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Gas Phase Structure and Vibrational Spectra of Dimethoxysulfane $(CH_3O)_2S$

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ABSTRACT

The vapor phase structure of $(CH_3O)_2S$ [1] has been investigated by electron diffraction and ab initio MO calculations, which both result in a C_2 symmetry for the most stable geometry, the C_s conformer being less stable by about 12 kJ/mol. The torsional barrier for rotation about one SO bond was calculated as 37 kJ/mol (trans barrier). The geometrical parameters (electron diffraction) of the C_2 conformer are: d_{SO} = 162.5(2), d_{CO} = 142.6(3), d_{CH} = 110.5(7) pm, angles OSO = 103(1)°, SOC = 115.9(4)°, HCH = 109(1)°, torsional angle COSO = 84(3)°. Geometrical data calculated with 6-31G basis set agree well with the diffraction data; calculated dipole moments 1.1 D (C_2) and 3.3 D (C_s).*

The infrared spectrum of gaseous $(CH_3O)_2S$ and the Raman spectra of liquid and solid $(CH_3O)_2S$ are reported and have been almost fully assigned to the 27 fundamental vibrations.

INTRODUCTION

Sulfoxylic acid, H_2SO_2, is one of the poorest characterized oxyacids of sulfur [2]. This molecule may exist as either sulfur dihydroxide, HOSOH **1**, or as HOS(O)H **2** containing an SH bond. Neither these species nor any ionic derivatives of **1** or **2** (salts) have ever been prepared. However, a number of stable organic sulfenic acids R–SOH have been obtained; and two of them were shown by X-ray crystallography and microwave spectroscopy to possess the structure R–S–O–H, derived from the H_2SO_2 isomer **1** by substitution of one OH by an organic group [3, 4]. In addition, the structure of the methyl ester of an aromatic sulfenic acid, $RSOCH_3$, has been determined in the solid state [5].

We here report for the first time the structure of $(CH_3O)_2S$ **3**, which is to be considered the bismethyl ester of the H_2SO_2 isomer **1**. Normally **3** is called dimethyl sulfoxylate, but the rational nomenclature would be dimethoxysulfane. The structure determination was performed by electron diffraction in the vapor phase. This study was undertaken as part of a systematic study on sulfur–oxygen compounds to obtain more accurate structural information about SO single bonds originating from two-coordinated sulfur. Such information has thus far been very scarce. In addition, we have measured and assigned the infrared and Raman spectra of **3**.

EXPERIMENTAL

Because pure **3** could not be obtained following the method of Thompson et al. [6], the compound was finally prepared according to Birkofer and Niedrig [7] but in a modified manner; all preparations were carried out with exclusion of moisture and air. To 25 g of solid di[imidazolyl-(1)]sulfide (0.15 mol) were added 12.1 mL of methanol (0.3 mol) with stirring

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and cooling to −60°C. The reaction mixture was allowed to warm up to 20°C and was stirred for an additional 45 min. The product was removed under reduced pressure (0.1 bar) from the yellow precipitated imidazole and was collected in a trap cooled by liquid nitrogen. A second distillation at normal pressure resulted in pure dimethyl sulfoxylate in 34% yield (4.9 g) as a colorless liquid, the vapor of which is strongly lachrymatory (bp 74°C/1013 mbar; mp −67°C). Analysis: C (calcd) 25.52%, (found) 25.61%, H (calcd) 6.42%, (found) 6.50%; ^{1}H NMR spectrum: *s* 3.96 ppm ($CDCl_3$; 80 MHz). Dimethyl-d_6 sulfoxylate was prepared following the above procedure; 12.5 g of di[imidazolyl-1-]sulfide reacted with 6.1 mL of methanol-d_4 (Fluka, >99.5 atom-% D) to yield 2.4 g of pure dimethyl-d_6 sulfoxylate (32%) (bp 73°C/1013 mbar).

For the electron diffraction study a sample of $(CH_3O)_2S$ was transported at Dry Ice temperature from Berlin to Tübingen. The electron diffraction intensities were recorded with the Gasdiffractograph KD-G2 [8] at two camera distances (25 and 50 cm). The electron wavelength (accelerating voltage ca. 60 kV) was calibrated with ZnO diffraction patterns. The sample reservoir was kept at −16°C, and inlet system and nozzle were at room temperature. The camera pressure did not exceed $2 \cdot 10^{-5}$ mbar during the experiment. Exposure times were 5–8 s and 20–26 s for the long and short camera distance respectively. Two photographic plates for each camera distance were analyzed by the usual procedures [9]. Numerical values of the total scattering intensities in the *s*-ranges 20–180 nm^{-1} and 80–350 nm^{-1} in steps of $\Delta s = 2$ nm^{-1} are available as supplementary materials.

Infrared spectra were recorded using a Perkin-Elmer grating instrument 580 B equipped with terminal for data storage and processing. Raman spectra were obtained utilizing an ISA spectrometer (U 1000 double monochromator by Jobin-Yvon, cooled GaAs detector, MAC 80 computer for spectrometer control and data handling) and a Spectra-Physics krypton ion laser operating at 647.1 nm.

Electron Diffraction Analysis

A preliminary structural model was derived by analysis of the radial distribution function (Figure 1). The peak at 325 pm, which corresponds to the nonbonded O· · ·C distances (O· · ·C′ and O′· · ·C), indicates that both dihedral angles COSO′ and C′O′SO are equal or nearly equal, i.e., the overall symmetry is C_2 or C_s. The small peak near 420 pm corresponding to the C· · ·C′-distance is compatible only with C_2 symmetry, that is, one methyl group lies below and the other above the OSO′ plane. The contribution of the C· · ·C′ distance is very weak, so the presence of a small amount (<20%) of a conformer with C_s symmetry cannot be excluded by the electron diffraction data. Because ab initio calculations (see below) predict the C_s conformer to be higher in energy by 12 kJ/mol relative to the C_2 form, we did not allow for the presence of a C_s conformer in the least squares refinement. The methyl groups were assumed to have C_{3v} symmetry and to stagger the S–O bonds, allowing for a possible tilt angle between the C_3 axis and the O–C bond direction. Vibrational amplitudes for nonbonded O· · ·H′ and C· · ·H′ distances were collected in groups, and further constraints are evident from Table 1. With these assumptions eight geometrical parameters and nine vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$: OSO/SOC = −0.65, OSO/COSO = 0.77, and SOC/COSO = −0.64. The final results are listed in Table 1 (vibrational amplitudes) and in Table 2 (geometrical parameters). Averaged molecular intensities are shown in Figure 2.

Ab Initio Calculations

HF calculations were performed with the GAUSSIAN 86 program [M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. F. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople; GAUSSIAN 86, Carnegie-Mellon Quantum Chemistry Publishing Unit; Pittsburgh, PA, 1984] on a CONVEX 220 computer (ZDV Tübingen).

RESULTS AND DISCUSSION

Table 2 compares the structural parameters of $(CH_3O)_2S$ derived for the gas phase by electron diffraction, for the solid state by X-ray diffraction [10], and by ab initio calculations. In the crystal the compound is present in the C_2 conformation. This is also the predominant form in the gas phase, but the electron diffraction analysis cannot exclude a small contribution of a second conformer of $(CH_3O)_2S$. Gas phase IR and liquid phase Raman spectra give no indication for the presence of a second conformer. The ab initio calculations predict the C_s structure to be ca. 12 kJ/mol higher in energy relative to the C_2 form.

The optimized parameters for both forms derived with 3-21G* and 6-31G* basis sets are listed in Table 3. The results for the two basis sets differ primarily in the CO bond distances and in the COSO dihedral angles. Both basis sets predict the C_s conformer (both methyl groups on the same side of the OSO′ plane) to be ca. 12 kJ/mol higher in energy. Its geometry differs from the C_2 structure mainly in the COSO angles, which increase by ca. 10° relative to the C_2 structure. The barriers to internal rotation about the S–O bonds were calculated with the 3-21G* basis set. Rotation of one methoxy group only (i.e., C_1 symmetry) resulted in barriers of 37

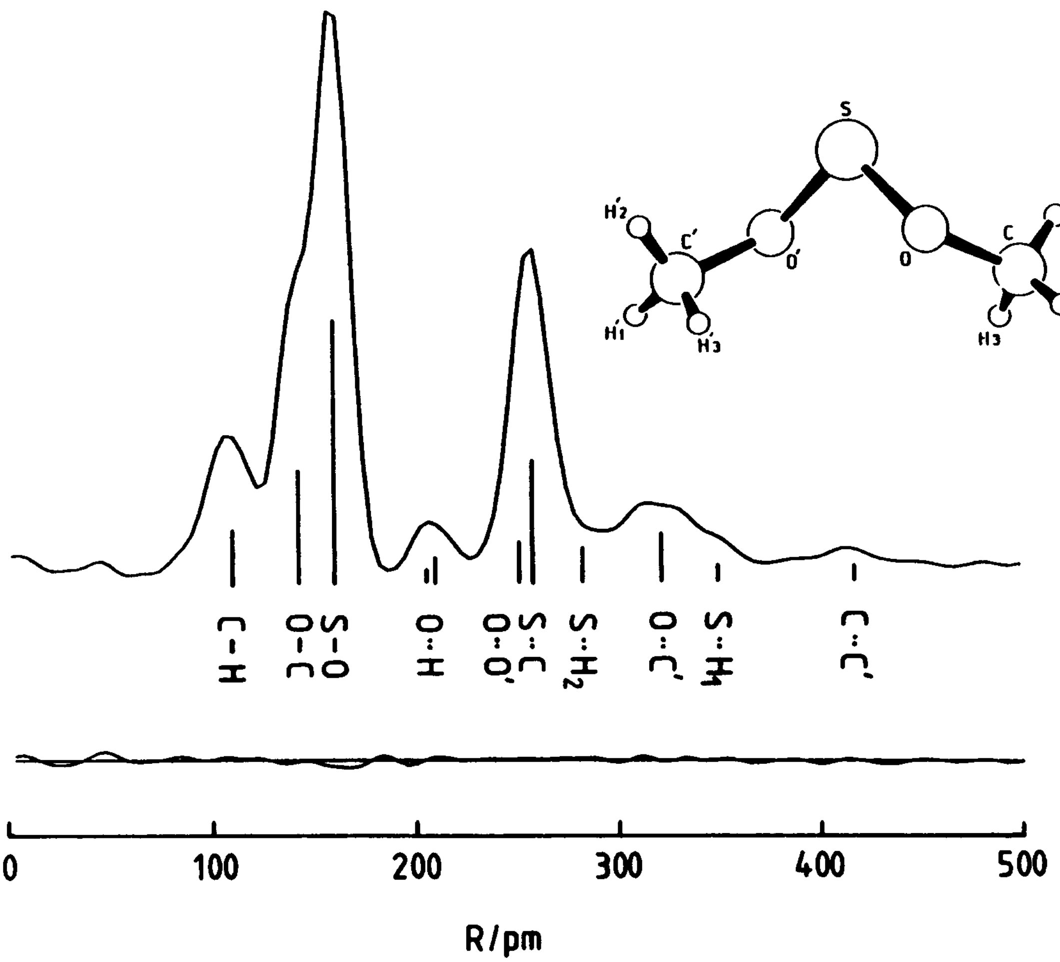


FIGURE 1 Experimental radial distribution function and difference curve of the electron diffraction experiment. The positions of O···H′, C···H′, and H···H distances are not shown.

and 38 kJ/mol for the trans and cis position, respectively. This trans barrier is much higher than such barriers in peroxides (e.g., ca. 1 kJ/mol in CH_3OOCH_3 [11]) or disulfides (e.g., 23 kJ/mol in CH_3SSCH_3 [12]). If both methoxy groups are rotated simultaneously, the energy increases by 78 kJ/mol for the planar trans structure (COSO′ =

TABLE 1 Interatomic Distances (first column) and Vibrational Amplitudes (in pm) of $(CH_3O)_2S$ from Electron Diffraction Analysis (without H···H distances)[a]

C–H	111	8.4(7)	S···H_2	282	21(6)
O–C	143	5.1(3)	O···C′	325	10[b]
S–O	162	5.1(2)	S···H_1	352	10[b]
O···H_1	205	11.2(14)	C···C′	421	23(11)
O···H_2	210		O···H′	297–414	17[b]
O···O	254	12(3)	C···H′	400–494	26(12)
S···C	259	6.0(5)			

[a] For atom numbering, see Figure 1.
[b] Not refined.

TABLE 2 Geometrical Structure of $(CH_3O)_2S$ by Electron Diffraction (gas phase), X-ray Diffraction (crystal), and Ab Initio Calculation

	Gas Phase[a]	*Crystal*[b]	*Ab Initio*[c]
C–H	110.5(7)	106.7(1)	108.2
O–C	142.6(3)	144.4(1)	141.5
S–O	162.5(2)	162.1(1)	162.6
O–S–O	102.7(14)	104.8(1)	102.4
S–O–C	115.9(4)	115.7(1)	116.6
H–C–H	108.7(10)	106–116	109.7
tilt (CH_3)[d]	3(2)		2.8
C–O–S–O	84(3)	81.75(2)	77.8

[a] Distances in pm, angles in degree. Error limits are 3σ values and include a possible scale error of 0.1%.
[b] Temperature 110 K; mean values are given for C–H and H–C–H [10].
[c] HF/6–31G*. Mean values are given for C–H and H–C–H.
[d] Tilt angle between assumed C_3 axis of CH_3 group and O–C bond direction toward oxygen lone pairs.

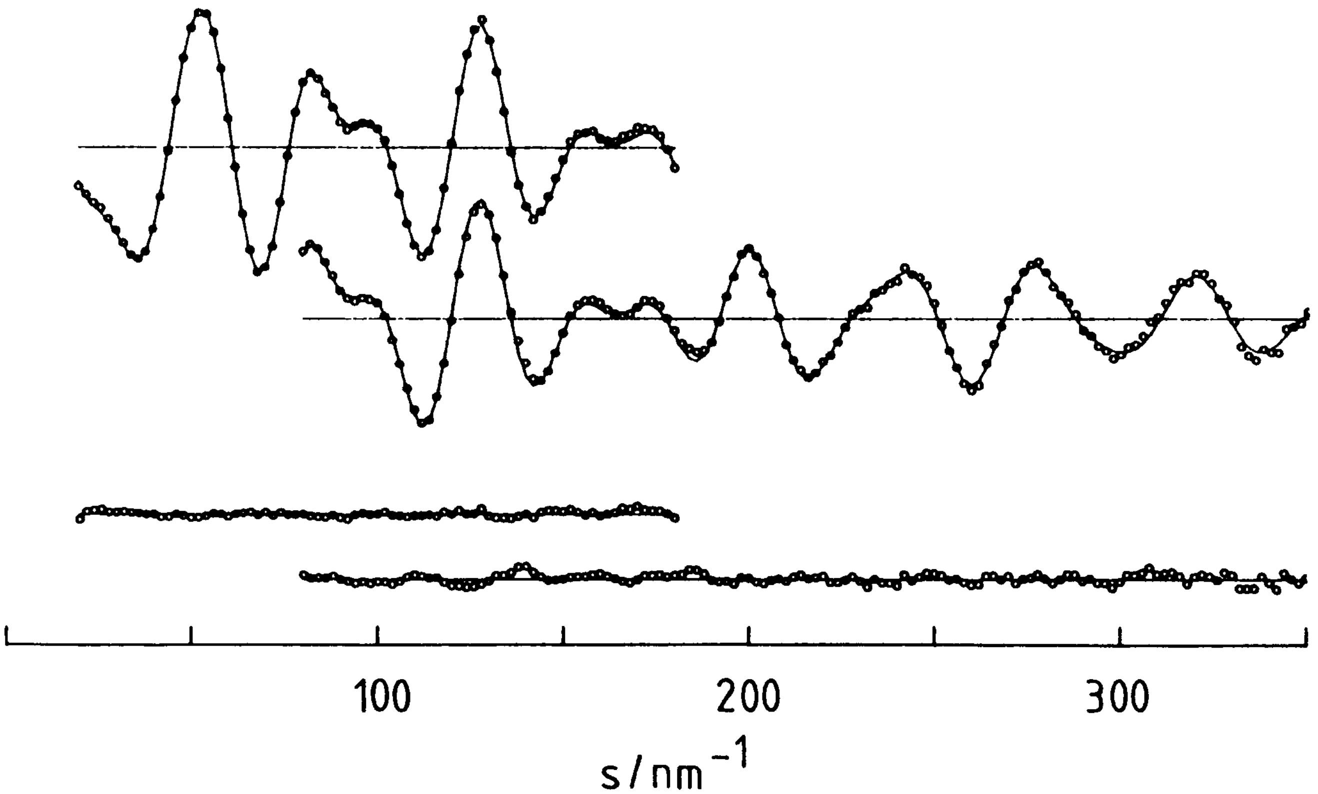


FIGURE 2 Experimental (dots) and calculated (full line) molecular intensities and intensity differences of the electron diffraction.

TABLE 3 Ab Initio Geometries, Relative Energies, and Dipole Moments for the Two Conformers (C_2 and C_s symmetry) of $(CH_3O)_2S$ Derived by Two Different Basis Sets (for atom numbering see Figure 1)

Basis set	*3-21G**		*6-31G**	
Symmetry	C_2	C_s	C_2	C_s
Distances/pm				
SO	163.1	162.6	162.6	162.4
OC	145.9	145.5	141.5	141.3
CH1	107.8	107.8	108.1	108.1
CH2	108.1	108.2	108.3	108.3
CH3	108.0	108.2	108.2	108.3
Angles/°				
OSO	101.7	104.9	102.4	104.6
SOC	117.4	120.2	116.6	118.8
COSO	74.8	84.9	77.8	88.4
OCH1	105.9	106.4	106.4	106.5
OCH2	110.4	110.6	110.6	110.9
OCH3	110.0	110.6	110.6	110.9
H1CH1	110.4	109.9	109.8	109.4
H1CH2	110.4	109.9	109.8	109.4
H1CH3	109.6	109.7	109.7	109.4
SOCH1	177.4	155.1	177.6	160.9
ΔE/kJ mol^{-1}	0.0	12.4	0.0	12.5
μ/Debye	1.4	3.7	1.1	3.3

C'O'SO = 180°) and by 101 kJ/mol for the planar cis structure (COSO' = C'O'SO = 0°). The conformational properties of dimethoxysulfane differ drastically from those of dimethyl sulfate. An electron diffraction study of the sulfate [13] indicated a mixture of C_2 (gauche, gauche) and C_{2v} (trans, trans) conformers of nearly equal energy.

Considering experimental uncertainties and systematic differences between gas phase and solid state structures, the geometrical parameters of both experimental methods are in very good agreement. The ab initio calculations at the HF/6-31G* level reproduce the experimental structures reasonably well except for the COSO dihedral angle, which is calculated to be several degrees smaller than the experimental values. This discrepancy is possibly due to the neglect of electron correlation, which has a very large effect on the calculated dihedral angles in peroxides [14]. From dihedral angles in peroxides RO-OR, which are typically larger than 110° (111.8° in HOOH [15], 114° in CH_3OOH [16], 119(4)° in CH_3OOCH_3 [11]), and those in disulfides RS–SR, which are typically near 90° (90.60(5)° in HS–SH [17], and 85(4)° in $CH_3S{-}SCH_3$ [18]), intermediate values are expected intuitively for the torsional angle about S–O single bonds. In contrast to this expectation, the COSO dihedral angle of $(CH_3O)_2S$ is small (84(3)° in the gas phase and 81.8(1)° in the crystal). For methanesulfenic acid (CH_3SOH) an HO–SC dihedral angle of 93.9(1)° has been obtained by microwave spectroscopy [4], and a planar trans structure for CH_3O–SR, R = *o*-nitrophenyl (i.e., CO–SC = 180°), has been reported in an X-ray study [5].

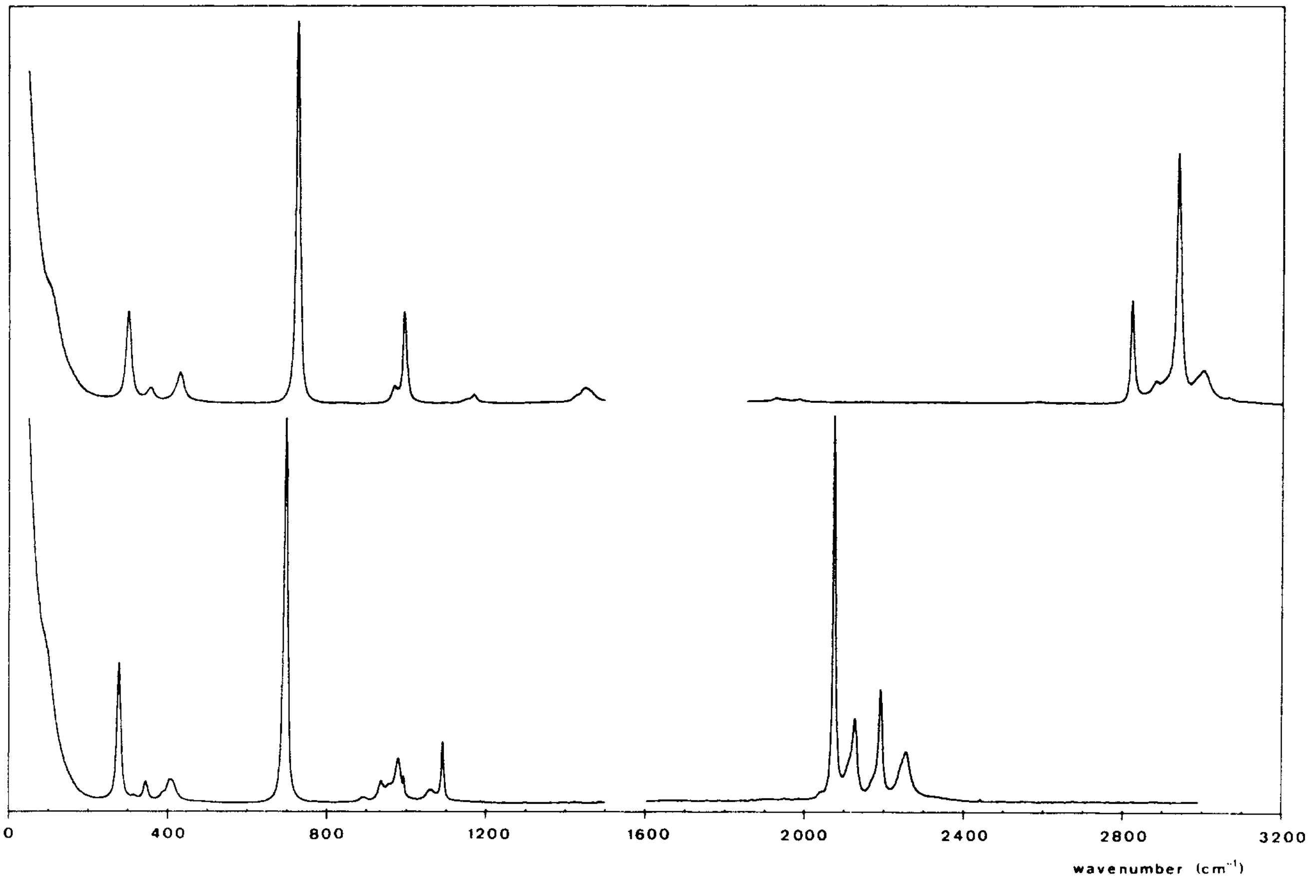
Only few experimental data are available for S–O single bond lengths in divalent sulfur compounds. For molecules containing a C–S–O moiety, values of 165.8(2) pm (CH_3S–OH) [4] and 164.8(12) pm (RS–OCH_3, R = *o*-nitrophenyl) [5] have been reported. The bond length derived for the present compound with an O–S–O moiety is 162.5(2) pm for the gas phase and 162.1(1) pm for the solid state. Shorter S–O single bonds occur in S(VI) compounds, with S–O = 156.7(3) pm in dimethyl sulfate. To our knowledge no structural data for S(II) compounds with an O–S–O moiety are known for comparison with the bond angle. In $(CH_3O)_2S$ this angle (103(1)° in the gas phase and 104.8(1)° in the solid) is larger than most other XSX angles: 92.12° in SH_2 [19], 99.05(4)° in $S(CH_3)_2$ [20], or 98.20° in SF_2 [21].

Vibrational Spectra

Vapor phase infrared spectra as well as Raman spectra of liquid and solid $(CH_3O)_2S$ and $(CD_3O)_2S$ have been measured; the signals observed are shown in Figures 3 and 4, and the wavenumbers are given in Tables 4 and 5.

Dimethyl sulfoxylate, as an eleven-atom molecule of C_2 symmetry, should exhibit 27 fundamental vibrations (14 of *A* and 13 of *B* symmetry). Among these are 10 stretching modes (ν), 13 deformation modes (9 δ and 4 ρ), and 4 torsional modes (τ), all expected to be infrared and Raman active because of the low molecular symmetry. However, the number of observed fundamental vibrations is lower than 27. This is due to the accidental degeneracy of some vibrations, especially of the methyl groups. In the case of the deuterated compound some of these bands split into their components. To simplify

FIGURE 3 Raman spectra of liquid $(CH_3O)_2S$ (*top*) and $(CD_3O)_2S$ (*bottom*); sample temperature 20°C; spectral slit width 2 cm^{-1}; sample sealed in glass capillary; ordinate: intensity.



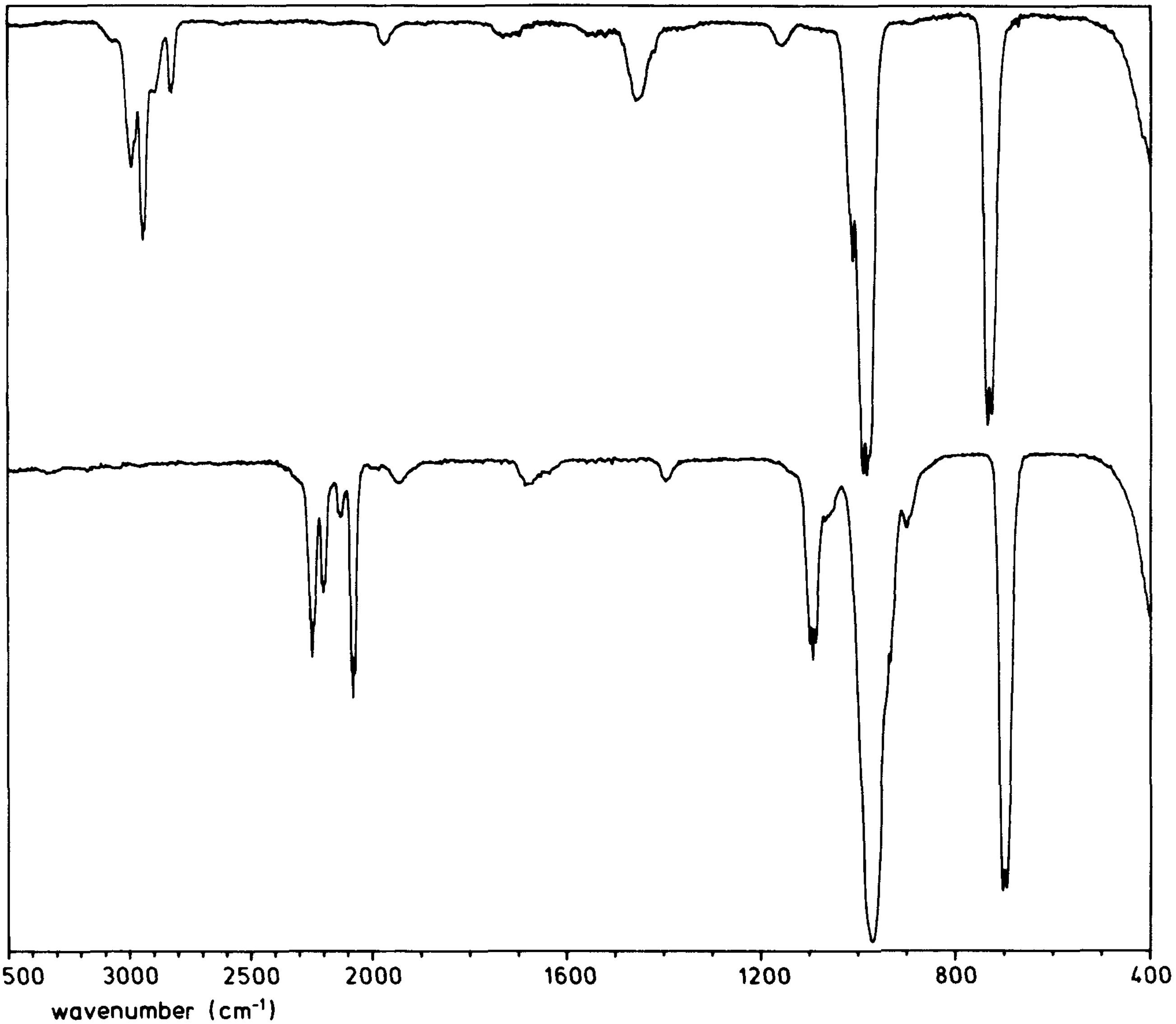


FIGURE 4 Infrared spectra of gaseous $(CH_3O)_2S$ (*top*) and $(CD_3O)_2S$ (*bottom*); sample temperature 25°C; ordinate: absorption.

the discussion, the methyl vibrations will be treated separately.

Methyl Stretching Modes

Six methyl stretching modes are expected, two symmetric (ν_s) and four asymmetric ones (ν_{as}). The vibrational coupling between the two methyl groups should be rather weak. Therefore, only one strong polarized Raman line is expected for ν_s (CH_3), and this is observed at 2936 cm^{-1}. The depolarized Raman line of medium intensity at 2998 cm^{-1} is assigned to $\nu_{as}(CH_3)$. The polarized signal at 2818 cm^{-1} is due to the first overtone of the methyl deformation, which is in Fermi resonance with the symmetric CH stretching mode. The remaining weak signals are attributed to combinations. In the spectra of the deuterated compound the CD stretching pattern is different. There are three medium-to-strong polarized and two depolarized Raman lines in the CD stretching region (Table 5). The latter two, located near 2250 cm^{-1}, are attributed to $\nu_{as}(CD_3)$. The signal at 2074 cm^{-1} is assigned to the symmetric CD_3 stretching mode. The remaining two polarized bands can be explained by analogy to the nondeuterated compound as combination vibrations and overtones of the CD_3 deformation vibrations, which are in Fermi resonance with $\nu_s(CD_3)$. This assignment is in agreement with that of dimethyl sulfate and dimethyl-d_6 sulfate [22].

TABLE 4 Vibrational Spectra (cm^{-1}) of Dimethyl Sulfoxylate, $(CH_3O)_2S$ (wave numbers in cm^{-1}; p = polarized, dp = depolarized)

Infrared	*Raman*		
Vapor (20°C)	*liquid (20°C)*	*solid (−100°C)*	*Assignment*
3065 vw	3064 vw		
2990 m	2998 m dp		ν_{as} CH$_3$
2942 s	2936 vs p		ν_s CH$_3$
2894 sh	2881 w p		Fermi resonance
2830 w	2818 s p		2 δ_s CH$_3$
—	—		
1976 vw	1982 vw p		2 × 993 = 1986
—	1926 vw p		2 × 969 = 1938
1726 vw	—		
1452 w	1456 sh dp	1453 w	$\delta_{s,as}$ CH$_3$
	1448 w dp	1437 w	
1421 sh	1426 sh dp	1422 vw	
1160 vw	1168 vw p	1167 vw	ρ CH$_3$
	1151 vw dp	1141 vw	
1012 m	—	993 w	
987 vs	993 m p	986 m	ν_s CO
979 sh	969 w dp	957 w	ν_{as} CO
731 s		723 m	ν_{as} SO
	727 vs p	719 vs	ν_s SO
	432 w p	425 w	δ_s COS
	423 sh dp	420 sh	δ_{as} COS
	355 vw p	317 sh	
	300 m p	309 w	δ SO$_2$
		168 vw	
		126 w	
	98 sh	92 m	τ SO
		74 sh	

Methyl Deformation Modes

The six expected methyl deformation modes, two $\delta_s(CH_3)$ and four $\delta_{as}(CH_3)$, only give rise to two absorptions in the infrared spectrum at 1452 and 1421 cm^{-1}. These signals are observed as three depolarized lines at 1456, 1448, and 1426 cm^{-1} in the Raman spectrum. Hence, there is no basis on which to discriminate between the symmetric and the asymmetric modes because both are expected to occur at almost the same frequency. For dimethyl sulfate, the methyl deformation vibrations have been observed at 1459 and 1443 cm^{-1} [22]. Dimethyl-d_6 sulfoxylate exhibits two absorptions, a sharp one at 1093 cm^{-1} and a weak broad one at 1060 cm^{-1} in the infrared spectrum. The former is polarized in the Raman spectrum and hence can be attributed to the symmetric deformation $\delta_s(CD_3)$. The latter is depolarized and splits in the Raman spectrum on solidification. It is assigned to the asymmetric methyl deformation. In the case of dimethyl-d_6 sulfate a polarized Raman line at 1077 cm^{-1} and a depolarized one at 1060 cm^{-1} have been assigned to the symmetrical methyl deformation [22].

Methyl Rocking Modes

The four methyl rocking modes are expected to lie in the 850–1150 cm^{-1} region [23]. The absorption at 1160 cm^{-1} in the infrared spectrum of $(CH_3O)_2S$ and the Raman lines at 1168 (p) and 1151 cm^{-1} (dp) are attributed to methyl rocking modes. A second infrared absorption at 1012 cm^{-1} that has no counterpart in the Raman spectrum can be assigned to this type of vibration, too. In dimethyl sulfate the methyl rocking modes occur at 1180 and 1165 cm^{-1} [22]. For dimethyl-d_6 sulfoxylate, three methyl rocking modes are observed at 959, 933, and 890 cm^{-1}. These wavenumbers are similar to those observed for dimethyl-d_6 sulfate, for which these modes have been observed at 941, 928, and 896 cm^{-1} [22]. In both cases, the line at 930 cm^{-1} is polarized in the Raman spectrum; the others are depolarized.

Stretching Modes of the COSOC Chain

The two CO stretching vibrations (ν_s and ν_{as}) occur as a very strong absorption at 987 cm^{-1} in the infrared spectrum of gaseous $(CH_3O)_2S$ and split into

TABLE 5 Vibrational Spectra of Dimethyl-d_6 Sulfoxylate, $(CD_3O)_2S$ (wavenumbers in cm^{-1}; p = polarized, dp = depolarized)

Infrared	*Raman*		
Vapor (20°C)	*liquid (20°C)*	*solid (−100°C)*	*Assignment*
2322 vw	2325 vw		
	2254 m dp		ν_{as} CD$_3$
2248 m	2244 sh dp		
2200 m	2190 m p		$2\,\delta_s$ CD$_3$ Fermi resonance
2132 w	2126 m p		
2079 s	2074 vs p		ν_s CD$_3$
—	2041 w p		
1946 vw	1951 vw		2 × 979 = 1958
—	1904 vw		2 × 959 = 1918
1679 vw	—		
1639 vw			
1397 vw			2 × 699 = 1398
1130 vw	1147 vw p(?)		
1093 m	1090 m-w p	1086 w	δ_s CD$_3$
1060 vw	1059 w dp	1058 vw	δ_{as} CD$_3$
		1049 vw	
	992 w p	990 vw	
970 vs	979 m p	977 wsh	ν_s CO
		969 w	ν_{as} CO
954 sh	959 w dp	943 vw	ρ CD$_3$
933 m	935 w p	933 vw	
900 w	890 vw dp	886 vw	
699 s		694 m	ν_{as} SO
	696 vs p	690 vs	ν_s SO
	405 w p	406 w	δ_s COS
	390 wsh dp	389 vw	δ_{as} COS
	345 w p		
	314 vw dp	292 vw	
	276 m p	282 w	δ SO$_2$
		158 vw	
		114 w	
	85 sh	84 m	τ SO
		68 sh	

two lines of medium and low intensity in the Raman spectrum, the former being polarized and the latter depolarized. Although these lines may be assigned as the symmetric and asymmetric CO stretching modes, it is likely that these vibrations are mixed to some extent with a methyl rocking or even the SO stretching modes. Such a coupling has been found for dimethylperoxide, for which it was shown by normal-coordinate analysis that the symmetric CO stretching vibration is coupled with a methyl rocking and the OO stretching mode [24]. Upon deuteration, the symmetric CO stretching mode shifts by 17 cm^{-1} to 970 cm^{-1}.

The most interesting fundamental vibrations of $(CH_3O)_2S$ are doubtless the two SO stretching modes because vibrations of SO single bonds originating from two coordinated sulfur atoms have only rarely been studied. The following wavenumbers for ν(S–O) have previously been published:

$C_2H_5OSSOC_2H_5$:	712 cm^{-1} [25]
$C_2H_5OSOC_2H_5$:	708 cm^{-1} [26]
$CH_3OS(O)OCH_3$:	694/735 cm^{-1} [27]
$CH_3OS(O)_2OCH_3$:	757/829 cm^{-1} [22]
$CH_3OS(O)CH_3$:	692 cm^{-1} [27]

The structural fragment OSO of $(CH_3O)_2S$ may be compared to the SF_2 molecule, the stretching vibrations of which occur at 813 and 839 cm^{-1} in the vapor phase [28]. The small difference of only 3% causes us to expect ν_s (SO) and ν_{as} (SO) of $(CH_3O)_2S$ to be closely neighboring in the spectra. In fact, there is only one strong absorption at 731 cm^{-1} in the IR spectrum of $(CH_3O)_2S$ (Table 4) that can be assigned to ν_{as} (SO), whereas the 20°C Raman spectrum shows a strong line at 727 cm^{-1} that is polarized and should therefore be assigned to ν_s (SO). Only the low-temperature Raman spectrum exhibits two lines at 723 and 719 cm^{-1}, the stronger of which is assigned to ν_s and the other one to ν_{as} (SO). As discussed earlier, both lines may represent SO vibrations coupled with other modes of this molecule. The deuterated sulfoxylate shows the same behavior; only the low-temperature Raman spectrum exhibits two lines to be assigned to ν_s and ν_{as} (SO). The wavenumber shift of ν(SO) on deuteration clearly indicates that these fundamentals are coupled to some degree to other vibrations, at least in the case of $(CH_3O)_2S$. The low-temperature Raman spectra also show weak lines to be assigned to ν_s(SO) of the ^{34}S substituted isotopomers as follows:

$(CH_3O)_2$ ^{34}S: 714 cm^{-1}
and $(CD_3O)_2$ ^{34}S: 684 cm^{-1}

With this discussion all stretching modes of $(CH_3O)_2S$ have now been assigned.

Bending Modes of the COSOC Chain

These vibrations comprise δ (COS), δ (SO_2), τ (COSO), and other fundamentals, the definite assignment of which is rather difficult. The tentative assignments given in Tables 4 and 5 certainly need confirmation by either additional data of related compounds or by a normal-coordinate analysis. The two torsional modes τ (COSO) should be almost degenerate and are assigned to the lowest observed Raman line of liquid $(CH_3O)_2S$, which occurs as a shoulder on the wing of the Raleigh line at 98 cm^{-1}; in solid $(CH_3O)_2S$ it is of medium intensity. The polarized line at 300 cm^{-1} is assigned to δ (SO_2) because in SF_2 the bending mode occurs at 357 cm^{-1} [28]. There is one weak, polarized Raman line each in the spectra of both $(CH_3O)_2S$ and $(CD_3O)_2S$, which disappears on crystallization of the samples (355 and 345 cm^{-1}, respectively). Although it is tempting to explain this observation in terms of a rotamer that disappears on cooling, one would expect more Raman lines to disappear in such a case. A rotamer of C_s symmetry as discussed earlier should, for example, have different CO stretching fundamentals, which have not been observed. We therefore discard this idea.

Finally, the Raman lines near 400 cm^{-1} may represent δ_s and δ_{as} (COS). This assignment leaves only some very weak signals unexplained, which may be combination vibrations or overtones or represent the unassigned fundamental (CH_3 torsion about CO bond).

ACKNOWLEDGMENTS

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