

Raman spectral studies of solutions of alkali metal perchlorates in dimethyl sulfoxide and water

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Received April 19, 1984

This paper is dedicated to Professor Camille Sandorfy on the occasion of his 65th birthday

M. I. S. SASTRY and SURJIT SINGH. *Can. J. Chem.* **63**, 1351 (1985).

Raman spectra of solutions of alkali metal perchlorates in dimethyl sulfoxide (DMSO) in the Cl—O, C—S, and S=O stretching regions, as well as of perchlorates in aqueous solutions in the Cl—O stretching region are reported. The results are discussed in terms of half-bandwidths, relative intensities, and depolarization ratios. For H₂O the half-bandwidth of the Cl—O stretching band at $\sim 935\text{ cm}^{-1}$ is almost double the value in DMSO solutions. Solutions of perchlorates in DMSO show two symmetric bands in the Cl—O stretching region, whereas in aqueous solutions only one band is observed. The half-bandwidths in perchlorate solutions in DMSO for the C—S stretching band increase with increase in concentration of perchlorate compared to that of liquid DMSO. The band contours in the S=O stretching region in DMSO solutions also show significant changes. These observations are explained on the basis of formation of ion pairs of metal perchlorates in solutions of DMSO and ion hydrates in the case of aqueous solutions.

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On rapporte les spectres Raman de perchlorates de métaux alcalins en solution dans le diméthylsulfoxyde (DMSO) dans les régions d'élongation du Cl—O, du C—S et du S=O ainsi que ceux de solutions aqueuses de perchlorates dans la région d'élongation du Cl—O. On discute des résultats en fonction de la largeur à mi-hauteur des bandes, des intensités relatives et des rapports de dépolarisation. Dans l'eau, la largeur à mi-hauteur de la bande d'élongation du Cl—O à 935 cm^{-1} est à peu près le double de la valeur dans le DMSO. Les solutions de perchlorate dans le DMSO montrent deux bandes symétriques dans la région d'élongation du Cl—O alors qu'on n'en observe qu'une seule en solution aqueuse. La largeur à mi-hauteur de la bande d'élongation du C—S des solutions de perchlorate dans le DMSO augmente avec une augmentation de la concentration de perchlorate par rapport à celle du DMSO liquide. Les contours des bandes dans la région d'élongation du S=O dans les solutions de DMSO changent d'une façon importante. On explique ces observations par la formation de paires d'ions dans les perchlorates métalliques en solution dans le DMSO et par la formation d'hydrate d'ions dans le cas de solutions aqueuses.

[Traduit par le journal]

Introduction

In the past two decades vibrational spectral studies of electrolytes have attracted considerable attention. Several reports (1–13) on this subject have appeared, dealing with various aspects of aqueous and nonaqueous solutions of electrolytes, molten salts, effect on solvent vibrational bands in aqueous and non-aqueous solutions of electrolytes, etc. While studying the vibrational spectra of solutions of electrolytes several effects, such as ion solvation, ion association, as well as the effect of dissolved electrolytes on the vibrational spectra of the solvent bands, are considered. Ionic and molecular associates found in solutions are often short-lived and may have a well-defined identity on the vibrational time scale only. Since Raman spectra can be recorded for the solute and solvent bands simultaneously for the same concentration of the solution with varying photon count and other such parameters, this branch of vibrational spectroscopy has been widely used for the study of electrolyte solutions. Several papers have appeared on the studies of ion association by vibrational spectroscopy. Alkali metal perchlorates have not been found to show any detectable ion pairs in aqueous solutions (14). The perchlorate band is often used in Raman spectra as an internal standard because of an apparent inability of ClO₄ ions to form inner-sphere ion pairs with most cations. No definite evidence has been reported to indicate the splitting of the $\nu_3(f_2)$ band of ClO₄⁻ in dilute aqueous solutions. Metal perchlorates in matrix isolation spectra show pronounced splitting of the ν_3 band (14), indicating the formation of ion pairs. Raman spectral studies of aqueous metal chlorates show $\nu_3(e)$ doublets even in the spectra of dilute solutions, similar to the doublets in aqueous metal nitrate solutions (15–17). A possible explanation for the difference between the ν_3 region of

ClO₄⁻ (aq) and ClO₃⁻ (aq) is that the ClO₄⁻ (aq) is less strongly hydrogen bonded to the water (1). Symons and Waddington (18) studied the ir spectra of aqueous perchlorate solutions and assigned a new band at a frequency higher than that of the stretching modes of pure water to the ClO₄⁻ . . . H₂O complex and computed a hydration number of 4 from intensity measurements. Sodium perchlorate in acetonitrile, tetrahydrofuran, and pyridine was found to show ion association by ²³Na nmr chemical shift and vibrational spectral studies (19). Similarly lithium, sodium, and magnesium perchlorates in acetone (20, 21), and lithium and sodium perchlorates in pyridine (22) show splittings. Definite support for the presence of ion pairs in solutions comes from analogous splittings observed in matrices (14) and crystalline perchlorate complexes (23).

All the above studies on vibrational spectra of solutions of ClO₄⁻ are confined to the splitting of the $\nu_3(f_2)$ Cl—O stretching vibrational band. A survey of the perchlorate vibrations under *T_d*, *C_{3v}*, and *C_{2v}* symmetries shows that for an equilibrium between free perchlorates (*T_d*) and singly (*C_{3v}*) or doubly (*C_{2v}*) associated perchlorates, additional bands should also be observed in the totally symmetric Cl—O stretching (*A₁*) region. In addition to these effects, the solvent bands may also show certain changes in the band profiles, in case the solvent structure changes during the equilibrium. We have recently reported results on the Raman spectral studies of the structure of DMSO and the effect of dilution when its solutions in water and CCl₄ (24, 25) are considered. We report here Raman spectra of solutions of alkali metal perchlorates in DMSO with a view to understanding the ion association and ion–solvent interactions. For comparison, spectra of aqueous solutions of perchlorates in the Cl—O stretching region are also included.

Experimental

Analar DMSO (Merck) was purified by vacuum distillation and kept on 4A Linde sieves. Sodium perchlorate monohydrate (Fluka), lithium perchlorate monohydrate (BDH), and potassium perchlorate (Reidel) were used as such without further purification. They were kept in a desiccator over calcium chloride. Vacuum distilled DMSO, and triple distilled water were used for preparation of solutions. The solutions were separately prepared in 25-mL standard flasks.

Raman spectral measurements were made at room temperature, on a Cary 82 laser Raman spectrometer equipped with a Spectra Physics argon ion laser (Model 165), with the sample contained in a glass cell. All the spectra were recorded employing a 514.5-nm exciting line, varying in the range 300–500 mW power. A 90° scattering geometry was employed. Slit widths of 1.2–2 cm⁻¹ were used for different concentrations, with 2–5 s time constant. Spectra were recorded with 0.10 cm⁻¹/s monochromator speed. Both parallel and perpendicularly polarized spectra were recorded at the same instrumental settings. The spectra are reproducible to within ±1 cm⁻¹.

Results and discussion

Raman spectra of solutions of lithium, sodium, and potassium perchlorates were recorded in solutions of varying concentrations in DMSO and water. The results are presented below.

Cl—O stretching region

In Figs. 1 to 4 are given Raman spectra of DMSO and solutions of metal perchlorates in the 900–1100 cm⁻¹ region. Pure DMSO shows band due to CH₃ rocking at ~953 cm⁻¹. The ClO₄⁻ ion in its *T_d* symmetry is known (2) to show a totally symmetric Raman band at ~935 cm⁻¹. In Figs. 2 to 4 perchlorates are found to show a sharp band in this region. In addition to this strong and sharp band, a low frequency band is observed in all the solutions of perchlorates in DMSO at ~910 cm⁻¹. Raman spectra of aqueous solutions of lithium and sodium perchlorates given in Figs. 5 and 6 do not show low frequency bands as observed in the respective solutions in DMSO. Matrix isolation studies on metal perchlorates were carried out by Smyrl and Devlin (14). Perchlorates when deposited in argon matrices only have ion pairs with definite dipole moments. Such ion pairs are assumed to have the perchlorate ions in *C_{3v}* symmetry, in contrast to free perchlorate ions which have *T_d* symmetry. In a system where both free perchlorate ions as well as their ion pairs are present, it is expected to observe separate bands because of totally symmetric Cl—O stretchings for the free ClO₄⁻ ion under the *T_d* symmetry, as well as for the ion-paired ClO₄⁻ ion under the *C_{3v}* symmetry. The low frequency band at ~910 cm⁻¹ may be assigned to the totally symmetric stretching vibration of the ion-paired ClO₄⁻. Weak bands in the ir spectra of matrix-isolated perchlorates have been reported in this region by Smyrl and Devlin (14). Neither of the two bands at ~910 cm⁻¹ and ~935 cm⁻¹ are shown in the Raman spectra in the perpendicular polarized mode. This shows that both the bands are totally symmetric. The lower frequency Cl—O stretching band was reported in the Raman spectra of perchlorates in acetonitrile, THF, and pyridine by Greenberg and Popov (19), and in acetone by James and Mayes (21), in the figures included in these reports, without giving any proper assignments for such bands. However, appearance of a weak band in this region in the matrix-isolated ir spectra of perchlorates may justify the assignment of this band to the ion-paired perchlorates. In the early reports (19, 21), components of the main Cl—O stretching band contour at frequencies higher than the 935 cm⁻¹ band are assigned to ion pairs. Since the Cl—(OH) stretching band in

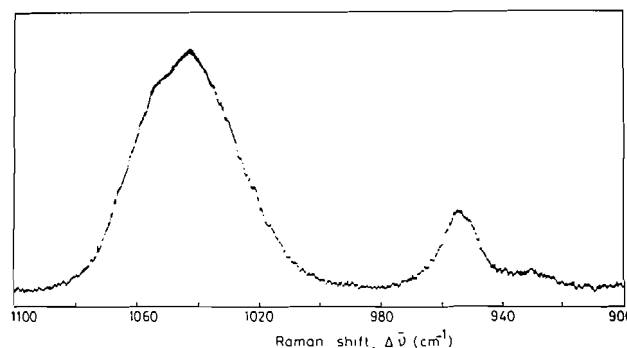


FIG. 1. S=O stretching band in Raman spectra of pure DMSO (*I_{||}*).

HClO₄ is assigned to the 734 cm⁻¹ band (26, 27), which is lower than the 935 cm⁻¹ band, as an analogy we believe the Cl—(OM⁺) stretching should be assigned to the lower frequency band at ~910 cm⁻¹ as reported in the present work. As mentioned above, in aqueous solutions of perchlorates no band is seen in this region. This is not surprising as ion pairs cannot be formed in aqueous solutions of perchlorates because of the greater possibility of hydration of M⁺ and ClO₄⁻ ions (1, 18). In Tables 1 and 2, spectral parameters of the Cl—O stretching bands in terms of band positions, half-bandwidths, and band heights are given for the various systems considered. The ratios of the intensities of the high frequency band to the low frequency band are shown in the last columns of Table 1. It is noticed that positions of the two bands do not change from system to system and from one concentration to another. The intensity ratio is found to decrease with higher concentrations of perchlorate, indicating greater possibility of association at higher perchlorate concentrations. It is noticed (Tables 1 and 2) that the half-bandwidth of the Cl—O stretching band at ~935 cm⁻¹ is about twice as great when ClO₄⁻ is in aqueous solution compared to when in DMSO solutions. For example, for a 1.0 M solution of sodium perchlorate in DMSO the Δ*v*_{1/2} is 4.0 cm⁻¹, whereas for the same concentration of sodium perchlorate in aqueous solution the value is found to be 8.5 cm⁻¹. It is further noticed that the half-bandwidth increases considerably with increasing concentration of perchlorate in aqueous solutions (varying from 8.5 cm⁻¹ for a 1.0 M solution to 14.5 cm⁻¹ for a 5.0 M solution). These observations support the possibility of hydration of ClO₄⁻ as suggested by Symons and Waddington (18), though the broadening of the Cl—O stretching bands can also be explained in part by the dynamics of the spherical perchlorate ions in aqueous solutions. Dean and Wilkinson have recently reported (28) that the *A₁* stretching bands for SO₄²⁻, WO₄²⁻, and MoO₄²⁻ ions in aqueous solutions shift to higher frequencies with increasing concentrations of the solutions. We have obtained similar results in sodium perchlorate solutions: the Cl—O stretching band is found to shift from 933.5 cm⁻¹ for a 1 M solution to 936 cm⁻¹ for a 5 M solution. In the case of LiClO₄, however, no significant shift is observed. The *v*₀ value extrapolated to infinite dilution is approximately 933.5 cm⁻¹ in both cases.

S=O Stretching region

Figure 1 shows the band contour for the S=O stretching mode of pure liquid DMSO. In earlier publications from this group (24, 25) it was shown that this band is made up of at least four bands at ~1070 cm⁻¹, ~1058 cm⁻¹, ~1040 cm⁻¹, and ~1025 cm⁻¹. It was suggested (25) that the high frequency

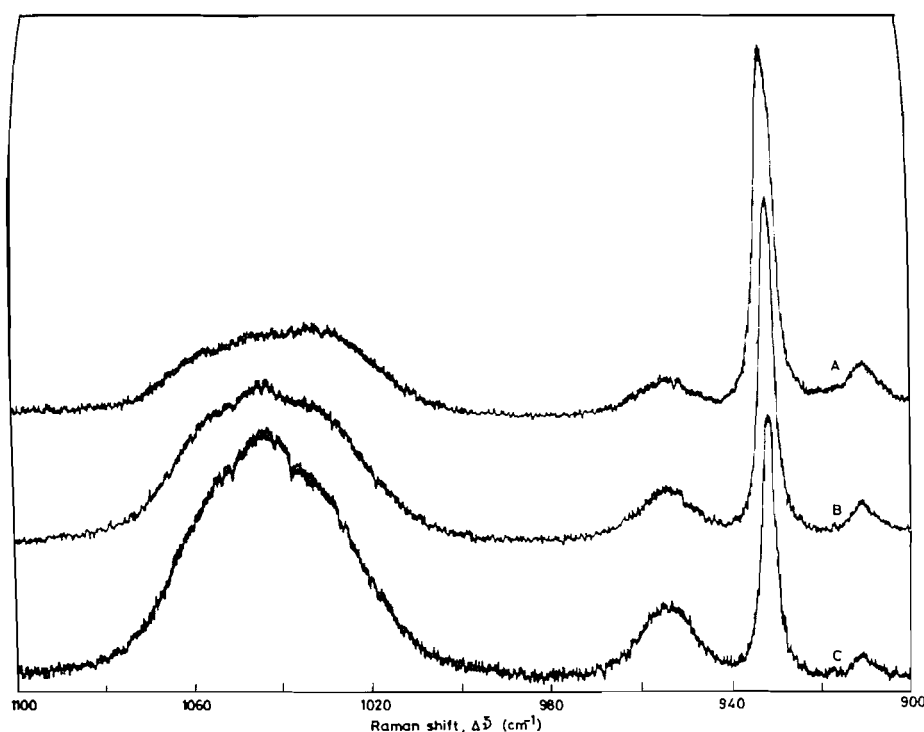


FIG. 2. S=O and Cl—O stretching bands in Raman spectra of solutions of lithium perchlorate in DMSO (I_{\parallel}) with concentrations: A, 2.0 *M*; B, 1.0 *M*; C, 0.5 *M*.

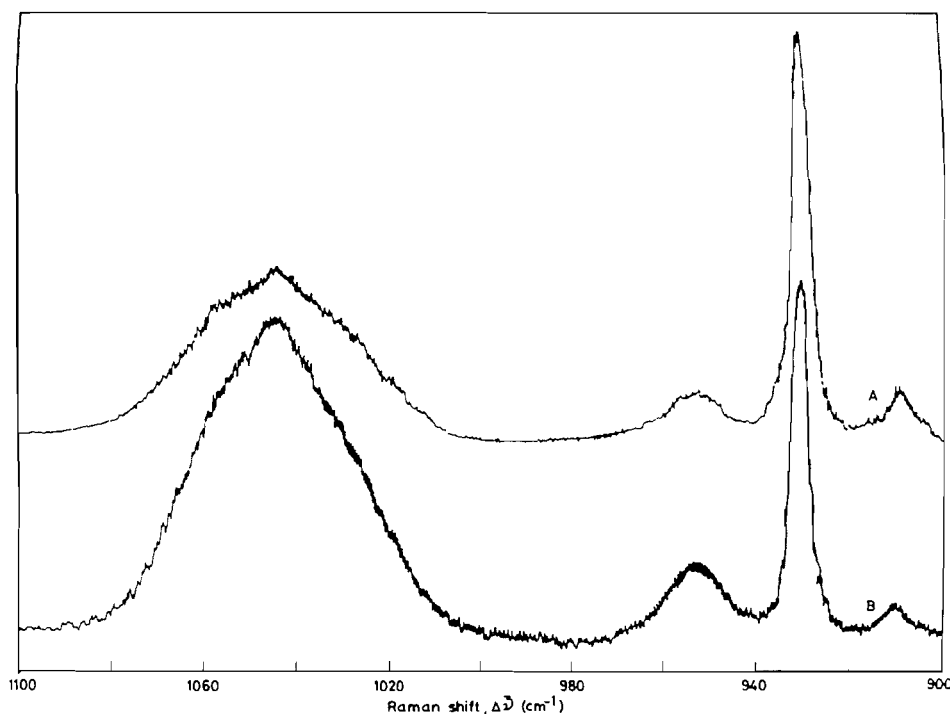


FIG. 3. S=O and Cl—O stretching bands in Raman spectra of solutions of sodium perchlorate in DMSO (I_{\parallel}) with concentrations: A, 1.0; B, 0.5 *M*.

band belongs to free S=O stretching, whereas the low frequency bands at $\sim 1058 \text{ cm}^{-1}$ and $\sim 1040 \text{ cm}^{-1}$ belong to a cyclic dimer and at $\sim 1025 \text{ cm}^{-1}$ to a linear dimer and other open-chain polymers. Addition of perchlorates clearly shows perturbation in the structure of the S=O stretching band (Figs. 2–4). The half-bandwidth is found to increase with the addition of perchlorates. The increase is of the order of 10–20% for 1.5

molar solutions of perchlorates. It is also noticed that the relative intensity of the low frequency band at $\sim 1025 \text{ cm}^{-1}$, with respect to higher frequency bands, increases considerably with increasing concentration of perchlorates. This may well indicate the presence of ion pairs and the structure making character of perchlorates for liquid DMSO. If the ions were to be solvated by DMSO one would expect structure breaking of

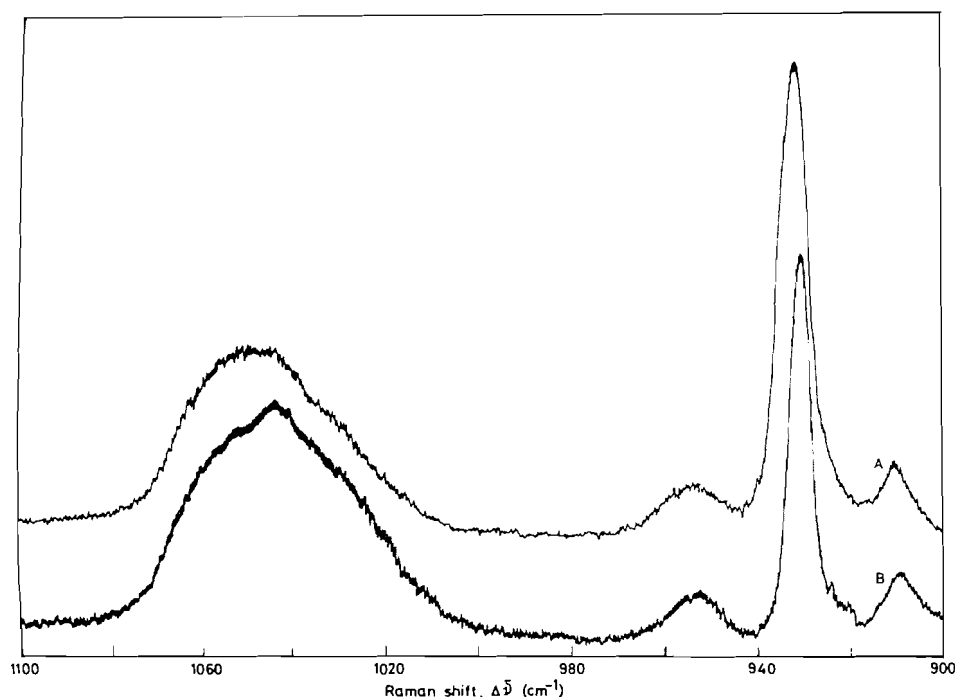


FIG. 4. S=O and Cl—O stretching bands in Raman spectra of solutions of potassium perchlorate in DMSO (I_{ij}) with concentrations: A, 2.0 M; B, 1.0 M.

TABLE 1. Raman spectral parameters for the Cl—O stretching band of alkali metal perchlorates in DMSO

System	Concentration (M)	$\bar{\nu}$ (cm ⁻¹)	$\Delta\bar{\nu}_{1/2}$ (cm ⁻¹)	Band heights, I	$A = I \times \Delta\bar{\nu}_{1/2}$	I_{935}/I_{910}	A_{935}/A_{910}
LiClO ₄	0.5	932.0	4.0	5.50	22.0	15.71	11.89
		911.5	5.0	0.35	1.85		
	1.0	932.0	4.0	7.10	28.4	11.83	8.61
		911.0	5.5	0.60	3.3		
	2.0	931.5	5.0	7.50	37.5	10.00	7.14
		911.0	7.0	0.75	5.25		
NaClO ₄	0.5	931.0	4.0	7.25	29.0	14.50	9.67
		910.5	6.0	0.50	3.0		
	1.0	931.5	4.0	8.40	33.6	9.33	6.22
		910.5	6.0	0.90	5.4		
	1.5	932.0	5.0	7.30	36.5	9.13	7.60
		910.5	6.0	0.80	4.8		
KClO ₄	1.0	931.0	5.0	7.70	38.5	7.33	6.11
		910.0	6.0	1.05	6.3		
	2.0	933.0	5.0	7.8	39.0	8.66	4.33
		911.0	10.0	0.9	9.0		

liquid DMSO leading to decrease of intensity of the low frequency band ($\sim 1025 \text{ cm}^{-1}$) which is assigned to various associated species of DMSO. In all the perchlorate solutions, concentrations more than 1.5 mol L^{-1} could not be considered because of the solubility limitation, except for KClO₄, where the spectra were also recorded for a 2 M solution. In the case of a 2 M solution of potassium perchlorate in DMSO it is further observed that the relative intensities of the 1040 cm^{-1} and $\sim 1050 \text{ cm}^{-1}$ components are nearly similar, unlike the case in dilute solutions, as well as in pure DMSO, where the relative intensity of the $\sim 1040 \text{ cm}^{-1}$ band is slightly higher than that of the $\sim 1050 \text{ cm}^{-1}$ band. This effect may be brought about by the lowering of the concentration of cyclic dimers and

TABLE 2. Raman spectral parameters for alkali metal perchlorates in water in the Cl—O stretching region

System	Concentration	$\bar{\nu}$ (cm ⁻¹)	$\Delta\bar{\nu}_{1/2}$ (cm ⁻¹)
LiClO ₄	1.0	933.5	9.0
	2.0	933.5	8.5
	3.0	934.0	11.0
	4.0	933.0	10.0
NaClO ₄	1.0	933.5	8.5
	2.0	934.5	9.5
	3.0	935.0	11.5
	4.0	935.0	13.0
	5.0	936.0	14.5

TABLE 3. Raman spectral parameters for DMSO – perchlorate systems in the C—S stretching region

System	Concentration (mol)	$\bar{\nu}$ (cm ⁻¹)	$\Delta\bar{\nu}_{1/2}$ (cm ⁻¹)	I_{\parallel}	I_{\perp}	$\rho = I_{\perp}/I_{\parallel}$
Pure DMSO		669.0	13.0	8.0	0.70	0.09
		698.5	15.0	1.85	1.20	0.65
LiClO ₄ + DMSO	0.5	670.0	13.0	7.30	0.55	0.08
		699.5	18.0	2.00	1.03	0.51
	1.0	671.0	18.0	9.40	0.90	0.09
		701.0	20.0	3.05	1.65	0.54
	2.0	673.5	18.0	8.30	0.75	0.09
		705.5	19.0	2.05	1.30	0.63
NaClO ₄ + DMSO	0.5	670.0	15.0	8.80	0.80	0.09
		700.0	17.0	2.55	1.50	0.59
	1.0	670.5	15.0	8.10	0.70	0.09
		700.0	18.0	2.00	1.30	0.65
	1.5	673.0	16.0	8.10	0.60	0.07
		702.0	19.0	2.10	1.15	0.55
KClO ₄ + DMSO	1.0	670.0	15.0	8.50	0.70	0.08
		699.5	17.0	2.35	1.35	0.57
	2.0	672.5	15.0	7.70	0.83	0.11
		702.0	16.0	1.90	1.15	0.61

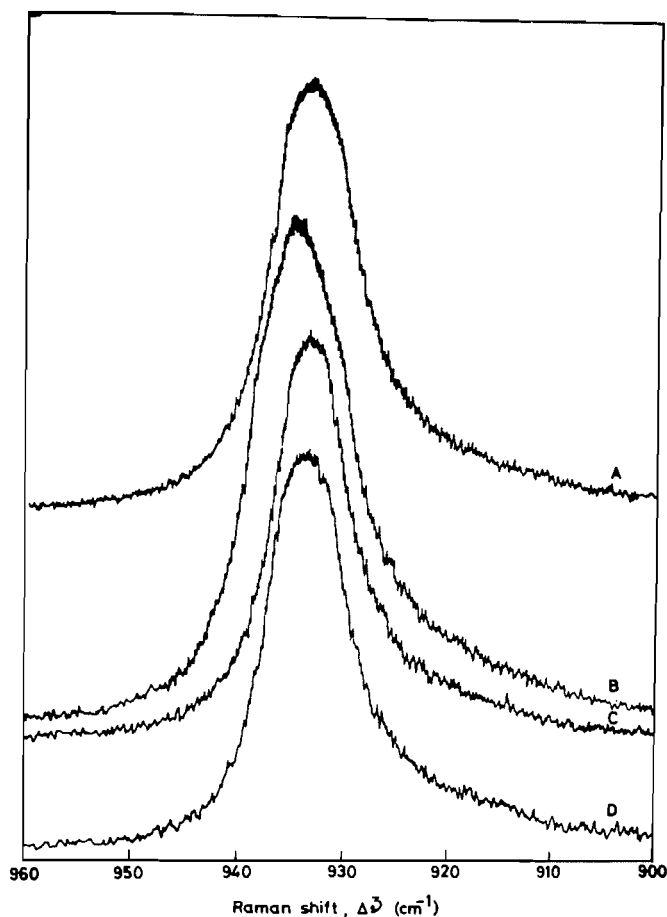


FIG. 5. Cl—O stretching bands in Raman spectra of aqueous solutions of lithium perchlorate (I_{\parallel}) with concentrations: A, 4.0 M; B, 3.0 M; C, 2.0 M; D, 1.0 M.

free DMSO molecules with increasing concentration of perchlorates, which is in conformity with the above observations on corresponding increase in intensity of the low frequency component of the S=O stretching band.

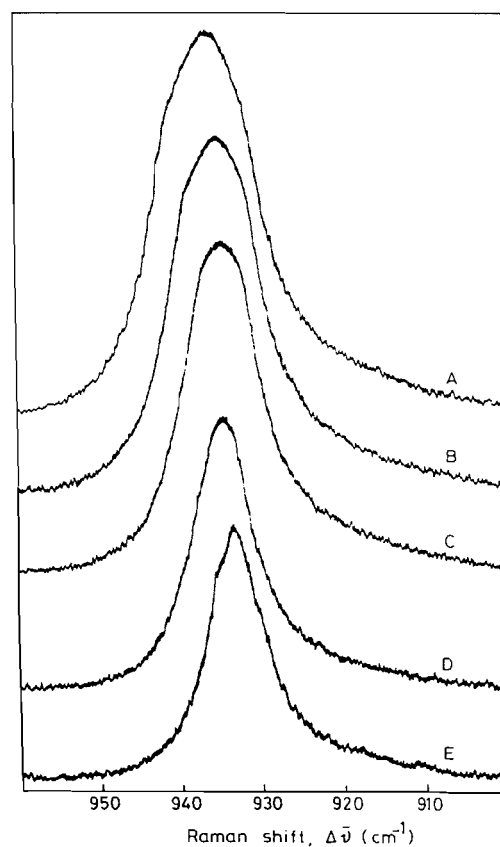


FIG. 6. Cl—O stretching bands in Raman spectra of aqueous solutions of sodium perchlorate (I_{\parallel}) with concentrations: A, 5.0 M; B, 4.0 M; C, 3.0 M; D, 2.0 M; E, 1.0 M.

C—S Stretching region

The spectral parameters of the C—S symmetric and asymmetric stretching bands are given in Table 3. The depolarization ratios for the low frequency band are in the range of 0.08 to 0.10; whereas for the high frequency band they range between 0.50 and 0.65. It is noticed that the half-bandwidth of

the high frequency band increases with increasing concentration of perchlorates, being 15 cm^{-1} for pure DMSO and nearly 20 cm^{-1} for a 1 M solution of LiClO_4 . Similar increases are observed in the half-bandwidths for other solutions as well. The low frequency symmetric stretching band for solutions of LiClO_4 shows a considerable increase in the bandwidth, whereas those for the solutions of potassium and sodium perchlorates have similar bandwidths for the concentration range of $0.5\text{--}2\text{ M}$, which is about 2 cm^{-1} higher than the pure DMSO band. Since the spectral parameters were different for different concentrations for recording the Raman spectra, the intensities of the bands cannot be accurately compared for the same system over a range of concentrations. However, the variation in half-bandwidths as well as depolarization ratios with varying concentrations of perchlorates definitely shows reordering of the DMSO molecules in the perchlorate solutions, when compared with pure liquid DMSO. Fourier transform of these bands may be helpful in determining the vibrational relaxation times, which may give extra support to the proposed structure-making properties of perchlorates for liquid DMSO. Work in this direction is under progress and will be published elsewhere.

Conclusions

Raman spectra of perchlorate solutions in DMSO suggest the presence of ion pairs in the solutions of DMSO on the basis of the Cl--O stretching bands. The band contours in the S=O stretching region also show significant changes. The bands in the C--S stretching region show increase in the half-bandwidths, and decrease in the depolarization ratio of the higher frequency asymmetric stretching bands. Raman spectra of aqueous perchlorate solutions do not show the low frequency Cl--O stretching band due to ion-paired ClO_4^- species with the C_{3v} point group observed in the case of solutions in DMSO, which is in accordance with earlier conclusions that ClO_4^- ions do not show evidence of ion association in aqueous solutions.

Acknowledgements

One of us (M.I.S.S) is grateful to I.I.T., Madras, for providing a Research Fellowship. This work was carried out under a joint Project from the Volkswagen Foundation with Prof. W.A.P. Luck of Uni-Marburg (W.-Germany), which is gratefully acknowledged.

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