understanding atomic and molecular phenomena. For the various types of association, however, quantum mechanics has to be augmented by statistical mechanics in order to study the properties and structure of these complex systems.

Molecular interactions determine the properties and the structure of matter. So it is not surprising that one observes increasing interest in their study which is of so much importance in chemistry, physics and biology.

Molecular interactions are the key to understanding the structure and properties of liquids and solids, and the properties of gases. In addition they provide some understanding of the fundamental problems concerned with the mechanisms of chemical and biochemical catalysis and the paths of chemical reactions. Molecular interactions are also of prime importance in deciding the structure and properties of biological systems as well as energy transfer in enzymes, phase transitions, etc.

In the last few years there has been great progress in the study of molecular interactions. This became possible as a result of the development of new theoretical approaches; the ease with which we can now carry out complex computations; and new physical experimental methods and techniques. These new methods have made it possible to study molecular systems in the vapour phase, in liquids, in solids, and in low-temperature matrices.

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* Festschrift of Professor Dušan Hadži.

In general systems in which intermolecular interactions occur, e. g., hydrogen bonding liquids, are very complicated from the point of view of structure. Hence, as a starting point it is wise to study a model system consisting of small clusters of molecules. One can then by step-wise addition approach the bulk system in a gradual manner. What this means in practice is that if one wants to study the bulk properties of water, one starts off studying monomeric water then the dimer followed by the trimer etc. etc.

Theoretical studies of molecular clusters (or complexes) are based on an examination of the complex *in isolation* and free from interaction with other species. Ideally then the parallel experimental studies should be carried out on a similar isolated system. Hence one should study low pressure gas phase systems containing small complexes. Using vibrational spectroscopy this poses many practical difficulties — low concentration of the species (e. g., dimer) of interest, overlapping rotational structure, etc.

In pure liquid or solid phases simple 1 : 1 interactions are certainly not being observed. Solutions in an inert solvent are better, but complicated by interactions with the solvent (which may be comparable in strength with the interaction being studied). The matrix isolation technique overcomes many of these difficulties.

Water is one of the main constituents of all living organisms. Its properties make it essential for life processes and it is important as a solvent for many physical proceses. An extensive network of H-bonding is responsible for the structure of bulk water. Information on the relative positions of the spatial units and quantitative information on the molecular interactions involved are necessary in order to understand the unique importance of water. In this paper some experimental and theoretical studies on water which throw some light on this basic problem are reported.

MATRIX ISOLATION SPECTROSCOPY

The use of low temperature as a controlling factor in chemical experiments is wide spread. All undergraduates are familiar with the use of slush baths or liquid nitrogen as important tools for certain chemical operations. For spectroscopists, however, the possibility of being able to cool samples under highly controlled conditions has added an entirely new dimension to research possibilities. Using cryogenic techniques new pathways to synthetic problems can be found, spectral features can be heightened, reactions can be slowed down, phase changes investigated, reactive species stabilised and examined at leisure and a broad range of charge-transfer species investigated in detail.

Matrix isolation is a technique for trapping isolated molecules of the species of interest in a large excess of an inert material by rapid condensation at a low temperature, so that the diluent forms a rigid matrix. At a sufficiently low temperature, diffusion of the solute species is prevented and thus, e. g., molecular complexes may be stabilised for leisurely spectroscopic examination.

In a simple way one can think of the solute species as a low pressure gas at low temperature. This is so because one expects little interaction between the inert matrix »cage« material (M) and the »trapped« solute (S). This is particularly true at high M : S ratios. In these circumstances, the matrix environment will have little influence on intramolecular processes occurring in the solute. This model predicts that the spectrum of the solute in the low temperature matrix will be very similar to that obtained for the free solute species in the gas phase. In practice matrix isolation (M. I.) spectra are often much simpler than those for the corresponding gas phase. This happens because the solute molecules, unless very small, do not rotate in the matrix and at the low temperature pertaining absorption transitions occur only from the lowest level thermally populated states.

The great advantages gained by using the matrix isolation technique in spectroscopy are now becoming more appreciated and in the near future the technique will be a standard one for studying both stable and unstable species. One of the greatest advantages is the great sharpening of solute absorptions compared with other condensed phases owing to the reduction of intermolecular interactions in the inert matrix environment. With the exception of very small molecules, rotation does not occur in matrices and the bands are therefore, much narrower than those obtained in the vapour phase.

The matrix technique is now used in most fields of spectroscopy. A monograph describing the present position in electronic (absorption and emission), MCD, Mössbauer, ESR and vibrational spectroscopy has recently been published[1]. Amongst the topics dealt with are computer processing of vibrational and spectroscopic data, vibrational and rotational relaxation, high pressure studies, intermolecular potentials, idealised matrices, the non-ideal matrix and spectroscopic matrices, molecular motion in matrices, vibrational band intensities in matrices, conformational isomerism, hydrogen bonded molecular complexes, and charge transfer molecular complexes. Details concerning experimental apparatus and methods are available in several texts (see ref. 1 for citations).

VIBRATIONAL SPECTROSCOPIC M. I. STUDIES ON WATER

(i) *Preamble*

The infrared spectrum of water trapped in low-temperature matrices has been the subject of many investigations. The rotation and nuclear spin conversion of water in noble gas matrices have been studied in detail[2-8]; in nitrogen[9-14] and deuterium[15] 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 concensus that the dimer has an open-chain structure. Dyke et al[16] have shown that the dimer is open chain in the gas phase using molecular beam-electric resonance spectroscopy.

In the earliest matrix study, Van Thiel et al.[9] 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[12,14] 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 Huong 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[10,19,20] gave contradictory results. A band at 218

cm^{-1} for water in a nitrogen matrix has been assigned[10] to libration of the monomer, which should be absent in an argon matrix (here 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. 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[9,17], but no conclusions were drawn as to the structures of these species. We have recently extended this work in order to obtain further information on the small multimers of water[22].

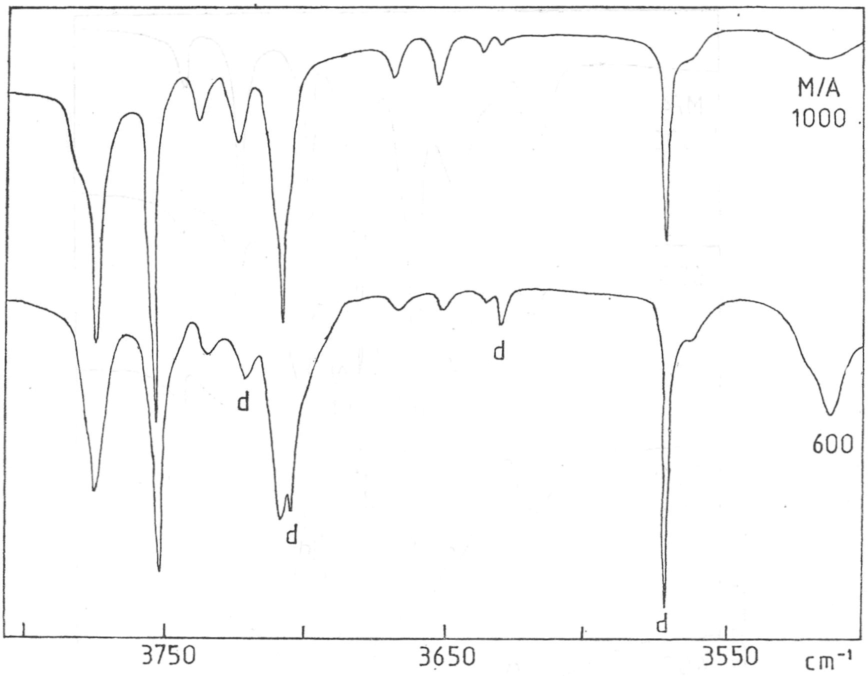
(ii) *Experimental*

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 mmol h^{-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.

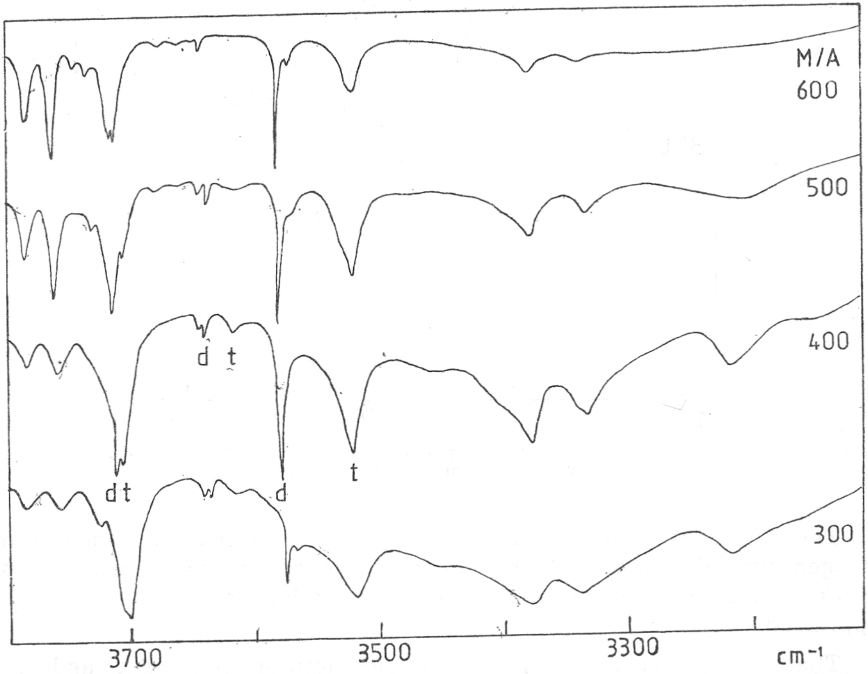
(iii) *Results*

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 (Figure 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 (Figure 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 to multimers of unspecified size.

The bending region showed similar changes (Figure 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.



1. Stretching region of H_2O in argon matrices at low concentrations (d indicates a dimer band)



2. Stretching region of H_2O in argon matrices at higher concentrations (d indicates a dimer band, t a trimer band)

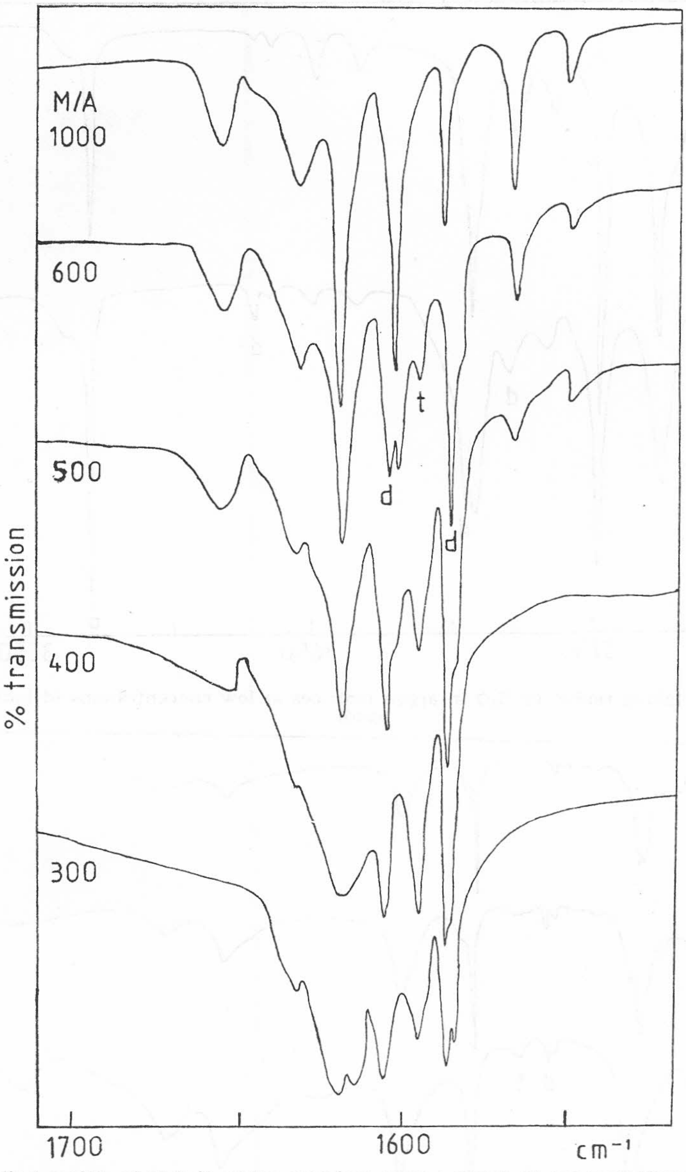


Figure 3. Bending region of H_2O in argon matrices over a range of concentrations (d indicates a dimer band, t a trimer band)

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.

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 is absent.

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
$(H_2O)_2 \cdot N_2$	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
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. 9, 10, 12, 14, 20 22

[b] vibration-rotation band centre.

[c] ref. 5

[d] J. A. Cugley and A. D. E. Pullin, *Chem. Phys. Lett.* **19** (1973) 203.

The bands observed for water in argon and nitrogen matrices, together with their assignments, are listed in Table I. Literature data for D_2O and HDO, assigned on a basis similar to that of the H_2O frequencies, are collected in Tables II and III.

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
	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. 12, 14. [c] vibration-rotation band centre.

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. 12, 14. [c] vibration-rotation band centre.

(iv) *Discussion — Monomer*

Redington and Milligan[4] successfully interpreted the infrared spectra of monomeric water in noble gas matrices as arising from water molecules undergoing essentially free rotation. Ayers and Pullin[7] reassigned the ν_1 regions of H_2O 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 non-rotating monomer, which can arise in two ways: at low concentrations, small trace 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 (Figures 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 (H_2O 1594 cm^{-1}, D_2O 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 H_2O, D_2O, and HDO in argon matrices is presented in Table IV. For H_2O, the assignments can be fitted best with effective rotational constants slightly smaller than the gas-phase values; for D_2O and HDO the gas-phase rotational constants were used to calculate the line positions. The lines listed as »band centre« are due to non-rotating monomer.

Dimer

The intramolecular modes of the water dimer in argon and nitrogen matrices are well established, and the present work agrees with previous assignments[12,14,17]. The number of bands observed (four stretching and two bending) 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 in the far-infrared spectrum are poorly defined, thus only a tentative assignment can be made. Dyke et al.[16] 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} 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.[23] 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}. 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.

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}	~1690(vw)	—	{2710}	1228(vw)	{3762}	..	{1472}
$1_{+1} \rightarrow 2_{+1}$	—	{3721}	1660(w)	—	{2708}		{3764}	..	{1474}
$1_{-1} \rightarrow 2_{-1}$	—	{3687}	1636(w)	—	{2688}	1204(vw)	{3732}	..	1439(w)
$1_{+1} \rightarrow 2_0$	3785(sh)	—	—	2795(w)	—	—	{3722}	{2743}	{1432}
$1_{-1} \rightarrow 2_{-2}$	3776(m)	—	—		—	—	3716(m)	2739(w)	1428(s)
$1_0 \rightarrow 2_{-1}$	{3772}	—	—		—	—		{2739}	
$0_0 \rightarrow 1_0$	—	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)	—	—	3703(s)	2725(m)	1414(s)
$1_{-1} \rightarrow 1_{+1}$	—	3654(w)	1607(m)	—	{2668}	1186(w)		..	
$1_0 \rightarrow 1_{+1}$	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)	3674(m)	..	1383(w)
$1_{-1} \rightarrow 0_0$	3711(m)	—	—	2761(w)	—	—		2695(w)	
$1_0 \rightarrow 0_0$	—	{3605}	1556(w)	—	{2638}	1155(w)	{3658}	..	1367(w)

[a] Calculated using H_2O: $A = 25$, $B = 14.5$, $C = 8$ cm^{-1} (cf. gas phase $A = 27.4$, $B = 14.6$, $C = 9.5$ cm^{-1}); D_2O: $A = 15.2$, $B = 7.3$, $C = 4.9$ cm^{-1} (gas phase) HDO: $A = 22.7$, $B = 9.1$, $C = 6.6$ cm^{-1} (gas phase). Gas phase constants from W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem Phys.* 24 (1956) 1139.

[b] Non-rotating monomer.

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	—

ref. 23

Trimer

The trimer bands closely parallel the dimer absorptions, particularly in the intramolecular 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. 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. It seems, therefore, that there may be a number of different tetramer structures, and possibly higher multimers, contributing to the spectrum.

THEORETICAL STUDIES ON WATER

(i) *Preamble*

The subject of electron donor-acceptor interactions has been one of intense activity in the past several years. The hydrogen bond, which is a specific type of electron donor-acceptor interaction, has particularly attracted considerable attention and there have been continued efforts to understand the nature of the bond by quantum mechanical methods. Since the early review by Bratos in 1967, a large number of papers dealing with quantum mechanical studies of the hydrogen bond have appeared in the literature[24].

(ii) *Semi-Empirical and ab Initio Calculations*

Results of calculations based on semi-empirical molecular orbital methods have been reviewed by Murthy and Rao[25], Kollman and Allen[26], and Schuster[27]. These reviews give a fair amount of the data reported in the literature on dissociation energies, equilibrium distances, and so on. Typical results on linear water dimer obtained by various methods are shown in Table VI. A comparison between energies of interaction and hydrogen bond distances obtained by ab-initio calculations with medium size basis sets and by the CNDO/2 method[28] shows that relative values are predicted correctly by the CNDO/2 method, although absolute values may vary. The CNDO/2 method appears to be a reliable and inexpensive procedure for the study of hydrogen bond interaction. This method is particularly useful in calculating properties of hydrogen bonds formed between large molecules where precise ab-initio methods would be difficult to employ. Where experimental enthalpies of association are available, CDNO/2 results on moderately strong hydrogen bonds compare favourably. It has been pointed out that the CNDO/2 method is superior to EHT or NNDO methods in predicting properties of such systems[26,29].

TABLE VI

Dissociation Energy of Linear Water Dimer (in kilocalories per mole) by Different Methods

Method	Dissociation energy
EHT	6.3
CNDO/2	5.0—8.7
INDO	4.0—6.9
NNDO	7.6
MINDO/1	10.4
STO-3G (counterpoise)	4.9
STO-3G (optimized)	6.0
6-31G	5.6
Extended Gaussian + polarization	4.7—5.1
HFAD Gaussian	5.3

Both semi-empirical and ab-initio molecular orbital methods have been employed to investigate hydrogen bonded chains of H_2O. The results show that the linear dimer is more stable than the cyclic or bifurcated dimer. The position is not quite so clear cut with the trimer. An early calculation[29] indicated that the open trimer is the more stable but later studies[30-32] suggest that a cyclic trimer, with three hydrogen bonds, is the more stable form. These calculations apply, of course, to an *isolated* water trimer but they are at variance with our experimental study[22] which shows that in a *low temperature matrix* the trimer has an open-chain structure. CNDO/2 calculations on H_2O chains have been extended to nonamers[27,32]. In the case of small oligomers, CNDO/2 energies of interaction are close to ab-initio values when experimental geometries are chosen[33]. Major contributions to the mean hydrogen bond energy come from up to the fifth neighbours in $(H_2O)_n$.[27]

Hydrogen bonding between water molecules forming the tetrahedral pentamer and its subunits[34-36], as well as clusters of pentamers[32] have been investigated because of the relevance of the pentamer unit to the structure of water. CNDO/2 and ab-initio calculations yield similar results on these systems, as can be seen from Table VII. The mean hydrogen bond energy of clusters (obtained by CNDO/2) converges faster than in chains. The stability of clusters appears to be mainly due to the large number of hydrogen bonds rather than their increased strength.

TABLE VII

Hydrogen Bond Energies (in kilocalories per mole) in Water Oligomers and Tetrahedral Clusters

n	Oligomer or cluster[a]	CNDO/2[b]	ab-initio[d]
2	Dimer (1)	8.7(6.0)	6.1
3	Trimer (2)	9.6(6.2)	7.3
4	Tetramer (3)	10.1(6.3)	8.2
5	Pentamer (4)	9.0(5.8)[c]	7.3
8	2-Tetrahedrons (7)	9.2—	—
11	3-Tetrahedrons (10)	9.3—	—
14	4-Tetrahedrons (13)	9.3—	—
17	5-Tetrahedrons (16)	9.3—	—

[a] Numbers in parentheses are numbers of hydrogen bonds; pentamer corresponds to one tetrahedron

[b] Values for minimized geometry are given along with those for experimental geometry in ice (in parentheses) from refs. 32, 35.

[c] Experimental geometry of r(OH) = 0.96A; R(0 . . . 0) = 2.72Å; <HOH = 107.1^0.

[d] From ref. 34.

Stereochemistry of hydrogen bonds has been examined in several systems, such as $(H_2O)_2$, $(HF)_2$, $H_2CO—H_2O$, etc., by CNDO/2 and ab-initio methods[27]. In genaral, it appears that linear hydrogen bonds are more stable than bent hydrogen bonds. In the case of $(H_2O)_2$, CNDO/2 calculations[37] predict that bending up to 10^0 or 20^0 can be tolerated without much loss of strength; lone pair direction does not appear to be the most stable orientation for the hydrogen bond in the dimer.

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IZVLEČEK

Matrična izolacija in študij vode z metodo molekulskih obrital

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Strukturo in lastnosti trdnin, tekočin in plinov določajo molekulske interakcije. Njihovo poznavanje je bistveno za razumevanje fizikalno-kemijskih pojavov, kot so npr. fazni prehodi, mehanizmi kemijskih in biokemijskih reakcij, prenos energije pri enzimih, kemična in biokemična kataliza ipd.

Določitev molekulskih interakcij pa ni lahka naloga niti s teoretično-računskega, niti z eksperimentalnega vidika. V prvem primeru pomagajo predvsem hitri računalniki, v drugem pa se zatekamo k tehniki matrične izolacije. Ta tehnika je postala standardna raziskovalna metoda že pri celi vrsti različnih eksperimentalnih tehnik — od Mössbauerjeve spektroskopije, preko infrardeče in Ramanske spektroskopije, do elektronske spinske resonance (ESR).

Pri matrični izolaciji v matriko inertnega plina, največkrat N_2 ali A, ujamemo molekulo, ki jo želimo preiskovati. Zaradi nizke temperature, molekule v matriki

ne difundirajo in ostanejo osamljene. Razmere, v katerih se nahajajo preiskovane molekule, so podobne kot v razredčenem plinu. Vibracijski spekter je celo enostavnejši, saj ne moti rotacijska fina struktura, ki je sicer prisotna v spektrih plinov. V matriki se večina molekul razen zelo majhnih prosto ne vrti. Nizka temperatura pa dovoljuje le absorbcijske prehode med najnižjimi termično zasedenimi stanji. V primerjavi z vibracijskimi spektri trdnin so trakovi izredno ostri zaradi zmanjšanega vpliva intermolekulskih interakcij.

Tudi voda sodi med snovi, v katerih se pojavlja prav določen tip intermolekulskih interakcij in t oso vodikove vezi. Poznavanje njihove vloge pri lastnostih, ki jih voda ima, je komplicirana in zahtevna naloga. Rešujemo jo postopoma. Izhodišče nam predstavlja majhen molekulski sistem, ki je v tem primeru kar monomer — molekula vode, v naslednji stopnji ji dodamo še eno molekulo, tako da dobimo dimer, nato trimer in tako naprej. S tem dograjujemo mrežo vodikovih vezi, ki so odgovorne za strukturo vode. Jasno je, da je poznavanje strukture dimera vode in drugih manjših multimerov bistveno in da predstavlja izhodišče za razumevanje strukture in dinamike tekoče vode.

Članek opisuje infrardeče spektre matrično izolirane vode v inertnih matrikah N_2 in A. V širokem koncentracijskem območju vode v matriki (od 1 : 1000 do 1 : 300) je zasledovano pojavljanje trakov, ki odgovarjajo nihanjem dimera, trimera in multimerov. Podano je podrobnejše poimenovanje teh trakov, ki vodijo do zaključka, da imajo dimeri in trimeri strukturo odprtih verig, medtem ko pa je struktura multimerov ciklična.

Podan je tudi pregled semi-empiričnih in ab-initio računov, ki so služili za račun disociacijske energije linearnega dimera vode in energije vodikovih vezi v oligomerih vode in tetraedričnih skupkih.