Pramāṇa, Vol. 1, No. 3, 1973, pp 161-64. Printed in India. © 1973

Dynamics of H_2O molecules in ferroelectric $K_4Fe(CN)_6 \cdot 3H_2O$

P KUMARA ACHARYA and P S NARAYANAN
Department of Physics, Indian Institute of Science, Bangalore 560012

MS received 7 May 1973; after revision 16 July 1973

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 $A_4M(CN)_6 \cdot 3H_2O$ (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_2O 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 ⟨010⟩ direction. PFCT also grows in the tetragonal form which undergoes an irreversible phase transition (Toyoda *et al* 1960) at −55°C to the monoclinic form *Cc*. On heating the crystal, this transition disappears and the crystal becomes paraelectric above −24·5°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 Å, 100 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 nondegenerate 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 H_2O molecules in the crystal are partially replaced by D_2O, the perturbation caused by asymmetric environment leads to the appearance of HDO vibrational modes and also an increase in the number of D_2O and H_2O vibrational frequencies (Seidl and Knop 1969).

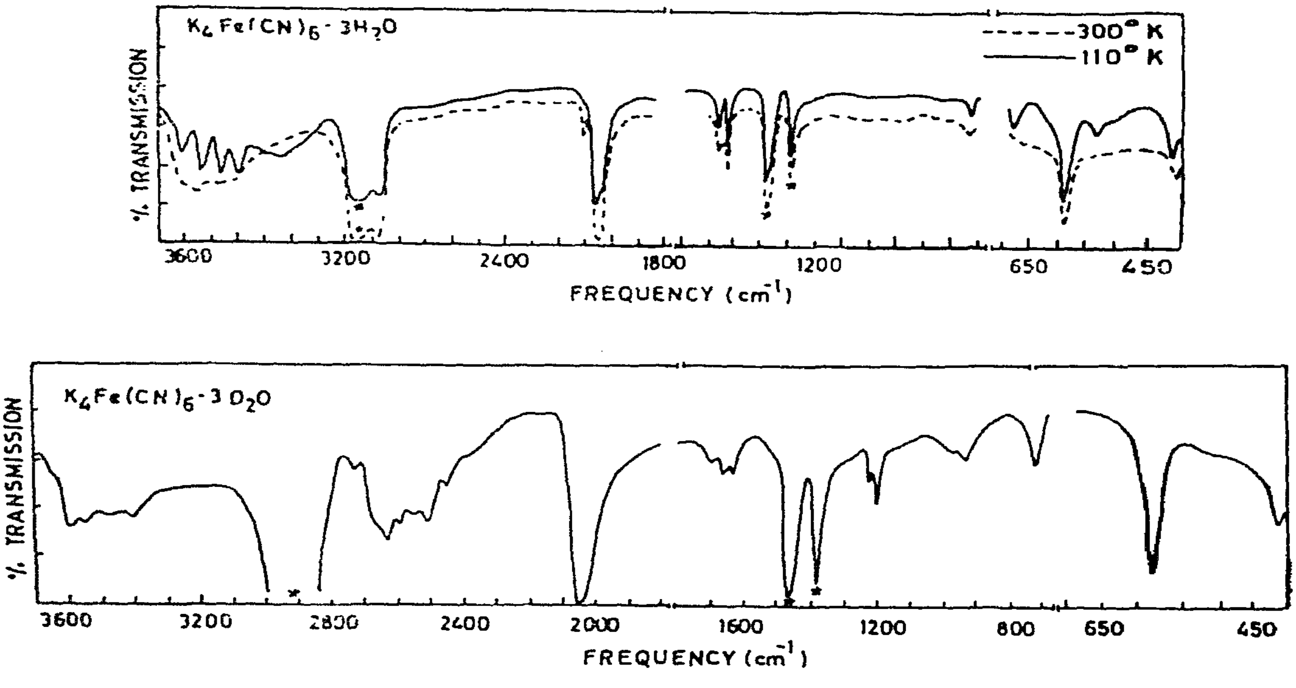

Figure 1. The infrared spectrum of PFCT in nujol mull.

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

Raman	Infrared		Assignments	Raman	Infrared		Assignments
	300 K	110 K			300 K	110 K	
22			lattice oscillations	—	—	2030	C≡N stretching
45				2060	2050	2055	
56				2065	2076	2080	
87				2091	2095	2100	
122				—	2500	2480	combinations
158				—	2700	2720	
175							
385	420	422	Fe-C stretching	—	—	3160	H_2O stretching
				—	—	3232	
—	—	518	H_2O librations	—	3320	3280	
—	560	538		3385	—	3388	
522	—	—	Fe-C stretching				
—	588	592		3400	3415	3453	
—	600	605	H_2O librations	3525	3470	3516	H_2O stretching
—	—	685		3537	3540	3534	
—	1630	1622	H_2O bending	—	—	3580	
—	1660	1662		—	3595	3600	
				—	—	3625	

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_2O around 1600 cm^{-1} shows three components and that of D_2O 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 duteration 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_2O 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 associated with an ordering of dipoles. In the present study no librational mode is observed around 400±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} ($C\equiv N$), 588 cm^{-1} (Fe—C) and 420 cm^{-1} observed in the IR spectrum are the triply degenrate (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 $C\equiv N$ vibrations and the $Fe—C_6$ vibrations, the high frequency bands (2100 cm^{-1}) can be assigned to pure $C\equiv N$ 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.

Acknowledgements

The authors thank Roy Clarke for recording the laser Raman spectrum. One of the authors (P.K.A.) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship.

References

Avogadro A, Cavelius E, Muller D and Peterson J 1971 *Phys. Status Solidi* **48B** 247

Blinc R, Brenman M and Waugh J S 1961 *J. Chem. Phys.* **35** 1770

Eisenberg D and Kauzmann W 1969 *The Structure and Properties of Water* (Oxford University Press)

Gleason T G and Walker J C 1969 *Phys. Rev.* **188** 893

Hazony Y and Earls D E 1968 *Phys. Rev.* **166** 507

Kiriyama R, Kiriyama H, Wada T, Niizeki N and Hirabayashi H 1964 *J. Phys. Soc. Japan* **19** 540

Lundin A G, Mikhailov G M and Gubuda S P 1961 *Dokl. Akad. Nauk SSSR* **136** 864

Nakagawa I and Shimanouchi T 1962 *Spectrochim. Acta.* **18** 102

Nakagawa T, Sawada S, Kawakubo T and Nomura S 1963 *J. Phys. Soc. Japan* **18** 1227

Rush J J and Taylor T I 1964 *Proc. IAEA Vienna* Vol. II, p 333

Seidl V and Knop O 1969 *Can. J. Chem.* **47** 1361

Taylor J C, Muller M H and Hilterman R L 1970 *Acta. Crystallogr.* **A26** 559

Tsang T and O'Reilly D E 1965 *J. Chem. Phys.* **43** 4234

Toyoda H, Niizeki N and Waku S 1960 *J. Phys. Soc. Japan* **15** 1831

Van der Elsken J and Robinson D W 1961 *Spectrochim. Acta.* **17** 1249

Waku S, Hirabayashi H, Toyoda H, Iwasaki H and Kiriyama R 1959 *J. Phys. Soc. Japan* **14** 973

Waku S, Masuno K, Tanaka T and Iwasaki H 1960 *J. Phys. Soc. Japan* **15** 1185

Waku S, Masuno K and Tanaka T 1960 *J. Phys. Soc. Japan* **15** 1698

Waku S, Masuno K and Tanaka T 1961 *J. Phys. Soc. Japan* **16** 1158