Dynamics of H$_2$O molecules in ferroelectric K$_4$Fe(CN)$_6$ · 3H$_2$O

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Abstract. The infrared spectrum of potassium ferrocyanide trihydrate has been recorded both in the para and ferroelectric phases. From a combined study of the IR and Raman spectra, it is concluded that there are two sets of water molecules present in the lattice, one set being involved in stronger hydrogen bonding than the other. The ferroelectric transition appears to be associated with an ordering of the water dipoles.

Keywords. Ferroelectric transition, hydrogen bonding, potassium ferrocyanide trihydrate.

1. Introduction

Potassium ferrocyanide trihydrate (PFCT) and its isomorphous compounds having the general formula A$_4$M(CN)$_6$ · 3H$_2$O (where A = K or NH$_4$ and M = Fe, Mn, Ru or Os) are ferroelectric at low temperatures (Waku et al 1959, 1960). At its ferroelectric Curie point —24.5°C, PFCT goes from monoclinic space group C2/c to the monoclinic space group Cc (Waku et al 1959) with a transition entropy of 0.38 cal mol$^{-1}$ deg$^{-1}$ (Nakagawa et al 1963). Since the deuteration of PFCT is found to raise its Curie point by about 6°C (Waku et al 1960), several workers (Lundin et al 1961; Blinc et al 1961; Kiriyama et al 1964; Tsang and O’Reilly 1965; Avogadro et al 1971) have carried out PMR and DMR studies on this crystal, in order to understand the role of the water molecules in triggering ferroelectric phase transition. Blinc et al (1961) have concluded from PMR studies that the onset of ferroelectric behaviour in this crystal is associated with a dynamical orientational ordering of the hydrogen bonded water molecules. Tsang and O’Reilly (1965) have shown from DMR results that the D$_2$O molecules are undergoing 180° flip motion about the DOD bisectrix. The Mössbauer studies carried out by Hazony and Earls (1968) and Gleason and Walker (1969) do not show a minimum in the recoilless fraction at the transition temperature and hence it is concluded that the transition is not of displacive type. Blinc et al (1961) have recorded the IR spectrum of powdered sample of PFCT dispersed in KBr pellet and have shown the existence of two sets of water molecules. The appearance of the water librational modes only in the ferroelectric phase has been attributed to a reorientation of the water molecules below the transition. No investigation of the Raman spectrum of this crystal has been reported so far. The present investigations on the IR absorption spectrum of PFCT both in the para and ferroelectric phases along with the Raman spectrum were undertaken with a view to understanding the role of water molecules in triggering phase transition in this crystal.
2. Experimental

Large plate like single crystals of PFCT can be grown from an aqueous solution, starting with the commercially available pure compound of PFCT. The crystals grown thus were twinned (Waku et al 1961) and have a perfect cleavage plane perpendicular to \( \langle 010 \rangle \) direction. PFCT also grows in the tetragonal form which undergoes an irreversible phase transition (Toyoda et al 1960) at \(-55^\circ\text{C}\) to the monoclinic form \( C\text{t} \). On heating the crystal, this transition disappears and the crystal becomes paraelectric above \(-24.5^\circ\text{C}\). The IR spectrum was recorded in the region 400 to 4000 cm\(^{-1}\) in nujol mull, using a Carl Zeiss UR10 infrared spectrometer. The deuteration was done by crystallizing anhydrous PFCT in heavy water. The Raman spectrum was recorded at room temperature using a Krypton ion laser source (\( \lambda = 5682 \text{ Å}, 100 \text{ mW} \)) and a Spex double monochromator. Figure 1 shows the IR spectrum of PFCT and partially deuterated PFCT. Table 1 lists the observed Raman shifts and the infrared band positions.

3. Results and Discussion

The water molecules in crystalline hydrates, apart from having the three non-degenerate intermolecular vibrations also have low frequency intramolecular vibrations arising due to their librations (Van der Elsken and Robinson 1961; Eisenberg and Kauzmann 1969). The frequency and shape of their bands in the IR and Raman spectra are sensitive to their chemical environment and the strength of coupling with their neighbours (H-bonding, metal-oxygen bonding). When the \( \text{H}_2\text{O} \) molecules in the crystal are partially replaced by \( \text{D}_2\text{O} \), the perturbation caused by asymmetric environment leads to the appearance of HDO vibrational modes and also an increase in the number of \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) vibrational frequencies (Seidl and Knop 1969).

![Figure 1](image_url). The infrared spectrum of PFCT in nujol mull.
Recent neutron diffraction studies by Taylor *et al.* (1970) on PFCT and deuterated PFCT show the existence of two types of water molecules, resulting from O–H⋯O and O–H⋯N types of hydrogen bonds. The IR spectrum of PFCT shows a broad band around 3200 cm\(^{-1}\) and four unresolved peaks in the region 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\). The presence of these bands indicate the existence of crystallographically inequivalent water molecules. The broad band around 3200 cm\(^{-1}\) may be an overtone of the bending mode or fundamental of stretching modes, lowered in frequency as a result of strong hydrogen bonding. The IR spectrum of a single crystal PFCT shows a single band extending from 3200 cm\(^{-1}\) to 3600 cm\(^{-1}\) and with the minimum thickness the fine structure could not be resolved. The bending mode around 1600 cm\(^{-1}\) shows two components. The existence of two sets of water molecules is also confirmed by the Raman lines around 3400 cm\(^{-1}\) and 3500 cm\(^{-1}\). The decoupling of the two O–H bond vibrations due to asymmetric bonding is clearly shown in the IR spectrum of partially deuterated PFCT, which shows six components in the region 2500 cm\(^{-1}\) to 2700 cm\(^{-1}\) and four components in the region 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\). The bending mode of H\(_2\)O around 1600 cm\(^{-1}\) shows three components and that of D\(_2\)O around 1200 cm\(^{-1}\) shows two components. The HDO bending mode around 1400 cm\(^{-1}\) is masked by the nujol peak (1395 cm\(^{-1}\)). These observations not only confirm the existence of inequivalent water molecules, but also the asymmetric bonding. The weak bands around 600 cm\(^{-1}\) and 560 cm\(^{-1}\) which were not observed by Blinc *et al.* (1961), are due to water librations. On deuteration one of them (600 cm\(^{-1}\)) shifts to 500 cm\(^{-1}\) and the other probably to a value less than 400 cm\(^{-1}\) and hence not observed in the present study.

In the ferroelectric phase the four weak bands in the region 3400 cm\(^{-1}\) to 3600 cm\(^{-1}\) become sharp and show fine structure. The broad band around 3320 cm\(^{-1}\) splits into four components. The splitting may be due to decoupling of H\(_2\)O vibrations, caused by their reorientations. Such a reorientation is confirmed by the appearance of new librational modes in the ferroelectric phase. Thus the ferroelectric transition is asso-

### Table 1. Raman shifts and IR absorption maxima (cm\(^{-1}\)) of PFCT

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ciated with an ordering of dipoles. In the present study no librational mode is observed around $400 \pm 40$ cm$^{-1}$ in contradiction to the inelastic neutron scattering results of Rush and Taylor (1964) on PFCT.

For the $O_h$ symmetry of the Fe(CN)$_6^{4-}$ complex ion, the 33 internal vibrational modes are distributed among six irreducible representations:

$$\Gamma = 2A_{1g} + 2E_g + F_{1g} + 4F_{1u} + 2F_{2g} + 2F_{2u}.$$  
Nakagawa and Shimanouchi (1962), through normal coordinate analysis have shown that while the $A_{1g}$ (2017, 414 cm$^{-1}$), $E_g$ (2010, 386 cm$^{-1}$) and $F_{2g}$ (430, 102 cm$^{-1}$) are Raman active, only the $F_{1u}$ modes (2020, 585, 414 and 98 cm$^{-1}$) are IR active. The strong peaks around 2100 cm$^{-1}$ (C≡N), 588 cm$^{-1}$ (Fe−C) and 420 cm$^{-1}$ observed in the IR spectrum are the triply degenerate ($F_{1u}$) modes. The corresponding Raman bands are around 2100 cm$^{-1}$, 522 cm$^{-1}$ and 385 cm$^{-1}$. In the presence of weak coupling between C≡N vibrations and the Fe−C$_6$ vibrations, the high frequency bands (2100 cm$^{-1}$) can be assigned to pure C≡N vibrations and the rest to the vibrations of the Fe−C$_6$ octahedron.

4. Conclusion

The vibrational spectra of PFCT and its deuterated analogue reveal that there are two sets of crystallographically inequivalent water molecules in the lattice, one of them having an asymmetric environment. The ferroelectric transition is associated with an ordering of the water dipoles.

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