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Infrared spectra, photochemistry, and ab initio calculations of matrix isolated methanethiol/sulfur dioxide complex[☆]

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Abstract

Intermolecular complexes of methanethiol with sulfur dioxide have been prepared by condensing the reagents diluted in argon and in nitrogen at 12–14 K. The 1:1 CH₃SH/SO₂ complexes were identified from the infrared spectra of the mixtures of methanethiol with sulfur dioxide in argon and nitrogen matrices. Perturbations to the vibrational energy spaces of some vibrational modes were identified and assigned. Ab initio calculations with the 6-311G** basis set have been performed to get some information about the structure, binding energy, dipole moment, and potential function governing the internal rotation of SO₂ for the complex. The calculated results have suggested that the dipole/dipole interaction held the constituent species together to form the complex. Photochemical reactions were performed by exposing the matrix mixtures to UV irradiation. The appearance of new bands indicated the presence of more than one photochemical reaction product. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Matrix isolation; Infrared spectra; Complex; Ab initio calculation; Sulfur dioxide; Methanethiol

1. Introduction

The matrix-isolation technique coupled with Fourier transform infrared (FTIR) spectroscopy has been applied to characterize weakly bonded complexes involving sulfur compounds [1,2] and to identify the reaction products with sulfur species [3–5]. In our previous studies, complexes of R₂S with SO₂ and SO₂ dimer [6], RSH with SO₂ [7], where R is CH₃,

C₂H₅, (CH₃)₂CH, or (CH₃)₃C, and C₂H₆S₂ isomers with SO₂ [8] were identified in argon matrices. Evidence of the complex formation through the disulfide interaction was obtained. For alkanethiols, they can form complexes either through the S atom when complexed with hydrogen halides, or through the thiol hydrogen atom when complexed with a base.

Owing to the continued use of large amounts of sulfur-containing fossil fuels, there is an increasing interest in organic sulfur compound reactions. Several gas phase oxidation reactions of organosulfur compounds have been reported [9–11]. A reaction between F atoms and CH₃SH was reported by Jacox [12] who identified the absorptions of CH₃S and CH₂SH hydrogen-bonded to HF in solid argon at 14 K. The reactions of ozone and oxygen atoms with dimethyl sulfide and methanethiol in argon matrices have been studied by Tevault et al. [9] who

[☆] Dedicated to Professor James R. Durig on the occasion of his 65th birthday.

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reported the production of CH_3SOH , CH_3OSH , $\text{CH}_3\text{S(O)H}$, and possibly $\text{CH}_3\text{SO}_2\text{H}$. Considering the similarities between SO_2 and O_3 , one may expect some possible reactions between alkanethiols and sulfur dioxide upon irradiation. As a continuation of our studies of the complexes between sulfur compounds, this paper reports an infrared matrix isolation studies of the interaction, photochemical reaction between methanethiol, CH_3SH , and sulfur dioxide, SO_2 , and ab initio calculations of the complex.

2. Experimental

The cryogenic, spectroscopic, and vacuum techniques used in this study have been described in detail previously [6]. In a typical experiment, the reactant gases were mixed, diluted with argon in a desired ratio in the vacuum manifold, and deposited onto the cold window until a proper amount was achieved. The spectra were recorded on a Mattson Polaris FTIR spectrophotometer equipped with ICON FTIR Analytical Software in the $400\text{--}4000\text{ cm}^{-1}$ spectral region using a 1-cm^{-1} resolution and 400 scans. The sample compartment was continuously purged with compressed air which had been pretreated by a Type 75-50 Balston Air Dryer (Balston) in order to eliminate H_2O vapor and CO_2 gas. The photochemical experiments were performed by exposing the matrix mixture on the cold window to the UV irradiation from a Model LH 151N high pressure mercury arc lamp (1000 W, Schoeffel Instrument) passed through a 10 cm water filter for a certain period of time, then a spectrum was collected. A comparison of the spectra before and after the UV irradiation reveals the information about the photochemical reaction.

Ar and N_2 gases (research grade, Air Product) were used without purification. The sulfur dioxide and methanethiol (both Matheson) were subjected to several freeze–thaw cycles at liquid nitrogen temperature, then dried by passing the sample several times through a U-tube filled with activated molecular sieves (4 \AA) in a high vacuum system, and kept in sample tubes with activated molecular sieves in order to eliminate trace water. A final freeze–thaw cycle at liquid N_2 temperature was applied to each sample prior to mixing with Ar or N_2 gas. The

CH_3SD was prepared by bubbling undeuterated methanethiol through a three-stage unit with 99.8% D_2O to which a few pellets of sodium were added in order to facilitate the hydrogen and deuterium exchange reaction, according to the method by May and Pace [13]. The final product was purified and dried the same way as that for the undeuterated methanethiol and identified by the gas phase IR spectrum.

3. Results

Prior to the methanethiol–sulfur dioxide formation experiments, blank experiments were carried out on each of the reactants in solid argon. The spectra obtained were in good agreement with literature spectra [14–17].

3.1. $\text{SO}_2 + \text{CH}_3\text{SH}$ complex

Several experiments were conducted with sulfur dioxide and methanethiol in different mole ratios. These two reactants were mixed, diluted in Ar, and then condensed on the cold CsI window through a single nozzle. First, a spectrum was recorded of a matrix with a ratio of $\text{SO}_2/\text{CH}_3\text{SH}/\text{Ar}$ equal to 1/3/3000. In addition to the parent species absorptions, several new IR bands were observed near the fundamental vibrations of the SO_2 subunit and the S–H stretching and CSH bending modes of the CH_3SH . These were located at 1338 cm^{-1} in the SO_2 antisymmetric stretching vibration region, partially overlapping with the isolated SO_2 band, at 1145 and 1143 cm^{-1} in the SO_2 symmetric stretching region, at 522 cm^{-1} in the SO_2 bending region. Other observed new bands included a weak line at 2590 cm^{-1} between the methanethiol monomer and dimer bands of SH stretching, a weak band at 797 cm^{-1} on the lower energy side of the CSH bending mode, and weak bands at 702 and 700 cm^{-1} on the lower frequency side of C–S stretching vibration of methanethiol. Fig. 1 shows the representative spectra in the SO_2 fundamental vibration regions. The spectrum collected after annealing the Ar matrix to 30 K revealed that the relative intensity of the metastable SO_2 monomer band at 1351 cm^{-1} decreased significantly while the dimer band around 1342 cm^{-1} , as well as the new bands due to the formation of the complex, increased. When an excess

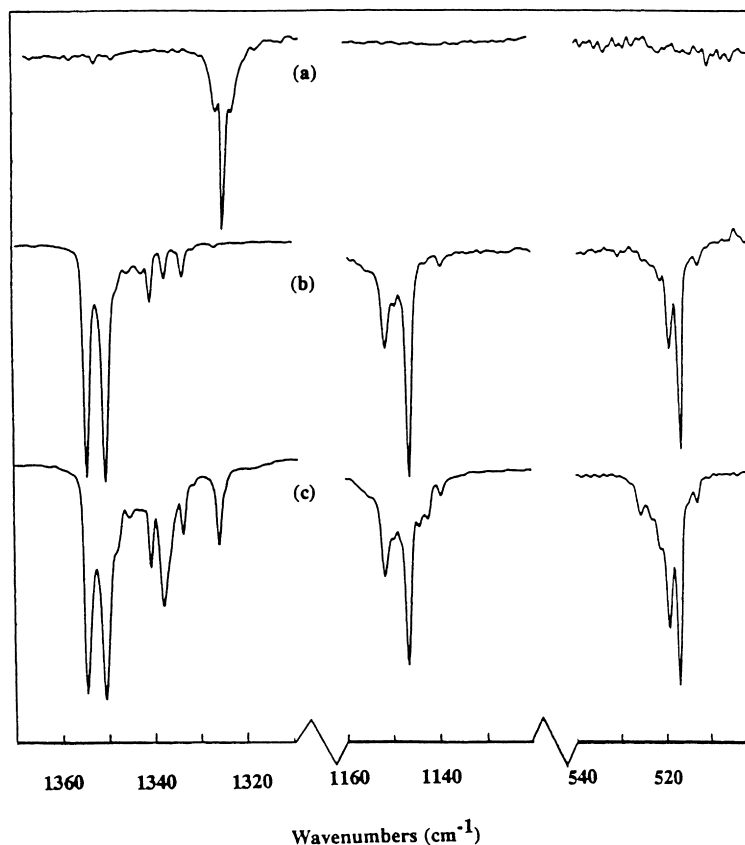


Fig. 1. FTIR spectra of: (a) Ar/CH₃SH = 500/1; (b) Ar/SO₂ = 3000/1; and (c) Ar/SO₂/CH₃SH = 3000/1/3.

amount of CH₃SH was used in the experiment with a SO₂/CH₃SH/Ar ratio of 1/6/3000, the same set of new bands were observed but the relative intensities of the 1338, 1145, 1143 and 522 cm⁻¹ bands grew more rapidly than the parent and the dimer SO₂ bands. In another series of experiments, the concentration of methanethiol was kept constant while different SO₂ amounts were used in the mixtures. It was found that the intensities of the bands at 2590, 797, 702 and 700 cm⁻¹ increased clearly in comparison with the corresponding fundamental vibrations of the parent methanethiol as the concentration of SO₂ increased in the mixtures. Fig. 2 shows the intensity variations of the CSH bending and the C–S stretching vibrations of the complex in the mixtures of methanethiol with SO₂ at different mole ratios.

Similar experiments were conducted for the reactant mixtures in nitrogen matrices in order to compare

the behaviors of the new complexes in different matrix environments. All the new bands were observed in different matrix conditions except for the relative intensities and the splitting due to matrix site effect. The new peak positions in nitrogen matrices differed slightly with those in argon matrices.

CH₃SD mixed with SO₂ in argon matrices at different ratios were also examined in this study, and similar results were obtained. New absorptions near the SO₂ fundamentals and near the SD stretching, CSD bending, and C–S stretching vibrations of CH₃SD were observed.

3.2. *Ab initio* calculations

In the matrix isolation IR experiment, we were able to confirm the formation of the 1:1 CH₃SH/SO₂ complex from the identification of new bands. All

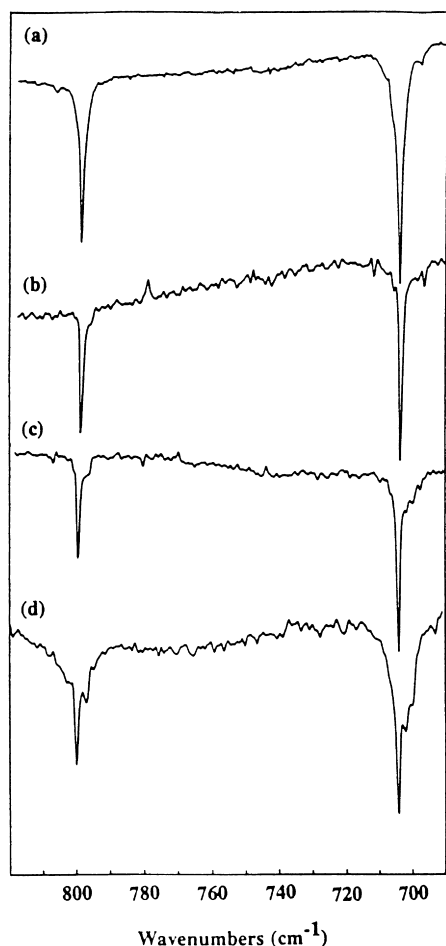


Fig. 2. FTIR spectra of argon matrices containing CH_3SH and SO_2 / CH_3SH at different mole ratios: (a) $\text{CH}_3\text{SH}/\text{Ar}$; (b) $\text{SO}_2/\text{CH}_3\text{SH} = 0.33/1$; (c) $\text{SO}_2/\text{CH}_3\text{SH} = 1/1$; and (d) $\text{SO}_2/\text{CH}_3\text{SH} = 3/1$.

these new IR bands were observed to shift less than 13 cm^{-1} from the parent species vibration modes, indicating that the interaction between the two parent species is weak. There is no experimental structure information available for the complex. For this reason, ab initio calculations were performed for the complex as well as for the parent species with the GAMESS program [18,19] using the 6-311G** basis set at the HF and MP2 levels. The energy minimum with respect to the nuclear coordinates for each of these molecules was obtained by the simultaneous relaxation of the geometric parameters.

Fig. 3 shows the structure of the lowest energy complex and Table 1 gives the calculated structural

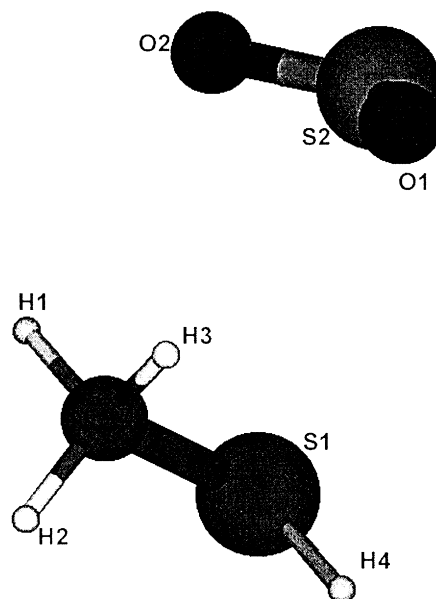


Fig. 3. Structure of the $\text{CH}_3\text{SH}/\text{SO}_2$ complex.

parameters. It is seen that the structures of the two constituent components in the complex are not much different from those of free CH_3SH and SO_2 . Thus, a weak interaction between the parent molecules is expected. The resulting weak interaction is in agreement with that derived from the experimental IR frequency shifts. Although the experimental structure of the complex is not available for comparison with the calculated result, the agreement between the calculated and the experimental structures for SO_2 [20] and CH_3SH [21] is better than 2%. The separation between the two sulfur atoms in the complex (3.45 \AA) is significantly larger than the sum of the atom covalent radii—another indication of weak interaction between the parent molecules.

The lowest energy structures calculated from HF and MP2 generally agree very well. However, Hartree–Fock also gives a second structure slightly higher in energy in which the SO_2 is slightly rotated. For both HF and MP2 we have examined the potential energy function governing the internal rotation of the SO_2 with respect to the S–S bond in the complex. Shown in Fig. 4 are the potential energy function curves obtained from the two methods. The general shapes of the curves are similar with both having a minimum near 60° with a very low

Table 1

Calculated structural parameters and dipole moments of methanethiol/sulfur dioxide complex and its parent molecules at the 6-311G** level (units are: Å for bond length, (*r*); degree for bond angle (*θ*) and dihedral angle (*δ*); Debye (D) for dipole moment (*μ*)

	SO ₂		CH ₃ SH		Complex	
	HF	MP2	HF	MP2	HF	MP2
r(S2O1)	1.407	1.467			1.409	1.467
r(S2O2)	1.407	1.467			1.409	1.467
θ(O1S2O2)	118.7	119.3			118.0	118.6
r(CH1)			1.082	1.091	1.081	1.090
r(CH2)			1.081	1.090	1.081	1.089
r(CH3)			1.081	1.090	1.081	1.090
r(CS1)			1.821	1.813	1.821	1.813
r(SH4)			1.331	1.334	1.331	1.335
θ(S1CH1)			106.4	106.6	106.4	106.5
θ(S1CH2)			111.1	111.7	110.6	111.4
θ(S1CH3)			111.1	111.7	110.8	111.3
θ(CS1H4)			98.3	96.3	98.2	96.6
δ(H1CS1H4)			180.0	180.0	178.3	176.4
δ(H2CS1H4)			−61.6	−61.8	−63.1	−64.8
δ(H3CS1H4)			61.5	61.8	59.8	58.8
r(S1S2)					3.541	3.454
θ(S1S2O1)					88.5	87.8
θ(S1S2O2)					88.8	83.4
δ(O1S2S1C)					64.6	58.8
δ(O2S2S1C)					−53.4	−60.3
<i>μ</i>	2.29	1.77	1.76	1.57	1.00	0.94

rotational barrier (2.2 kcal/mol from MP2 and 1.2 kcal/mol from HF). The difference is that the second minimum near 0° in HF has been lifted up to a shoulder with MP2.

In the complex formation, the interaction sites may arise from the sulfur atoms in the parent molecules. The sulfur atom in the thiol is expected to have a negative charge and the one in the sulfur dioxide has a positive charge. Listed in Table 2 are the calculated atomic Mulliken charges in the parent species and the complex. These quantities may not be totally reliable as useful atomic charges but they do reveal the possible sites of the interactions. The Mulliken charges and structure of the complex (see Fig. 3 and Table 1) reveal that the dipole moments of the parent species in the complex are nearly parallel and opposite in direction. From the moderate values of experimental dipole moments for methanethiol (1.26 D) [21] and sulfur dioxide (1.62 D) [22], a dipole/dipole interaction between the two molecules is expected. Fig. 5 shows the

calculated dipole moments of the complex at different dihedral angles (O2S2S1C). Results from both HF and MP2 methods give minimum dipole moment of the complex at the same dihedral of 30°. This angle is close to the equilibrium value (~60°) obtained from the minimization of the total energy of the complex—an indication that the dipole/dipole interaction is important in the formation of the complex from the constituent molecules. Also listed in Table 2 are the energies for the complex, from which the binding energy for the complex is less than 5 kcal/mol. The small binding energy of the complex also suggests that the interaction between the parent species is weak.

Fundamental frequencies of vibrations have been calculated with the GAMESS program for the parent molecules and the complex. In the calculations, the potential function governing each vibrational mode was assumed to be harmonic and a scale factor of 0.9 was used for all frequencies calculated with the HF method. Given in Table 3 are some calculated Hartree–Fock frequencies along with the

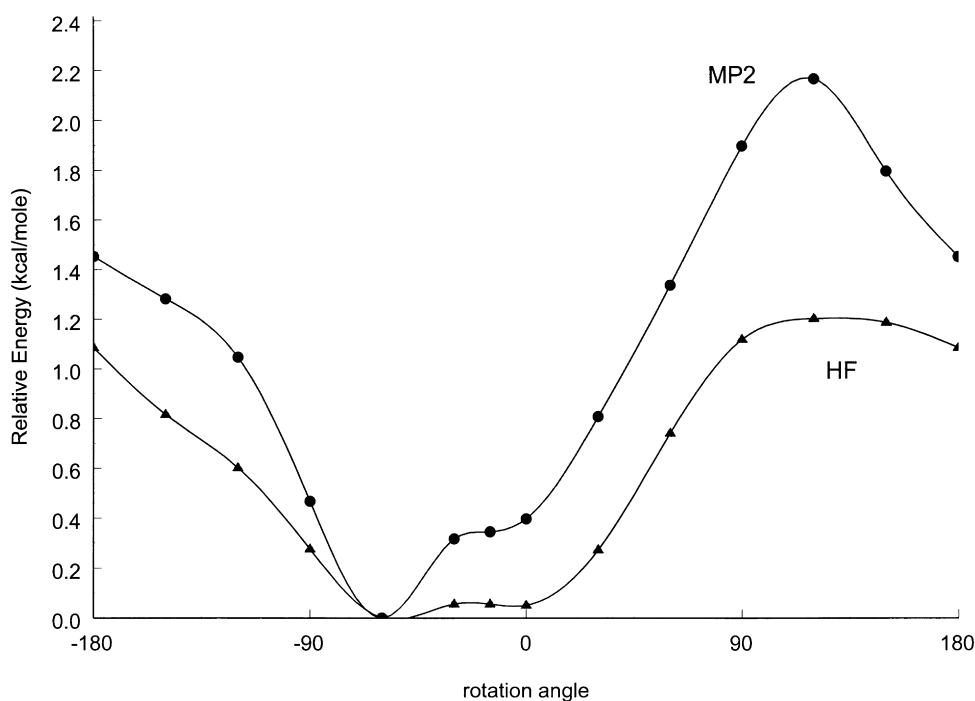


Fig. 4. Potential functions governing the internal rotation of SO_2 in the complex as determined by ab initio calculations with the 6-311G** basis set.

corresponding frequencies measured in the present investigation. The root-mean-square deviation of the calculated frequencies from the observed ones is 4%. It is of interest to note that the directions of both the calculated and the experimental frequency shifts arising from the formation of the complex agree well with the exceptions of the S–H stretching and

the CSH bending. According to our HF calculations, the calculated S–H stretching frequency for the thiol molecule blue shifts by 2 cm^{-1} while the observed frequency red shifts by 14 cm^{-1} . The MP2 harmonic frequencies show a small 2 cm^{-1} red shift for the S–H stretching frequency but are further off in the other shifts.

Table 2

Mulliken atomic charges (Coul) and binding energy (kcal/mol)

	SO_2		CH_3SH		Complex	
	HF	MP2	HF	MP2	HF	MP2
S2	1.05	0.77			+1.08	+0.81
O1	−0.52	−0.39			−0.54	−0.40
O2	−0.52	−0.39			−0.55	−0.41
C			−0.39	−0.45	−0.39	−0.48
H1			0.13	0.14	+0.15	+0.14
H2			0.13	0.14	+0.13	+0.15
S1			−0.02	0.00	−0.06	−0.02
H4			0.03	0.04	+0.04	+0.04
Binding energy					3.21	4.68

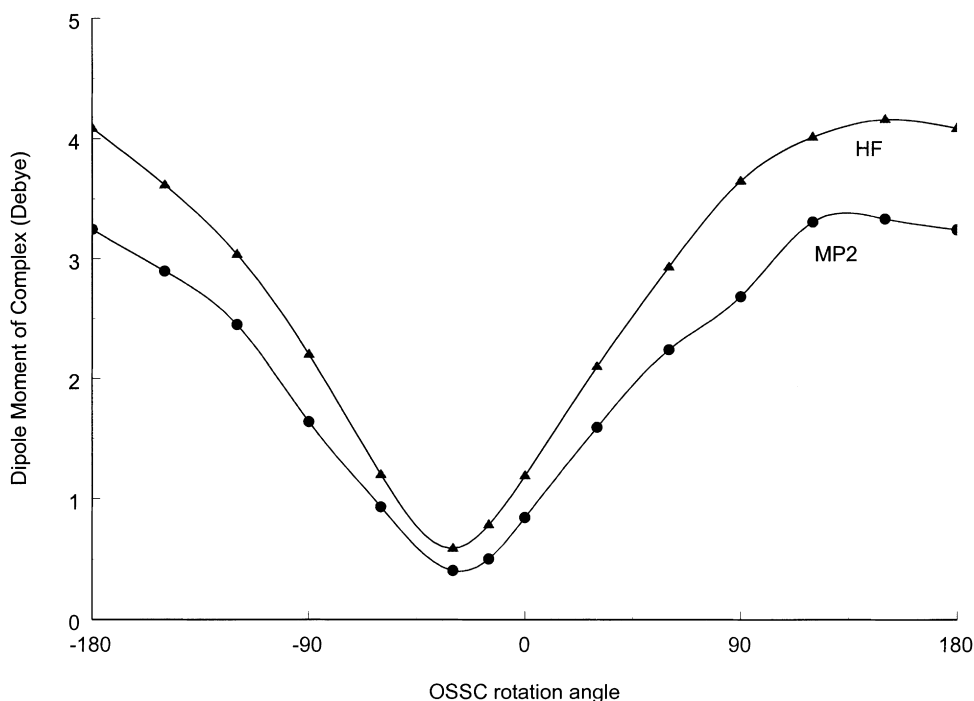


Fig. 5. Dipole moments of the complex as determined by ab initio calculations with the 6-311G** basis set.

3.3. $\text{CH}_3\text{SH} + \text{SO}_2$ photochemical reactions

The gas mixture of methanethiol and sulfur dioxide in argon matrices with a ratio of 3/1/3000 was prepared and deposited onto the cold CsI window as mentioned previously. After the IR spectrum was collected, the mixture was exposed to UV irradiation for about 30 min and another spectrum was collected. It was found that there were some new absorption bands appeared after exposing the mixture to the

Table 3
Some vibrational frequencies (cm^{-1}) of methanethiol/sulfur dioxide complex and its parent molecules (s, strong; m, moderate; w, weak)

	SO ₂		CH ₃ SH		Complex	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$\delta(\text{OSO})$	544	519(s)			544	522(w)
$\nu_s(\text{SO}_2)$	1220	1152(s)			1218	1145/43(w)
$\nu_a(\text{SO}_2)$	1401	1355(s)			1343	1338(w)
$\nu(\text{C-S})$			688	704(s)	682	702/00(w)
$\delta(\text{CSH})$			771	800(m)	772	797(w)
$\nu(\text{S-H})$			2572	2604(w)	2574	2590(w)

UV light. They are neither from the parent species nor from the molecular complexes between the parent molecules. Fig. 6 shows part of spectra of $\text{CH}_3\text{SH}/\text{SO}_2$ in argon matrices before and after the UV irradiation. These new bands were located at 3508, 3503, 3498 cm^{-1} as a triplet, at 1194, 1187 cm^{-1} and 492, 489 cm^{-1} as doublets, and at 1100, 758 cm^{-1} as singlets with relatively strong intensities. Weak absorption bands were also found at 1316, 1176, 1171, 1129, 1121, 1094, 1090, 1078, 792, 787, 781, 771, 766, 764, 751, 743 and 735 cm^{-1} . The bands at 751, 743 and 735 cm^{-1} disappeared after annealing the irradiated mixture. When the relative amount of SO_2 in the mixture was increased, for example, with $\text{CH}_3\text{SH}/\text{SO}_2/\text{Ar} = 1/1/3000$, all new bands due to the UV irradiation were observed. Additionally, the following changes were noticed: (1) the relative intensities of bands at 3508, 3503, 3498, 1194, 1187, 1100, 758, 751, 743, 735, 492 and 489 cm^{-1} did not change significantly; (2) the absorption intensities at 792, 787, 771, 766 and 764 cm^{-1} increased. On the other hand, when more methanethiol was used in the mixture, such as $\text{CH}_3\text{SH}/\text{SO}_2/\text{Ar} = 6/1/3000$, only

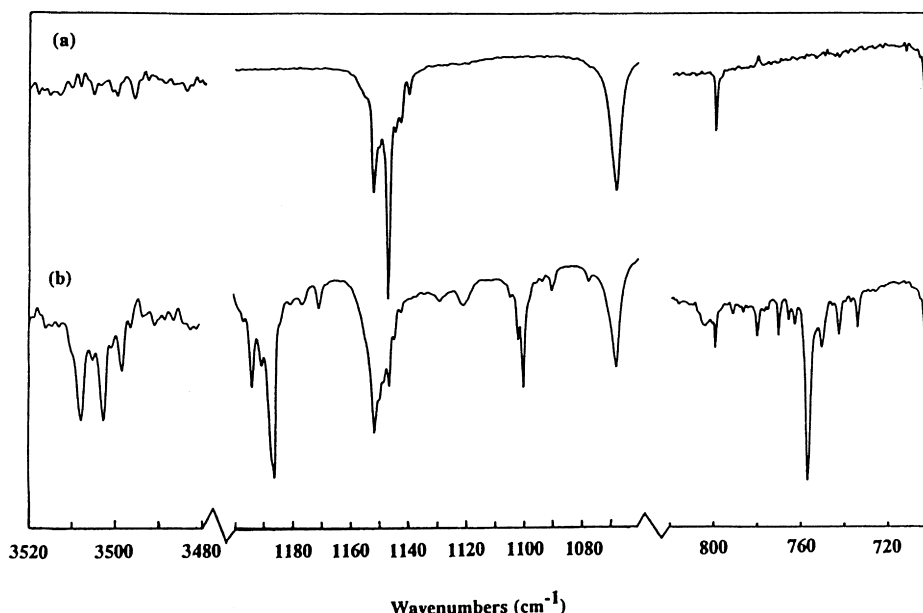


Fig. 6. FTIR spectra of Ar/SO₂/CH₃SH = 3000/1/3: (a) recorded before the UV irradiation; and (b) recorded after 30 min of UV irradiation.

1187, 1100, 787, 758, 492 and 489 cm⁻¹ absorptions were observed after the UV irradiation.

CH₃SD mixed with SO₂ in argon matrices was also examined in this study. Similar to the non-deuterated isotopic species, a mixture of CH₃SD/SO₂/Ar was prepared and deposited, then spectra before and after the UV irradiation were collected and compared. New absorption bands at 2590, 2585, 2584, 1316, 1194, 1190, 1186, 1184, 1170, 1165, 1101, 764, 758, 577, 750, 747, 743, 741, 735, 732, 492, 489, 485, 482 and 479 cm⁻¹ were observed after exposing the mixture to UV light. Annealing experiment revealed that the bands at 747, 743, and 741 cm⁻¹ disappeared after arising the temperature to 30 K (about 30% of the melting point of argon) for about 10 min, then recooling to 12 K and collecting the spectrum.

4. Discussion

The matrix-isolated IR spectrum of methanethiol has been reported by Barnes et al. [16]. Singlet absorptions at 2630 and 2576 cm⁻¹, and a doublet at 2552 and 2550 cm⁻¹ were assigned to the S–H stretching vibration of the methanethiol monomer,

dimer and multimer, respectively. The IR spectrum of methanethiol in solid Ar obtained in the present study is essentially in agreement with theirs. In addition, two very weak absorptions were observed at 808 cm⁻¹ on the higher energy side of the CSH bending mode (800 cm⁻¹) and at 698 cm⁻¹ on the lower energy side of the C–S stretching mode (704 cm⁻¹) of the monomer.

The codeposition of methanethiol with SO₂ in this study gave rise to new IR absorption bands, which could not be accounted for those of the isolated parent species and therefore must be assigned to a product species. All these new bands in the SO₂/methanethiol mixtures were only shifted slightly from the parent species vibration modes, which is a typical character for the formation of a weakly bound molecular complex. Furthermore, only one set of new absorptions was observed in several different concentration experiments suggesting that the complex in the SO₂/methanethiol mixtures in the matrices is most likely in a 1:1 stoichiometry. Thus, the new bands at 1338, 1145 and 1143, 522 cm⁻¹ were assigned to the anti-symmetric stretching, symmetric stretching, and the bending vibrations of SO₂ subunit in the 1:1 SO₂/methanethiol complex. The new absorption bands at 2590, 797, 702 and 700 cm⁻¹ were assigned to the SH

stretching, CSH bending and C–S stretching vibrations of the methanethiol subunit of the complex, respectively. The interaction between methanethiol and sulfur dioxide was suggested through the two sulfur atoms in these two molecules. Detailed discussions about the interaction site were given in our previous report on complexes between alkanethiols and sulfur dioxide [7].

Hashimoto et al. [17] have investigated the reaction of SO₂ with OH prepared by the photolysis of H₂O₂ or H₂O during deposition. They assigned the weak absorptions at 3540, 1309, 1097 and 760 cm⁻¹ to the HOSO₂ radical in argon matrix at 11 K, with the 3540 cm⁻¹ band to OH stretching vibration, the 1309 and 1097 cm⁻¹ bands to S(=O)₂ antisymmetric and symmetric stretching vibrations, respectively, and the 760 cm⁻¹ band to S–OH stretching. ¹⁸O-labeled species of the same kind was also obtained by using H₂¹⁸O as the hydroxyl radical source. Similar observation has been reported by Kuo et al. [23].

Our ab initio calculations have shown that the constituent molecules (CH₃SH and SO₂) are held together by dipole/dipole interaction. The binding energy has been calculated to be less than 5 kcal/mol. Due to the weak “intermolecular” bonding, the parent species are only mildly perturbed by the interaction as evidenced from the small frequency shift due to the complex formation. The weakly bonded complex is rather non-rigid with large zero-point excursions from equilibrium positions. The calculated frequencies of the intermolecular modes are less than 122 cm⁻¹.

After a UV irradiation of the CH₃SH/SO₂ mixture in argon matrices in this study, the observation of absorption bands at 3508, 1316, 1100 and 758 cm⁻¹, along with the absorptions at 3540, 1309, 1097 and 760 cm⁻¹ for HOSO₂ radical [17], suggested a possible structure of HOSO₂ in one of the reaction products. This suggestion was supported by the observation of isotopic shifts in the CH₃SD/SO₂/Ar experiment, in which a triplet at 2590, 2585 and 2584 cm⁻¹ due to DOSO₂ instead of a triplet at 3508, 3503 and 3498 cm⁻¹ and an absorption at 751 cm⁻¹ instead of 758 cm⁻¹ were observed, while the bands at 1316 and 1100 cm⁻¹ did not change.

In a photo-detachment study by Lineberger and co-workers [24], a band spacing of 1040 ± 80 cm⁻¹ was assigned to the CH₃ “umbrella” vibration of CH₃S

radical. The observation of bands at 1194 and 1187 cm⁻¹ for CH₃SH/SO₂ after UV exposition in our experiment is at a little bit higher frequency than their band spacing, but nevertheless would be reasonable to consider these two absorption bands as vibrations from a CH₃ group. Further supports for this argument are: (1) almost same new bands at this region were observed in CH₃SD/SO₂ photolysis experiments, in which the same CH₃ group existed; (2) when a C₂H₅SH/SO₂/Ar mixture, in which no CH₃ group but a similar C₂H₅ group exists, was exposed to the UV irradiation, similar bands appeared in this region, but with notable changes in the band positions; (3) the UV photolysis of (CH₃)₂S/SO₂/Ar showed similar new band formation in this region at 1199, 1180 and 1172 cm⁻¹. All these experimental evidences suggest that the new absorption bands in this region are related to the R group in the RSH/SO₂ or R₂S/SO₂ UV irradiation experiment, and consequently, the CH₃ vibrations may appear in the irradiation of the CH₃SH/SO₂ and CH₃SD/SO₂ systems.

Another interesting region of new bands were located as weak bands around 792 to 732 cm⁻¹, where two types of vibration are most favorable for this study: the S–O single bond stretching and the C–S stretching. Indeed, these absorptions can be classified into two groups according to their different behaviors upon the deuteration of the sulfhydryl hydrogen: the bands at 758, 743 and 735 cm⁻¹ which shifted to 751, 741 and 732 cm⁻¹ in the CH₃SD/SO₂ system, and those at 792, 787, 781, 771 and 764 cm⁻¹ which did not show the isotopic shift upon the deuteration of methanethiol. Concentration experiment for the CH₃SH/SO₂ system indicated that the 758, 743 and 735 cm⁻¹ bands did not change with the SO₂ concentration in the mixture while the 792, 787, 781, 771 and 764 cm⁻¹ bands increased in intensity when more SO₂ was used in CH₃SH/SO₂/Ar mixture. These results also supported the separation of these two groups of bands. Therefore one can conclude from these argument that at least two species were formed in the photochemical reaction of CH₃SH + SO₂. The bands at 758, 741 and 735 cm⁻¹ belong to one species, most likely a molecule with a SOH group, while the bands at 792, 787, 781, 771 and 764 cm⁻¹ are associated with other species.

From the above discussions, together with the most

possible radicals of CH_3S and H in the CH_3SH photo-detachment studies [25–27], a molecule of $\text{CH}_3\text{S}-\text{S}(=\text{O})-\text{OH}$ might be suggested as the major product for the $\text{CH}_3\text{SH} + \text{SO}_2$ photochemical reaction. The observation of bands at 492 and 489 cm^{-1} , which are near the $\text{S}-\text{S}$ stretching vibration region, provides a support to this suggestion. Although a complete vibrational assignment of the product molecule is not possible from the present study, a rough picture of the absorptions suggested to the $\text{CH}_3\text{SS}(=\text{O})\text{OH}$ may be summarized from this report. The 3508, 3503 and 3498 cm^{-1} triplet was assigned to the $\text{O}-\text{H}$ stretching vibration, the 1316 cm^{-1} band to the CH_3 vibration, the 1100 cm^{-1} singlet to the $\text{S}=\text{O}$ stretching vibrations, the 758 cm^{-1} band to the $\text{S}-\text{OH}$ stretching, and the 492 and 489 cm^{-1} doublet to the $\text{S}-\text{S}$ stretching vibration of the $\text{CH}_3\text{SS}(=\text{O})\text{OH}$ molecule. The non-singlet nature for some of the absorption spectra may be explained by the possibility of more than one conformer existing, or by the matrix effect, or by the possible further interaction of this product molecule with other species presented in the system under the experimental conditions.

It is interesting to note that the spectra resulted from the $\text{CH}_3\text{SH} + \text{SO}_2$ photochemical reaction were simpler in the case of $\text{CH}_3\text{SH}/\text{SO}_2/\text{Ar}$ mixture with a ratio of 6/1/3000 than that with a ratio of 3/1/3000. Only the suggested $\text{CH}_3\text{SS}(=\text{O})\text{OH}$ absorption bands were observed in this case. Combining this information with the fact that those $\text{CH}_3\text{SS}(=\text{O})\text{OH}$ absorptions did not show an intensity dependence on the amount of SO_2 used in the mixture, one may suggest that the formation of this product is controlled by the production rate of CH_3S and H radicals in the system. The simplicity of the spectra observed at higher CH_3SH concentration is probably due to the matrix cage effect which limits the diffusion of the radicals formed by UV irradiation and force them to recombine. Consequently, only few radicals can further reach and react with the SO_2 molecules, especially for those less stable radicals or for those with a lower quantum yield such as CH_2SH .

The possible formation of a $\text{HSCH}_2-\text{S}(=\text{O})\text{OH}$ molecule during the UV irradiation of $\text{CH}_3\text{SH}/\text{SO}_2$ mixture in argon matrices cannot be ruled out in this study, considering the possible presence of CH_2SH

and H radicals in the photo-detachment experiment [27]. The appearance of the new band around 780 cm^{-1} might be attributed to the $\text{C}-\text{S}$ vibration in the product molecule. A conclusive and substantial identification of the UV irradiation products will require further studies including ab initio calculations and normal coordinate analyses.

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