Proton conduction in solids—A Raman spectral study

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Abstract. The mechanism of proton conduction in hydrogen-bonded solids and the importance of Raman investigations to understand it are discussed here. The results of Raman investigations on the protonic conductors $(NH_4)_3 H(SO_4)_2$ and $Li_2SO_4 \cdot H_2O$ under small d.c. electric fields have been discussed. The enhancement in intensity of the 859, 829 and 330 cm^{-1} bands of $(NH_4)_3 H(SO_4)_2$ has been explained on the basis of proton movement along the N–H....O bond. Spectral changes of the bands due to torsional oscillation of the ammonium ion indicate the probability of hindered rotation of this group. The appearance of new bands at 773 and 1680 cm^{-1} in $Li_2SO_4 \cdot H_2O$ indicates the formation of H_3O^+ during electrolysis. The changes in stretching and bending modes of water are explained on the basis of polarizability changes induced by the migration of proton along the O–H....O bond and reorientation motion of water molecules.

Keywords. Proton conduction; Raman spectroscopy; hydrogen-bonded system; polarizability change.

1. Introduction

Electrical conduction in solids is due to the motion of charge carriers which can either be electrons/holes or ions/vacancies. Ionic conductivity implies diffusion of matter into the interior of the solid and/or on its surface. Ionic compounds can be divided into three groups: (i) insulators, (ii) ionic conductors (IC) and (iii) superionic conductors (SIC). The distinction between IC and SIC lies in the difference in the corresponding activation energies (E_a). For SIC, E_a is < 0.6 eV and for IC it is between 0.6 and 1.2 eV. In SIC the mobile species responsible for conduction are available in plenty in addition to the loose-packed nature of the solid (Colomban and Novak 1988). Protonic conductors are superionic in which the conduction is mainly due to protons.

2. Mechanism of proton conduction

In nonhydrogen bonded materials the conduction is by interstitial migration (Glasser 1975). Such materials are usually studied in a hydrogen atmosphere. The bare proton is expected to move more or less freely in the lattice due to its small ionic radius. In chain hydrogen-bonded systems, the conduction is mainly due to cooperative proton transfer (Grotthus mechanism) in addition to interstitial motion (Glasser 1975). In this process a hydrogen atom is transferred from one end of the chain to another (figure 1). This introduces a proton at one end or removes a proton from the other, which results in a hydrogen bond chain in the reverse orientation. In order to make the chain ready for further proton transfer a reorientation motion follows (Glasser 1975; Chandra et al 1986) which makes the chain ready for further proton transport (figure 2).

In certain materials surface conduction effects due to different protonic species such as H_2O, H_3O^+, OH^- etc bound to the surface cannot be neglected. In such materials
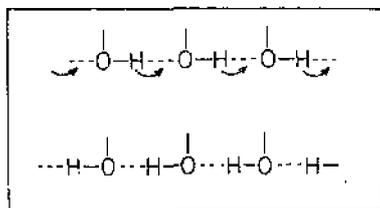
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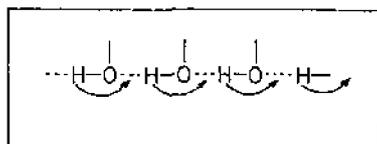Figure 1. Proton transport along a chain hydrogen bonded system.

Figure 2. Reorientation mechanism in a chain hydrogen bonded proton conduction.

the conductivity is due to both intrinsic factors and surface conduction. Migration or transport of a proton along a chain by means of tunnelling is more rapid in certain cases. This effect is predominantly observed in metals (Kreuer 1988). Here the neighbouring potential wells may have overlapping energy levels due to the shifting of energy levels by thermal agitation (Goodenough 1986). This overlapping makes the tunnelling process easier. In hydrogen-bonded systems mutual interaction between the bonds can also cause tunnelling (Bruinink 1979; Kreuer 1988).

3. Experimental techniques

In order to understand the mechanism of proton conduction in solids, it is necessary to determine the structure of the rigid framework as well as that of potentially mobile species. X-ray and neutron diffraction methods are well suited for accurate determination of the structure, but less efficient for understanding the exact nature of protonic species and their localisation in the material. These details can be obtained by various methods such as conductivity measurements (Vander Kooy et al 1964; Kawada et al 1970; Casciola and Constantino 1986), NMR spectroscopy (Schmidt and Uekling 1962; Janik and Rachwalska 1974; Iwahara et al 1983) and optical spectroscopy (Colomban et al 1977, 1988; Pham-Thi et al 1987). The unambiguous experiment to demonstrate protonic conductivity is the electrolysis of the specimen between two electrodes (Workman et al 1954; Krasucki et al 1960; Reddy et al 1982; Chandra et al 1986).

3.1 Raman spectroscopic method

Raman and IR spectra are related to movement of proton within a bond and hence are fundamental techniques to study the mechanism of proton conduction in solids. The Raman and IR spectra of a number of protonic conductors have been reported (Colomban et al 1977, 1985, 1987a, b; Pham-Thi and Colomban 1986; Pham-Thi et al 1987). The conductivity $\sigma(\omega)$ is proportional to the scattered Raman intensity $I(\omega)$

as $I(\omega)/[n(\omega) + 1]$ where $n(\omega)$ is the Bose Einstein population factor (Collongues *et al* 1984). Broadening and shifting of frequencies of Raman bands, appearance and disappearance of bands and intensity changes are noticed (Colomban *et al* 1987a, b). Hence, the intensity measurements of Raman bands under different conditions are expected to provide information about the proton transport dynamics.

The application of an external low d.c. electric field is expected to modify the spectra of protonic conductors (Pham-Thi and Colomban 1986; Chandra *et al* 1986, 1987; Colomban and Novak 1988). Under the influence of small electric fields the intensity of Raman bands associated with bonds involved in proton movement is found to change. Appearance and disappearance of certain bands are another predominant feature. Hence it can be employed as a powerful tool to study the mechanism of proton conduction and the degree of structural disorder in protonic conductors.

To investigate the Raman spectrum under small d.c. electric field, single crystal or pellet cut in the form of a rectangular parallelopiped is usually used. It is mounted with its faces normal to the incident and scattered radiations, as shown in figure 3. Quick drying silver paint is applied on both the other parallel faces (figure 3) for good electrical contact. Low d.c. voltages are applied and spectral measurements carried out at different intervals of time.

To highlight the importance of this dynamic method for understanding the mechanism of proton conduction, the Raman spectral investigation under low d.c. electric field was carried out for the single crystal $(NH_4)_3H(SO_4)_2$ and for the polycrystalline $Li_2SO_4 \cdot H_2O$. Chandra *et al* (1987) reported a similar study in $MoO_3 \cdot 2H_2O$. They explained the changes observed on the basis of the electrolysis of one of the H_2O molecules in it forming H_3O^+.

4. Results and discussion

4.1 $(NH_4)_3H(SO_4)_2$

From DTA and coulometric studies, Reddy *et al* (1982) established that it is a good protonic conductor and that the transfer of protons along the N-H....O bond is mainly responsible for conduction in this crystal. The estimated activation energy for
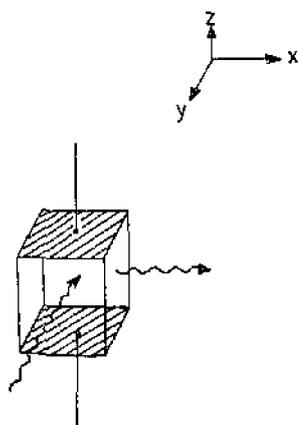

Figure 3. Sample illumination geometry.

proton transfer is 0·33 eV, which is within the range for superionic conductors (< 0·6 eV). The results of d.c. conductivity measurements of this crystal were explained on the basis of proton defects in the ammonium group (Syamaprasad and Vallabhan 1981). From a detailed vibrational analysis, Rajagopal and Aruldhas (1988) found that the SO_4^{2-} and HSO_4^- ions co-exist in the crystal. Their observation of the torsional mode of the NH_4^+ ion around $330\,cm^{-1}$ and the combination of this mode with the bending modes in the region 1785–$2200\,cm^{-1}$ show that the ion is locked in the crystal lattice (Waddington 1958). As the conductivity was maximum along the c-axis (Reddy $et\ al$ 1982), d.c. voltages (10, 20, 30 V) were applied in this direction. Spectral measurements were made at different intervals of time (3, 5, 7 and 9 h) with the voltage on. The exciting radiation was directed at the sample near the cathode and then at the anode.

The significant changes noticed on the application of the d.c. electric fields were (i) the enhancement in intensity of 859, 829 and $330\,cm^{-1}$ bands, (ii) the appearance of additional bands at 908 and $318\,cm^{-1}$, (iii) enhancement of the intensity was more pronounced at the cathode end and (iv) the intensity of all these bands was found to increase with time.

In the crystal SO_4^{2-} and HSO_4^-, ions coexist and the band at $829\,cm^{-1}$ was assigned to the S–O....H stretching vibration. In the presence of the field, the migration of protons from NH_4^+ to SO_4^{2-} group along N–H....O bond took place. This movement of protons is expected to distort the polarizability of the band resulting in increase in intensity. The increase in intensity with field of the OH out-of-plane bending vibration at $859\,cm^{-1}$ is also due to the proton movement along the N–H....O bond. The new band observed at $908\,cm^{-1}$ may arise out of the combination of SOH bending modes 499 and $411\,cm^{-1}$ or the overtone of the symmetric bending mode of SO_4^{2-} ion ($454\,cm^{-1}$). The intensity growth of this band under d.c. bias also points out that the S–OH bond becomes distorted due to proton transfer thereby changing the anharmonicity.

The NH_4^+ ion was found to be locked in the crystal lattice and the band at $330\,cm^{-1}$ assigned to its torsional oscillation (Rajagopal and Aruldhas 1988). The application of the field decreased the barrier height for rotation thereby increasing the probability for tunnelling. This is likely to result in the hindered internal rotation of NH_4^+ ion. This can cause the observation of the additional band at $318\,cm^{-1}$ and enhancement in intensity of the torsional vibration at $330\,cm^{-1}$.

The variation in intensity of 829 and $318\,cm^{-1}$ bands as a function of time for different applied voltages is shown in figure 4. For the torsional oscillation mode 318 and $330\,cm^{-1}$ there is no appreciable difference in intensity between the cathode and anode ends. This is understandable as the torsional oscillation of the ion is not likely to depend much on proton transfer.

4.2 $Li_2SO_4 \cdot H_2O$

The Raman spectra of a pressed pellet of the sample were subjected to low d.c. electric fields (20, 30, 40 and 50 V). Electrodes were connected to the opposite sides of a cylindrical pellet. The remaining curved portions were cut off and the laser beam directed into the sample perpendicular to the electric field. Spectra at different intervals of time (2, 4, 6 and 8 h) are investigated.
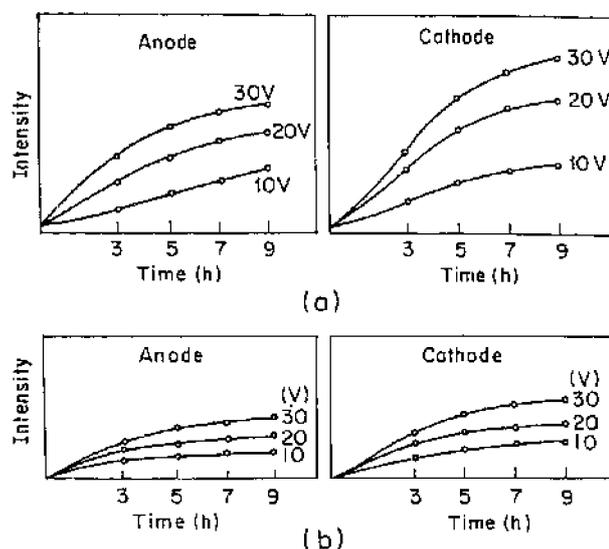
Figure 4. Variation of intensity (arbitrary units) with time for different applied voltages of the (a) $829\,cm^{-1}$ band and (b) $318\,cm^{-1}$ band of $(NH_4)_3H(SO_4)_2$.
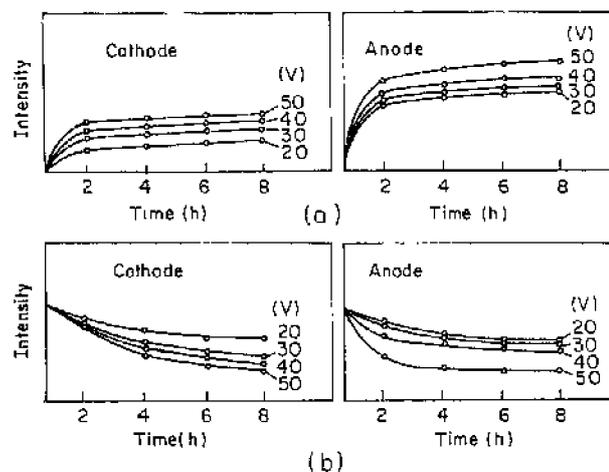

Figure 5. Variation in intensity (arbitrary units) with time for different applied voltages of (a) $773\,cm^{-1}$ band and (b) $1605\,cm^{-1}$ band of $Li_2SO_4\cdot H_2O$.

Under application of the field, the following changes were noticed. (i) Appearance of a new band at $773\,cm^{-1}$, whose intensity increased with voltage and time (figure 5). (ii) An additional band ($1680\,cm^{-1}$) was observed in the bending region of water about 6–8 h after application of the field. This was more prominent at higher voltages. (iii) The stretching region of water broadened with time and finally the bands at 3500 and $3448\,cm^{-1}$ coalesced into a single broad band. This was more pronounced near the cathode end. (v) The intensity of the bending mode of H_2O ($1605\,cm^{-1}$) showed slight decrease with applied voltage and time (figure 5).

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It was earlier reported (Smith et al 1968) that water molecules in $Li_2SO_4 \cdot H_2O$ were weakly hydrogen-bonded, weaker than that in the fast proton conductor ice. Such a loosely-packed structure favoured proton movement from one end of a chain to another by Grotthus mechanism. During this process, after the first proton jump along the O–H....O bond, it is necessary that the bond undergoes a reorientation motion to facilitate further proton transfer along the chain. This proton movement and the reorientation motion is expected to induce and/or distort the polarizability of the bond (Colomban et al 1985). The reduction in intensity of the $1605 cm^{-1}$ band and the coalescing of the stretching modes of water were probably due to the highly disordered structure which resulted from the proton movement along the O–H....O bonds and reorientation motion of water molecules. Colomban et al (1987) observed the collapsing of external modes due to reorientation and subsequent disordering of HSO_4^- ions in $CsHSO_4$.

The appearance of the new bands at 773 and $1680 cm^{-1}$ clearly indicated the formation of H_3O^+ ion during electrolysis (Chandra et al 1987; Kreuer 1988). As the voltage and time increased, the production rate of H_3O^+ also increased. The band at $1680 cm^{-1}$ corresponded to the bending mode of H_3O^+ ion. However, the stretching vibrations of H_3O^+ which was expected just below the stretching modes of H_2O was not observed. It might have got superimposed on the broad stretching bands of H_2O.

Changes in site symmetry might have caused the growth in intensity and appearance of new bands. As the applied voltages were very low, the symmetry of the vibrating groups was not likely to change. Mobility of protons through hydrogen bonds was possible without changing the overall symmetry though distortions were possible (Colomban et al 1985). The observed time dependence also pointed out that the site symmetry of the ion was not destroyed during electrolysis.

Thus Raman investigations of a crystal or pellet under low d.c. electric fields offer an easy and direct dynamical method to understand the mechanism of conduction in proton conducting solids.

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