

The Vibrational Spectra of Dimethyl Sulphite

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The infrared spectra of dimethyl sulphite as a liquid and as a solid at -180° were recorded in the region $4000-220\text{ cm}^{-1}$. A Raman spectrum of the liquid sample was obtained and polarization data presented.

The spectra have been interpreted in terms of C_s symmetry. Tentative assignments of the skeletal vibrational modes have been proposed.

We have for some time been interested in the donor-acceptor complexes between various organic sulphur compounds and iodine.¹ Among these donors, we investigated dimethyl sulphite which forms considerably weaker complexes than the sulphoxides. In connection with this work we decided to study the vibrational spectrum of dimethyl sulphite, since only a few infrared absorption frequencies²⁻⁴ and Raman data^{4,5} without polarization measurements have been reported. Our present spectral data have been compared with the vibrational analysis reported for dimethyl sulphoxide⁶ and the structurally related dimethyl carbonate.⁷ Since dimethyl sulphite consists of 12 atoms and therefore has 30 fundamental vibrations, no complete interpretation of the vibrational spectra is possible, but a tentative assignment of the skeletal modes will be proposed.

EXPERIMENTAL

Dimethyl sulphite from Aldrich was fractionated two times over dryerite in a Vigreux column under reduced pressure. No impurity peaks were detected in a gas chromatogram.

The infrared spectra were recorded in the region $4000-220\text{ cm}^{-1}$ with a Perkin-Elmer model 621 spectrometer. No satisfactory vapour spectrum was obtained in a 1 m cell, and the sample was recorded as a capillary, in 0.1 mm sealed KBr and polyethylene cells and as a capillary at -180°C .

The Raman spectrum was recorded with a Cary model 81 spectrometer, using the 7 mm tube and the 4358 \AA Hg-radiation. Semiquantitative polarization measurements were performed by the standard procedure.

Table 1. Infrared and Raman spectral data and tentative assignments of dimethyl sulphite.

Infrared		Raman		Interpretation
Liquid	Solid -180°C	Liquid		
3910 vw				
3548 vw				
3105 vw				
3011 vs	3004 s	3026 s, bd	D	a'' } a' } CH stretch
2957 vs	2958 vs	2955 vs	P	
	2920 w			
		2898 w, sd	P?	a' } a' }
2837 s	2838 s	2838 s	P	
2607 m	2585 w, bd	2604 m		
	2530 w			
2407 m	2382 w			
2363 w				
2140 m				
1934 s	1910 w, bd			
1903 s				
1695 w, sd				
1650 w	1654 w, bd			
1540 w	1530 vw			
	1463 s			
1456 vs	1455 vs	1461 vs	D	a'' } a' } CH ₃ deformation
	1435 s, sd	1434 w, sd	P	
1378 vw?	1385 vw			
1334 w	1327 w			
1209 vs	1208 vs	1207 vs	P	a' S=O stretch
1193 m, sd	1192 vs			} CH ₃ rocking
1170 vw	1177 s, sd	1166 m	D?	
	1114 w			
	1062 w			
	1033 w, sd			
987 vs	1000 vs	982 s	P	a' in phase COS stretch
959 vs	968 vs	960 s	D	a'' out of phase COS stretch
	890 w			
	857 w			
	838 w			
822 vw	817 w			
770 w		768 vw		
733 vs	732 vs	732 s	P	a' sym OSO stretch
688 vs	695 vs	698 m, bd	D	a'' asym OSO stretch
611 w	603 m	607 vw		
579 m	582 s, sp	579 s, sp	P	a' in plane O ₃ SO bend
526 m	530 w	519 m	P	a' OSO bend
518 m				a'' out of plane O ₃ SO bend
				bend
442 m	450 w	444 s	P	a' in phase COS bend
412 s	419 s, sp	412 s	D	a'' out of phase bend
390 w	385 vw			overtone OCH ₃ torsion?
299 w		295 w, sd	P	a'' SO torsion
260 s, bd	270 s	260 s, bd	P	a' SO torsion

Abbreviations: s, strong; m, medium; w, weak; v, very; sp, sharp; sd, shoulder; bd, broad; P, polarized and D, depolarized.

RESULTS AND DISCUSSION

The infrared spectra of dimethyl sulphite in the liquid and solid states are shown in Fig. 1 and the Raman spectrum is shown in Fig. 2. The observed frequencies are listed in Table 1 and various new infrared ^{2,3} and Raman ^{4,5} bands compared to the earlier data were observed. Dimethyl sulphite undoubtedly has a pyramidal configuration around the S atom like dimethyl sulphoxide ⁸ and the molecule can therefore have no further symmetry elements than a plane of symmetry. Assuming the point group C_s for dimethyl sulphite, the 30 fundamental vibrations divide into 16 a' and 14 a'' . Out of these, 12 fundamentals (7 a' and 5 a'') should be mainly associated with the skeletal

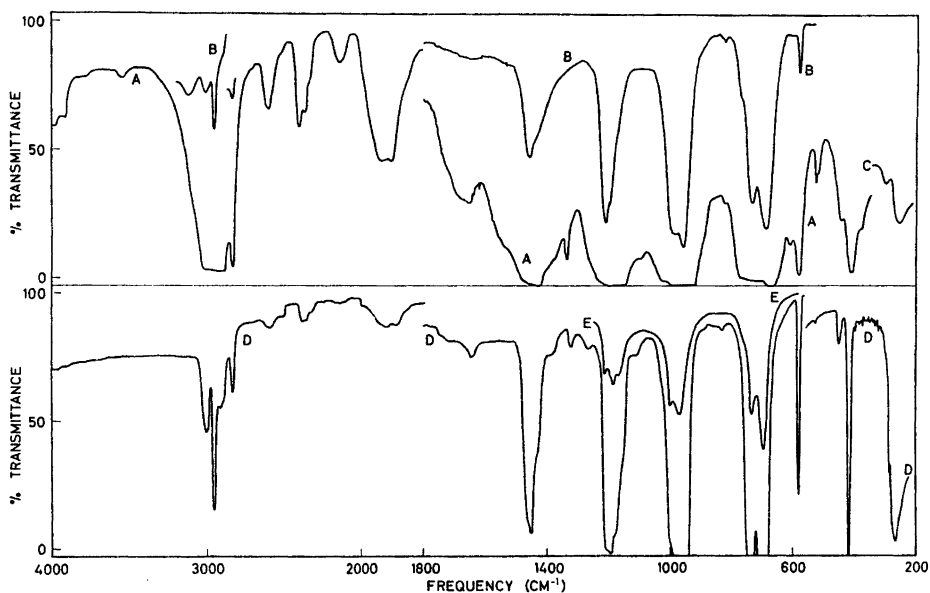


Fig. 1. The infrared spectra of dimethyl sulphite as a liquid (upper curves; A 0.1 mm, B capillary, C 0.1 mm polyethylene cell) and as a solid (lower curves, -180°).

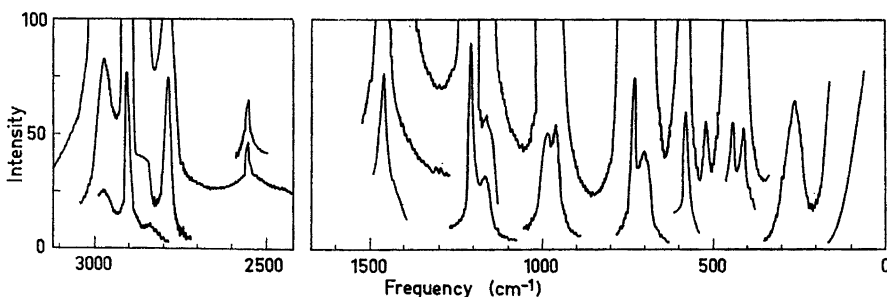


Fig. 2. The Raman spectrum of liquid dimethyl sulphite.

stretching (5), bending (5), and SO torsional (2) modes. The remaining 18 fundamentals should be predominantly connected with the methyl stretching, deformation, rocking, and torsion and fall inside the well established regions for these modes. Moreover, all the fundamentals should be infrared as well as Raman active; those of species a' and a'' should be polarized and depolarized in Raman, respectively.

The six CH stretching modes should be situated around 3000 cm^{-1} leaving 24 fundamentals below 1500 cm^{-1} . However, only 16 Raman bands which all are believed to be fundamentals were observed in this region. Four low frequency bands connected with the SO and the OCH_3 torsional modes are expected in dimethyl sulphite and may have been unobserved since they are generally weak in Raman and the infrared spectrum below 220 cm^{-1} was not recorded. It seems likely, however, that there is a very weak coupling between the two OCH_3 halves of the molecule which means near degeneracy between certain in-phase and out-of-phase modes. This assumption was also proposed by Detoni and Hadzi³ to account for the observation that some of the strong infrared bands appeared as doublets. Our present data indicate that many of the skeletal in-phase and out-of-phase modes appear as closely spaced bands and some of the methyl modes coincide completely. In dimethyl carbonate with a planar configuration and a "stiffer" structure these modes interact more strongly, and a much higher number of infrared and Raman bands were observed.⁷

The possibility of rotational isomerism in dimethyl sulphite, caused by a restricted rotation around the SO bonds cannot be excluded, and has been advocated for the corresponding trialkyl phosphites.⁹ The present data do not support the assumption of rotational isomerism since no simplification in the infrared spectra occurred upon solidification (Fig. 1). However, there is some doubt if our solid sample at -180° was really crystalline in spite of prolonged annealing a little below the freezing point, since the spectrum lacks the sharp peaks generally present in crystalline samples. We plan to study dimethyl sulphite with NMR technique at lower temperatures to further investigate the possibility of rotational isomerism.

Our tentatively assigned fundamentals are listed in Table 1, and only some of the skeletal modes will be discussed. The very strong infrared and Raman bands at 1209 and 1207 cm^{-1} , respectively, are undoubtedly connected with the $\text{S}=\text{O}$ stretching mode. The shoulder at 1193 cm^{-1} which is prominent in the low temperature infrared spectrum is probably a CH_3 deformation or rocking mode enhanced by Fermi resonance with the $\text{S}=\text{O}$ stretching mode. We have assigned the two COS stretching modes to the close bands around 970 cm^{-1} and the two OSO stretching modes around 700 cm^{-1} . The five skeletal bending modes ($3 a'$ and $2 a''$) are assigned to bands in the region $600-400\text{ cm}^{-1}$. The infrared band at 390 cm^{-1} may tentatively be assigned to the first overtone of a methyl torsional mode expected around 200 cm^{-1} .¹⁰ Finally, the two infrared bands with Raman counterparts around 280 cm^{-1} have been assigned to the SO torsional modes in agreement with recent data reported for aliphatic ethers.¹¹

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