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A Matrix Isolation and ab Initio Study of the Hydrogen Peroxide Dimer

Anders Engdahl,[†] Bengt Nelander,*[,†] and Gunnar Karlström[‡]

Chemical Physics, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden, and Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden

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The infrared spectrum of the hydrogen peroxide dimer has been studied in argon matrices at 17 K. The spectra have been assigned from concentration dependencies, experiments with different H/D ratios, photolysis experiments, and quantum chemical ab initio SCF calculations. The dimer has a cyclic structure with both components acting as hydrogen bond donors and as hydrogen bond acceptors. There is a significant coupling between the two bonded OH stretches in the two molecules and a relatively strong coupling between the corresponding HOO bends.

Introduction

The water dimer has an open structure with one molecule forming a hydrogen bond to the other;[1] the cyclic structure with two equivalent water molecules is unstable with respect to the open structure.[2] However, the water trimer has a cyclic structure, where each molecule acts both as a hydrogen bond donor and as a hydrogen bond acceptor.[3−5] It has been found that a water molecule which accepts a hydrogen bond becomes a stronger hydrogen bond donor. This cooperativity effect and the extra hydrogen bond more than compensate for the large deviations from linearity of the trimer hydrogen bonds. The hydrogen peroxide molecule is long enough to make it possible to form a cyclic dimer, with hydrogen bonds which deviate from linearity about as much as those of the water trimer. It is an open question if there is a cooperativity effect in hydrogen peroxide, when one oxygen accepts a hydrogen bond and a hydrogen in the other is engaged in a hydrogen bond. Very little has been published on small aggregates containing hydrogen peroxide. Hydrogen peroxide in low-temperature matrices has been studied by a few groups,[6−8] and a reliable assignment of the monomer spectrum has been published by Pettersson et al.[8] Goebel et al. have studied the complex between hydrogen peroxide and dimethyl ether and shown that hydrogen peroxide forms a single, relatively strong hydrogen bond to the ether oxygen.[9] We have recently completed an investigation of the complex between water and hydrogen peroxide.[10] The results clearly show that this complex is cyclic, with water and hydrogen peroxide both acting as hydrogen bond donors and as hydrogen bond acceptors. In this complex, the cooperativity effect in water probably helps to compensate for the deformation of the hydrogen bonds. In this paper, we present the results of a study of the infrared spectrum of the hydrogen peroxide dimer in argon matrices. The results suggest that the dimer is cyclic. We have investigated the effect of deuteration and found that both hydrogen bonds and deuterium bonds are formed, and there seems to be no clear indication of which is the more stable.

In a typical deuteration experiment, there are 10 different isotopomeric dimers present. Concentration dependencies are therefore insufficient as a basis for an assignment. Vibration spectra for different isotopomeric dimers, calculated from a SCF vibrational potential function, were used to guide the assignment. The calculated shifts for the stretches agreed qualitatively with the experimental observations, and the calculated bend shifts were in semiquantitative agreement with the observed shifts, where these could be obtained from measured monomer bands.

Computational Details

The interpretation of infrared spectra for molecular complexes is a difficult task. This is partly due to the fact that the structure of the studied complex is unknown, but also partly due to the fact that even if the structure of the complex were known it is not straightforward to predict how different lines in the spectrum would shift due to complex formation. To facilitate the interpretation of the obtained spectra, we have performed a series of ab initio calculations on the H_2O_2 molecule and on the dimer of this molecule. All calculations have been carried out with the MOLCAS program system.[11] A 10s, 6p, 3d primitive basis set was contracted to 4s, 3p, 1d for the oxygen atoms, and a 7s, 3p primitive basis set was contracted to 3s and one p function for the hydrogen atoms.[12]

In a first set of calculations, we performed full geometry optimizations for the monomer and the dimer at the SCF level of approximation. The dimer geometry is presented in Figure 1. The two H_2O_2 molecules are identical in the obtained structure, and the binding energy is calculated to be 5.41 kcal/mol at the SCF level and 6.31 kcal/mol at the MP2 level. Both these energies have been corrected for the basis set superposition error (BSSE) according to the method of Boys and Bernardi.[13] By comparison with extensive calculations on the H_2O dimer,[14] one would expect that calculations at the basis set limit would increase this binding energy by ∼1 kcal/mol. The main purpose of these calculations was to calculate dimer shifts of the vibrational frequencies for the H_2O_2 dimer, and this was done at the SCF level of approximation using the analytical Hessian matrix calculated by the MOLCAS program. The results for the H_2O_2 dimer as well as for a set of isotope-substituted dimers are presented in Table 3 together with experimental results as shifts compared to the free H_2O_2 molecule.

It is well-known that the SCF approximation yields force constants that are too large, particularly for stretching modes. In practice, this means that the deformation of the molecules as calculated in the SCF approximation is smaller than what is

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[†] Chemical Physics.

[‡] Theoretical Chemistry.

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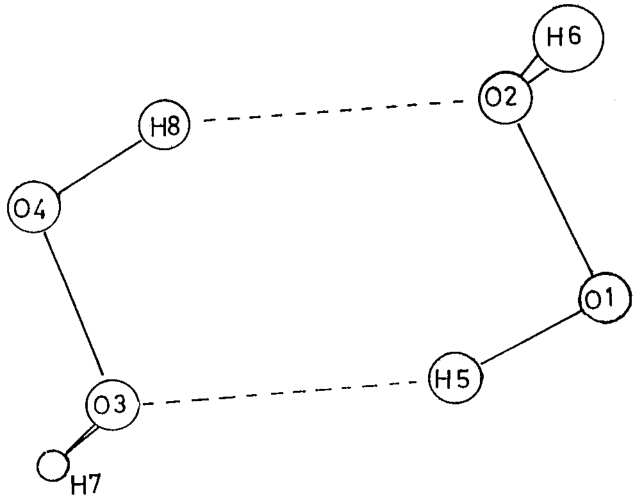

Figure 1. Structure of the hydrogen peroxide dimer. The complex is characterized by the following geometry parameters. Values in parentheses refer to the free monomer. Only unique parameters are presented. r(O1−O2) = 1.394 Å (1.392 Å). r(H5−O1) = 0.947 Å (0.943 Å). r(H6−O2) = 0.943 Å (0.943 Å). r(H8−O2) = 2.126 Å. α(H6−O2−O1) = 103.0° (102.8°). α(H5−O1−O2) = 102.3° (102.8°). α(O4−H8−O2) = 148.9°. The H6−O2−O1−H5 dihedral angle = 114.0°. The two molecules are equivalent, and the dimer has a center of inversion. The four oxygen atoms lie in the same plane, and the two hydrogens in the hydrogen bonds are 0.14 Å above and below the oxygen plane, respectively. The "free" hydrogen is on the same side of the oxygen plane as the "bound" hydrogen of the same molecule.

experimentally observed. This also means that the shifts that are calculated for modes involving the OH stretches are smaller than the observed ones. To look into this problem, we have calculated the potential energy curve for when one of the OH bonds in the H_2O_2 molecule is changed but keeping the rest of the molecular structure fixed, at both the SCF and MP2 level of approximation. The calculations showed that the SCF potential had a harmonic OH stretch frequency of 4144 cm^{-1}, while the $1 \leftarrow 0$ transition energy for an anharmonic SCF potential was 4038 cm^{-1}. The MP2 calculations gave a harmonic frequency of 3840 cm^{-1} and a $1 \leftarrow 0$ transition energy of 3728 cm^{-1}.

The H_2O_2 molecule contains a dihedral angle. The barriers associated with this motion are low, and one may expect this to result in the effective structure of the molecule being sensitive to the isotope substitution of the hydrogens. To look into this problem and analyze its effects for the IR spectra, we have performed calculations for a H_2O_2 molecule for different dihedral angles. (The rest of the molecule has been relaxed to minimize the energy of the system.) For each dihedral angle that has been studied, we have calculated the vibrational spectrum in the harmonic approximation. The result showed that the coupling between the bending vibrations varies strongly with the dihedral angle for HOOH and for DOOD, and the variation in HOOD is as expected relatively weak. We used our calculated torsion potential to estimate average dihedral angles for HOOH, HOOD, and DOOD in their ground torsional states and obtained values of 122.5°, 120.9°, and 119.2°, respectively. The calculated increase in the extent of coupling between the two bends due to the change in dihedral angle from the calculated minimum (113.52°) was 41.6 cm^{-1} for HOOH, 10.6 cm^{-1} for HOOD, and 23.6 cm^{-1} for DOOD. However, the calculated change in dihedral angle upon dimer formation was close to 0. The figures therefore only serves as warnings. Even a rather small change in the torsion potential when the dimer forms may produce important bending shifts, with isotope shifts which differ significantly for HOOD compared to those for HOOH or DOOD.

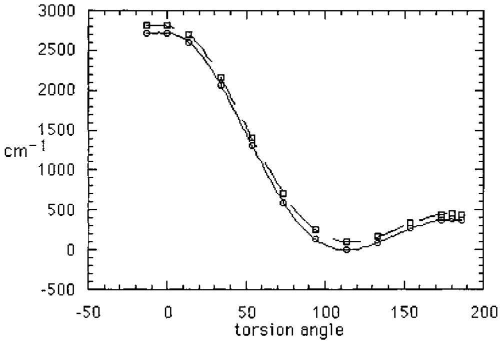

Figure 2. Calculated torsion potentials of monomeric HOOH: (□) SCF and (○) MP2. The SCF potential has been shifted 100 cm^{-1} vertically for clarity. The cis barriers are 2717.5 (SCF) and 2711.9 cm^{-1} (MP2), and the trans barriers are 380.7 (SCF) and 352.1 cm^{-1} (MP2).

Two potential energy curves, one at the SCF level of approximation and one at the MP2 level, are also obtained from this study. The potential minimum was found at a dihedral angle of 113.5° in the SCF approximation, and at 115.6° at the MP2 level, the experimental value is 111.9°.[16] The calculated trans barriers were 381 (SCF) and 352 cm^{-1} (MP2), which can be compared with the experimental trans barrier[16] (387.07 cm^{-1}). For the cis barrier, we obtained values of 2718 (SCF) and 2712 cm^{-1} (MP2), and the experimental value is[16] 2562.8 cm^{-1}. The calculated torsion potential curves are presented in Figure 2.

Experimental Section

Hydrogen peroxide was prepared from its urea complex as described in ref 8. Deuterated hydrogen peroxide was prepared by mixing urea, hydrogen peroxide, and an excess of D_2O. When all the urea had been dissolved, the solution was heated to a maximum of 60 °C. After it was allowed to cool to room temperature, the excess water was pumped away. To improve the degree of deuteration, the product might then be dissolved in D_2O and the procedure repeated until a sufficient deuterium concentration has been obtained. It is also essential to treat the deposition system with deuterated water vapor prior to an experiment to avoid deuterium−hydrogen exchange with the formation of HDO_2 during deposition. The matrices were prepared by passing argon over the urea complex, kept at a fixed temperature. The hydrogen peroxide concentrations could be varied by variation of this temperature.

A cryostat, based on a Leybold closed cycle cooler (RDK 10-320), was used in this work. It can operate between 10 and 100 K. The sample is condensed on a combined CsI−sapphire window, mounted in an OFHC copper frame. The temperature of the frame is measured with a Lake Shore silicon diode. The outer shroud of the cryostat can rotate relative to the frame, allowing different windows to be aligned with the frame. The outer shroud has a pair of CsI windows for infrared transmission spectroscopy, and a pair of sapphire windows for UV−vis spectroscopy. A blade valve allows the use of different sample preparation devices together with the cryostat. Windows in the same vertical planes as the CsI windows and as the blade valve and with a 45° entrance angle make it possible to irradiate the matrix during the recording of an infrared spectrum or during deposition.

The matrices were deposited and spectra recorded at 17 K. Infrared spectra were recorded between 450 and 4000 cm^{-1} using a Bruker 113v FTIR spectrometer.

TABLE 1: Observed Monomer Hydrogen Peroxide Bands

assignment (cm^{-1})	HOOH	HOOD	DOOD
ν_1, ν_5	3597		
	3588.0	3587.5	
		3587.0	
		2650.5	2646.1
		2645.5	2645.5
$\nu_2 + \nu_6$	2644.2	2330.6	1965.7
ν_2		1350.6	
		1342.8	
ν_6	1277.0		
	1271.0	981.2	951.7

Irradiation of the matrix with the quadrupled radiation from a YAG laser (Continuum NY 20C) at 266 nm rapidly eliminated the bands of hydrogen peroxide dimers and, at a slower rate, the bands of free hydrogen peroxide.

Assignment

The calculations described above predict a cyclic dimer structure. As will be shown below, the vibration spectra of the hydrogen peroxide dimer are consistent with a cyclic dimer structure with two equivalent components. To show which hydrogens are participating in the hydrogen bonds, we will write the dimers with the free hydrogens first and last and with the bonded hydrogens next to the other dimer component. A dimer of two HOOD molecules with one hydrogen and one deuterium bond will be denoted as HOOD−HOOD or DOOH−DOOH, while HOOD−DOOH has two deuterium bonds. ν_n(HOOH−DOOD) represents the *n*th fundamental of HOOH bound to DOOD. When the isotopic composition of the dimer partner is immaterial, we represent it as Hpo. The calculations indicate that the blue shift of ν_2(HOOH−DOOD) is significantly larger than that of ν_6(HOOH−DOOD), and consequently, ν_2(HOOH−Hpo) is the HOO bend of the hydrogen bond and ν_6(HOOH−Hpo) the HOO bend of the free hydrogen. We therefore use ν_2 to denote the HOO (DOO) bend of the hydrogen-bonded H (D) and ν_6 to denote the HOO bend of the free H (D) for all isotopomers of hydrogen peroxide dimers.

Pettersson et al.[8] have assigned the monomer spectra of HOOH, HOOD, and DOOD in noble gas matrices. In the same paper, they also assign a few bands to hydrogen peroxide multimers. We have made a systematic study of these and other bands, which have concentration dependencies indicating that they are due to species which contain more than one monomer hydrogen peroxide. In these studies, we have made the observation that under 266 nm irradiation, the hydrogen peroxide dimer decomposes significantly faster than monomeric hydrogen peroxide, which in turn decomposes faster than the hydrogen peroxide water complex. For comparisons, the spectra of different isotopomers of hydrogen peroxide in argon matrices are collected in Table 1. Table 2 gives the positions of the observed dimer bands, and Table 3 compares the calculated and observed dimer shifts.

The ab initio calculations give a cyclic dimer structure with two equivalent components. When the two dimer components have identical isotopic composition with identical isotopes in inversion-related positions, all intramolecular fundamentals split into two components, one infrared active and one inactive. The only exception is the free OH stretches, which are calculated to be closely degenerate.

When the hydrogen peroxide concentration is increased from low levels, a relatively sharp band at 3471.3 cm^{-1} grows more rapidly than the bands of monomeric hydrogen peroxide. Its strength leaves little doubt that it is due to dimeric hydrogen peroxide. We assign this band to the bonded OH stretch of HOOH, ν_1(HOOH−HOOH). According to the calculations, this is the upper, active component of the bound OH stretches.

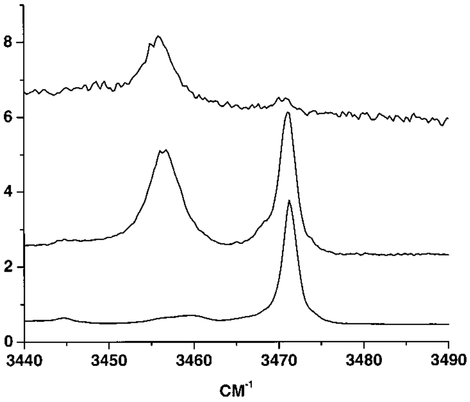

Figure 3. Bound OH stretch region of the dimer, with only HOOH (bottom) an intermediate H/D ratio (middle), and a low H/D ratio (top). The upper curves have been scaled and shifted for clarity. The HOOH−HOH complex absorbs at 3460.3 cm^{-1}.[10] The DOOH−HOH and DOOH−DOD complexes absorb at 3457 and 3454.3 cm^{-1}, respectively.

The free OH stretch of HOOH−HOOH, ν_5(HOOH−HOOH), appears as a doublet at 3581.7 and 3576.7 cm^{-1}. The calculations give two, almost equal free OH stretches. From the data for different isotopomers, it is clear that the two observed bands should be assigned to a site splitting. We note that the free OH stretches are directed out from the plane of the dimer oxygen atoms and are more sensitive to the structure of the trapping site than other dimer fundamentals. The splitting may, for instance, be due to an asymmetry of the trapping site.

Two other bands, at 1417.9 and at 1293.5 cm^{-1}, have constant intensity ratios with respect to the 3471.3 cm^{-1} band and are assigned to ν_2(HOOH−HOOH) and ν_6(HOOH−HOOH), respectively. A comparison with the calculations shows that the 1417.9 cm^{-1} band is the lower, active component of the bound HOO bendings and the 1293.5 cm^{-1} band is the upper active component of the free HOO bends. A very weak band at 866.6 cm^{-1} is assigned to ν_3(HOOH−HOOH) on the basis of its photolysis rate.

It is straightforward to identify the bands of DOOD−DOOD, which corresponds to the HOOH−HOOH bands assigned above. ν_1(DOOD−DOOD) is found at 2564.4 cm^{-1}, ν_2(DOOD−DOOD) at 1055.0 cm^{-1}, ν_5(DOOD−DOOD) at 2645.3 and 2542.0 cm^{-1}, and ν_6(DOOD−DOOD) at 963.0 cm^{-1}.

In studies of strongly deuterated samples, where HOOH is present at a very low concentration, a weak but sharp band is observed at 3470.7 cm^{-1}, close to the bonded OH stretch of HOOH−HOOH but significantly shifted from this band (Figure 3). The SCF calculations indicate that the OH stretches engaged in hydrogen bonding in the two dimer components interact to form one allowed and one forbidden transition even in dimers formed from different isotopomers. The shifts between HOOH and HOOD in the three dimers (HOOH−HOOH, HOOH−HOOD, and DOOH−HOOD) are calculated to be very small. We therefore assign this band to the bonded OH stretch of DOOH−HOOD, ν_1(DOOH−HOOD). When the H/D ratio is intermediate, the band is observed between the two extreme positions. We therefore believe that ν_1(HOOH−HOOD) is found between 3471.3 and 3470.7 cm^{-1}. When the H/D ratio is increased from almost pure deuteration, the bound OD stretch shifts from 2564.4 to 2565.2 cm^{-1}, which we believe is the position of ν_1(HOOD−DOOH). ν_1(DOOD−DOOH) is probably situated between these two values.

TABLE 2: Experimental Hydrogen Peroxide Dimer Bands

	HOOH−(HOOH)	HOOH−(HOOD)	HOOH−(DOOH)	HOOH−(DOOD)
ν_1	3471.3	3471.3	3456.5	3456.5
ν_5	3581.6, 3576.9			
ν_2	1417.9	1448.6	1436.2	1436.2
ν_6	1293.5	1290.3	1290.3	1290.3
ν_3	866.6			
	DOOH−(HOOH)	**DOOH−(HOOD)**	**DOOH−(DOOH)**	**DOOH−(DOOD)**
ν_1	3470.7	3470.7	3455.4	3455.4
ν_2			1402.0	1400.4
ν_6	969.9	970.6	969.9	969.9
	HOOD−(HOOH)	**HOOD−(HOOD)**	**HOOD−(DOOH)**	**HOOD−(DOOD)**
ν_1	2555.3	2555.3	2565.2	2565.2
ν_5				3581.2, 3576.5
ν_2	1050.1	1048.8	1035.5	1037.9
ν_6	1330.4	1330.4	1326.9	1330.4
	DOOD−(HOOH)	**DOOD−(HOOD)**	**DOOD−(DOOH)**	**DOOD−(DOOD)**
ν_1	2553.9	2553.9	2564.4	2564.4
ν_5				2645.2, 2642.0
ν_2	1062.9	1062.9		1055.0
ν_6	960.6	960.6	960.6	963.0

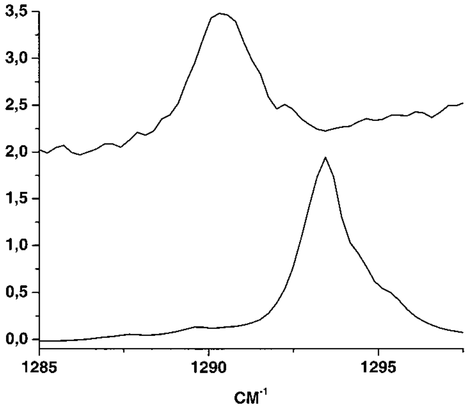

Figure 4. Free HOO bend of the dimer, with only HOOH in the matrix (bottom) and with a low H/D ratio (top). The upper curve has been shifted and scaled for clarity.

When a dimer is formed from one H-bonding and one D-bonding component, the bound OH stretch is calculated to fall between the active and inactive OH stretches of HOOH−HOOH and the bound OD stretch is to be found midway between the active and inactive OD stretches of DOOD−DOOD. The intensities of the two bands are half of that of the corresponding homodimer bands. We observe bound OH stretches at 3556.5 cm^{-1} at high H/D ratios and at 3555.4 cm^{-1} at low H/D ratios. On the basis of the calculations, we assign 3556.5 cm^{-1} to ν_1(HOOH−DOOH) and ν_1(HOOH−DOOD) and 3555.4 cm^{-1} to ν_1(DOOH−DOOD) and ν_1(DOOH−DOOH). The ν_1(HOOD−HOOH) and ν_1(HOOD−HOOD), and ν_1(DOOD−HOOH) and ν_1(DOOD−HOOD), bands are similarly found between 2555.3 and 2553.9 cm^{-1}. Figure 3 shows the spectrum of the bound OH stretching region at different H/D ratios.

From the calculations, ν_5(HOOH−Hpo) is expected to be almost independent of the isotopic composition of Hpo. Experimentally, the upper component shifts from 3581.7 cm^{-1} with only HOOH in the matrix to 3581.1 cm^{-1} when the H/D ratio is low. We therefore assign the two bands at 3581.2 and 3576.5 cm^{-1} in strongly deuterated experiments to ν_5(HOOD−DOOD). We have not been able to observe any bands which we can assign to ν_5(DOOH−Hpo), and we therefore believe that these bands coincide with ν_5(DOOD−Hpo), like what has been found for the corresponding monomer bands.

The intensities of ν_2(HOOH−Hpo) and ν_6(HOOH−Hpo) do not follow the intensity of the 3471 cm^{-1} band in partially deuterated samples but decrease faster when the H/D ratio decreases. In partially deuterated samples, a band at 1290.2 cm^{-1} appears, its position independent of the H/D ratio, and we assign this band to ν_6(HOOH−HOOD), ν_6(HOOH−DOOH), and ν_6(HOOH−DOOD). This assignment is supported by the calculations, which indicate a weak interaction between the two free HOO bends in HOOH−HOOH, which are split into two components, and only the upper component is infrared active. Compare the entries for HOOH−HOOH and HOOH−DOOD in Table 3 (Figure 4). It is considerably more difficult to find ν_2(HOOH−DOOD) and the related bands. In partially deuterated samples, bands appear at 1436.2 and 1448.6 cm^{-1} which photolyze as dimer bands. From the calculations, they seem to be possible candidates for ν_2(HOOH−DOOH), ν_2(HOOH−DOOD) (1436.2 cm^{-1}), and ν_2(HOOH−HOOD) (1448.6 cm^{-1}). Their assignment to these bands is based entirely on the SCF calculation, which predicts that the inactive component of ν_2(HOOH−HOOH) is found at a higher frequency than the active component, and also indicate an interaction between the bound HOO bends in HOOH−HOOD.

ν_6(DOOD−Hpo) appears at 960.6 cm^{-1} when Hpo differs from DOOD (Figure 5). This shift is also predicted by the SCF calculation (Table 3). It is more difficult to find the ν_2 bands of DOOD−Hpo. A weak band at 1062.9 cm^{-1} is assigned to ν_2(DOOD−HOOD) and ν_2(DOOD−HOOH) on the basis of the SCF calculation (Figure 6).

A band at 969.7 cm^{-1} appears as soon as there is reason to expect HOOD-containing dimers to be present in the matrix (Figure 5). Its photodecomposition rate and its general concentration dependency make it clear that it should be assigned to ν_6(DOOH−Hpo). The calculations indicate that ν_6(DOOH−HOOD) is found slightly above ν_6(DOOH−Hpo); we therefore assign a shoulder at 970.4 cm^{-1} to this band. At the same time, a band appears at 1330.4 cm^{-1} and usually also a weaker band at 1326.9 cm^{-1}. A band in the CsI window which has a variable intensity and a weak photosensitivity makes it difficult to study their photodecomposition rates, but we believe that they are decomposed at the same rate as other dimer bands. On the basis

TABLE 3: Experimental and Calculated Dimer Shifts (cm^{-1})

	HOOH−HOOH	HOOH−(HOOD)	HOOH−(DOOH)	HOOH−(DOOD)
ν_1	−116.7	−116.7	−131.5	−131.5
	−47.86	−47.82	−56.18	−56.03
	(−64.15)	(−64.51)		
ν_5	−6.4, −11.1			
	−2.91	−3.23	−3.41	−3.58
	(−2.63)			
ν_2	16[a]	47[a]	34[a]	34[a]
	23.69	56.42	44.42	43.63
	(62.94)			
ν_3	1[c]			
	−2.28	0.31	−1.70	−1.73
ν_6	22.6	19.4	19.4	19.4
	22.34	17.93	17.48	17.89
	(13.57)			
	DOOH−(HOOH)	DOOH−(HOOD)	DOOH−(DOOH)	DOOH−(DOOD)
ν_1	−116.8	−116.8	−132.1	−132.1
	−47.82	−47.65	−56.20	
ν_2			59.2	57.6
	63.90	56.42	74.68	
ν_6	−11.0	−11.0	−11.0	−11.0
	−10.06	−8.98	−10.29	
	HOOD−(HOOH)	HOOD−(HOOD)	HOOD−(DOOH)	HOOD−(DOOD)
ν_1	−90.2	−90.2	−80.3	−80.3
	−41.03	−41.12	−35.43	
ν_5				−6.8, −11.5
	−3.56	−3.21	−3.78	
ν_2	69.2	67.9	54.6	57.0
	52.08	52.45	48.50	
ν_6	−12.4	−12.4	−15.9	−12.4
	−12.57	−13.45	−9.28	
	DOOD−(HOOH)	DOOD−(HOOD)	DOOD−(DOOH)	DOOD−(DOOD)
ν_1	−90.2	−90.2	−81.1	−81.1
	−38.93			
ν_5				−0.2, −3.5
	−4.79			
ν_2	21[b]	21[b]		13.5[b]
	29.25			
ν_6	9.6	9.6	9.6	11.7
	10.42			

[a] $\nu_2(H_2O_2/Ar) = 1402$ cm^{-1}, estimated from $\nu_2 - \nu_6$(gas) = 131.30 cm^{-1}, and $\nu_6(H_2O_2/Ar) = 1271.0$ cm^{-1}. [b] $\nu_2(D_2O_2/Ar) = 1041.5$ cm^{-1}, estimated from $[(\nu_2 - \nu_6)(gas)][(\nu_2 - \nu_6)(SCF\text{-}D_2O_2)]/[(\nu_2 - \nu_6)(SCF\text{-}H_2O_2)]$ and $\nu_6(D_2O_2/Ar) = 951.7$ cm^{-1}. The upper row for each fundamental gives the experimental shifts and the lower row the calculated shifts. For HOOH−HOOH, the forbidden transitions from the calculation are given in parentheses on a third row. [c] Based on the gas-phase value of ν_3 (ref 15).

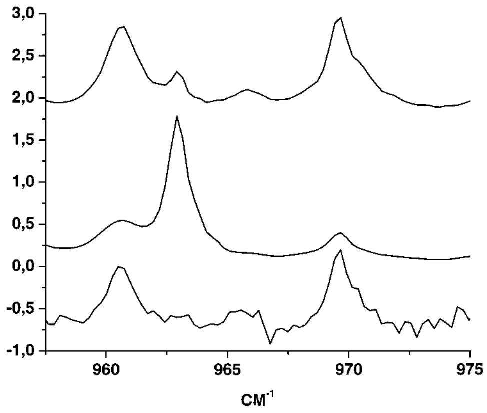

Figure 5. Free DOO bend. The peak at 960.6 cm^{-1} is due to DOOD in mixed dimers; the peak at 963.0 cm^{-1} is due to DOOD−DOOD, and the peak at 969.9 cm^{-1} is due to H-bonded HOOD. The curves have been shifted and scaled for clarity.

of the calculations, we assign these bands to ν_6(HOOD−Hpo) and ν_6(HOOD−DOOH), respectively. Petterson et al.[8] assign a band at 1346.4 cm^{-1} to dimers or multimers of HOOD. We believe that this band is due to monomers of HOOD where the tunneling over the trans barrier is hindered by electric fields from impurities in the matrix, like what is observed for ν_6(HOOH/Ar).[10]

The bands due to the HOO and DOO bends of the H or D engaged in the hydrogen bond, ν_2(DOOH−Hpo) and ν_2(HOOD−Hpo), are difficult to assign. Two bands at 1402.0 and 1400.4 cm^{-1}, which can be observed between the HOD bands, and are photolyzed rapidly, are assigned to ν_2(DOOH−DOOH) and ν_2(DOOH−DOOD), respectively, on the basis of the SCF calculations. A sharp band at 1050.1 cm^{-1} can be assigned to ν_2(HOOD−HOOH), since it is the last band to disappear in this region at very high H/D ratios. At low H/D ratios, a band appears at 1048.8 cm^{-1}, and we assign this band to ν_2(HOOD−HOOD) since the calculations indicate that this band should be close to ν_2(HOOD−HOOH). Another weak band which appears at low H/D ratios at 1037.9 cm^{-1} is assigned to ν_2(HOOD−DOOD). A weak band at 1035.5 cm^{-1} may be due to HOOD−DOOH. The DOO- bending region at different H/D ratios is shown in Figure 6.

Discussion

The OH stretches of monomeric hydrogen peroxide are almost degenerate. In the dimer, one stretch shifts approximately 10 cm^{-1} toward lower frequencies and splits into two components.

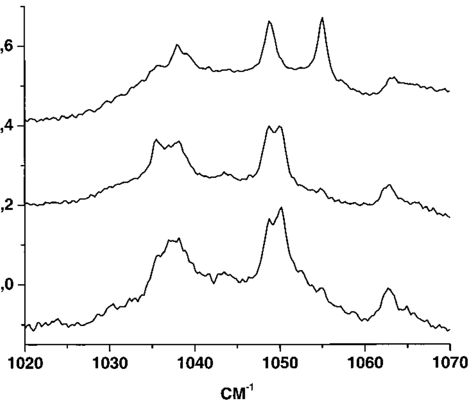

Figure 6. Bound DOO bend of dimers of DOOD and D-bonded HOOD. The upper curve shows a spectrum from an experiment with a low H/D ratio. The peaks at 1037.9, 1048.8, and 1055.0 cm^{-1} are assigned to HOOD−DOOD, HOOD−HOOD, and DOOD−DOOD, respectively, and the peak at 1062.9 cm^{-1} has been assigned to DOOD−HOOH and DOOD−HOOD. The two lower curves are obtained with intermediate H/D ratios. The peaks at 1035.5 and 1050.1 cm^{-1} are assigned to HOOD−DOOH and HOOD−HOOH, respectively. HOOD−HOH and HOOD−DOD absorb at 1031 cm^{-1}.

The other stretch shifts approximately 110 cm^{-1} in the same direction. The OH stretches thus behave like the OH stretches of the hydrogen bond donor of the water dimer, where the OH engaged in the hydrogen bond is strongly red shifted and the free OH stretch is red shifted by a small amount. We therefore assign the strongly shifted band to a bound OH stretch, ν_1, and the split, slightly downshifted band to a free OH stretch, ν_5. We note that the free OH stretch is expected to be sensitive to the shape of the trapping site and suggest that the split is due to trapping site asymmetry.

The SCF calculations predict that the hydrogen peroxide dimer is cyclic, with two equivalent components. The interactions between the two OH stretches, engaged in the hydrogen bonds and between the bends of these OH groups, are calculated to be easily observable. Also, the interaction between the bendings of the two free OH groups is predicted to give an observable splitting. As seen from the above discussion, summarized in Table 3, it is possible to assign the observed dimer bands using the SCF calculations as a guide. The question is whether it is possible to assign the dimer spectrum assuming an open dimer structure, with one acceptor and one hydrogen bond donor component.

For an open dimer, one would have to assign the 3471.3 cm^{-1} band to the bound OH stretch of the donor. The 3581.6, 3576.9 cm^{-1} band could be assigned to the free OH stretch of the donor, to an acceptor OH stretch and the free OH stretch of the donor, or to two acceptor OH stretches. The 3470.7 cm^{-1} band in partially deuterated experiments would be assigned to HOOH bound to DOOD. Similar shifts of hydrogen bond donor bands between different isotopomeric acceptors have been observed for the water dimer.[18] The two bands at 3456.5 and 3455.4 cm^{-1} have to be assigned to HOOD being H-bonded to another hydrogen peroxide and not to, for instance, ν_1 of HOOH bound to DOOD since a 15 cm^{-1} shift between HOOH bound to HOOH and HOOH bound to DOOD would be at least 5 times larger than the largest such, secondary, isotope shift observed. However, the assignment of the bands at 3455 cm^{-1} to an the OH stretch of HOOD, acting as a H-bond donor, is also unreasonable since one would then have a difference of more than 15 cm^{-1} between the bound OH stretches of HOOH and HOOD. In the monomer, the OH stretches of HOOH and HOOD coincide. When one takes into account the fact that the two OH stretches of monomeric HOOH are almost degenerate, it is not possible to imagine a mechanism which can produce a significantly larger dimer shift in HOOD than in HOOH. We are therefore convinced that the hydrogen peroxide dimer is cyclic. We also note that the assumption of a cyclic dimer structure makes it possible to assign the observed HOO and DOO bending vibrations of Hpo dimers. This conclusion is strongly supported by the quantum mechanical calculations.

In contrast to HDO, HOOD forms both hydrogen bonds and deuterium bonds with approximately equal probabilities. HDO prefers deuterium bonds, since the libration of the complexed molecule around the free OH bond has a significantly lower frequency then the libration around the free OD bond of the hydrogen-bonded isomer.[18] The remaining contributions to the zero-point vibration energy (ZPE) approximately cancel. There is no corresponding difference expected for the intermolecular fundamentals of the two isomers in the HOOD case. If we try to estimate the ZPE difference between HOOH−HOOD and HOOH−DOOH from the experimentally observed intramolecular stretches and bends, we obtain a value of −23 cm^{-1}. We clearly expect the torsion of the H-bonded form to have a higher frequency than the D-bonded form, and this effect may well compensate for the contributions from the other fundamentals. The SCF calculations give a 32 cm^{-1} higher ZPE for HOOH−HOOD than for HOOH−DOOH. However, the intramolecular stretch shifts are underestimated and the intramolecular bend shifts overestimated by the calculation and make a 6 cm^{-1} higher contribution to HOOH−HOOD than to HOOH−DOOH. If we combine the experimental estimate for the ZPE difference from the intramolecular stretches and bends with the SCF estimate for the torsions and intermolecular fundamentals, we obtain a ZPE for HOOH−HOOD 2 cm^{-1} higher than that for HOOH−DOOH. The difference is consequently expected to be too small to influence the observed ratio between the two isomers.

References and Notes

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