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Proton conduction in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$: a Raman spectral study

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Abstract. The Raman spectra of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ under small DC electric fields (20, 30, 40 and 50 V) have been obtained in order to study the conduction mechanism and group vibrations for this compound. New bands have been observed at 1680 and 773 cm^{-1} owing to the formation of H_3O^+ during electrolysis. With an increase in voltage and time the stretching bands of water broaden and finally coalesce into a single band. A slight reduction in the intensity of the bending mode of water (1605 cm^{-1}) is also noticed. These are due to the polarizability changes induced by the proton movement along the O—H . . . O bond, reorientation of the bonds and subsequent distortion of the lattice.

1. Introduction

Raman investigations under low DC electric fields are a new technique used to understand the mechanism of proton conduction (Chandra *et al* 1986, 1987, Rajagopal *et al* 1989). Lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), a well known proton conductor, has been studied by various methods in order to determine the nature of conduction in this compound (Van Beek 1963, 1964, Thomas and Clarke 1969). The reported Raman and IR spectra deal mainly with the vibrations of the water molecule in it (Janik *et al* 1971, Price and Stuart 1973, Hayward and Schiffer 1976, Jungermann 1977, Lang and Claus 1983). In the present work, Raman spectra of a pressed pellet of the sample subjected to low electric fields are reported.

2. Experimental details

Commercially available AR grade $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ has been used for the study. Raman spectra were obtained using a Spex Ramalog 1401 double monochromator. The 514.5 nm green line from an Ar^+ laser was used as the excitation source. Electrodes are connected over silver paint to the opposite sides of the cylindrical pellet. The pellet (diameter, 10 mm; thickness, 1.5 mm) was prepared by pressing the sample with a pressure of 20 ton. The remaining curved portions are cut off and flattened as shown in figure 1.

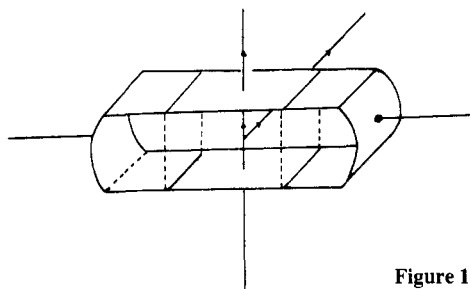


Figure 1. Sample illumination geometry.

The laser beam was directed into the sample perpendicular to the direction of the electric field (20, 30, 40 and 50 V). Spectra were obtained by directing the laser beam near the cathode and then at the anode. Spectra at different intervals of time (2, 4, 6 and 8 h) were studied, after the application of the field.

3. Results and discussion

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic system with the space group $P2_1 (C_2^2)$, $Z = 2$ (Smith *et al* 1968). The observed spectral data and band assignments are given in table 1. The Raman spectrum in the absence of an electric field is reproduced in figure 2, spectrum A.

The shifting of the ν_1 band of the SO_4^{2-} ion to a high frequency in the Raman spectrum (1001 cm^{-1}) and its activity in the IR spectrum (1010 cm^{-1}) show that the tetrahedron has suffered considerable distortion. The complete lifting of the degeneracy of the ν_3 mode in the Raman spectrum and its partial removal in the IR spectrum also support this argument. This result is contrary to the S—O bond length of 1.472 \AA observed from neutron diffraction studies (Smith *et al* 1968), which is close to the free-state value. The water bands observed are in agreement with earlier studies (Price and Stuart 1973, Hayward and Schiffer 1976, Lang and Claus 1983).

The bands in the low-frequency region (below 400 cm^{-1}) are assigned on the basis of the following.

(i) The compound contains two types of Li atom (Smith *et al* 1968, Jungermann 1977), namely Li(1) and Li(2), the Li(1) being attached to the oxygen atom of SO_4^{2-} , and the Li(2) to the oxygen atom of the water molecule.

(ii) The translational and librational modes of the SO_4^{2-} ion fall in this region with translational modes on the lower side, usually with higher intensities (Carter 1976).

Under the application of the electric field (figure 2, spectra B and C) the following changes have been observed.

(i) A new band appears at 773 cm^{-1} , the intensity of which increases with increasing voltage and time (figure 3(a)).

(ii) An additional band (1680 cm^{-1}) is observed in the bending region of water about 6–8 h after the application of the field. This is more prominent at higher voltages.

(iii) As time proceeds, the stretching region of water broadens and finally the bands at 3500 and 3448 cm^{-1} coalesce into a single broad band. This is more pronounced near the cathode end.

Table 1. Observed spectral data and band assignments of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{D}_2\text{O})$. The relative intensities are indicated as follows: vs, very strong; s, strong; m, medium; br, broad; w, weak; vw, very weak; sh, shoulder.

Wavenumber (cm^{-1})				
Raman		IR		Assignment
H_2O	D_2O	H_2O	D_2O	
73 w	73 w			t SO_4^{2-}
113 s	113 m			
171 m	171 m	235 vw	235 vw	
205 w	205 w	300 w	290 vw	l SO_4^{2-}
391 m	391 m	350 w	350 w	t Li(1)-O
418 w		415 w		t Li(2)-O
465 w	465 w	450 w	450 w	
486 s	486 m		470 sh	$\nu_2 \text{SO}_4^{2-}$
635 vs	635 s	600 m	600 m	$\nu_4 \text{SO}_4^{2-}$
697 w		640 s	640 s	
794 w, br	555 vw			1 H_2O
922 w				$2\nu_2 \text{SO}_4^{2-}$
1006 vs	1006 vs	1010 w		$\nu_1 \text{SO}_4^{2-}$
1101 vs	1101 s	1110 vs	1110 vs	
1119 s	1120 s	1170 sh	1170 sh	$\nu_3 \text{SO}_4^{2-}$
1147 vs	1147 s			
1176 vs	1176 m			
1605 br	1216 w	1610 s	1200 vw	$\nu_2 \text{H}_2\text{O}$
3448 br	2550 w, br	3400 —	2600 m, br	$\nu_1 \text{H}_2\text{O}$
		3650 s, br		
3500 w, br	2622 w, br		2630 m, br	$\nu_3 \text{H}_2\text{O}$

(iv) The intensity of the bending mode of H_2O (1605 cm^{-1}) shows a slight decrease with increasing applied voltage and time (figure 3(b)).

The water molecules in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ are weakly hydrogen bonded (O—H . . . O distances, 2.86 and 2.95 Å), weaker than that in the fast proton conductor ice (Hirahara and Murakami 1956, Smith *et al* 1968). Such a loose-packed structure favours proton movement from one end of a chain to another by the Grotthuss mechanism (cooperative proton transfer) (Glasser 1975, Colombari and Novak 1988). During the process, after the first proton jump along the O—H . . . O bond, it is necessary that the bond should undergo a reorientation motion in order to facilitate further proton transfer along the chain, as explained by Thomas and Clarke (1969).

From the appearance of the new band at 773 cm^{-1} , it is inferred that the H_3O^+ ion is formed during electrolysis (Chandra *et al* 1987, Kreuer 1988). The intensity dependence of this band shows that, as the voltage and time increase, the production rate of H_3O^+ increases. The additional band appearing (1680 cm^{-1}) in the bending region of water may also be due to the formation of H_3O^+ . This corresponds to the bending mode of H_3O^+ (Pham-Thi and Colombari 1985). However, the stretching vibrations of H_3O^+ , which are expected just below the stretching modes of H_2O , are not observed. They might have become superimposed on the broad stretching bands of H_2O .

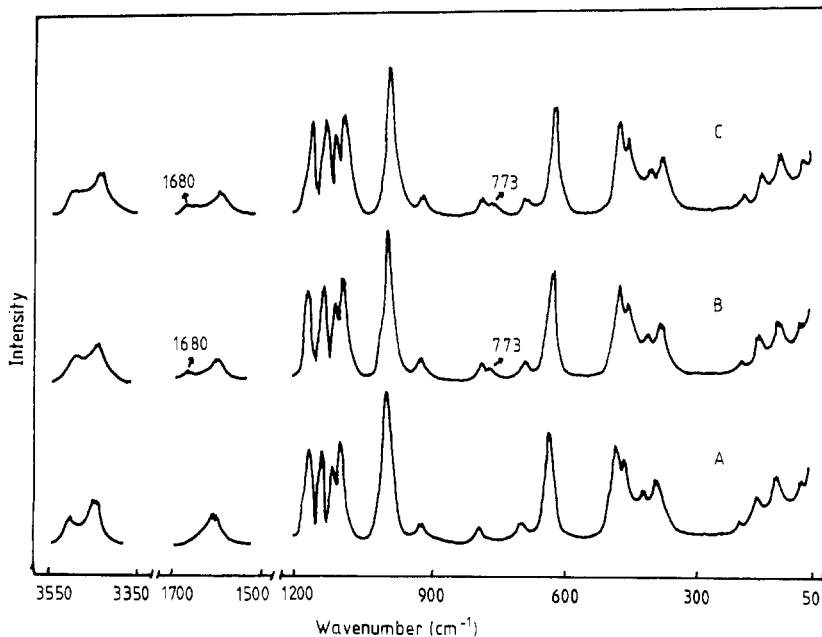


Figure 2. Raman spectra of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$: spectrum A, without a field; spectrum B with a 30 V field (cathode end); spectrum C with a 30 V field (anode end).

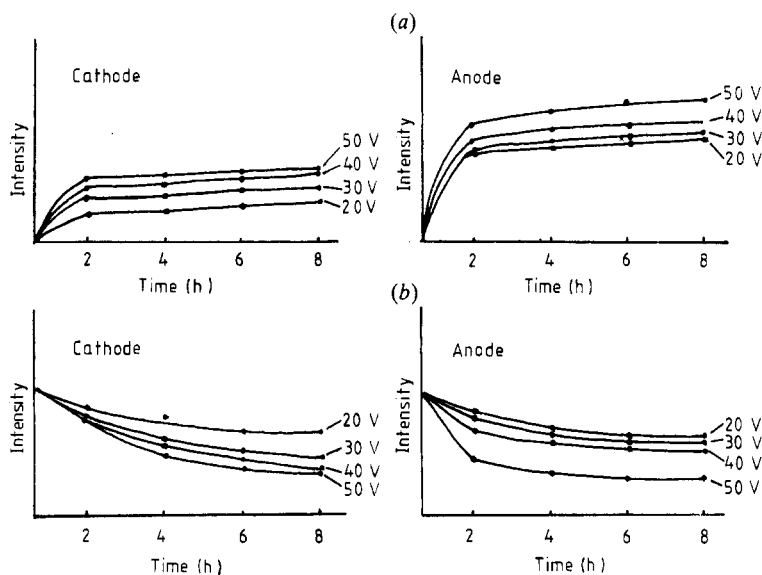


Figure 3. Variation in intensity (arbitrary units) with time for different applied voltages: (a) 773 cm^{-1} band; (b) 1605 cm^{-1} band.

The proton movement along the $\text{O}-\text{H} \dots \text{O}$ bonds is expected to induce polarizability changes. Further, the reorientation motion of the bonds can also distort its polarizability. The electric quadrupole interaction studies of $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ by Ketudat

and Pound (1957) revealed the presence of hindered rotation of water molecules at room temperature. The observed slight reduction in intensity of the bending mode of H_2O (1605 cm^{-1}) may be due to these net polarizability changes during the proton transport and reorientational process. The intensity decrease of this band with increasing voltage and time indicates a continuous increase in disorder.

As the applied voltage and time increase, it is observed that the stretching modes of H_2O broaden and finally coalesce into a single band. This is due to the highly disordered structure, resulting from the proton movement along the $\text{O}-\text{H} \dots \text{O}$ bonds and reorientation motion of water molecules. Colombari *et al* (1987) observed the collapse of external modes due to reorientation and subsequent disordering of HSO_4^- ions in CsHSO_4 .

The mobility of protons through hydrogen bonds is possible without changing the overall symmetry, although distortions are also possible (Colombari *et al* 1985). The observed time dependence of the intensity of the bands indicates that the site symmetry of the ion is not destroyed, even though the crystal suffers considerable distortion during the electrolysis.

In pressed pellets, effects due to surface conduction cannot be neglected. Hence the changes in conductivity may not be completely due to the bulk. Work on single crystals and deuterated samples which is expected to provide more information about the conduction mechanism is in progress.

4. Conclusions

(i) The appearance of new bands at 773 and 1680 cm^{-1} is due to the formation of H_3O^+ ions during electrolysis.

(ii) The coalescing of the stretching modes of water is due to the increased structural disorder and reorientation motion of water molecules.

(iii) The intensity dependence of the ν_2 band of H_2O (1605 cm^{-1}) on voltage and time reveals the polarizability changes induced by the proton movement along the $\text{O}-\text{H} \dots \text{O}$ bond and reorientation motion of water molecules.

(iv) From the variation in intensity of different bands with respect to time it is inferred that the site symmetries of the ions are not changed during the experiment.

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