Reactions in Mixed Non-aqueous Solutions containing Sulphur Dioxide. Part 7.[1] A Raman Spectroscopic Study of Adduct Formation between Sulphur Dioxide and Dimethyl Sulphoxide

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Details are given of the $v(SO)_{dmso}$ stretching (dmso = dimethyl sulphoxide), $v_1(SO_2)$, $v_3(SO_2)$, and $v_2(SO_2)$ regions of the Raman spectra of SO_2–dmso mixtures at 293 K and sub-ambient temperatures. Analysis of the $v(SO)_{dmso}$ region, which contains at least seven component bands, provides evidence of several component species. Bands at 1 067, 1 057, and 1 044 cm^{-1} are due to monomers and associates of dmso, and a band whose frequency varies between 1 029 and 1 025 cm^{-1} is due to a methyl-rocking mode of dmso. Bands at 1 013, 1 006, and 997 cm^{-1} are attributed to the adducts $SO_2 \cdot 2dmso$, $SO_2 \cdot dmso$, and $2SO_2 \cdot dmso$ respectively. An example of the use of band fitting to a difference spectrum supports these assignments.

Many metals and their oxides dissolve spontaneously in binary mixed solvents containing sulphur dioxide with cosolvents such as dimethyl sulphoxide (dmso).[2–5] Cosolvents supporting metal dissolution have both high donor number and moderate or high dielectric constant.[5] Metal dissolution can occur if the cosolvent has either a low donor number or a low dielectric constant if the metal is used as a sacrificial anode.[5,6] By use of solvent mixtures containing SO_2, reactions of the solvent, or its components, with metals such as Fe, Mn, Mo, or Zn lead to salts of sulphur oxyanions.[2–5] When a SO_2–dmso mixture is used disulphates $(S_2O_7^{2-})$ are produced, but with other SO_2–cosolvent mixtures the anion formed is normally dithionite $(S_2O_4^{2-})$. Accordingly we conclude that dmso oxidises S^{IV} to S^{VI} in a reaction sequence following metal dissolution. Liberation of dimethyl sulphide provides good supporting evidence.

In order to understand the mechanisms of metal dissolution reactions it is important for us to improve our knowledge of the constitution of SO_2–dmso mixtures. The large exothermic enthalpy of mixing SO_2 and dmso[2,3] suggests formation of compounds or adducts, and a preliminary melting point study[2] confirmed the presence of a species with 1 : 1 stoicheiometry. We believe this to be a simple donor–acceptor interaction between dmso and SO_2; dmso forms adducts with many molecules, *e.g.*, water, methanol, and ethanoic acid, through hydrogen bonding[7] and low donicity aprotic solvents such as I_2, ICl, ICN, $CHCl_3$, and CH_3CN.[8]

Some time ago we observed that the maximum of the $v(S–O)$ region of the Raman spectrum of dmso shifts from *ca.* 1 050 to 1 010 cm^{-1} when SO_2 is added.[2] This is greater than is observed for many other dmso adducts. We also noted that the spectra depend on the composition.

With recent improvements to, (*i*) the spectrometer, and (*ii*) data handling and processing methods, spectroscopic data can now be treated analytically. Our Coderg RS100 Raman spectrometer has been upgraded to provide multiple scanning and digital data collection, and with coaddition of spectra we can achieve much improvement in signal/noise ratio. We have a computer-assisted curve resolution procedure, VIPER,[9,10] but, of vital importance to this work, we now have the powerful curve resolution–enhancement program TREAT based on smoothing and derivative convolution.[11]

Fortunately the 1 000—1 100 cm^{-1} region of the Raman spectra of the mixtures has a flat baseline free from any interfering features. A careful assignment of the i.r. and Raman spectra of dmso by Horrocks and Cotton[12] showed that only the $v(SO)_{dmso}$ stretching vibration occurs in this region. We have undertaken a careful and detailed analysis of the region over

all compositions and have attributed the component bands to discrete species in equilibria.

To complement the spectroscopic analyses we also present a more detailed phase study of SO_2–dmso mixtures in Part 8 of this series.[13]

Experimental

Sample Preparation.—SO_2–dmso samples were prepared in glass tubes by condensing SO_2 onto dmso as in the preparation of liquid ammonia solutions for Raman spectroscopy.[14,15] Pure dry redistilled dmso was introduced by syringe, the tubes were evacuated, and the samples deoxygenated by recycling through the melting point of dmso. Sulphur dioxide was condensed and the tubes sealed from the atmosphere. Compositions, established by weighing tubes and contents at appropriate stages, are quoted as the mol fraction, $F = (mol\ SO_2)/[(mol\ dmso) + (mol\ SO_2)]$. When not in use all samples were stored in the dark at 220 K.

Spectrometer Technique.—Spectra, recorded on the recently upgraded double-monochromator Coderg RS100 Raman spectrometer, were irradiated with the 488.0 nm line of a Coherent Radiation model 52 argon ion laser at >1 W continuous. Digitised data were collected by a Datalab DL4000 signal averager. The main spectrometer drive, modified to facilitate multiple scanning through any preselected wavenumber range, allows any number of multiple scans to be chosen and data to be recorded at 0.125, 0.25, 0.5, or 1.0 cm^{-1} intervals. All available data were collected at 0.125 cm^{-1} intervals. Spectra were calibrated to ± 0.2 cm^{-1} against neon emissions. Spectrometer conditions were optimised by (*i*) alignment of irradiating beam and sample, (*ii*) use of longest acceptable amplifier time constant to maximise *RC* smoothing, and slow scan speeds to minimise *RC* distortion, (*iii*) photomultiplier cooling to 240 K, and (*iv*) using slitwidths $\leqslant 0.125\ w_{\frac{1}{2}}$ ($w_{\frac{1}{2}}$ = half-width). Mirrors at 180 and 270° to the incident beam and sample improved the signal with a second light pass, and collection of unused Raman emission 270° to the incident beam. Spectra were obtained for lower temperatures with an Oxford Instruments cryostat DN704 controlled to ± 0.2 °C.

Data Handling.—The coadded signal-averaged data were transferred from the DL4000 to a Hewlett Packard 9845A minicomputer for processing. Programs for the 9845A were written to accommodate a maximum 512 data points across a spectrum; in the case of $v(SO)_{dmso}$ only, 969 data points were reduced to

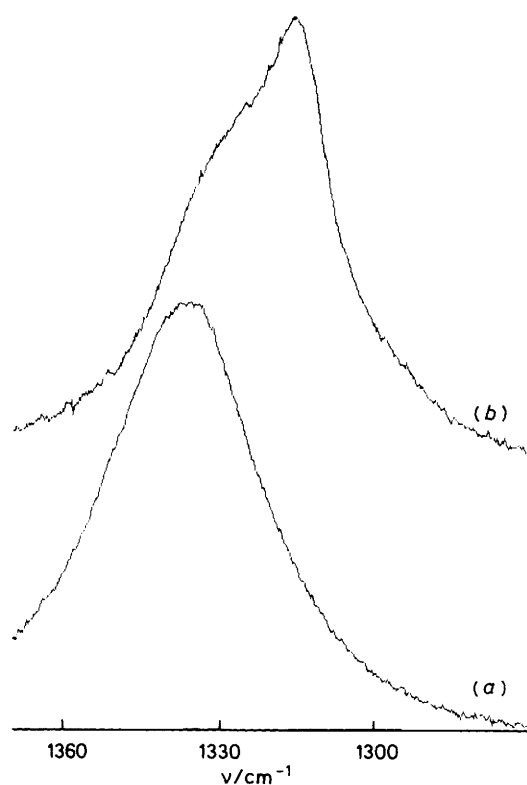**Figure 1.** The $v_3(SO_2)$ antisymmetric stretching region of the Raman spectra of (*a*) pure liquid SO_2, and (*b*) a SO_2–dmso mixture with $F = 0.67$ at 293 K: four coadded scans (401 points) at 5 cm^{-1} min^{-1}; spectrometer slitwidth, 1.0 cm^{-1}

Figure 2. The $v_1(SO_2)$ symmetric stretching region of the Raman spectra of SO_2–dmso mixtures at 293 K: four coadded scans (241 points) at 1 cm^{-1} min^{-1}; spectrometer slitwidth, 0.25 cm^{-1}; signal/noise ratio $> 1\,000$

485. The first 4 cm^{-1} of the spectra were discarded to avoid baseline distortion resulting from the fast back–forward spectrometer drive between successive scans.

Underlying band positions were established by the smoothing and derivative convolution process TREAT.[11] We have shown that maximum noise reduction with minimum signal distortion is achieved with a quadratic function and two passes of a first-derivative filter, rather than a single pass of a second-derivative filter. The only variable to be determined in this program is the number of data points N encompassed in successive segments of polynomial fit; N is chosen for the best compromise between preventing the smoothing function from following the spectral noise (when N is small) and avoiding spectrum distortion (when N is large). Successive trial integral values of N between preset lower and upper limits find the inflexion where $d^2(x)/dN^2 = 0$; x is the variance of residuals between observed and smoothed data. For the second-derivative spectra of $v(SO)_{dmso}$ quadratic functions with $N = 11$, 13, or 15 were used. The program produces a bar chart of residuals which indicates any distortion of the signal caused by smoothing, checks on the random distribution of positive and negative residuals, and assesses the signal/noise ratio.

Results

The spectrum was carefully surveyed between 250 and 2 500 cm^{-1}. The only vibrations with significant perturbations due to SO_2–dmso interactions were the S–O stretching mode of dmso, $v(SO)_{dmso}$, and the v_1, v_3, and v_2 modes of SO_2. Other vibrations likely to contain structural information are $\delta(CSC)$ at *ca.* 305 cm^{-1}, $\delta_{asym}(CSO)$ at *ca.* 329 cm^{-1}, and $\delta_{sym}(CSO)$ at *ca.* 378 cm^{-1}. These are all weak features and changes in composition cause only small frequency shifts with no discernible changes in the spectra. No bands were found due to simultaneous transitions,
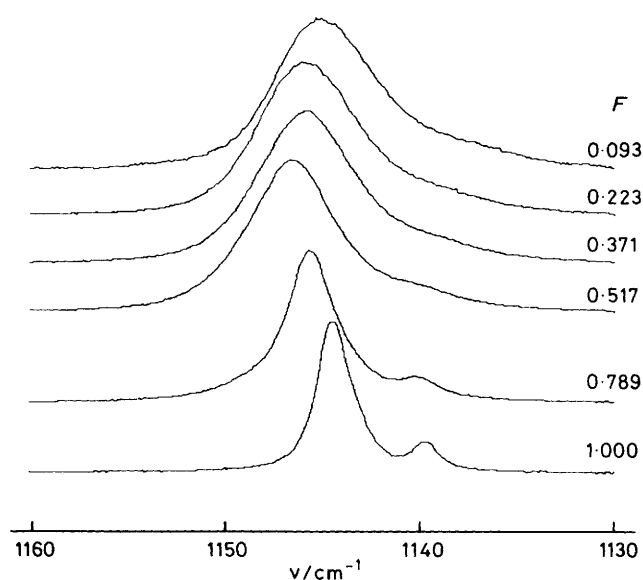
$[v_1(SO_2) + v(SO)_{dmso}]$ and $[v_3(SO_2) + v(SO)_{dmso}]$, between 2 150 and 2 330 cm^{-1}. Only the $v(SO)_{dmso}$ mode shows significant changes with temperature or polarisation of the incident beam.

$v_3(SO_2)$ *Antisymmetric Stretching Region.*—In the past it was the $v_3(SO_2)$ antisymmetric stretching region which received attention because it was considered to be sensitive to intermolecular interactions in SO_2 solutions.[16] When SO_2 is added to dmso the band between 1 270 and 1 370 cm^{-1} shifts only a small amount (3—5 cm^{-1}) with little change in the shape of the band maximum at 1 336 cm^{-1}. It can be seen from Figure 1 that analyses of the spectra are impaired by the overlap of a more intense band at 1 315 cm^{-1} attributable to dmso vibrations, probably the two components of the symmetrical distortion vibration $\delta(CH_3)A'$ and $\delta(CH_3)A''$.[12,17] Uncertainty of baseline position and shape also arises in this region.

$v_1(SO_2)$ *Symmetric Stretching Region.*—This is by far the most intense region. Using the best possible spectrometer recording conditions it was examined between 1 130 and 1 160 cm^{-1}. The baseline is flat and the band separated from other features. Figure 2 shows a stacked set of spectra scaled numerically so that their peak maxima have equal ordinate values.

Two sharp bands in the spectrum of liquid SO_2 at 1 144.5 ($w_{\frac{1}{2}} \sim 2.1$ cm^{-1}) and 1 139.5 cm^{-1} are attributable to the v_1 vibrational modes of $^{32}SO_2$ and $^{34}SO_2$. A low-intensity band outside the range surveyed, at *ca.* 1 120 cm^{-1}, is due to the $v_1(SO_2)$ vibration of $S^{16}O^{18}O$. On reduction of F the band due to $^{34}SO_2$ merges into a set of features of increasing intensity in the 'tail' of the $v_1(SO_2)$ band on its low-frequency side. Confirmation of the attribution of the bands at 1 144.5 and 1 139.5 cm^{-1} came from two-band VIPER fits of the spectra of mixtures between $F = 1.0$ and 0.517. The two resolved bands remain in the same intensity ratio when the composition of the mixture is changed.

As the mol fraction decreases to $F = 0.517$ the band experiences a small shift to higher frequency (1 146.7 cm^{-1}) and considerable broadening ($w_{\frac{1}{2}} \sim 5.1$ cm^{-1}), suggesting changes in the distribution of the components of the mixtures. Further
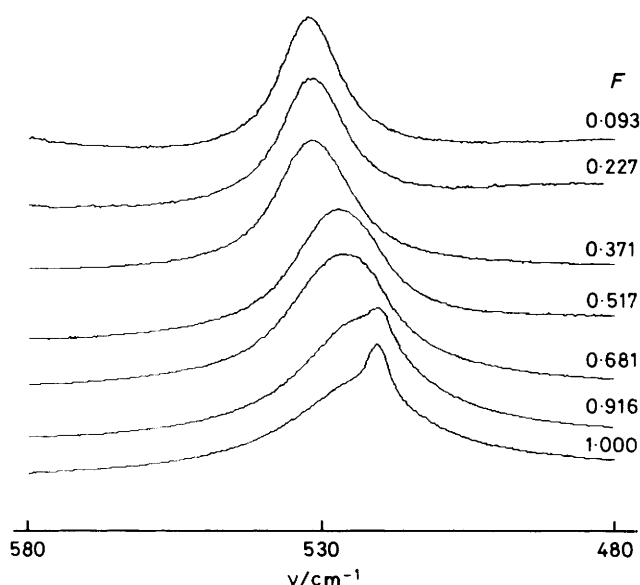
Figure 3. The $v_2(SO_2)$ deformation region of the Raman spectra of SO_2-dmso mixtures at 293 K: four coadded scans (397 points) at 5 cm^{-1} min^{-1}; spectrometer slitwidth, 1.0 cm^{-1}

Figure 4. The $v(SO)_{dmso}$ stretching region of the Raman spectra of SO_2-dmso mixtures at 293 K: four coadded scans (797 points reduced to 397) at 2.5 cm^{-1} min^{-1}; spectrometer slitwidth, 0.5 cm^{-1}; signal/noise ratio > 500

decrease of F to 0.093 causes a reversal of direction of the shift, albeit small, to 1 145.0 cm^{-1} with broadening to $w_{\frac{1}{2}} \sim 6.2$ cm^{-1}. These small shifts, encompassed within only 14 data points on the sharpest spectrum, and the nearly symmetrical bandshapes present an impossible task for computer resolution. The second derivatives of the spectra have a small asymmetry which can only be accounted for by the presence of underlying features, too closely spaced for resolution, and whose variations in intensity must be related to the changes in the distribution of components of the mixtures. Although this is the most intense region of the spectrum, and excellent signal/noise levels were obtained, further analyses of the derivative spectra were impossible because the data were at the absolute limit of spectrometer resolution.

It is noted that the spectra are similar to those of solutions of halogenosulphinates in SO_2,[18] where the halide anion is a powerful donor to the SO_2 acceptor, cf. the strong electron donation from dmso to SO_2.

$v_2(SO_2)$ *Symmetric Deformation Region.*—The spectrum of liquid SO_2, consisting of a broad asymmetric feature at ca. 528 cm^{-1} ($w_{\frac{1}{2}} \sim 20$ cm^{-1}) on which is superimposed a sharp band at 521 cm^{-1} ($w_{\frac{1}{2}} \sim 3$—5 cm^{-1}), has been previously reported[19] but not interpreted. Increase in the concentration of dmso causes the feature at 521 cm^{-1} to disappear and the centre of the main band to shift from 528 to 532 cm^{-1}, together with a marked reduction in bandwidth (Figure 3). Further increase in concentration of dmso causes little discernible shift in the position of the band.

The second derivatives indicate that the spectra are structured with a number of underlying components. However, changes occur mainly in the SO_2-rich mixtures and the sharp band at 521 cm^{-1} precludes analysis of this region.

$v(SO)_{dmso}$ *Stretching Region.*—This region is well separated from other features of the SO_2-dmso spectrum. The nearest band at 953 cm^{-1} was previously attributed[12] to a methyl-rocking vibration of dmso. The baseline at both ends of the region is flat, and it is reasonable to assume that a flat baseline exists throughout.

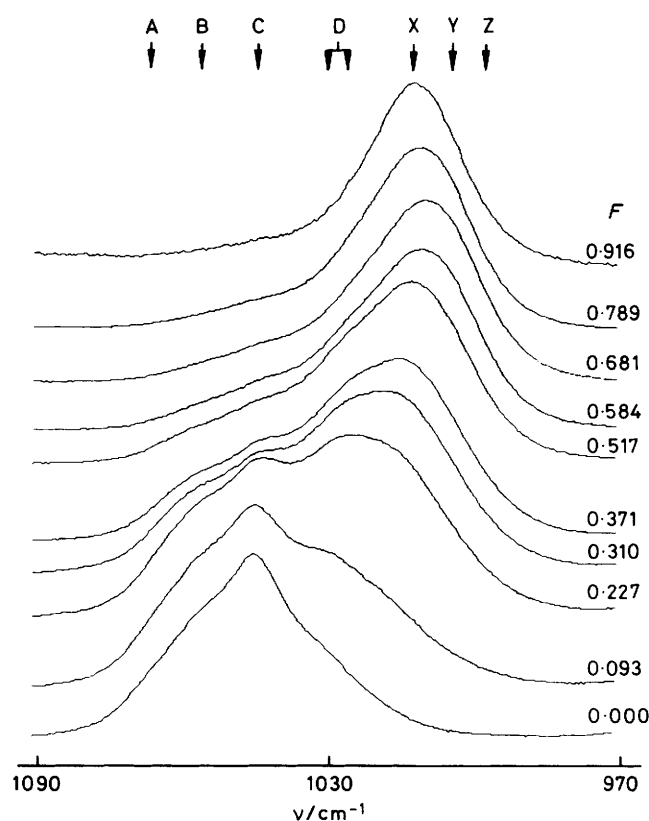Considerable changes occur in the spectra with changing

SO_2-dmso composition, and it is clear from Figure 4 that different component bands dominate at different compositions. Although the data presented in this paper are much better they are, nevertheless, consistent with our earlier observations[2,3] that the main feature due to solvent dmso (ca. 1 044 cm^{-1}) gives way to another maximum which shifts between 1 009 and 1 024 cm^{-1} as the SO_2 concentration increases. These changes in the spectra as SO_2 is added to dmso are entirely different from the vibrational spectra observed when dmso is diluted by an 'inert' solvent such as carbon tetrachloride.[17,20] On addition of CCl_4, dmso–cosolvent interaction was not detected and association between dmso molecules was being monitored.

The spectrum of the solvent dmso contains at least four underlying bands. Two, at 1 067 (A) and 1 057 cm^{-1} (B), appear on the high-frequency side of the maximum at 1 044 cm^{-1} (C). The fourth band (D), previously undetected in the Raman but reported as a weak feature in the i.r.,[17] produces an inflexion at ca. 1 029 cm^{-1} (D). Increase in F causes the intensities of bands A, B, and C to diminish and to be replaced by a broad feature 30—40 cm^{-1} lower in frequency. This new band is already a significant contributor to the spectrum at $F = 0.093$, but at $F > 0.227$ it has become the major contributor to the spectrum. Bands A, B, and C are still detectable at $F = 0.517$, but have effectively disappeared at $F = 0.584$. The broad feature, centred at ca. 1 024 cm^{-1} at $F = 0.227$, contains at least three components. As F is increased it shifts to lower frequency, ca. 1 009 cm^{-1} between $F = 0.5$ and 0.6, but reverts to higher frequency as the mixture becomes richer in SO_2; 1 012 cm^{-1} at $F = 0.916$. This behaviour matches that observed in the $v_1(SO_2)$ symmetric stretching region.

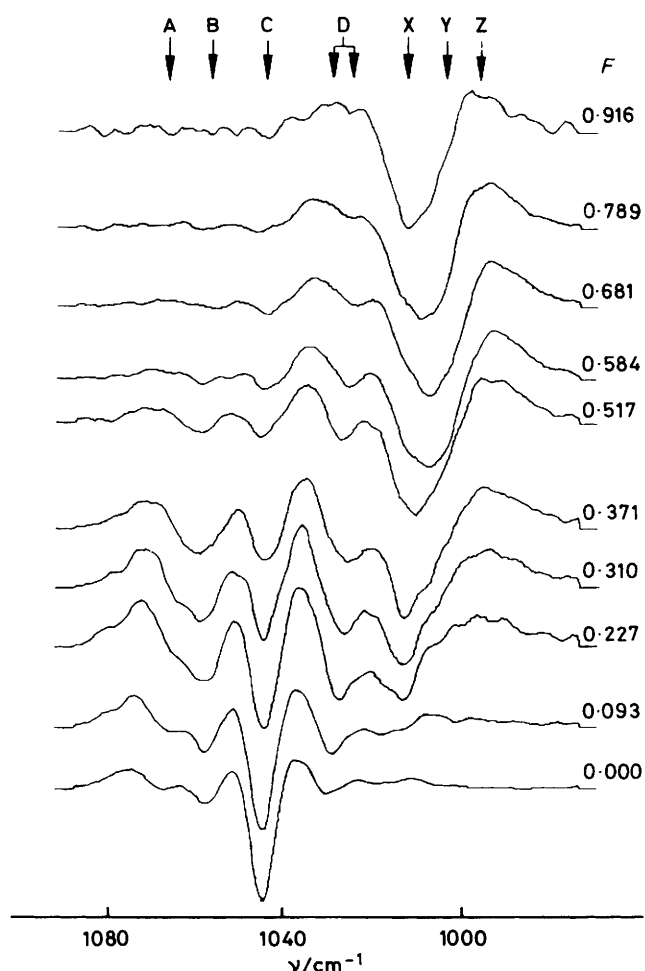The spectra of SO_2-rich mixtures consist of a number of very

Figure 5. Second derivative of the $\nu(SO)_{dmso}$ stretching region of the Raman spectra of SO_2–dmso mixtures at 293 K

Figure 6. The $\nu(SO)_{dmso}$ stretching region of the Raman spectra of SO_2–dmso mixtures at various temperatures for (a) $F = 0.52$, and (b) $F = 0.79$

closely spaced bands, three of which can be positively identified at 1 013 (X), 1 006 (Y), and 997 cm^{-1} (Z). Because these are separated by less than half of the width of the bands at half-height, computer resolution using VIPER is impracticable. Such close spacing of bands always results in fits with highly correlated band parameters.[21] It is the second derivatives of the $\nu(SO)_{dmso}$ stretching region, shown in Figure 5, from which the positions of the underlying components can be identified.

Band D at 1 029 cm^{-1} was not observed in the Raman until recently[20] although it has been noted as a weak feature in i.r. spectra of dmso.[17] It appears as a discrete feature on the profile on the second derivative with an intensity well above background noise, and is present in the spectra of all the mixtures at approximately the same relative intensity. There is also a small shift in its frequency, 1 029 to 1 025 cm^{-1}, as the SO_2 concentration is increased to $F = 0.5$; above $F = 0.52$ the band remains fixed at 1 025 cm^{-1}.

To establish the positions of bands, X, Y, and Z, it was necessary to apply the second-derivative treatment to spectra of the mixtures at both ambient and sub-ambient temperatures. Two of these bands, X and Y, can be identified by following the intensity changes of the second derivatives of the spectra of mixtures between $F = 0.2$ and 0.6 at 293 K (see Figure 5). Band Z is only positively identified in the second derivative of low-temperature SO_2-rich mixtures (Figures 6 and 7). Temperature reduction causes the bands to sharpen and the relative intensity of Z to increase. At corresponding temperatures the spectra of
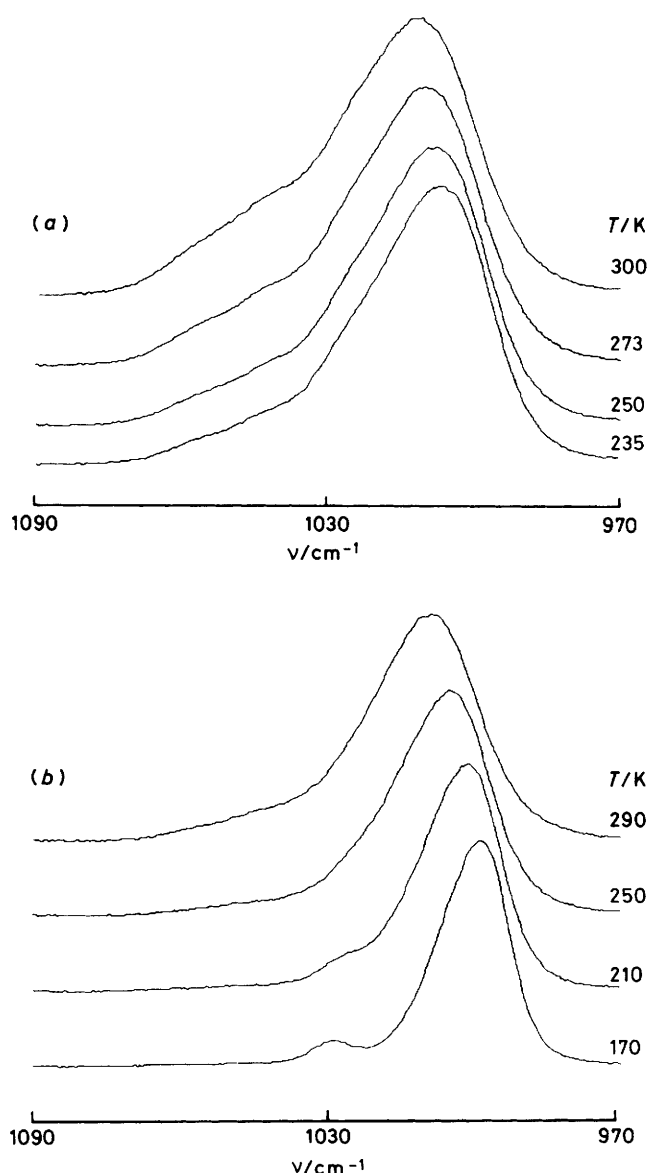
mixtures of $F = 0.310$, 0.517, 0.681, and 0.789 show a consistent trend in the variation of the relative intensities of X, Y, and Z. In the particular case of the sample with $F = 0.789$ the temperature could be reduced to 170 K without its solidification. The spectrum in Figure 6 indicates that the species attributable to Z dominates this mixture at low temperature. It should also be noted that, at $F = 0.789$ and 170 K, the band at 1 025 cm^{-1} (D) is seen as a separate feature because of the sharpening of band Z and the absence (or reduction) of the species attributable to bands X and Y.

Because they were likely contaminants spectra were obtained for dmso containing added water and dimethyl sulphide (dms). Liquid dms has a low-intensity band at 1 029 cm^{-1}, ca. 0.1% as intense as the $\nu(SO)_{dmso}$ feature. The assignment[22,23] of this to a methyl-rocking vibration is consistent with the similar assignment to band D at the same frequency in the dmso spectra. Addition of both dms and water up to a 5% level produced no changes in the spectra of dmso. Thus it is reasonable to assume that interferences due to these impurities can be ignored.
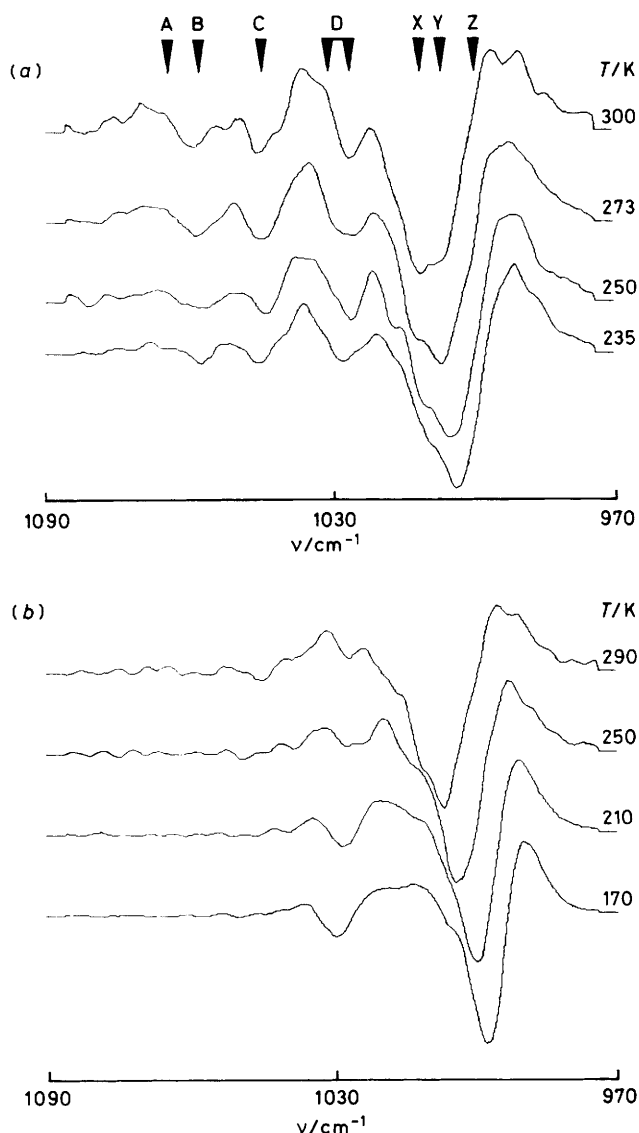
Figure 7. The second derivatives of the $\nu(SO)_{dmso}$ stretching region of the Raman spectra of SO_2–dmso mixtures at various temperatures for (a) $F = 0.52$, and (b) $F = 0.79$

Discussion

Many reports on the association of dmso have appeared in the literature. Early work [24] identified frequencies in the i.r. and Raman spectra of the liquid with skeletal vibrations. Definitive assignments were made by Horrocks and Cotton [12] who identified most of the 24 vibrations of dmso and presented a normal co-ordinate analysis. Spectra of dmso mixed with other solvents indicated that the bands assigned to the solvent were susceptible to the concentration of the added cosolvents. [25-27]

Figueroa *et al.*[25] suggested autoassociation of dmso involving a closed dimer and other more highly associated forms. Later Forel and Tranquille [17] substantially agreed with Horrocks and Cotton,[12] and concluded that dimers and higher aggregates exist but found no conclusive evidence for auto-association at concentrations <0.5 mol dm^{-3}. Their i.r. spectrum contained an intense peak at 1 058 cm^{-1} with shoulders at 1 042 and 1 022 cm^{-1}, and the band at 1 044 cm^{-1} in the Raman was declared to be a polarised feature with a depolarised shoulder at 1 058 cm^{-1}. Addition of CCl$_4$ caused the band at 1 042 cm^{-1} to disappear as another band appeared at

1 070 cm^{-1}. Claiming this to indicate the absence of auto-association Forel and Tranquille [17] assigned the band at 1 070 cm^{-1} to monomeric dmso. A small band in the i.r. at 1 022 cm^{-1} was left as an isolated feature after addition of CCl$_4$. Forel and Tranquille [17] attributed this to a methyl-rocking vibration $r(CH_3)$, unlike Figueroa *et al.*[25] who had previously assigned it to a closed dimer. Some support for the closed dimer assignment has been claimed by Sastry and Singh [20] in their Raman study of dmso–CCl$_4$ mixtures. They assigned the three bands at *ca.* 1 070, 1 058, and 1 040 cm^{-1} to the monomer, and the anti-symmetric and symmetric stretching modes of a closed-ring dimer respectively. They then claimed that the band at *ca.* 1 025 cm^{-1} was due to linearly associated polymers. We find this assignment dubious. Because of the way the intensities of the two bands at 1 058 and 1 040 cm^{-1} vary independently when dmso is diluted, these bands should not be ascribed to two different vibrations of the same dimeric species. Also it has been reported [20] that the band at *ca.* 1 025 cm^{-1} appears in the i.r. spectrum of gaseous dmso. If so, it seems inappropriate to ascribe it to a polymeric form of dmso.

Our results are in accord with an assignment of the band at 1 025 cm^{-1} (D) to the methyl rocking vibration. It appears in all the spectra in Figures 4—7, and is particularly well resolved in the low-temperature spectra of SO$_2$-rich samples. The frequency shift from 1 029 to 1 025 cm^{-1} which occurs with increase of SO$_2$ concentration is informative. Such a shift of the methyl-rocking vibration will be apparent only if a number of adducts, each with slightly different methyl-rocking frequencies, exist in equilibrium.

The relative intensities of bands A and B both increase with respect to band C on dilution of dmso with SO$_2$. This supports the assignment of band A to the dmso monomer, band B perhaps to a linear associated species, and the polarised band C to the symmetrical movement of a closed-ring dimer. If band B is a composite derived from all chain interactions its intensity would be expected to vary slightly with both temperature and composition as we observe.

The changes in the spectra with composition and temperature leave no doubt that a minimum of three bands, X, Y, and Z, must be included below 1 025 cm^{-1}. Band X is the dominant feature between $F = 0.1$ and 0.4 with the other bands as a shoulder. Between $F = 0.4$ and 0.7 band Y becomes important, but it is not the only feature present. At ambient temperatures band Z is present only at low intensity, but it becomes the dominant feature of the spectra of mixtures between $F = 0.6$ and 0.8 just above their freezing points. Based on the stoicheiometric compositions at which the bands X, Y, and Z manifest themselves we attribute them to SO$_2$–dmso adducts of 1:2, 1:1, and 2:1 stoicheiometry respectively. The phase diagram for the SO$_2$–dmso system presented in the following paper [13] clearly indicates the two adducts, 2SO$_2$·dmso and SO$_2$·dmso; these account respectively for bands Z and Y. No species of the appropriate composition was found in the phase diagram to correspond with band X which we attribute to the adduct SO$_2$·2dmso. However, band X dominates the Raman spectra of mixtures with $F < 0.5$ and we must associate it with the 1:2 species. The only satisfactory explanation is that SO$_2$·2dmso is stable in the liquid phase and unstable as a solid and therefore cannot be identified in the phase study.

To test the validity of our computer analysis we always aim to compare calculated second-derivative spectra derived from the resolved components obtained from VIPER curve fitting with the second derivatives of observed spectra.[14] The complexity of the spectra of the SO$_2$–dmso mixtures and the closeness of underlying components render curve resolution and an estim-ation of equilibrium constants between adducts impossible. However, we have provided alternative support to the identific-ation of bands X, Y, and Z, by the numerical analysis of spectra
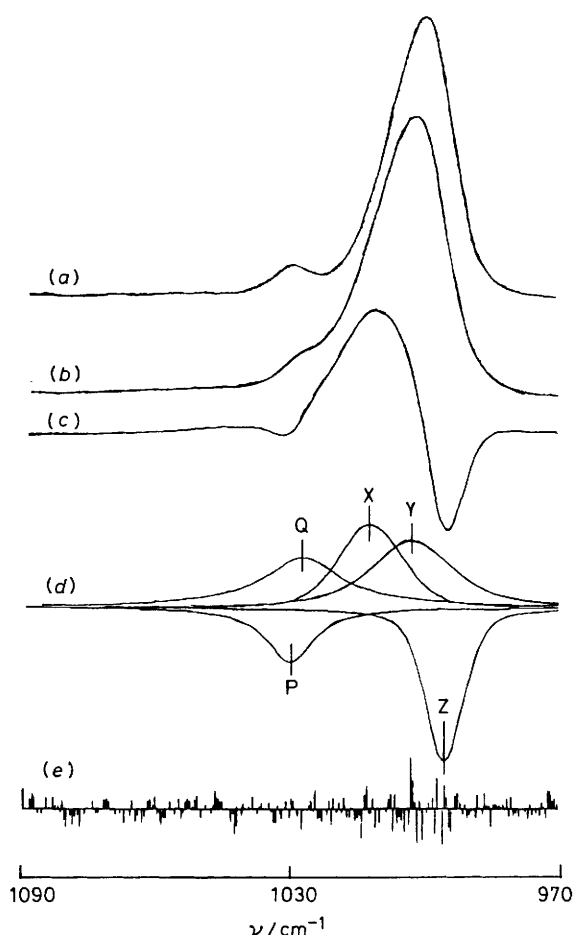
reduction of temperature. A VIPER band fit of this difference spectrum gives a result well within the noise level of the original spectrum. From the relative intensity changes of the X, Y, and Z components, the need to include them in the spectra is confirmed. Two closely spaced bands of low intensity, P and Q, opposite in sign, were used to account for the shift in frequency of the methyl rocking vibration (band D) which results from the change in the distribution of the component species when the temperature is lowered.

Acknowledgements

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Figure 8. VIPER fitting of a difference spectrum obtained from the subtraction of the $v(SO)_{dmso}$ region of the Raman spectra of a SO_2 dmso mixture with $F = 0.79$ at 170 and 210 K: (*a*) spectrum at 170 K, (*b*) spectrum at 210 K, (*c*) subtraction of (*b*) $-$ (*a*), (*d*) component bands fitted by VIPER to (*c*), (*e*) residuals ($\times$ 10), *i.e.*, difference between calculated spectum (*d*) and spectrum (*c*)

of mixtures with $F = 0.789$ at low temperatures. These spectra simplify to a two-band system consisting of the methyl-rocking feature D and a composite of the two bands Y and Z. Band fits using VIPER still give highly correlated band parameters for Y and Z, and the result is not necessarily unique, but the fitting process justifies the inclusion of two bands, in their correct positions under the main feature.

Recently we have developed another approach to support the results of numerical band-fitting. Here the numerical subtraction of two different spectra within a set is performed. The sample in Figure 8 shows the difference between the spectra of the sample with $F = 0.789$ at 170 and 210 K. This new difference profile emphasises the intensity changes of the underlying bands, caused by changes in species distribution on