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Infrared Spectroscopic and ab Initio Study of HOOCIO₂

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The HOO complex with SO₂, a matrix isolation study

Thomas Svensson, Bengt Nelander*

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

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Abstract

The complex formation between HOO and SO₂ in argon matrices has been studied with FTIR spectroscopy. The complex shifts of the intramolecular fundamentals of the complex components suggest the formation of a complex, where HOO acts as a lone pair donor to the sulfur atom of SO₂ while its hydrogen atom is sufficiently close to one of the oxygen atoms of SO₂ to give a significant blue shift of the HOO bend. The complex is rapidly decomposed by irradiation at 266 nm. A comparison between the spectrum of the photoproduct and the spectrum of matrix isolated sulfuric acid suggests the possibility that the photoproduct is the radical formed by dissociation of one of the OH bonds of sulfuric acid.

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1. Introduction

Very little is known about the interactions between free radicals and unreactive, stable molecules. Lester and co-workers [1] have studied OH radical complexes for instance with Ar, H₂ [2], and CO [3]. In a few cases, matrix isolated radical complexes have formed as a result of the method used to create the radical. No systematic studies seem to have been made of matrix isolated radicals. This paper is part of a series of studies of the interactions between peroxy radicals and small molecules [4–7].

Sulfur dioxide and peroxy radicals are important constituents of the atmosphere and their interaction is consequently of significant interest. In

our previous studies, the peroxy radical has been observed to form hydrogen bonds to molecules which can act as hydrogen bond acceptors. The hydrogen bonds formed appear to be stronger than those of the corresponding water complexes. The peroxy radical can also accept hydrogen bonds, and whenever possible as for instance with water [4,8], it prefers to form cyclic complexes.

Sulfur dioxide is a weak Lewis acid and a number of binary sulfur dioxide complexes have been studied, both in molecular beams and in noble gas matrices. Strong acids as HF and HCl form a hydrogen bond to one of the oxygen atoms of sulfur dioxide [9,10]. Lone pair donors such as water [11], ammonia [12], and amines [12,13] form complexes where the lone pair of the donor points to the sulfur atom with the lone pair approximately orthogonal to the SO₂ plane. HCN, which can act both as a lone pair donor and form

*Corresponding author.

hydrogen bonds, binds to SO₂ via the lone pair on the nitrogen atom [14]. The peroxy radical forms stronger hydrogen bonds than HCN and is also a good lone pair donor, it is therefore not easy to predict the structure of an SO₂ HOO complex.

2. Experimental

Gas mixtures were prepared by standard manometric techniques. In one volume argon (L'Air Liquide 99.9995%) was mixed with O₂ (L'Air Liquide, 999995%) and SO₂ (BDH Chemicals). SO₂ was purified by two or more freeze-thaw cycles before use. Other gases were used as delivered. The Ar/O₂ ratio was varied between 50/1 and 75/1 and the Ar/SO₂ ratio was varied between 150/1 and 500/1. In a second volume argon was mixed with H₂ (AGA) or D₂ (L'Air liquide). The Ar/hydrogen mixture was passed through a microwave discharge. The gas flows were regulated by Nupro needle valves. The gas mixtures were deposited on a CsI-window, cooled by a Leybold RDK 10-320 closed cycle cryocooler, at 17 K. The deposition time was 2 h and the deposition rate 10 mmol/h.

Infrared spectra were recorded between 500 and 4000 cm⁻¹ with a Bruker 113v spectrometer. The widths of the SO₂ bands were much less than 0.5 cm⁻¹ [15,16] therefore spectra were recorded at both 0.1 and 0.5 cm⁻¹. After the initial spectra had been recorded the matrix was irradiated at 266 nm from a quadrupled Continuum NY 20 C YAG laser, and new spectra were recorded.

3. Assignment

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 $\nu_i(\text{A-B})$.

The spectrum of SO₂ in argon matrices has been assigned by Schriver–Mazzuoli et al. [15]. According to these authors, SO₂ may be trapped both in stable and metastable sites. Our observations of the SO₂ spectrum are in good agreement with [15] and [16].

In order to see the effect of hydrogen atoms on SO₂, we carried out an experiment where we left out the oxygen and codeposited SO₂ mixed with argon from one line and argon mixed with hydrogen through the microwave discharge from the other. New weak bands were observed in the SO₂ fundamental regions. These bands were not observed when peroxy radicals and SO₂ were codeposited, i.e. when SO₂ mixed with argon and oxygen was codeposited with argon and hydrogen through the discharge. The bands were close to the vibrational fundamentals of SO₂, which perhaps indicates that the bands were due to a weak complex between a hydrogen atom and SO₂. We did not observe bands close to the positions of the different isomers of HSO₂ given by Isoniemi et al. [17].

When peroxy radicals and SO₂ were codeposited a set of new bands were observed near the peroxy radical and SO₂ fundamentals. Their intensities were dependent on the concentration of SO₂ in the matrix. Their relative intensities were in constant ratios in different experiments. They were practically eliminated from the matrix after a few minutes of irradiation at 266 nm in contrast to the bands of SO₂, HOO, H₂O, and H₂O₂. The last two species form as a result of reactions involving peroxy radicals and hydrogen atoms. We observed a few of the strongest bands of the HOOH–HOO complex as weak bands. These bands are also rapidly eliminated by 266 nm irradiation. They were identified from sets of experiments with different isotopomers of hydrogen peroxide and peroxy radicals, which will be the subject of a later publication. The bands which require both peroxy radicals and SO₂ are assigned to a HOO–SO₂ complex. They are collected in Table 1.

The SO₂ ν_1 , region. A new strong band was observed at 1140.4 cm⁻¹ (Fig. 1). It is assigned to $\nu_1(\text{O}_2\text{S-OOH})$. With DOO, a band appeared at 1133.5 cm⁻¹ with DOO (Fig. 1). A careful search of the SO₂ band showed a band in the D experiments at 1149.6 cm⁻¹, which also was eliminated by irradiation. When the spectra before and after irradiation were subtracted for different experiments, it scaled with the 1133.5 cm⁻¹ band. There was no corresponding band in the H experiments. The 1133.5 cm⁻¹ band is assigned to $\nu_3(\text{DOO-SO}_2)$ and the 1149.6 cm⁻¹ band to $\nu_1(\text{O}_2\text{S-OOD})$.

Table 1
The observed bands of the peroxy radical SO₂ complex

	HOO	DOO	SO ₂	HOO–SO ₂	DOO–SO ₂
HOO, ν_1	3413.0			Not obs.	
HOO, ν_2	1388.9			1455.8 ^c	
				1458.2	
HOO, ν_3	1100.9			Not obs.	
DOO, ν_1		2530.2			2456.2
					2468.2
DOO, ν_2		1020.3			1071.0
					1071.9 ^c
					1073.4
					1074.1
DOO, ν_3		1122.9			1133.6
SO ₂ , ν_1			1152.3 ^{a,c}	1140.4	1149.6
			1151.7 ^a		
			1150.1 ^b		
			1147.3 ^{b,c}		
SO ₂ , ν_2			520.0 ^{a,c}	522.4	522.3
			519.2 ^a		524.3
			517.4 ^{b,c}		
			517.0 ^b		
SO ₂ , ν_3			1355.0 ^{a,c}	1330.1	1333.5
			1351.3 ^{b,c}	1329.1	1332.7
			1351.1 ^b		1331.9

^a Stable site.

^b Metastable site.

^c Strong component in a multiplet.

The SO₂ ν_2 , region. A broad and weak band, possibly with a multiplet structure, was observed near 523.0 cm⁻¹. In D experiments the band a doublet was observed at 522.2 and 524.2 cm⁻¹. The band is assigned to $\nu_2(\text{O}_2\text{S–OOH})$.

The SO₂ ν_3 , region. A broad band was observed at 1330.1 cm⁻¹ which shifted to 1333.6 cm⁻¹ with DOO (Fig. 2). It was assigned to $\nu_3(\text{O}_2\text{S–OOH})$.

The HOO and DOO ν_1 , region. No band was observed in the OH region. In the OD region, a weak doublet was observed at 2456 and 2468.2 cm⁻¹. This band is likely to be due to $\nu(\text{OOD–SO}_2)$. Its weakness makes a definitive assignment impossible.

The HOO and DOO ν_2 , region. A band with its major component at 1455.8 cm⁻¹ was shifted to a band with its major component at 1070.8 cm⁻¹ in D experiments. These bands are assigned to $\nu_2(\text{HOO–SO}_2)$ and $\nu_2(\text{DOO–SO}_2)$, respectively.

The HOO ν_3 , region. No band in this region which could be assigned to a peroxy radical SO₂ complex was observed.

In the SO₂ spectrum only very small decreases of the band absorptions at metastable sites were observed when the matrix was irradiated. When peroxy radicals and SO₂ were codeposited the same bands were observed but now irradiation at 266 nm produced a significant decrease of the metastable bands. Energy released from decomposing HOO–SO₂ complexes may produce a local annealing that eliminates the metastable site. A similar effect was observed when matrix isolated peroxy radicals and CO₂ were irradiated [7]. Chaabouni et al. [16] report a similar observation when ozone was photolysed in an SO₂ containing matrix.

3.1. Unassigned bands in the initial spectra

In addition to the bands assigned to the OSO–HOO complex there were a number of bands in the spectra that were not observed in HOO or SO₂ spectra. When the matrices were irradiated some of these bands decreased. We note that the pho-

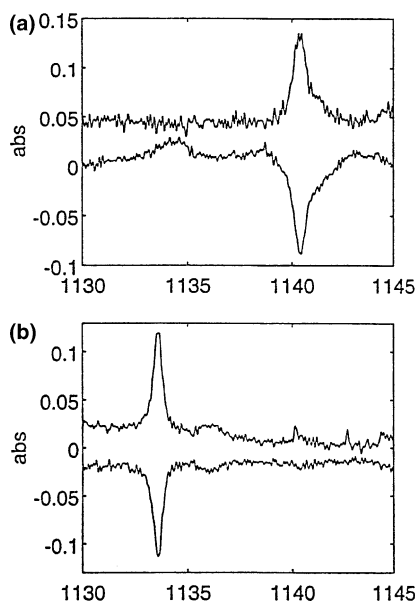


Fig. 1. The $\nu_1(\text{SO}_2)$ region. Upper curves, initial spectra after deposition. Lower curves after 5 min of irradiation ratioed against the initial spectra (cm^{-1}). The curves are in absorbance and have been shifted for clarity. (a) An H experiment; (b) a D experiment.

tolysis rate of the HOO-SO_2 complex is very high, much higher than that of HOO , the HOO-CO complex or the $\text{H}_2\text{O-HOO}$ complex. CO is in general present in small amounts when a discharge has been used. Water forms as a byproduct of the preparation of HOO [4]. Therefore trace amounts of the OC-HOO and $\text{H}_2\text{O-HOO}$ complexes are in general present in these experiments. Hydrogen peroxide is another byproduct from the HOO preparation. Its HOO complex seems to photolyse at approximately the same rate as the HOOH-HOO complex. This complex has been the subject of a separate study. The matrices contain trace amounts of ozone, probably due to traces of water passing through the discharge. It seems likely that ozone complexes will also photolyse at the very high rate. Most bands of these complexes should be too weak to be observable but possibly the shifted ozone asymmetric stretch might be observable. This may explain the 1037.5 cm^{-1} band below.

A few bands decreased at the same rate as the peroxy radical- SO_2 bands when the matrix was

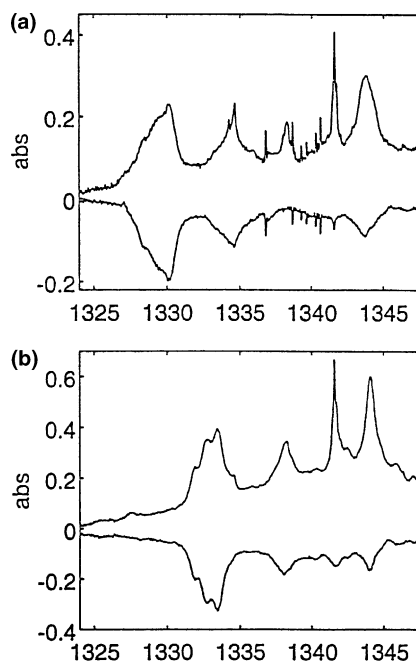


Fig. 2. The $\nu_3(\text{SO}_2)$ region. Upper curves, initial spectra after deposition. Lower curves after 5 min of irradiation ratioed against the initial spectra (cm^{-1}). The curves are in absorbance and have been shifted for clarity. (a) An H experiment; (b) a D experiment.

irradiated. We are not sure if they can be assigned to this complex. Two weak bands with H to D shifts were observed at 1037.5 cm^{-1} (D: 1036.9 cm^{-1}) and 685.6 cm^{-1} (D: 682.4 cm^{-1}). Two bands were observed at 1229.0 cm^{-1} and at 1470.0 cm^{-1} in the D experiments (no corresponding H band observed) and one weak band at 1285.4 cm^{-1} in the H experiments (no corresponding D band observed).

Two bands in the SO_2, ν_3 , region, decreased when the matrices were irradiated, but at a slower rate than the peroxy radical SO_2 complex. They were observed both in H and D experiments. The band intensities were approximately the same as $\nu_3(\text{O}_2\text{S-OOH})$ at 1330.0 cm^{-1} . They were observed at 1334.6 cm^{-1} (D: 1338.2 cm^{-1} and at 1343.8 cm^{-1} (D: 1344.0 cm^{-1} (Fig. 2). The concentration dependences of the bands were also approximately the same as for $\nu_3(\text{O}_2\text{S-OOH})$, but the photolysis rates varied. The photolysis rate of the 1343.8 band was approximately half of that of the 1330.0

band and the photolysis rate of the 1334.6 band was between those of the 1330.0 and the 1343.8 band. No other bands in the spectra could definitively be assigned to the species which caused these two bands.

3.2. Product bands

Two sets of product bands with H to D shifts were observed upon photolysis. The rapid growth during the first minutes correlated well with the decrease of the HOO–SO₂ bands. After the growth period the product bands in set 2 slowly increased at the expense of the product bands in set 1. The bands in set 1 were observed at 542.4, 858.0, and 3552.9 cm⁻¹ (D: 540.7, 854.5, and 2622.3 cm⁻¹) and the peaks in set 2 at 544.4, 863.4, and 3555.1 cm⁻¹ (D: 543.0, 860.2, and 2624.8 cm⁻¹). Apparently the growth of the set 2 bands was due to secondary photolysis. Possibly the bands of the first set are due to a product trapped at a metastable site, and the set 2 bands to the same product trapped at a stable site. A band at 1134.5 cm⁻¹ (secondary photolysis band: 1138.6 cm⁻¹) with the same rapid growth, followed by the same slow decrease, was observed in the H experiments. No D band corresponding to this band was observed. In addition a band was observed in the D experiments at 1052.3 belonging to set 1 with the corresponding set 2 band at 1050.4 cm⁻¹. The bands are collected in Table 2.

A weak band at 528.9 cm⁻¹ was observed both in H and D experiments, which grew long after the HOO–SO₂ complex was eliminated. A weak triplet at 1391.5, 1392.1, and 1392.8 cm⁻¹ grew fast during the first minutes of irradiation. These bands have been assigned to SO₃ in an experiment where matrix isolated SO₂ and O₃ were irradiated [16].

Weak bands observed at 658.9 and 2350.1 cm⁻¹ after irradiation were probably due to OH–OCO since traces of OOH–CO at 2160.6, 1423.8, and 3342.5 cm⁻¹ were observed after deposition. The formation of HO–CO₂ by irradiating matrix isolated OOH–CO has been observed earlier [7].

4. Discussion

The spectra obtained in this work clearly show that peroxy radicals form a complex with SO₂. Shifted bands are observed in all SO₂ fundamental regions and in some peroxy radical regions. The irregular appearance of the ν_3 regions of HOO and DOO and the ν_1 region of SO₂ can be understood as strong interaction between the complexed fundamentals in the complex partners, with the ν_3 (HOO–SO₂) band being too weak to be observable.

HOO can act both as a hydrogen bond donor as in the ammonia complex [5] and as a lone pair donor as in the Cl₂ complex [4]. SO₂ can accept hydrogen bonds from for instance HF and HCl [9], but it seems to prefer acting as an electron acceptor as exemplified by the water [11] and HCN [14] complexes. Relatively few SO₂ complexes have been studied in matrices and there seems to be a significant difference between the complex shifts observed in nitrogen matrices and the shifts in argon matrices [18]. However it seems as the antisymmetric stretching fundamental of SO₂ is significantly redshifted when SO₂ acts as an electron acceptor. In the ammonia complex, this band is shifted –14 cm⁻¹ in nitrogen matrices [19] and in argon, the shift seems to be even larger [18]. Andrews et al. [20] do not observe any shifted ν_3 (O₂S–HF) band and Nord [19] finds a –4.7 cm⁻¹

Table 2
Reaction product bands

H experiments	Relative strength	D experiments	Relative strength
542.4 (544.4)	m	540.7 (543.0)	m
858.0 (863.4)	m	854.5 (860.2)	m
1134.5 (1138.6)	m	1052.3 (1050.4)	m
3552.9 (3555.1)	s	2622.3 (2624.8)	s

Secondary photolysis product bands in parenthesis (cm⁻¹).

shift of $\nu_3(\text{O}_2\text{S-HBr})$ in a nitrogen matrix. The -25 cm^{-1} [$\nu_3(\text{O}_2\text{S-OOD} : -22\text{ cm}^{-1})$] shift of $\nu_3(\text{O}_2\text{S-OOH})$ therefore suggests that HOO acts as a lone pair donor towards SO_2 . The slightly larger shift in the HOO case may be due to an interaction with the HOO bend of the complex partner. The HOO bend is significantly blue shifted in the complex. This seems to indicate an important perturbation of the bending motion in the complex. When a hydrogen bond is formed, the OH stretch is expected to be significantly intensified, and we have had no problem in finding the OH stretch vibrations of the hydrogen bonded peroxy radical complexes studied in our earlier work. In this case we observe a weak band with maxima at 2456 and 2468 cm^{-1} , shifted -74 cm^{-1} from the band of free DOO. The limited data available for peroxy radical complexes indicate that the stretch shift is smaller than expected from the shift of the bend. Taken together, the data suggest that a peroxy radical acts as a lone pair donor with the end oxygen close to the S-atom and with the hydrogen pointing towards one of the sulfur dioxide oxygens.

The strength of the complex is hard to estimate. The complex shift of ν_3 of SO_2 is comparable to that of the ammonia complex, which is calculated to have a dissociation enthalpy at 25°C of -4.5 kcal/mol [12]. The interaction of the OH group may perhaps help to stabilize the complex further.

The bands of the initial photoproduct, 542.4 , 858.0 , 1134.5 , and 3552.9 cm^{-1} are relatively close to the bands of matrix isolated H_2SO_4 , 548.1 , 881.7 , 1216.1 , and 3566.7 cm^{-1} reported by Givan et al. [21]. We therefore suggest that the initial product is a sulfuric acid radical, OSO_2OH (sulfuric acid minus one hydrogen).

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