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Infrared spectrum of H₂O matrix isolated in CO at 10 K: Evidence for bifurcated dimers

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(Received 4 May 1981; accepted 24 June 1981)

The spectrum of H₂O in a CO matrix is qualitatively different from that of H₂O in other matrices. Not only are the frequency shifts of the monomeric absorptions with respect to the gas phase larger than in any other matrix, the pattern of the dimeric absorptions is also markedly different. It is concluded that the H₂O dimer in a CO matrix has a bifurcated structure. A number of absorptions due to CO strongly interacting with H₂O are also reported.

INTRODUCTION

Infrared absorbance spectroscopy has been employed extensively to study the properties of H₂O isolated in inert matrices at low temperatures. It has revealed the self-association through hydrogen bonding leading to formation of dimers, trimers, etc.,¹ and the nearly free rotation of the H₂O monomer in the noble gas matrices Ar, Kr, and Xe.²⁻⁶ The study of the small hydrogen bonded aggregates may help to elucidate the structure of liquid water.⁷

Matrix isolated dimeric water has received particular attention which has led to a debate about linear versus cyclic dimer structure (see for instance Ref. 8 and references therein). A bifurcated structure has also been considered as contributing to the spectrum in an inert gas matrix, but has been rejected.¹ We have found that in a CO matrix this may be the most stable form, and to the best of our knowledge the spectra presented in this paper constitute the first published evidence for the existence of this structure. Published matrix isolation spectra of H₂O are limited to inert matrices with the exception of the H₂O bending mode absorption in a CO₂ matrix.⁹ Surprisingly although CO is well known as a matrix material,¹⁰ the spectrum of H₂O in a CO matrix is not available in the literature. The effect of matrix material on the structure of a hydrogen bonded dimeric molecular complex has been illustrated recently for the H₂CO·H₂S complex. It has been suggested that in an Ar matrix a bifurcated structure exists while in N₂ both a bifurcated and a linear structure are present.^{11,12}

The investigations presented here have been carried out to study the infrared absorption of the mantles of low temperature interstellar grains. Observations of heavily obscured interstellar infrared sources reveal the presence of molecular grain mantles.¹³ It has been observed that under certain conditions these mantles consist of H₂O in large concentrations leading to a perturbed amorphous solid H₂O ice band at 3250 cm⁻¹ in interstellar spectra.^{14,15} However in many circumstances this band is not observed. Model calculations of interstellar chemistry in the gas phase and on grain surfaces indicate that under some interstellar conditions grain mantles will have a composition resembling the labora-

tory matrices reported here.¹⁶ Extension of the special regions covered by present observations of interstellar infrared sources to the regions studied in this paper, where matrix isolated H₂O absorbs, will contribute greatly to a better understanding of interstellar conditions.

EXPERIMENTAL

A description of the apparatus is given in Ref. 17. Mixtures of H₂O (triply distilled demineralized water purified by four freeze thaw cycles) and CO (Matheson research grade) are deposited at a thickness growth rate of 0.5 μm min⁻¹ onto a CsI window at 10 ± 2 K. Cooling is provided by an Air Products CSW-202 A refrigerator. The temperature of the cold tip is varied by electric heating. Infrared absorption spectra (4000–550 cm⁻¹) are taken with a Digilab 15 B/D fourier transform spectrometer at a resolution of 0.5 cm⁻¹. The measurement of a spectrum takes 10 min. Interpolation of the spectra for better peak shapes is done by zero filling of the interferogram. While the samples are free of air impurities it is comforting to note that addition of 0.5% air to a H₂O/CO (1:200) mixture does not alter its matrix spectrum in the regions studied.

RESULTS, IDENTIFICATIONS

The infrared spectra of H₂O in CO matrices at various concentrations are displayed in Fig. 1. Figure 2 shows the changes that occur when the H₂O is allowed to diffuse through the matrix by rising the sample temperature to 25 K for a short time. A study of the evolution of the spectrum upon variation of concentrations (Fig. 3) and upon diffusion (Fig. 4) combined with gas phase data¹⁸ and earlier matrix work^{1,19-26} including double doping experiments of CO and H₂O in Ar^{27,28} and in N₂²⁹ permits the identification of the H₂O absorptions given in Table I. Symbols ν_1 , ν_2 , and ν_3 refer to the symmetric OH-stretching mode, the bending mode, and the asymmetric stretching mode, respectively.

The assignments are made according to the following procedure. In order to facilitate the important discrimination between features due to monomeric, dimeric and trimeric H₂O the peak heights plotted in Figs. 3 and 4 are ratioed against the height of the dimer absorption at 3493 cm⁻¹. This peak is well separated from other peaks belonging to small aggregates of H₂O, although it appears on top of a broad polymer absorption. The spec-

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FIG. 1. (a)–(d) Infrared absorption spectra of H₂O in CO matrices at various concentrations (mole fractions of H₂O) indicated in the figure. Scales arbitrarily expanded.

trum with $M/A = 10$ shows many partly overlapping bands. The peakheights of this spectrum plotted in Fig. 3 are therefore quite uncertain.

Peaks of which the intensity remained constant relative to the absorption at 3493 cm^{-1} at all concentrations and during warm up are attributed to dimers. The sharp peaks of which the relative intensities increase with decreasing H₂O concentration are identified with the monomer. The trimer absorptions grow upon increase of the concentration or upon diffusion, and larger polymers are only present at high concentrations or after considerable diffusion. Assignments of the monomeric absorptions to specific vibrational modes are based on a comparison with gas phase data and earlier matrix work (Table III). A discussion of the assignments of the dimeric absorptions is given later.

Free rotation of H₂O in the matrix is excluded since the peak intensities in the spectra show no reversible temperature dependence.

In view of the results above we conclude that the assignments to monomeric and dimeric absorptions are very firm except for perhaps the weak dimer band at 3458 cm^{-1} which is partly overlapped by the two neigh-

boring trimer absorptions. Assignments to tetramers and higher polymers are somewhat speculative.

New features in the CO stretching region are shown in Fig. 5. On the basis of experiments carried out at different concentrations, diffusion experiments and literature spectra of pure solid CO,^{31,32} and of CO and H₂O mixed in solid Ar²⁷ and in N₂²⁹ we have assigned these features to the respective CO isotopes perturbed by H₂O (Table II). Absorptions showing the same concentration and diffusion dependence as the monomeric H₂O absorptions are easily ascribed to CO interacting with one H₂O molecule. The assignment of the peak at 2097 cm^{-1} to such a monomeric complex for ¹²C¹⁸O is uncertain because it is extremely weak and close to the strongly absorbing unperturbed ¹³C¹⁶O. The peaks tentatively attributed to ¹²C¹⁶O interacting with a H₂O dimer are not sufficiently pronounced to measure their peakheights accurately. Thus, this assignment should accordingly be considered speculative.

DISCUSSION

Monomer absorptions

The relative intensities of the monomeric H₂O absorptions in CO are approximately $\nu_3 : \nu_1 : \nu_2 = 1 : 0.15 : 0.58$ as

FIG. 2. Infrared absorption spectra of H₂O in a CO matrix ($M/A = 100$) in a diffusion experiment. From top to bottom: (a)—spectrum before diffusion, (b)—same sample after 5 min at 25 K; (c)—after additional 10 min at 25 K; (d)—20 min at 25 K, note expanded absorption scale; (e)—5 min at 27 K, note expanded scale.

compared to the gas-phase ratio of 1:0.05:1.5.³⁶ These differences are due to distortion of the H₂O molecule by the matrix and vibration induced polarization changes in the matrix molecules.

The monomeric absorptions of H₂O have undergone a large shift with respect to the gas phase and H₂O isolated in inert, nonpolar matrices (Table III). From the comparative study of hydrogen halides in various matrices¹⁰ it is well known that a CO matrix gives rise to these large shifts (Table IV). Model calculations cannot explain the exceptional behavior of CO matrices.¹⁰ Matrix isolated NH₃ also shows extremely large frequency shifts in a CO matrix.³⁵ The shifts in our spectra are larger than those of the isolated CO·H₂O complex in Ar (Ref. 28, Table IV) and can therefore not be attributed to a simple one-to-one complex. Instead they have to be caused by a combined interaction with all neighboring molecules.

The very small peak at 3695 cm⁻¹ is presumably due to the ν_3 vibration of monomeric H₂O trapped in a different matrix site. Two monomeric ν_3 absorptions are also seen in a D₂ matrix where they are attributed to site effects²⁵ and possibly in Ar²² and N₂.¹⁹

Apart from the matrix shifts of H₂O, the presence of H₂O in turn induces a frequency shift in the stretching vibration of neighboring CO molecules. The induced shifts of 8 cm⁻¹ to higher frequencies with respect to the nonperturbed CO absorption (Table II) are similar to the values of 10.4 and 9.2 cm⁻¹ found for the ¹²C¹⁶O·H₂O complex isolated in Ar²⁷ and N₂,²⁹ which is largely attributed to dipole-dipole interactions²⁷ (see Table IV). The shift with respect to the gas phase absorption of ¹²C¹⁶O at 2143.3 cm⁻¹³¹ is much smaller. Interactions of a CO molecule with its neighbors in pure solid CO gives rise to a shift of 5.2 cm⁻¹ to lower frequencies,³¹

FIG. 3. Concentration dependence of peak intensities. All intensities in absorbance units are ratioed against the dimer absorption at 3493 cm⁻¹ and plotted against the cube root of the H₂O mole fraction. The absorptions are identified with the peak frequencies: (a)—intensities of peaks attributed the monomer absorptions; (b)—dimers; (c)—trimers.

but replacing a CO neighbor by H₂O adds to the existing interactions a dipole-dipole term resulting in an opposite frequency shift.²⁷ This shift is given by $\Delta\nu_{\text{elec}} = -2 \mu_{\text{H}_2\text{O}} \Delta\mu_{\text{CO}} / (r^3_{\text{H}_2\text{O}-\text{CO}} hc)$, where μ is the dipole moment, $\Delta\mu$ is the change in dipole moment during the transition from ground to first excited vibrational state, and r is the intermolecular distance. Taking the values summarized by Barnes *et al.*¹⁰ and $\mu_{\text{H}_2\text{O}} = 1.85D$ ³⁷ we find for the additional frequency shift $\Delta\nu_{\text{elec}} = 7.0 \text{ cm}^{-1}$ a number which is in excellent agreement with our experimental data.

Dimer absorptions

Proper assignments of some of the absorption features due to dimeric H₂O is difficult, because the pattern of features in the present CO matrix spectra does not resemble that encountered in Ar, D₂, and N₂ matrices. Dimeric absorptions in the latter matrices have tentatively been assigned to a closed cyclic structure,^{1,8,20,24} an open linear structure,^{19,22,23,25,26} or a mixture of both.²¹ The water dimer in a supersonic molecular beam is

linear.³⁸ In carbontetrachloride solution the dimer is thought to be cyclic,^{39,40} although arguments in favor of a linear structure have also been expressed.⁴¹

The three possible dimer structures as suggested by Van Thiel¹ are shown in Fig. 6. Geometries are based on recent quantum mechanical calculations.⁴²⁻⁴⁵ Assignments to linear structures have received some support from *ab initio* calculations of the vibrational frequencies of linear dimers.⁴²

Although *ab initio* calculations of the dimerization energies for H₂O are sensitive to choice of basis set and inclusion of configuration interaction^{44,45} the following qualitative conclusions seem justified. The calculated dimerization energy for a free linear dimer [Fig. 6(a)] is approximately 6 kcal/mol.⁴³⁻⁴⁵ The cyclic dimer [Fig. 6(b)] is metastable with respect to the linear dimer⁴³ and its dimerization energy is about 1–2 kcal/mol less.⁴³⁻⁴⁵ Finally, a free bifurcated structure [Fig. 6(c)] is again 0.3–0.7 kcal/mol less stable.^{44,45}

The stability of a particular dimer configuration in a

FIG. 4. Diffusion behavior of peak intensities of trimers and higher polymers. All intensities are given in absorbance units ratioed against the dimer absorption at 3493 cm⁻¹ and plotted against the monomeric absorption at 3707 cm⁻¹ which decreases upon diffusion.

TABLE II. Infrared absorption of a CO matrix perturbed by H₂O.

Frequency [cm ⁻¹]	Linewidth [cm ⁻¹]	Relative peak height ^a	Assignment
2151.0		10	¹² C ¹⁶ O • (H ₂ O) ₂
2149.5		10	¹² C ¹⁶ O • (H ₂ O) ₂
2146.3	1.2	92	¹² C ¹⁶ O • H ₂ O
2138.46 ^b		∞	¹² C ¹⁶ O
2112.7	1.4	8	¹² C ¹⁷ O
2098.8	1.5	1	¹³ C ¹⁶ O • H ₂ O
2097			¹² C ¹⁸ O • H ₂ O
2092.3	1.3	177	¹³ C ¹⁶ O
2088.7	1.3	43	¹² C ¹⁸ O

^aMeasured at $M/A = 60$ on an absorbance scale; H₂O mono ν_1 (3707.0) = 100.

^bPeak saturated, frequency taken from Ref. 29.

matrix is not only determined by the "free" dimerization energy, but also by the interaction with its environment. This interaction consists of attractive (electrostatic, inductive, dispersive) and repulsive contributions (see for instance Ref. 10). We will first show that the attractive matrix interaction may compensate for a large part the difference in dimerization energy of the free linear and bifurcated dimer, irrespective of the

TABLE I. Infrared spectrum of H₂O in CO matrix.

	Frequency (cm ⁻¹)	Linewidth (cm ⁻¹)	Relative peak height ^a	Assignment
	3707.0	2.5	100	mono ν_3
	3694.7		4	mono ν_3 (site?)
	3685.8		7	tri ν_3
I	3673.3	4.3	35	di ν_3
	3659.3		5	tetra, poly
	3648.2		3	tri ν_3
	3640			poly
	3617.3	1.7	22	mono ν_1
II	3597.5	2.5	8	di (+poly) ν_1
	3505		2	poly
III	3492.7	5.0	27	di ν_3
	3490			poly
	3478.2		4	tri
IV	3458.2	8.0	2	di ν_1
	3437.4		2	tri
	3404		1	poly
	3360.3		1	tetra, poly
	3332			poly
	3257 (3223) ^b			H ₂ O (as)
	3238			poly
	3226			poly
	3196			poly
	1665 (1630) ^b			H ₂ O (as)
	1652.5			tri ν_2
	1645			tetra, poly ν_2
	1638.6	3.0	5	di ν_2
	1637			poly ν_2
	1630.8			tri ν_2
	1622			poly ν_2
	1608.7	3.0	11	di ν_2
	1601.7	2.0	72	mono ν_2
	710			poly, intermolecular mode
	647			poly, intermolecular mode

^aMeasured at $M/A \approx 60$ in absorbance units.

^bThe frequencies in parentheses are of H₂O (as) annealed to 130 K but not crystallized (Ref. 15).

TABLE III. Comparison of recently published OH stretching and bending frequency values for monomeric and dimeric H₂O.

Matrix	gas	Ar	Ar	D ₂	N ₂	CCl ₄ liquid	CO
Authors	Benedict <i>et al.</i> 1956 ^a	Mann <i>et al.</i> 1974 ^b	Barnes <i>et al.</i> 1980 ^c	Murby <i>et al.</i> 1979 ^d	Fredin <i>et al.</i> 1977 ^e	Magnusson 1970 ^f	This work
Identification							
ν_3 mono	3755.59	3729	3733	{3737.7 3733.5	3726.9	3708	3707.0
di		3715	3726	3728.6	3715.0	3693	3673.3
di		3544	3709	3707.9	3698.8		3492.7
ν_1 mono	3656.65	3641	3638	3642.0	3634.5	3616	3617.3
di		3626	3634	3637.0	3627.2	3552	3597.5
di		3485	3574	3561.8	3550.0		3458.2
ν_2 mono	1594.59	1599	1590	1597.6	1597.6		1601.7
di		1616	1593	1599.4	1601.1		1608.7
di			1611	1617.2	1618.6		1638.6

^aReference 18.^bReference 24.^cReference 26.^dReference 25.^eReference 23.^fReference 30.

matrix material. Then in the discussion of the repulsive forces it is suggested that matrix ordering is the decisive factor for the actual dimer structure.

The electrostatic and inductive terms are functions of the dipole moment of the solute molecule. Therefore, these two contributions depend strongly on the dimer

FIG. 5. Infrared absorbance spectra of CO perturbed by the presence of H₂O at concentrations indicated in the figure. Same units as in Fig. 1.

TABLE IV. Vibrational frequencies of some related binary molecular complexes in matrices.

Solute	Matrix	Authors	ν_3 (cm ⁻¹)	$\Delta\nu_3^a$ (cm ⁻¹)	ν_1 (cm ⁻¹)	$\Delta\nu_1^a$ (cm ⁻¹)	ν_2 (cm ⁻¹)	$\Delta\nu_2$ (cm ⁻¹)	ν_4 (cm ⁻¹)	$\Delta\nu_4^a$ (cm ⁻¹)
H ₂ O·CO	N ₂	Fredin <i>et al.</i> 1975 ^b	3724.8	-30.8	3632.1	-24.6	1598.1	3.5		
H ₂ O	CO ₂	Jacox Milligan 1961 ^c					1615	20		
HCN	CO	King Nixon 1968 ^d	3261.2	-50	2104	+7	{761.3 739.0	49 27		
HCl	CO	Barnes <i>et al.</i> 1969 ^e			2806.0	-79.5				
HBr	CO	<i>ibid.</i> ^e			2504.8	-53.9				
H ₂ O·CO	Ar	f	3724	-32	3628	-29	1596	1		
H ₂ O	CO	This work	3707.0	-48.6	3617.3	-39.4	1601.7	7.1		
NH ₃	CO	Hagen 1981 ^g	3427.8	-16	3320.3	-17	981.0	31	1619.5	-7
CO·H ₂ O	N ₂	Dubost 1975 ^b			2147.6	4.3				
CO·H ₂ O	CO	This work			2146.3	3.0				

^a $\Delta\nu$ is defined as $\nu_{\text{solute}} - \nu_{\text{gas}}$.^bReference 33.^cReference 9.^dReference 34.^eReference 10.^fReference 28.^gReference 35.^hReference 29.

FIG. 6. H₂O dimer configurations: a—linear dimer; b—cyclic dimer (the two H₂O molecules are in different but parallel planes, Ref. 43); c—bifurcated dimer (O-O separation is from Ref. 44).

structure. The contribution of the electrostatic interaction in a CO matrix however can be neglected compared to the inductive interaction because the dipole moment of CO is much smaller than the dipole moment of H₂O. The dispersive contribution is hard to quantify. However, it does not depend strongly on the dimer structure and we will therefore neglect it. We have calculated the inductive interaction energy of the H₂O monomer and the different dimers in a CO matrix (Table V) employing the point polarizable atom model and the cavity model.¹⁰ These are expected to give lower and upper bounds to the interaction energy.¹⁰ For our estimate of the stabilization of the dimer structure (Table V) we use the dipole moments calculated by Kollman and Buckingham⁴⁰ and the dipole moment of the gaseous dimer in a molecular beam measured by electric resonance spectroscopy.³⁸ Symmetrical cyclic dimer structures do not have a dipole moment and consequently benefit from inductive stabilization only through higher electric moments. A comparison of these attractive matrix interaction energies with the dimerization energies of free dimers discussed above shows that the difference in dimerization energy of the linear or cyclic and bifurcated structure may well be compensated by matrix effects. (It should be noted that these model calculations of the attractive matrix interaction do not take into account the nonsymmetrical cavity shape of the CO matrix; in fact the results would be similar

TABLE V. Typical inductive dipole interaction energies of H₂O in a CO matrix.

Model	Interaction energy (kcal/mol)	
	PPA ^a	CM ^b
Monomer	0.34	0.90
Linear dimer ($\theta = 25^\circ$) ^c	0.84	2.2
Linear dimer ($\theta = 57^\circ$) ^c	0.46	1.2
Linear dimer (expt) ^d	0.67	1.8
Bifurcated dimer	1.4	3.6
Cyclic dimer	0	0

^aPoint polarizable atom model (Ref. 10).^bCavity model (Ref. 10) $\epsilon_\infty = 1.67$ (Ref. 46).^cThe angle θ is defined in Fig. 7, dipole moments from Ref. 40.^dBased on $\mu = 2.6$ D obtained from gaseous dimer (Ref. 38).for Ar and N₂ matrices.)

The repulsive matrix interaction is due to short range valence forces. Because it depends strongly on the geometry of solute and matrix it may be decisive in the determination of the dimer configuration in different matrices. For instance, although N₂ and CO have identical crystal structures (fcc at low temperatures) and nearly equal site dimensions the repulsive potential of the asymmetric CO is more anisotropic. Because of this anisotropy it is likely that during deposition the interaction of matrix and guest molecules leads to ordering in the solid matrix, at least locally. Even in pure solid CO some degree of ordering exists, as implied by the amount of residual entropy.⁴⁷ The asymmetric CO molecules with the large O and the smaller C atom may prefer a sort of head to tail arrangement. It is anticipated that in such an arrangement the most favorable orientation of a solute molecule as determined by the repulsive short range forces is well defined. Dimeric solute molecules will then accept a similar head to tail configuration as their environment. Consequently it is quite conceivable that a bifurcated dimer is the preferred configuration in a partly ordered CO crystal, even when the dimer in a N₂ matrix is linear or cyclic.

FIG. 7. Schematic infrared spectra of the linear (top) and bifurcated H₂O dimer (bottom)—visualization of Table VI.

We will now discuss the infrared characteristics expected for the linear cyclic and bifurcated dimer structure of H₂O.

The infrared spectrum of the linear H₂O dimer [Fig. 6(a)] should consist of two series of fundamental vibrational absorptions (see Fig. 7). The OH-stretching and bending vibrations (ν_{3A}^{in} , ν_{1A}^{in} , and ν_{2A}^{in}) of the nonbonded (H accepting) H₂O molecule are narrow and only slightly shifted with respect to the monomeric absorption (Table VI). Their relative intensities are about the same as in the monomer. The absorptions due to the vibrations in the hydrogen donating molecule however are broader and undergo much larger shifts. In this case, the absorption attributed to the stretching of the free OH (ν_f , Ref. 42, also referred to as the asymmetric stretching mode ν_{3D}^{in}) is located between the stretching frequencies found in the H accepting H₂O molecule. The other OH stretching vibration of the donor molecule is naturally shifted much further to lower frequencies (ν_b , Ref. 42, or symmetric stretching mode ν_{1D}^{in}). The bending mode ν_{2D}^{in} of the donor molecule is shifted to the blue while that of

TABLE VI. Identifications, frequency shifts with respect to the monomer and relative intensities of the OH-stretching modes of dimeric H₂O.

	Identification	$\nu_{di} - \nu_{mono}$ (cm ⁻¹)	Relative intensity	Identification	$\nu_{di} - \nu_{mono}$ (cm ⁻¹)	Relative intensity
Matrix		N ₂			CO	
Authors		Fredin <i>et al.</i> 1977 ^a	Tursi <i>et al.</i> 1970 ^b		This work	
	ν_{3A}^{in}	-11.9	1.00	I	ν_{3A}^{inf}	-33.7 1.00
	ν_{3D}^{in}, ν_f	-28.1	0.38	III	ν_{3D}^{inf}	-214.3 0.77
	ν_{1A}^{in}	-7.3	0.25	II	ν_{1A}^{inf}	-19.8 0.23
	ν_{1D}^{in}, ν_b	-84.5	0.62	IV	ν_{1D}^{inf}	-159.1 0.06

^aReference 23.^bReference 19.

the acceptor is hardly affected at all. The intensity ratios of the two stretching modes ν_f/ν_b has decreased compared with that found in the monomer or the H accepting dimer molecule.

The six intermolecular modes one expects for a cyclic dimer [Fig. 6(b)] can be thought of as in-phase and out-of-phase combinations of the three fundamental vibrations of the two H₂O molecules constituting the dimer.³⁹ All vibrations are expected to have undergone large frequency shifts with respect to the monomer. The out-of-phase vibrations are infrared active and in first order, their relative intensities should be the same as in monomeric H₂O. Since in the out-of-phase stretching modes the two hydrogen bonded H atoms approach the same O atom at the same time, while in the in-phase mode they alternate, it is likely, that the out-of-phase stretching modes absorb at higher frequencies.³⁹ Because of the symmetry the in-phase modes of the cyclic H₂O dimer should only be Raman active. If strong and asymmetric matrix perturbations are present they may absorb weakly in the infrared.

The spectrum predicted for a bifurcated H₂O dimer [Fig. 6(c)] is quite different from that expected of the linear dimer (Fig. 7). The vibrations (ν_{3A}^{bf} , ν_{1A}^{bf} , and ν_{2A}^{bf}) of the hydrogen accepting part of the dimer will have undergone small shifts with respect to the monomer and will have maintained the monomer intensity ratios just as in the linear dimer case. The absorptions by the hydrogen donating molecule should however show significant differences. The H-bonded molecule has maintained its C_{2v} symmetry which permits assignments to ν_{3D}^{bf} and ν_{1D}^{bf} (in contrast to ν_f and ν_b), and both modes are shifted about equally with respect to the monomeric absorptions. Because in a bifurcated dimer both H atoms of the H donating molecule are hydrogen bonded to the acceptor, the frequency shift of the bending mode ν_{2D}^{bf} will be larger than those of the other possible dimer structures. The intensity ratio of all vibrational modes of the donor part of the bifurcated dimer is similar to that of the monomer and the H accepting dimer molecule.

In five ways our dimer spectra show essential differences from those tentatively attributed to linear dimers in Ar, N₂, and D₂ matrices. We focus on the shifts to lower frequencies of the symmetric and asymmetric OH stretching vibrations ν_3 and ν_1 of the dimeric absorptions with respect to those attributed to the monomer (see Table VI and Fig. 7).

1. The two dimer bands indicated by I and II in Tables I and II seem to be related to the monomeric ν_3^{mon} and ν_1^{mon} absorptions, respectively, because of their frequency positions and intensity ratios. Their shifts with respect to the monomer absorptions however are considerably larger than for ν_{3A}^{lin} and ν_{1A}^{lin} of the presumably linear dimer absorptions in Ar and N₂ matrices.

2. The intensity ratio and frequency positions of bands III and IV (Tables I and II) suggest that these bands are related to ν_3^{mon} and ν_1^{mon} , respectively. Band III has then shifted more than band IV, whereas in the linear dimer ν_f has undergone a much smaller shift than ν_b . Unlike the ν_f absorption band III is not located in between ν_3^{mon} and ν_1^{mon} but has shifted beyond ν_1^{mon} .

3. The most shifted dimer band IV has the lowest intensity in contrast to the linear dimer spectra where the most shifted band ν_b is relatively intense.

4. Polymeric (presumably trimeric) absorption is present at the blue side of band I. This is contrary to what would be expected for a linear dimer and linear or cyclic polymers.

5. In addition the OH bending region also shows slightly larger dimer-monomer frequency shifts but no essential difference with respect to the dimer spectra in Ar and N₂ matrices.

Because of the above we exclude the possibility that the dimer in a CO matrix is linear. The cyclic dimer an alternative proposed for Ar and D₂ matrices^{1,8,20,24} is ruled out for the CO matrix because of the strength of the six dimer absorptions. In contrast the frequency shifts and intensity ratios in the measured spectrum are consistent with a bifurcated dimer structure. We attribute the different dimer structure in a CO matrix to a specific interaction with the matrix host molecules. The anisotropic field caused by the shape of the CO molecule is an obvious source of the exceptional behavior of CO, which deviates from that of N₂ although the respective matrix sites are nearly identical.

Recently obtained infrared spectra of NH₃ matrix isolated in CO suggest that this species may also have a bifurcated dimer structure.³⁵

CONCLUDING REMARKS

The infrared spectrum of H₂O in a CO matrix exhibits strong matrix shifts of monomeric and dimeric absorptions. Intensity ratios and frequency shifts of bands attributed to dimeric H₂O suggest that the structure of the dimer differs significantly from that of the dimers in Ar, N₂, and D₂ matrices. The only dimer structure that can explain the measured spectra is the bifurcated dimer. This is the first time that the bifurcated H₂O dimer structure has been observed matrix since the possibility was originally suggested by Van Thiel *et al.*, in 1957.¹

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