

Second derivative analysis of S=O stretching band in Raman spectra of dimethyl sulphoxide in carbon tetrachloride and water

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Abstract. Raman spectra of solutions of DMSO (dimethyl sulphoxide) are studied in the S=O stretching region by second derivative analysis. Broad bands observed in the normal Raman spectra show well resolved components in the derivative plots. On the basis of the various components obtained in these plots for solutions of DMSO in carbon tetrachloride and water, existence of equilibria between various associated species, involving dipolar and hydrogen bonding interactions, is suggested. It is concluded that solutions of DMSO in CCl_4 may have monomers, cyclic and linear dimers and polymers, whereas its aqueous solutions show the existence of 1:1 and 1:2 hydrogen bonded complexes of water with DMSO in addition to smaller concentrations of monomers, dimers and polymers.

Keywords. Raman spectra; second derivative; hydrogen bonding; DMSO interactions.

1. Introduction

The high boiling point, the entropy of evaporation (higher than that of water) and cryoscopic investigations in benzene show that liquid dimethyl sulphoxide (DMSO) is highly associated (Lindberg *et al* 1961). Recent Raman spectral studies on solutions of DMSO in carbon tetrachloride and water by Singh and Krueger (1982) as well as Sastry and Singh (1984) show definite evidence for the associative properties of DMSO. It was shown that the broad bands in the S=O stretching region could be fitted by considering four components for solutions of DMSO in CCl_4 whereas the corresponding bands in aqueous solutions were fitted by considering five components. On the basis of these observations it was concluded that liquid DMSO is a mixture of monomers, cyclic dimers, linear dimers and higher polymers. When dissolved in CCl_4 the concentration of monomers and cyclic dimers increases. Solutions of DMSO in water show the presence of hydrogen bonded DMSO molecules with water in addition to the free and dimerised DMSO molecules.

Derivative spectroscopy was introduced in the early 50's by Hammond and Price (1953), Tannenbauer *et al* (1953), Morrison (1953) and Giese and French (1955). Recently Vandeginste and De Galan (1975), Talsky *et al* (1978), Maddams (1980), Maddams and Mead (1982), Hawkes *et al* (1982), Maddams and Souton (1982) and Barker and Fox (1980) have outlined methods to resolve IR and Raman spectral bands employing derivative spectroscopy (see appendix). As an extension to our work on the Raman spectra of solutions of DMSO in the S=O stretching region reported earlier (Sastry and Singh 1984), we report here the second derivative spectra to justify our model for the structure of liquid DMSO and its solutions.

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2. Experimental and computational details

Details regarding spectral measurements and purity of chemicals used are as reported earlier (Sastry and Singh 1984). The second derivatives of the S=O stretching bands were computed using the 13 point polynomial method of Savitzky and Golay (1964). The calculations were performed on a Perkin Elmer Infrared Data system Model 3600 using a BASIC computer program developed in this laboratory.

3. Results and discussions

Raman spectra in parallel, polarized mode (I_{\parallel}) of DMSO in CCl_4 at various concentrations and their second derivatives in the S=O stretching regions are shown in figures 1 and 2 respectively. The broad bands with weak shoulders in Raman spectra are found to resolve in the derivative spectra. The probable positions of the components, on the basis of the plots obtained from the derivative spectra for various solutions, are summarised in table 1. Pure DMSO shows three clear bands in the derivative spectrum at ≈ 1055 , 1041 , and 1029 cm^{-1} . Upon dilution in carbon tetrachloride a high frequency band starts rising at ≈ 1065 to 1070 cm^{-1} and the low frequency band at 1029 cm^{-1} shows significant lowering in intensity. The bands at ≈ 1055 and $\approx 1041 \text{ cm}^{-1}$ also

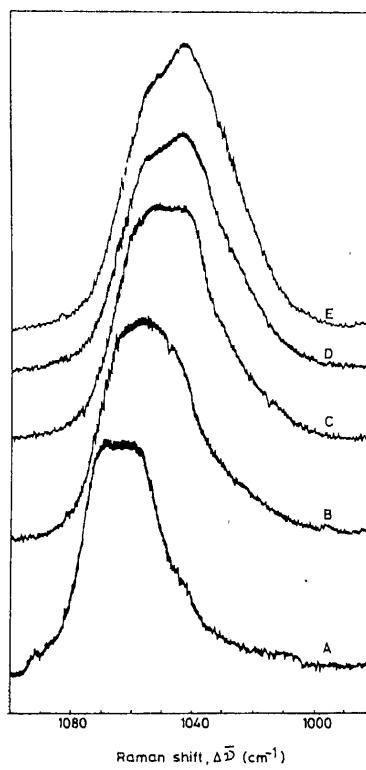


Figure 1. Raman spectra (I_{\parallel}) of solutions of DMSO in CCl_4 at different dilutions (mf), A-0.06; B-0.20; C-0.50; D-0.82; E-1.0 (taken from Sastry and Singh 1984).

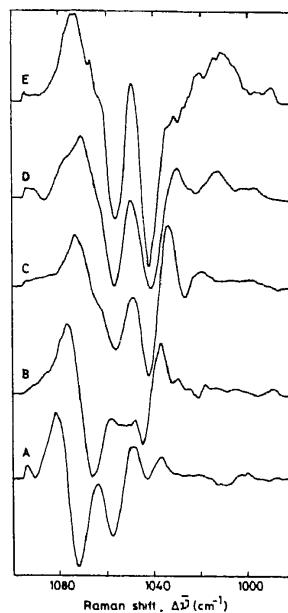


Figure 2. Second derivative plots for I_{\parallel} spectra of solutions of DMSO in CCl_4 at different dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

Table 1. Spectral parameters of the component bands for the DMSO- CCl_4 system.

Mole fraction of DMSO	Present work		Results from Sastry and Singh (1984)		
	$\bar{v}(\text{cm}^{-1})$	$\bar{v}(\text{cm}^{-1})$	$\Delta\bar{v}_{1/2}^*$ (cm^{-1})	Peak height	Integrated intensity (cm^{-1})
1.0	1029.0	1027.26	16.03	0.373	10.60
	1041.0	1042.06	12.43	0.631	13.89
	1055.0	1056.54	9.83	0.447	7.79
	1068.40		8.52	0.130	1.96
0.82		1028.70	20.41	0.263	9.61
		1040.0	12.87	0.554	12.28
		1055.0	10.77	0.382	7.29
		1069.72	12.01	0.105	2.23
0.50	1027.0	1028.51	18.79	0.261	8.70
	1042.0	1044.30	11.33	0.582	11.68
	1056.0	1057.56	9.45	0.422	7.03
	1062.0	1067.28	11.24	0.185	3.68
0.20		1025.93	15.05	0.200	5.35
		1044.5	11.69	0.500	10.37
		1052.0	11.25	0.341	6.84
		1066.0	11.43	0.450	9.11
0.06		1023.87	18.02	0.099	3.17
		1048.11	11.85	0.334	7.02
		1057.5	5.77	0.265	2.71
		1072.0	12.00	0.862	18.34

* $\Delta\bar{v}_{1/2}$ is half width of the band at $1/e$ of the amplitude.

show lowering in intensities. In all the cases the $\approx 1055\text{ cm}^{-1}$ band is found to be lower in intensity than the $\approx 1041\text{ cm}^{-1}$ band. The solution with 0.5 mf concentration shows all the four bands centered at $\approx 1062, 1056, 1042$ and 1027 cm^{-1} . These results show that DMSO solutions exhibit equilibria between species having Raman spectral bands at these four frequencies. In figure 3 is shown the second derivative spectrum of the isotropic Raman spectra of the above solutions for reference. As is well known the I_{\parallel} , I_{\perp} , I_{iso} and I_{aniso} spectra are respectively proportional to $(45\alpha^2 + 4\beta^2)$, $3\beta^2$, α^2 and β^2 where α and β represent the isotropic and anisotropic components of the polarisability tensor. The I_{\perp} spectra directly give the I_{aniso} Raman components whereas I_{iso} components are obtained by subtracting $4/3 I_{\perp}$ from I_{\parallel} spectra ($I_{\text{iso}} = I_{\parallel} - 4/3 I_{\perp}$).

The DMSO molecule is pyramidal in shape with two of the corners occupied by C atoms, one by an S atom and the fourth by an O atom. The S atom is sp^3 hybridised and the S–O bond is formed by an $sp^3 - p_x$ σ -overlap with a π -bond of the type $d_{xz} - p_z$ or $d_{yz} - p_y$ leading to a strongly polar S–O bond. As mentioned earlier (Sastry and Singh 1984, and references therein) associations through O–H bridging and S–H bridging appear improbable because of the low acidity of the C–H bond, while S–O bridging appears to be more probable because of the strong polar character of the S–O bond. Referring to the model based on the coexistence of equilibria between monomers, cyclic dimers, linear dimers/polymers in solutions of DMSO in CCl_4 the asymmetric S=O stretching bands in the Raman spectra of DMSO solutions were fitted with four Gaussian bands (Sastry and Singh 1984). It was argued, on the basis of relative intensities of the four components, that the band centered at $\sim 1070\text{ cm}^{-1}$ belongs to the S=O stretching fundamental of monomers, whereas the two bands centered at ~ 1058 and 1040 cm^{-1} belong to out-of-phase and in-phase S=O stretching bands of

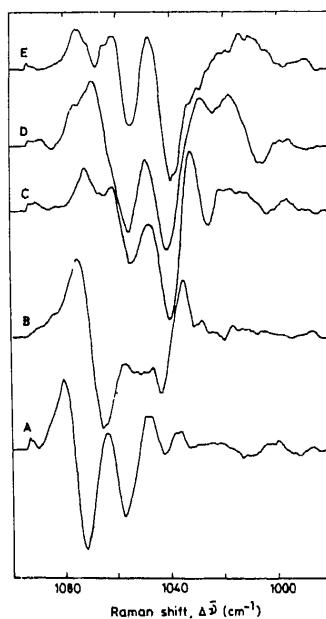


Figure 3. Second derivative plots for I_{iso} spectra of solutions of DMSO in CCl_4 at different dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

distorted cyclic dimers and the broad band at $\sim 1025\text{ cm}^{-1}$ belongs to linear dimer/polymer species. These conclusions are found to be in conformity with the results obtained by the derivative spectra of I_{\parallel} in figure 2. The derivative spectra of the I_{iso} for a 0.5 mf solution also shows four components as for I_{\parallel} (figure 3). If the cyclic dimer with C_{2h} symmetry is considered then I_{\parallel} and I_{iso} should show only one in-phase S=O stretching band. In case a slightly distorted cyclic dimer is considered without a centre of inversion then I_{\parallel} may show both in-phase and out-of-phase S=O stretching bands whereas I_{iso} should show only an in-phase band. Only in an extreme case where a distorted cyclic dimer has no effective symmetry element and belongs to C_1 symmetry, both S=O stretching bands are expected to be observed in I_{\parallel} and I_{iso} spectra. Two alternative assignments can therefore be proposed for the four components observed in I_{\parallel} and I_{iso} spectra of DMSO solutions: (i) as suggested above the cyclic dimer is highly distorted having a C_1 symmetry thus leading to a high frequency band assigned to the monomer, the next two bands assigned to the cyclic dimer and the lowest frequency component assigned to the linear dimer/polymer species, (ii) in case the cyclic dimer has an inversion centre with or without slight distortion, the four components at ~ 1070 , 1055, 1040 and 1025 cm^{-1} can respectively be assigned to S=O stretching modes of monomer, cyclic dimer (in-phase), linear dimer and polymer species. The band due to the terminal S=O stretch of linear dimer is expected to be coincident with the monomer band.

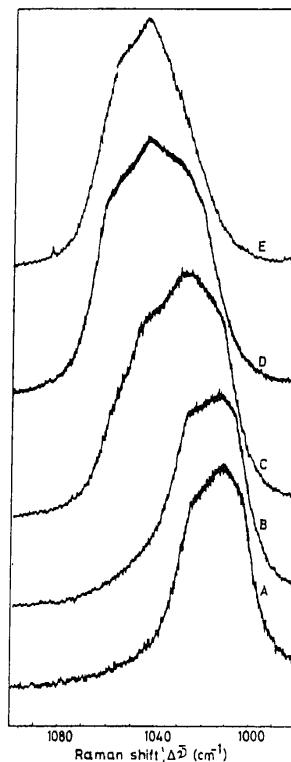


Figure 4. Raman spectra (I_{\parallel}) of solutions of DMSO in water at different dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0 (taken from Sastry and Singh 1984).

In figure 4 are given the I_{\parallel} bands in the S=O stretching region for several aqueous solutions of DMSO. The second derivative plots for these solutions for I_{\parallel} and I_{iso} spectra are shown in figures 5 and 6 respectively. The probable positions of the components are given in table 2. In the previous publication it was suggested (Sastry and Singh 1984) that with increase in concentration of water a new band in the low frequency region of 1012 cm^{-1} starts rising in intensity such that for 0.06 mf of DMSO, 80% of the total intensity of the S=O stretching band is attributed to this component. The band was assigned to the S=O stretching mode of DMSO molecules hydrogen bonded to water molecules. The derivative plots for I_{\parallel} spectra of these solutions show that the three main components of pure DMSO at $\sim 1055, 1041$ and 1029 cm^{-1} grow into four for 0.82 and 0.50 mf of DMSO in its aqueous solutions, the fourth band appearing at 1020 and 1012 cm^{-1} in the two solutions respectively. For 0.20 and 0.06 mf solutions the low frequency component is replaced by two components at ~ 1015 and 1005 cm^{-1} . It may be surmised that at lower concentrations of DMSO in aqueous solutions, two types of hydrogen bonded complexes may be present where one water molecule hydrogen

Table 2. Spectral parameters of the component bands for the DMSO-water system.

Mole fraction of DMSO	Present work		Results from Sastry and Singh (1984)		
	$\bar{\nu}(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\bar{\nu}_{1/2}^*$ (cm^{-1})	Peak height	Integrated intensity (cm^{-1})
1.0	1029.0	1026.26	16.03	0.373	10.60
	1041.0	1042.06	12.43	0.631	13.89
	1055.0	1056.54	9.83	0.447	7.79
	1068.40	1068.40	8.52	0.130	1.96
0.82	1020.50	1017.70	22.74	0.096	3.34
	1030.00	1025.00	12.14	0.325	7.00
	1043.00	1042.80	11.83	0.442	9.28
	1061.00	1059.00	10.36	0.334	6.14
	1072.80	1072.80	10.75	0.037	0.72
0.50	1012.00	1014.90	17.11	0.178	5.38
	1027.50	1027.30	16.89	0.222	6.66
	1044.50	1044.90	12.12	0.182	3.91
	1057.50	1058.60	9.27	0.086	1.42
	1072.60	1072.60	12.50	0.020	0.46
0.20	1008.50				
	1015.00	1010.30	14.08	0.249	6.69
	1027.00	1026.90	11.24	0.175	3.14
		1042.60	12.78	0.047	0.86
		1057.60	11.97	0.023	0.54
		1066.20	7.25	0.013	0.25
0.06	1005.00				
	1012.00	1012.00	17.78	0.268	8.40
	1025.50	1026.80	7.17	0.072	0.92
		1039.60	7.95	0.033	0.47
		1051.40	9.23	0.022	0.37
		1066.70	12.50	0.013	0.29

* $\Delta\bar{\nu}_{1/2}$ is half width of the band at $1/e$ of the amplitude.

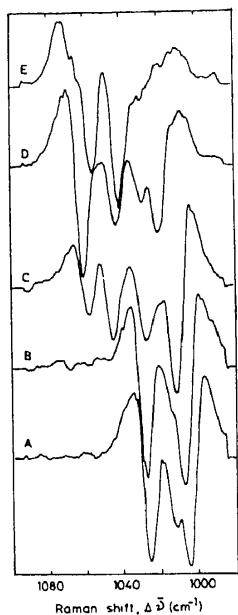


Figure 5. Second derivative plots for I_{\parallel} spectra of solutions of DMSO in water at various dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

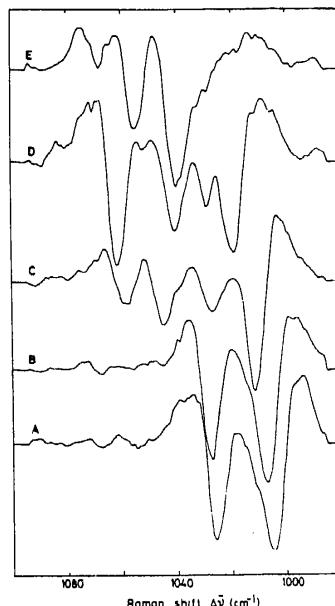


Figure 6. Second derivative plots for I_{iso} spectra of solutions of DMSO in water at various dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

bonds with one or two DMSO molecules, respectively, giving rise to asymmetrically and symmetrically hydrogen bonded water complexes. The two types of hydrogen bonded complexes may give rise to two low frequency components observed for dilute solutions of DMSO in water. The band components observed in the derivative spectra of I_{iso} are similar to those obtained for I_{\parallel} derivative plots as expected from the analysis given above.

Acknowledgements

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Appendix. Derivative spectroscopy

The two common band shapes usually considered are the Lorentzian (Cauchy) and the Gaussian functions. Morrey (1968) reported the mathematical relationships between the first and higher derivatives of Lorentzian and Gaussian functions (table A1). In the case of Lorentzian or Gaussian functions the ratio of the half-width of the primary function to the half width of the second derivative is 1:0.33 i.e. it decreases to a third of its original value (Talsky *et al* 1978, and references therein). It has also been shown (Butler and Hopkins 1970; Fell 1980; Maddams and Tooke 1982) that in general the n th derivative peak amplitude varies inversely with the n th power of the band width.

Table A1. Relationships for derivatives of Lorentzian and Gaussian bands.

Band shape \rightarrow	Lorentzian	Gaussian
Form	$I(\bar{v}) = I_0 [1 + X_3^2 (\bar{v} - \bar{v}_0)^2]^{-1}$ $X_3 = I_{\text{HWHM}} / \bar{v}_0$; \bar{v}_0 = band centre	$I(\bar{v}) = I_0 \exp(-X_4^2 (\bar{v} - \bar{v}_0)^2)$ $X_4 = (\ln 2)^{1/2} / \text{HWHM}$; \bar{v}_0 = band centre
1st derivative	$dI(\bar{v})/d\bar{v}$	$dI(\bar{v})/d\bar{v}$
Root	$dI(\bar{v})/d\bar{v} = 0 = \bar{v}_0$	$dI(\bar{v})/d\bar{v} = 0 = \bar{v}_0$
Extremal values	$\bar{v}_0 \pm 0.5774 \text{ HWHM}$	$\bar{v}_0 \pm 0.8494 \text{ HWHM}$
2nd derivative	$d^2 I(\bar{v})/d\bar{v}^2$	$d^2 I(\bar{v})/d\bar{v}^2 = 0 = \bar{v}_0 \pm 0.8494 \text{ HWHM}$
Root	$d^2 I(\bar{v})/d\bar{v}^2 = 0 = \bar{v}_0 \pm 0.5774 \text{ HWHM}$	$\bar{v}_0 \pm 1.471 \text{ HWHM(max)}$ $\bar{v}_0 \pm 1.471 \text{ HWHM(min)}$
Extremal values	$\bar{v}_0 \pm \text{HWHM(max)}$ $\bar{v}_0 \pm \text{HWHM(min)}$	$\text{Max}(\bar{v}_0 \pm 1.471 \text{ HWHM})/\text{min}(\bar{v}_0) = 0.4462$
Ratio of extremal values	$\text{Max}(\bar{v}_0 \pm \text{HWHM})/\text{min}(\bar{v}_0) = 0.25$	
4th derivative	$d^4 I(\bar{v})/d\bar{v}^4$	$d^4 I(\bar{v})/d\bar{v}^4$
Root	$d^4 I(\bar{v})/d\bar{v}^4 = 0 = \bar{v}_0 \pm 0.3250 \text{ HWHM}$ and $\bar{v}_0 \pm 1.3764 \text{ HWHM}$	$d^4 I(\bar{v})/d\bar{v}^4 = 0 = \bar{v}_0 \pm 0.6302 \text{ HWHM}$ and $\bar{v}_0 \pm 1.9828 \text{ HWHM}$
Extremal values	$\bar{v}_0 \pm 0.5774 \text{ HWHM (minimum)}$ $\bar{v}_0(\text{max}), \bar{v}_0 \pm 1.732 \text{ HWHM}$	$\bar{v}_0 \pm 1.150 \text{ HWHM (minimum)}$ $\bar{v}_0(\text{max}), \bar{v}_0 \pm 2.4264 \text{ HWHM}$
Ratio of extremal values	$\text{Min}(\bar{v}_0 \pm 0.5774 \text{ HWHM})/\text{max}(\bar{v}_0) = 0.4219$	$\text{Min}(\bar{v}_0 \pm 1.150 \text{ HWHM})/\text{max}(\bar{v}_0) = 0.6182$

HWHM-half width at half maximum.

The criterion for a peak to be observed is that the first derivative $dI(\bar{v})/d\bar{v} = 0$, and the second derivative $d^2 I(\bar{v})/d\bar{v}^2$ is negative. Morrey (1968) used the following conditions to define a peak:

$$d^2 I(\bar{v})/d\bar{v}^2 < 0; d^3 I(\bar{v})/d\bar{v}^3 = 0; d^4 I(\bar{v})/d\bar{v}^4 > 0.$$

On the higher derivatives, the adjacent bands have much less effect because of the narrower half-widths of the derivatives.

Westerburg (1969) defined two limits for the overlap of two component bands called the shoulder limit and the detectability limit. The point at which two peaks overlap to such a degree that the valley between them just disappears is defined as the shoulder limit and is expressed by the following equations:

$$dI(\bar{v})/d\bar{v} = d^2 I(\bar{v})/d\bar{v}^2 = 0.$$

The detectability limit occurs, when an inflection point of the profile and the maximum of the minor peak coincides, which is expressed mathematically by the following equation:

$$d^2 I(\bar{v})/d\bar{v}^2 = d^3 I(\bar{v})/d\bar{v}^3 = 0.$$

The shoulder and detectability limits of overlapping Gaussian and Lorentzian bands of various half-widths and intensity ratios have been reported by Vandeginste and De Galan (1975).

Maddams and Mead (1982) and Maddams and Sounth (1982) studied the effects of background and half-widths of component bands on the measurement of derivatives. Baker *et al* (1978) have examined the problem in context with the quantitative use of derivative spectra to characterize band shapes, following the procedure of Grushka and Monacelli (1972). They pointed out that the intensity ratio of the positive and negative lobes of the second derivative is a measure of the band shape: it is found to be 0.250 for a Lorentzian profile and 0.446 for a Gaussian band.

In the present study, for calculation of second derivatives we have used the convolution least squares method introduced by Savitzky and Golay (1964). The method provides a combined approach to smoothing and derivatization. A set of data points, collected at equal abscissal intervals is fitted to a polynomial by a least squares calculation. This set of points is moved forward sequentially by one data point until the whole spectrum has been covered. The degree of the polynomial, n , sets the limit to the highest derivative that may be obtained. This method is mathematically equivalent to convoluting the original data with a numerical function, and Savitzky and Golay (1964) have provided values for these functions for polynomials of various degrees and derivatives of various orders. The various mathematical steps involved in the convolution least squares method can be found in the pioneering work of Savitzky and Golay (1964). Steinier *et al* (1972) have subsequently noted errors in some of these numerical values and have supplied corrected tables. In our calculation we have used a 13 point quadratic polynomial for second derivative calculations.

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