

The structure of the water–hydrogen peroxide complex. A matrix isolation study

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Received 20th July 2000, Accepted 7th August 2000

Published on the Web 29th August 2000

The infrared spectrum of the water–hydrogen peroxide complex was studied in argon matrices. The complex is cyclic, with each molecule acting both as a hydrogen bond donor and a hydrogen bond acceptor. The assignment is supported by experiments with combinations of completely and partially deuterated hydrogen peroxide and water. The water–hydrogen peroxide complex is slowly decomposed when irradiated with 266 nm radiation. When the $D_2O-H_2O_2$ complex is irradiated, $H_2O-D_2O_2$ forms and *vice versa*.

Introduction

Hydrogen peroxide has a vapor pressure which is much lower than expected from its molecular weight. The reason is the same as for water: hydrogen peroxide forms a three dimensional hydrogen bonded network. Unfortunately, pure hydrogen peroxide is difficult to handle, which is probably the reason why its hydrogen bonding properties have been much less studied than those of water.

Since both hydrogen peroxide and water are present in the atmosphere, their interaction may be of importance, in particular at low temperatures. Tso and Lee observed a water–hydrogen peroxide complex in oxygen matrices but were unable to decide its structure.¹ Pettersson *et al.* studied the infrared spectrum of hydrogen peroxide in argon, krypton and xenon matrices and made a reliable assignment of its monomer absorption spectrum.² They demonstrated that the urea complex of hydrogen peroxide is a very good source of hydrogen peroxide for matrix isolation spectroscopy. The Helsinki group also studied the interaction between hydrogen peroxide and nitrogen.³ Recently, Goebel *et al.*⁴ published an investigation of the dimethyl ether complex of hydrogen peroxide. They showed that one of the OH groups of hydrogen peroxide forms a relatively strong hydrogen bond to the ether oxygen.

We are currently investigating the complex formation between peroxy radicals and different small molecules.^{5–7} The method we use to prepare peroxy radicals also produces varying amounts of water and hydrogen peroxide. We were therefore forced to investigate the interaction between these two compounds. We were able to observe all the OH stretches of the binary complex both with H_2O and H_2O_2 and with deuterated components. The spectra were assigned from concentration dependences and isotope shifts. The results clearly point to a cyclic structure, with both molecules acting as proton donors and as proton acceptors.

Experimental

Water was doubly distilled and de-gassed and D_2O (Norsk Hydro, 99.5%D) was degassed. Hydrogen peroxide was prepared from its urea complex as described.² Deuterated hydrogen peroxide was prepared by mixing urea, hydrogen peroxide and an excess of D_2O . When all the urea had dissolved, the solution was heated to a maximum of 60 °C. After allowing it

to cool to room temperature, the excess water was pumped away. To improve the degree of deuteration, the product could then be dissolved in D_2O and the procedure repeated until a sufficient deuterium concentration was 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.

A cryostat, based on a Leybold RDK 10-320 closed cycle cooler was used. It can operate between 10 and 100 K. The sample was condensed on a combined CsI–sapphire window, mounted in an OFHC copper frame. The temperature of the frame was measured with a Lake Shore silicon diode. The outer shroud of the cryostat could rotate relatively to the frame, allowing different windows to be aligned with the frame. The outer shroud had a pair of CsI windows for infrared transmission spectroscopy and a pair of sapphire windows for UV-Vis spectroscopy. A blade valve allowed 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 made it possible to irradiate the matrix during the recording of an infrared spectrum or during deposition.

The matrices were deposited and spectra were recorded at 17 K. Infrared spectra were recorded between 450 and 4000 cm^{-1} using a Bruker 113v FTIR instrument. 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 lower rate the bands of free hydrogen peroxide. The water complex of hydrogen peroxide decreased slowly under irradiation. When a DOD–HOOH complex was irradiated, we observed the formation of traces of HOH–DOOD, and when HOH–DOOD was irradiated, small amounts of DOD–HOOH were formed.

Nomenclature

In complexes of the type studied here, the intramolecular vibrations of the complex components retain their original character in the complex. Therefore, the perturbed *i*th fundamental of A in a complex with B will be denoted as $\nu_i(A-B)$. When the isotopic composition of B is immaterial, water will be denoted as Aq and hydrogen peroxide as Hpo. We indicate the presence of an H-bond from HOOD to water by writing the complex as DOOH–HOH (or HOH–HOOD) and a

D-bond as HOOD-HOH (or HOH-DOOH). Analogous expressions are used for HOD.

Assignment

When hydrogen peroxide is deposited in an argon matrix at a low concentration, one observes two bands, at 1271.0 and at 1277.0 cm^{-1} , as described by Pettersson *et al.*² When the concentration is increased, these two bands decrease strongly in intensity and are replaced with a band at 1274.0 cm^{-1} (Fig. 1). An identical change takes place when hydrogen peroxide at a low concentration is co-deposited with water at a relatively high concentration. No similar change takes place in the bending region of DOOD. The two peaks in the HOOH spectrum were assigned to a tunneling doublet by Pettersson *et al.*² When matrix isolated hydrogen peroxide tunnels through its *trans* barrier, its dipole moment is reversed. If an electric field exists at the trapping site, the two potential minima are no longer equivalent and a sufficiently strong field will stop the tunneling completely. In the presence of a strong field, the tunneling doublet will collapse to a band at an intermediate position. Both hydrogen peroxide and water have significant dipole moments and will therefore produce significant electric fields in the matrix, which can stop the hydrogen peroxide tunneling. A similar phenomenon has been observed when ammonia is trapped in nitrogen matrices, when the ammonia inversion is inhibited at higher ammonia concentration.⁸

A band at 3460.0 cm^{-1} is the easiest HOH-HOOH band to observe; even traces of water in the matrix induce this band. It shifts to 3457.1 cm^{-1} with HDO and to 3454.5 cm^{-1} with D_2O (Fig. 2). These bands are assigned to $\nu_5(\text{HOOH-HOH})$, $\nu_5(\text{HOOH-DOH})$ and $\nu_5(\text{HOOH-DOD})$, respectively. At the same time, a band appears at 3590 cm^{-1} , on the high wavenumber side of the strongest component of the monomer hydrogen peroxide band. It is assigned to $\nu_1(\text{HOOH-Aq})$. In the antisymmetric bending region of HOOH, a strong and easily observed band at 1295.9 cm^{-1} is assigned to $\nu_6(\text{HOOH-Aq})$. In addition, a very weak band at 869.7 cm^{-1} could be assigned to $\nu_2(\text{HOOH-Aq})$.

The hydrogen peroxide bands of the complex are relatively sharp and easy to observe. In contrast, the bands due to the water part of the complex are weak and broad and appear in regions where they are difficult to observe owing to the presence of water aggregate bands. Experiments with low concentrations of water and photolysis experiments showed that H_2O bound to hydrogen peroxide has one OH stretch at 3701 cm^{-1} and another at 3520 cm^{-1} . These bands are assigned to $\nu_3(\text{HOH-Hpo})$ and $\nu_1(\text{HOH-Hpo})$, respectively. With D_2O and Hpo a band at 2584 cm^{-1} appears and, since none of the

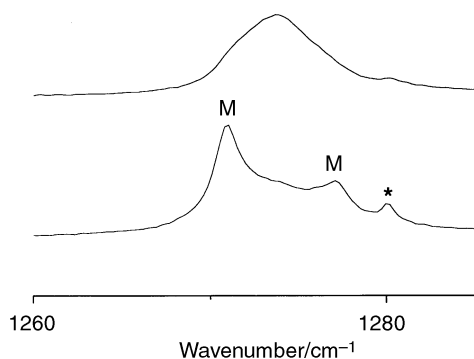


Fig. 1 Effect of impurities on the antisymmetric bending vibration of HOOH. Top curve: absorption of HOOH, present as an impurity in a DOOD- H_2O experiment. Ar matrix, 17 K. Bottom curve: absorption of HOOH, present as an impurity in a DOOD experiment with lower concentration of DOOD. M indicates the position of the HOOH monomer band. The asterisk indicates the HOOH- N_2 complex. Ar matrix, 17 K.

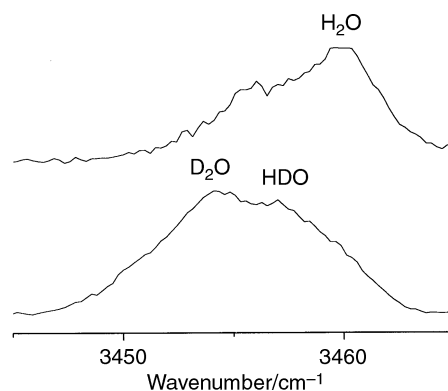


Fig. 2 The bound OH stretch of HOOH bound to H_2O (top) and D_2O (bottom). The complex partner of HOOH is indicated above the curves. Top curve: HOOH-HOH, Ar : H_2O = 187, 20 mmol Ar deposited, 17 K. Bottom curve: HOOH-DOD; Ar : D_2O = 209, 11 mmol Ar deposited, 17 K.

different isotopomers of the water trimer absorbs here,⁹ it is assigned to $\nu_1(\text{DOD-Hpo})$. The corresponding HOD band, $\nu_1(\text{HOD-Hpo})$, seems to be on the high wavenumber side of the $\text{H}_2\text{O}-(\text{HOD})_2$ band at 2595.5 cm^{-1} . Unfortunately, the photolysis of hydrogen peroxide dimers produces water dimers in a strongly perturbed site and the tail of the $(\text{D}_2\text{O})_2$ absorption extends to 2595 cm^{-1} , making it impossible to find the precise position of the hole in the absorption, from the destruction of HOD-Hpo. The free OH stretch of the HOD-Hpo complex was relatively easy to observe, since there was no monomer or aggregate HDO absorption at its position. Irradiation consistently decreased the absorption close to the bend of the acceptor part of the water dimer of the dominating isotopomer of water, indicating the position of the bending fundamental of complexed water.

Experiments with high and low degrees of deuteration clearly showed that HOOD can form both H- and D-bonds to water. We found no evidence for HDO which was H-bonded to Hpo. The free OD stretch of such a complex should be easy to observe since it is expected to appear near 2700 cm^{-1} where there are relatively few and sharp bands due to HDO monomer and HDO as the D-bond acceptor of water dimers. The complete assignment of the water hydrogen peroxide complex is given in Table 1.

The assignment of the HOH-HOOH and DOD-DOOD bands is straightforward, since one isotopomer of the complex is completely dominating. Also, DOD-HOOH presents no complications. The assignment of the HOH-DOOD bands is more difficult since the need to pre-treat the deposition line for DOOD with D_2O introduces an observable concentration of D_2O in the matrix and therefore some DOD-DOOD is present together with the HOH-DOOD. The assignment of the HOOD bands is complicated since the lack of coupling between the OH (OD) stretches in hydrogen peroxide makes the OH (OD) stretch of HOOD almost coincide with an OH (OD) stretch of HOOH (DOOD). For the OD regions, we used experiments where we deposited HOOH through a deposition line which was pre-treated with D_2O . This procedure gave matrices, where HOOH was the dominating isotopomer, with significant concentrations of HOOD and low concentrations of DOOD. For the OH regions we used experiments with a batch of DOOD, that was low in HOOD. It is difficult to have complete control over the degree of deuteration of the water in these experiments and the assignment of bands to a particular isotopomer of water bound to HOOD may be more uncertain than the assignments for the corresponding HOOH and DOOD cases. One further complication is that HOOD dimer bands coincide with the bound OH and bound OD stretches of hydrogen peroxide com-

Table 1 Intramolecular fundamentals of the water–hydrogen peroxide complex

	HOH–HOOH	HOD–HOOH	DOD–HOOH
$\nu_1(\text{Aq})$	3522	(2597)	2584
$\nu_2(\text{Aq})$	1593.5	1398.5	1177.2
$\nu_3(\text{Aq})$	3701	3686.6	
$\nu_1(\text{Hpo})$	3590	3590	3590
$\nu_3(\text{Hpo})$	869.8	869.8	869.8
$\nu_5(\text{Hpo})$	3460.3	3457.1	3454.3
$\nu_6(\text{Hpo})$	1295.9	1295.9	1295.5
	HOH–HOOD	HOD–HOOD	DOD–HOOD
$\nu_1(\text{Aq})$			
$\nu_2(\text{Aq})$			
$\nu_3(\text{Aq})$			
$\nu_1(\text{Hpo})$	2652	2652	2652
$\nu_2(\text{Hpo})$			
$\nu_5(\text{Hpo})$	3457	3457	3454.9
$\nu_6(\text{Hpo})$	976.1	976.1	976.1
	HOH–DOOH	HOD–DOOH	DOD–DOOH
$\nu_1(\text{Aq})$			
$\nu_2(\text{Aq})$			
$\nu_3(\text{Aq})$			
$\nu_1(\text{Hpo})$	3590	3590	3590
$\nu_2(\text{Hpo})$	1329.7	1329.7	1329.7
$\nu_5(\text{Hpo})$	2556.8	2556	2553.6
$\nu_6(\text{Hpo})$	1031	1031	1031
	HOH–DOOD	HOD–DOOD	DOD–DOOD
$\nu_1(\text{Aq})$			2584
$\nu_2(\text{Aq})$	1592	1398.5	1177.2
$\nu_3(\text{Aq})$			
$\nu_1(\text{Hpo})$	2652	2652	2652
$\nu_2(\text{Hpo})$			
$\nu_3(\text{Hpo})$	871.7	871.7	871.7
$\nu_5(\text{Hpo})$	2556.2		2553.5
$\nu_6(\text{Hpo})$	966.0	966.0	966.0

plexes. Fortunately, the dimer is rapidly photolysed, which makes it relatively easy to extract the water complex bands.

Discussion

Both the water and the hydrogen peroxide components of their binary complex have strongly shifted OH stretching fundamentals. Complexed hydrogen peroxide also has an almost unshifted OH stretch. The second water fundamental of complexed water is downshifted, but only as much as one would expect from the change in the coupling between its two OH stretches; the free OH stretch of complexed HDO is almost unshifted. The complex then has to have a cyclic structure with both molecules donating and accepting hydrogen bonds. The bifurcated structure, where HOOH forms two hydrogen bonds to the water oxygen, discussed by Tso and Lee¹ is clearly ruled out.

The complex shift of the bound OH stretch of water is very close to the corresponding shift of the water trimer, where the hydrogen bond deviates from linearity by a similar angle. We may therefore assume that the strength of the hydrogen bond from water to hydrogen peroxide is of a similar strength as a hydrogen bond in the water trimer, 3.4 kcal mol⁻¹ per hydrogen bond.¹⁰ The shift of the bound OH stretch of hydrogen peroxide is approximately -135 cm^{-1} , much less than the corresponding shift of the hydrogen peroxide dimethyl ether complex, -234 cm^{-1} .⁴ The red shifts of water forming a hydrogen bond to dimethyl ether and to another water molecule are -132 ¹¹ and -64 cm^{-1} ,¹² respectively. However, the complex shifts of water are misleading, since they are contaminated with the coupling between the symmetric and anti-

symmetric OH stretches, as one clearly sees when one compares the complex shifts of HOD and DOD D-bonded to the same hydrogen bond acceptor. For the HOD and D₂O complexes with dimethyl ether the shifts are -125 and -85 cm^{-1} , respectively. For the not observed H-bonded DOH–dimethyl ether complex, we expect a complex shift of -169 cm^{-1} , based on the complex shifts of HDO H and D-bonded to another water molecule¹³ and for HOD H-bonded to another water molecule the shift is -92 cm^{-1} .¹³ For these complexes there are no problems with coupling and the shifts may be used as estimates of the strength of the respective hydrogen bonds. In hydrogen peroxide, the two OH stretches coincide,² and therefore the coupling between the stretches is very small. Based on the complex shift of the hydrogen peroxide dimethyl ether complex, -234 cm^{-1} , for the water hydrogen peroxide complex, we therefore expect a complex shift of -127 cm^{-1} . This is very close to the observed shift, -135 cm^{-1} , even though the hydrogen bond in the water complex is deformed in order to make it possible to form a hydrogen bond from water to the other oxygen of hydrogen peroxide. Possibly the destabilization due to the deviation of the hydrogen bond from linearity is compensated for by the gain due to the other hydrogen bond. The OH shift of complexed hydrogen peroxide is between the OH shifts of the donor OH in the water dimer and trimer, respectively. This probably indicates that the hydrogen bonds are of similar strengths. The dissociation energy of the water–hydrogen peroxide complex is therefore expected to be slightly smaller than twice the dissociation energy of the water dimer.

HDO is known to prefer to form deuterium bonds rather than hydrogen bonds to acceptor molecules.¹⁴ The reason is that the zero point vibration energy is lower for the deuterium bonded isomer than the hydrogen bonded isomer. The main contribution to this difference comes from the difference in libration frequency around the free OH or OD bond of the complexed HDO. For the D-bonded isomer this frequency is approximately 0.75 times the frequency of the H-bonded isomer. The contributions from the intramolecular fundamentals to the zero point vibration energy difference cancel to a good approximation. The intermolecular fundamentals of complexed HOOD are expected to be almost independent of H- or D-bonding since both the mass and the moments of inertia are dominated by the oxygen atoms. The HOO bending of H-bonded HOOD and the DOO bending of D-bonded HOOD were not observed, but the HOO bend is expected to be not far from 1400 cm^{-1} and the DOO bend somewhere around 1040 cm^{-1} . The contribution from the torsion to the zero point vibration energy difference is expected to favor the D-bonded form, since the H-amplitude is larger than the D-amplitude and therefore the frequency of the H-bonded isomer is expected to increase more than that of the D-bonded isomer when the complex forms. If we accept the estimated bending vibrations above, the difference in zero point vibration energy from the intramolecular fundamentals, except the torsion, is approximately 50 cm^{-1} lower for the H-bonded isomer than for D-bonded isomer. It seems reasonable that the torsion more or less compensates for the contributions from the other fundamentals, and therefore the H- and D-bonded isomers are almost isoenergetic.

Fig. 3 shows the DOO bending region of a matrix with HOOH and D₂O, before and after irradiation with 266 nm radiation. The matrix contained a small amount of monomer HOOD before the irradiation, probably from the deposition system. We found that HOOH which passes through a glass tube which has been exposed to D₂O vapor undergoes partial isotope exchange to HOOD and DOOD.

As is seen from Fig. 3, a significant amount of water complexed DOOD forms as a result of the irradiation. In addition, smaller amounts of water complexed HOOD and monomer DOOD are formed. It seems clear that the DOOD forms from

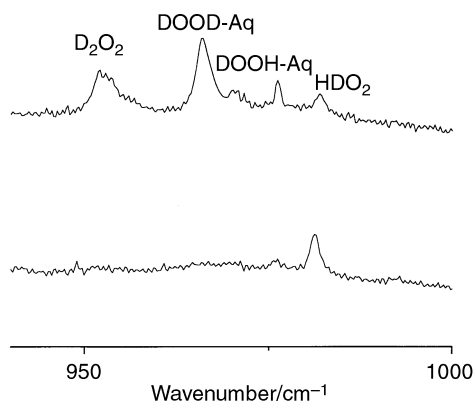


Fig. 3 Photoisomerisation of HOOH–DOD to DOOD–HOH. Top curve: the change in absorbance after photolysis for 1 h with 266 nm radiation. Bottom curve: directly after deposition at 17 K of H₂O₂ from +6 °C mixed with argon, and D₂O mixed with argon. Ar matrix, at 17 K.

D₂O. The only deuterated compounds present at significant concentrations before irradiation are D₂O and a much smaller amount of HDO. The initial step in the photolysis of HOOH is the formation of two OH radicals.¹⁵ These radicals may escape from the cage, recombine to HOOH or react to produce H₂O and an oxygen atom.¹⁵ Pehkonen *et al.*¹⁶ observed the formation of a complex between an oxygen atom and water when hydrogen peroxide was photolysed in argon matrices. They also showed that this complex transformed back to hydrogen peroxide after absorbing a photon in its charge transfer band with a maximum around 260 nm. Therefore, photolysis at 266 nm is expected to produce water oxygen atom complexes at a low rate,¹⁵ and consequently we see only very weak bands at the positions given for the oxygen atom water complex by Pehkonen *et al.*¹⁶ in spite of the fact that we decompose significant amounts of monomeric hydrogen peroxide. It is possible that the presence of the water molecule from the hydrogen peroxide complex prevents the cage escape of the hydroxyl radicals. We would then expect the formation of a water dimer–oxygen atom complex, which will

be rapidly photodecomposed to a new water–hydrogen peroxide complex, either with the old isotope distribution or with the roles of H and D reversed. This mechanism would keep the two hydrogen or deuterium atoms in a water or hydrogen peroxide molecule together, in agreement with the lack of isotope scrambling observed. There is also a possibility that the oxygen atom transfer between the two complex forming molecules takes place on the excited state surface. It should be noted that the decomposition of the water–hydrogen peroxide complex is slow compared with the decomposition of monomer hydrogen peroxide, which in turn is slow compared with the decomposition of the hydrogen peroxide dimer. We do not know if the low photolysis rate of the water complex is due to a blue shift of the absorption of complexed hydrogen peroxide, lowering the rate of absorption compared with monomer hydrogen peroxide, or if a decomposed complex rapidly reforms *via* the charge transfer absorption mechanism of ref. 15.

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