Matrix-isolation photolysis of SO_2, O_3 and H_2O: evidence for the $H_2O:SO_3$ complex

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The mechanism of H_2SO_4 formation via the reaction steps, $SO_2+O_3\xrightarrow{h\nu}SO_3\xrightarrow{H_2O}(SO_3:H_2O)\rightarrow H_2SO_4$, has been investigated at low temperature in an argon matrix. Photooxydation of SO_2 mainly occurs through the $SO_2:O_3$ pairs. Photolysis of a SO_2–H_2O–O_3 mixture did not lead to the H_2SO_4 molecule. The 1:1 $H_2O:SO_3$ complex was identified in nitrogen matrix. Observed isotope shifts in the IR absorption of the water submolecule suggest that the complexation proceeds through charge transfer with an O...S interaction.

1. Introduction

Sulfur dioxide, which enters the atmosphere from anthropogenic sources and the melting of sulfur metals, is a primary species implicated in the formation of acid rain. Once in the atmosphere, it can be transformed by a manifold of oxidation pathways into sulfuric acid as possible product. A large number of models and mechanisms have been proposed involving both homogeneous and heterogeneous processes, not yet well understood [1–6]. In most of them, sulfur trioxide is assumed to be a terminal product of the atmosphere oxidation mechanism followed by the reaction of SO_3 with H_2O, which may occur in the gas phase or on the surface of aerosol particles. Reaction could proceed via an adduct $H_2O:SO_3$ which arranges spontaneously to H_2SO_4. From measurements of the ratio constant of the gas-phase reaction of SO_3 with H_2O, RRKM theory and ab initio calculations, the energy barrier for $H_2O:SO_3$ isomerization has been found between 13 and 31 kcal [7–9]. There are few and contradictory results in IR spectroscopic identification of the $H_2O:SO_3$ complex. Using low-temperature photooxidation of H_2S in O_2, Tso and Lee characterized the complex by perturbed OH absorptions at 3678 cm^{-1} (ν_3) and 3562.8 cm^{-1} (ν_1) [10]. In neon matrices, Bondybey identified the $H_2O:SO_3$ complex by absorptions at 3612.9–1591.4 cm^{-1} (ν_3 and ν_2 of H_2O entity) and 1401–490.9 cm^{-1} (ν_3 and ν_2 of SO_3 part) [11].

In order to understand the complex chemical pathways related to the conversion of SO_2 to H_2SO_4 in the atmosphere, we must first examine the reaction of sulfur dioxide with atomic oxygen produced in situ by the photolysis of matrix-isolated ozone. Previous work showed that the UV photolysis of monomeric SO_2 in solid oxygen (λ, 270–420 nm) gives no product and the photooxidation of sulfur dioxide appears to proceed through either the intermediary of a $(SO_2)_2$ dimeric form [12] or a photodissociated molecular complex such as the $H_2CO:SO_2$ complex [13]. In this paper, we first describe results on the O_3–SO_2 oxidation system in argon. We also report results concerning the photoreaction involving SO_2, O_3, H_2O, trapped in solid argon. We have carried out a series of experiments to gain information about the $H_2O:SO_3$ complex.

2. Experimental

All the experiments were conducted in a closed

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cycle Air Product displex refrigerator, model 202. The gas mixtures were prepared by standard manometric techniques and sprayed through a dual jet system onto the cold window at 5 mmol/h. SO_2 (Matheson) was dried over P_2O_5 and distilled at low temperature. Ozone was prepared by Tesla coil discharge through oxygen at low pressures in a Pyrex finger cooled with liquid nitrogen. Solid SO_3 from Aldrich was placed in an all-metallic vacuum system, and was purified by removing the vapor above the solid phase at 0°C. Infrared spectra were recorded on a FTIR Bruker 113 with a resolution of 0.5 or 0.1 cm^{-1}. Ozone photolysis was carried out with a xenon lamp (150 W) or a 90 W medium-pressure mercury lamp used together with cut-off filters such as Schott WG 345 producing only $O(^3P)$ as the atomic fragment and Schott WG 280 producing a mixture of $O(^1D)$ and $O(^3P)$ [14].

3. Phototransformation of the SO_2/O_3 system in argon. Results and discussion

Before the reaction products of SO_2 with atomic oxygen were investigated, some experiments were performed to test the presence of observable products in the SO_2/O_3 system in argon.

Infrared spectra of SO_2 in rare-gas matrices have been previously reported [15,16]. In argon matrix, the three fundamental modes appeared in two absorptions. Increasing the temperature above 30 K led to the irreversible disappearance of features at lower frequency whereas the intensity of the higher-frequency absorptions remained unchanged. Such a behavior can arise from two distinct sites: a metastable hexagonal-close-packed due to stacking faults and a stable cubic-close-packed site [17,18]. Fig. 1a illustrates the ν_3 region of monomeric SO_2 ($SO_2/Ar=1/2000$); the stable absorption (referred to as S) and the metastable absorption (referred to as M) appear in doublets respectively at 1355.5–1355.1 cm^{-1} and 1351.3–1350.9 cm^{-1}. When ozone ($O_3/Ar=1/500$) was codeposited with SO_2 diluted in argon (1/2000), new sharp satellites absorptions were observed at 1352.4, 1350.6, 1350.1, 1349.5 (the strongest) and 1348.3 cm^{-1} (fig. 1b). These absorptions characterize a weak van der Waals complex between SO_2 and O_3 whose structure and bonding will be subject of a separate report. Irradiation photolysis at 12 K with the full light of a mercury lamp without heating of the matrix caused the disappearance of these bands, and a slight decrease in the intensity of the monomeric SO_2 band in the metastable site whereas the monomeric SO_2 band in the stable site remained unchanged (fig. 1c). Concurrently, a new set of bands about 1391, 529 and 489.5 cm^{-1} assigned, respectively, to the ν_3, ν_4 and ν_2 modes of the SO_3 molecule, and also at 1353 cm^{-1} in the ν_3 region of SO_2, appeared; this last unassigned band was neither observed upon irradiation of SO_2 in the absence of O_3 nor in the spectrum of SO_2–SO_3 mixture in Ar. The most intense and characteristic band of the ν_3 mode of compressed SO_3 appears as a triplet at 1392.2, 1391.7, 1391.5 cm^{-1} with a weak satellite at 1389.7 cm^{-1} (fig. 1). In contrast with the monomeric ν_3 band observed at 1385.2 cm^{-1} in a SO_3 argon matrix with the same 0.1 cm^{-1} resolution, it is shifted and split. The 6 cm^{-1} shift could be due to the presence of an O_2 molecule produced with SO_3 in the reaction cage. The splitting of the SO_3 ν_3 band appears similar to that seen for SO_2:O_3 pair.

Upon prolonged photolysis, two new weak bands appeared at 1442.9 and 1272 cm^{-1}. These bands were tentatively assigned to the SO_4 species produced by secondary reaction of SO_3 with atomic oxygen. The mechanism of this secondary process and the structure of neutral monomeric SO_4 have been previously reported by Kugel and Taube from direct reaction of SO_3 with atomic oxygen using the matrix-isolation method [19]. The positions and peak optical densities of the major infrared absorption characteristic of the parent molecules and of the products of the $O+SO_2$ reaction are summarized in table 1.

Other experiments were carried out with the xenon lamp with a cutoff 345 nm filter. Although the product yield was considerably diminished from that in previous experiments, formation of SO_3 was again observed, indicating that the ground-state $O(^3P)$ was sufficiently reactive for the photoproduction of SO_3.

Thus, the photooxidation reaction of SO_2 appears to proceed essentially through O_3–SO_2 pairs with a low activation energy, though monomeric SO_2 in a reactive site (metastable) seems also photochemically active.

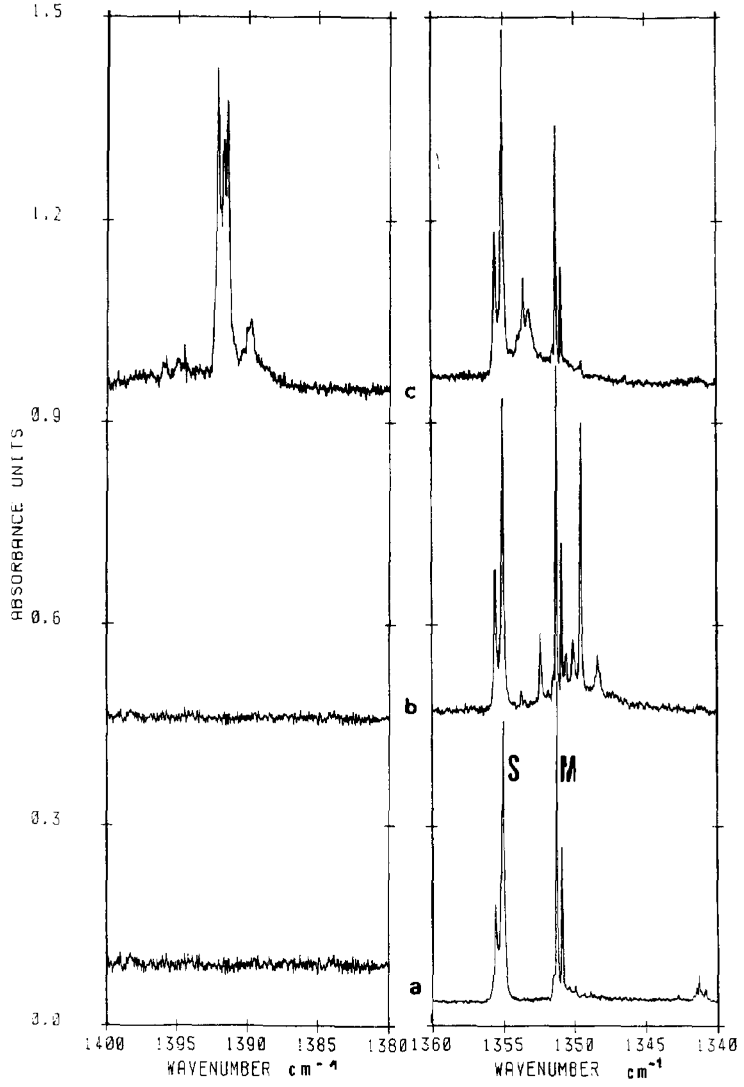

Fig. 1. FTIR spectra recorded at 10 K in the $SO_2(\nu_3)$ and $SO_3(\nu_3)$ absorption regions of: (a) SO_2/Ar mixture (1/2000) after deposition; (b) $SO_2/O_3/Ar$ mixture (1/4/2000) after deposition; (c) previous $SO_2/O_3/Ar$ sample after photolysis with full light of a mercury lamp for 3 h. S, M: monomer in the stable and metastable sites, respectively.

4. Phototransformation of the ternary $SO_2/H_2O/O_3$ system in argon

Irradiation experiments using the full light of the xenon lamp performed on an $SO_2/H_2O/O_3/Ar$ mixture (typically 1/1/5/100 ratio) led to two intense new bands about 1391 and 1276 cm^{-1}. These bands were respectively due to ν_3 of SO_3 and to ν_6 of H_2O_2 [20]. Thus, the photoreaction products which are observed in triply doped matrices are the same as those obtained in the $H_2O/O_3/Ar$ [21] and $SO_2/O_3/Ar$ experiments. Under the experimental conditions used, no trace of H_2SO_4 was detected. These results prompted us to reexamine the SO_3/H_2O system in argon and nitrogen matrices.

Table 1
Major product frequencies and peak absorbances (A) before and after 3 h 30 min mercury lamp photolysis of a $SO_2/O_3/Ar$ (1/4/4000) mixture (resolution 0.1 cm^{-1})

Before photolysis		After photolysis		Assignment
ν (cm^{-1})	A	ν (cm^{-1})	A	
–	–	1442.9	0.05	SO_4
–	–	1392.2	0.26	$SO_3(\nu_3)$
–	–	1391.7	0.20	
–	–	1391.5	0.23	
–	–	1389.7	0.06	
1355.5	0.22	1355.5	0.21	$SO_2(\nu_3)S$
1355.1	0.49	1355.1	0.48	
–	–	1353.6	0.13	not identified
–	–	1353.2	0.10	
1352.4	0.12	–	–	$SO_2{:}O_3$
1351.3	0.55	1351.3	0.3	$SO_2(\nu_3)M$
1350.9	0.27	1350.9	0.15	
1350.6	0.09	–	–	$SO_2{:}O_3$
1350.1	0.11	–	–	
1349.5	0.46	–	–	
1348.3	0.09	–	–	
–	–	1272	0.015	SO_4
1152.4	0.011	1152.4	0.011	$SO_2(\nu_1)S$
1151.5	0.015	1151.5	0.015	
1149.5	0.048	–	–	$SO_2{:}O_3$
1147.2	0.1	1147.2	0.042	$SO_2(\nu_1)M$
1146.7	0.03	1146.2	0.020	
1044.6	0.23	–	–	$SO_2{:}O_3$
1042.2	0.50	–	–	
1041.2	$\gg 1$	1041.2	0.3	$O_3(\nu_3)$
1039.6	$\gg 1$	1039.6	0.9	
1038.8	1.1	–	–	$SO_2{:}O_3$
1037.9	1.3	–	–	
–	–	529.7	0.07	$SO_3(\nu_4)$
–	–	528.7	0.08	
519.7	vw [a]	519.7	vw [a]	$SO_2(\nu_2)S$
517.3	vw [a]	517.3	vw [a]	$SO_2(\nu_2)M$
–	–	489.5	0.2	$SO_3(\nu_2)$

[a] vw = very weak.

5. $H_2O{:}SO_3$ complex

5.1. *Results*

Prior to the investigation of the reaction products arising from the codeposition of SO_3 with water at high dilution, blank experiments were conducted on each reactant alone in argon and nitrogen. The spectra of water in solid argon and nitrogen have been studied in great detail in the literature [22–25] and the spectra of SO_3 in Ar, Xe, Ne matrices have been reported by Bondybey [11]. In nitrogen, the ν_3 mode of SO_3 appears as a doublet at 1397.7 and 1395.3 cm^{-1} whereas the ν_4 and ν_2 modes are, respectively, characterized by bands at 532.1–531.5 and 488.1 cm^{-1}. The ν_3 mode is very sensitive to the matrix nature: in regard to gas phase, we observe a substantial blue-shift in solid nitrogen whereas red-shifts in argon and xenon were reported by Bondybey [11].

5.1.1. *Argon matrices*

Addition of water traces to SO_3/Ar mixtures, typically $H_2O/SO_3/Ar = 1/1/1500$, showed no change from the initial spectra. After annealing, only the polymeric water bands appeared without other new bands.

5.1.2. *Nitrogen matrices*

The spectrum of SO_3 in a nitrogen matrix codeposited with H_2O/N_2 mixtures ($H_2O/SO_3/N_2 = 1/1/1500$) gave rise to two new weak bands in the ν_{OH} region at 3648.8 and 3562.7 cm^{-1} (fig. 2) without an observable counterpart in the δ_{OH} region. In the SO_3 spectral regions, only new sharp bands at 1399.1, 1390.3 and 1079.30 cm^{-1} were observed. When the matrix was weakly annealed at 25 K and recooled to 10 K, the above bands strongly grew in intensity while maintaining the same relative intensity. An additional product band appeared at 3536 cm^{-1}. No evidence was found for the existence of H_2SO_4. Some experiments with D_2O using the same procedure as for H_2O with an H_2O/D_2O varying from 0.5 to 0.2 were performed. Two lines at 3600.0 and 2649.4 cm^{-1}, mainly observed at low D/H ratio, and two features at 2710.0 and 2600.6 cm^{-1} were, respectively, assigned to HOD and D_2O perturbed by SO_3 (figs. 1 and 2). The positions of the 2650 and 2601 cm^{-1} bands are close to those of ν_1 modes charac-

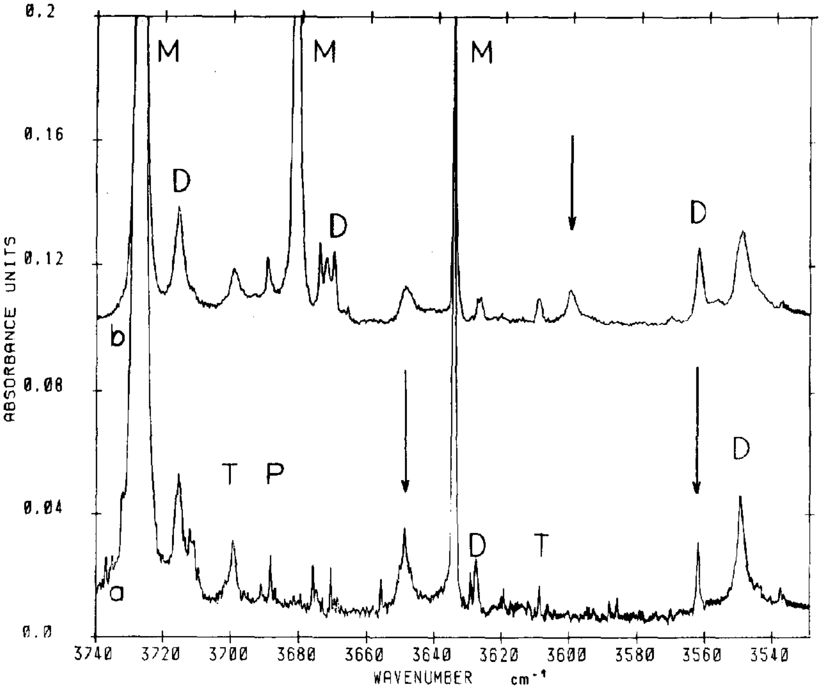

Fig. 2. FTIR spectra recorded at 10 K of: (a) $H_2O/SO_3/N_2$ (1/1/1000) and (b) $(D_2O+H_2O)/SO_3/N_2$ (2/1/1000) mixtures in the ν_{OH} region. The bands assigned to the $SO_3:H_2O$ complex are marked by arrows. M, D, T, P: monomer, dimer, trimer, polymer water bands. Observed relative intensity increasing of the 3560 cm^{-1} band in (b) spectrum is due to the closeness of the band with the HOD trimer band.

terizing the electron donor and the electron acceptor D_2O in $(D_2O)_2$. Nonetheless, their assignment seems correct because these bands increased in intensity after weak annealing at 25 K without counterpart in the ν_3 water dimeric bands as illustrated in fig. 3.

5.2. *Discussion*

The two weak bands observed in the nitrogen matrix at 3648 and 3560 cm^{-1} in the ν_3 and ν_1 water region for which relative intensities I_{ν_3}/I_{ν_1} of the absorption are independent of temperature indicate the formation of only one product species, which is tentatively assigned to the 1:1 $H_2O:SO_3$ molecular complex under the high dilution employed. The doublet at 1399, 1390 cm^{-1} can be assigned to the two split components of the antisymmetric stretch of the SO_3 subunit in the 1:1 complex. This splitting upon complexation has been previously reported by Ault for 1:1 molecular complexes of sulfur trioxide with various oxygen-containing bases and explained as a consequence of the lowering of symmetry in the complex [26]. The other product absorption at 1079 cm^{-1} lies near the forbidden symmetric stretch of parent SO_3; such a mode can be activated in the molecular complex and is readily so assigned.

Two possible structures which might be invoked for the 1:1 complex are either a complex with a hydrogen bond or a complex with a bonding between the water oxygen atom and sulfur atom as previously observed in the $H_2O:SO_2$ complex [27]. As suggested by quantum-mechanical treatment, the second one appears most likely [8]. Spectral features obtained in isotopic D_2O/H_2O experiments are consistent with the second structure. The decoupling effect between the two OH and OD oscillators is nearly symmetrical leading to the conclusion that the two oscillators are equivalent. Unfortunately, the absence of observable δ_{OH} bands does not allow us to perform a force-field calculation on the water molecule. The relative intensities of the water bands in the complex ($I_{\nu_3}/I_{\nu_1}=2.1$) are different from those

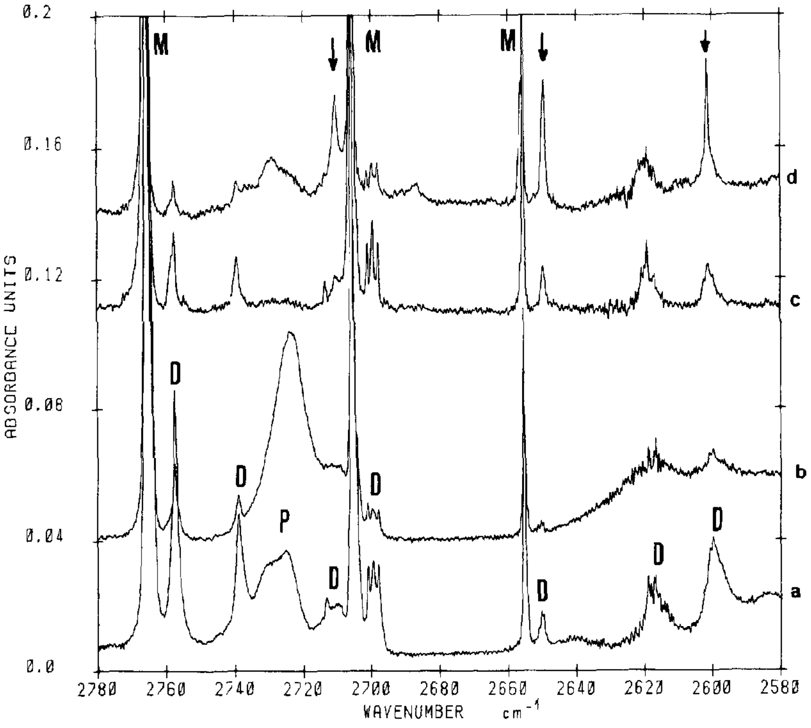

Fig. 3. FTIR spectra of $D_2O/SO_3/N_2$ (1/1/1000) in the ν_{OD} region showing: (a) blank spectrum D_2O/N_2 (1/350) recorded at 10 K; (b) blank spectrum D_2O/N_2 (1/350) recorded at 25 K; (c) reaction run (10 K); (d) temperature behavior (25 K). Bands assigned to the SO_3–H_2O complex are marked by arrows. M, D, T, P: monomer, dimer, trimer, polymer water bands.

measured for free water ($I_{\nu_3}/I_{\nu_1}=29$) in the gas phase [28]. Such a change is typical of charge-transfer complexes and has been explained in terms of change of the atomic polar tensors upon complexation [29–31]. In the $H_2O:SO_3$ complex, the observed effect is close to that found for the $H_2O:SO_2$ complex although SO_3 is a stronger Lewis acid than SO_2 as proved by a larger OH frequency shift. The absence of the $H_2O:SO_3$ complex in argon may be due to less complex stabilization in argon compared to nitrogen, because of the absence of the quadrupole moment in argon. Previous observation of $H_2O:SO_3$ at high concentrations in neon may not be at variance with this explanation.

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