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SECOND ORDER IR SPECTRUM OF THE $K_4Fe(CN)_6 \cdot 3H_2O$ CRYSTAL

Key Words: Infrared spectra, crystal vibrations, combination and overtone frequencies, anharmonicity, H - bond.

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INTRODUCTION

The investigation of second order vibrational spectra of solid hydrates is a complicated experimental and theoretical problem. Up to now, there is a small number of IR-absorption studies and a few Raman ones, which consider multiphonon processes. Recently, the theoretical works of Agranovich ^{1,2} and Ruvaldis and Zawadowski ³ have appear which treat some aspects of two-phonon processes in molecular crystals. The emphasis of these works is placed on some effects characteristic only for the second order spectra - Fermi resonance, two-bound states, simultaneous excitations of two molecules etc.

The publications devoted to the above points usually analyze concrete overtones or combination bands, not concerning the rest part of the spectrum and its total interpretation on the basis of the fundamental vibrations. The main reason is the difficulty to understand the origin of the numerous overtones and combinations which often give rise to closely situated or overlapped bands. It is not easy to find a leading principle for identification of the observed spectral picture. The limitations posed from the group-theory rules are rather weak in the case of low symmetry crystals.

Despite of the complex situation, a considerable interest has been shown in this field during the last years. The second order spectra can give a valuable information about the anharmonicity of the normal vibrations. Sometimes they can throw an additional light on the spectrum of fundamentals and, thus, can help their examinations. Interesting, carefully studied class of second order spectra is that of H-bonded alcohols⁴ and different forms of ice⁵.

The present work is a part of our systematic studies on the crystal $K_4Fe(CN)_6 \cdot 3H_2O$ (KFCT). Up to now our interest was concentrated on the first order vibrational spectrum of this hydrate and especially on the dynamics of its crystallographically different water molecules⁶⁻⁸ (H_2O -I, H_2O -II, H_2O -III). Here we present the first investigation of the second order spectrum of KFCT in the near infrared region ($3700 - 7200 \text{ cm}^{-1}$), where

neither Fermi resonance nor any other type of interactions between overtones and fundamentals are expected. An interpretation of the observed bands is given based on our knowledge of the IR and Raman fundamental frequencies.

EXPERIMENTAL

Single crystalline plates of KFCT, grown perpendicularly to the crystallographic b axis with a thickness of about 1 mm, were used. Spectra were recorded on a Carl-Zeiss spectrometer Specord, model 61 NIR with a scan speed $30 \text{ cm}^{-1}/\text{min}$. The time constant was chosen to be 1 sec and the spectral split width - $1 \pm 3 \text{ cm}^{-1}$. In order to improve the quality of the spectra and to extend the wavenumber scale, a parallel registration of the signal amplified 2 ± 10 times has been carried out (recorder K 201 Carl-Zeiss). Because of the broadness of the bands at room temperature, the spectra were obtained at 90 K using a Carl-Zeiss temperature cell.

SPECTROSCOPIC DATA AND DISCUSSION

The infrared spectra of the KFCT crystal in the region of $3700 - 7200 \text{ cm}^{-1}$ are shown in Fig.1a,b. One can see distinct band systems which may be assigned as follows:

1. Combinations of water stretching modes ν_{OH} and water librations $\delta_{\text{H}_2\text{O}}$ or vibrations of the ferrocyanide ion of the type $\nu_{\text{Fe-C}\equiv\text{N}}$ ($3700 - 4300 \text{ cm}^{-1}$).

2. Overtones and combinations of C=N stretching vibrations ν_{CN} (4070 - 4200 cm^{-1}).

3. Combinations of water stretchings ν_{OH} and bending δ_{OH} modes (5000 - 5200 cm^{-1}).

4. Combinations of water stretchings ν_{OH} and C≡N vibrations ν_{CN} (5400 - 5700 cm^{-1}).

5. Overtones $2\nu_{OH}$ and combinations $\nu_{OH}^i + \nu_{OH}^j$ of water stretching vibrations (6500 - 7200 cm^{-1}).

The distribution of the second order spectrum of KFCT in distinct spectral series is rather strange but it has been found to be very useful for its interpretation. The unambiguous assignment of the series as a whole has helped us to interpret the observed bands in detail and to evaluate the anharmonicity constants. It also allowed us to draw some conclusions about the interactions between the different groups in the crystal unit cell.

The spectrum in the region of 3700 - 4300 cm^{-1} is very complicated due to numerous possible combinations of the type $\nu_{OH} + \delta_{H_2O}$ and $\nu_{OH} + \nu_{Fe-C\equiv N}$ which may exist there (Fig.1a - solid line). The comparison between the spectra of pure and deuterated KFCT (Fig.1a-dashed line) allows us to establish the participation of ν_{OH} modes in this part of the spectrum. The spectrum of partially deuterated KFCT (Fig.1a - dotted-dashed line) helps us for the assignment of the bands. Probably the bands which do not shift by deuteration are combinations of the type $\nu_{OH} + \nu_{Fe-C\equiv N}$, as the stretching modes of

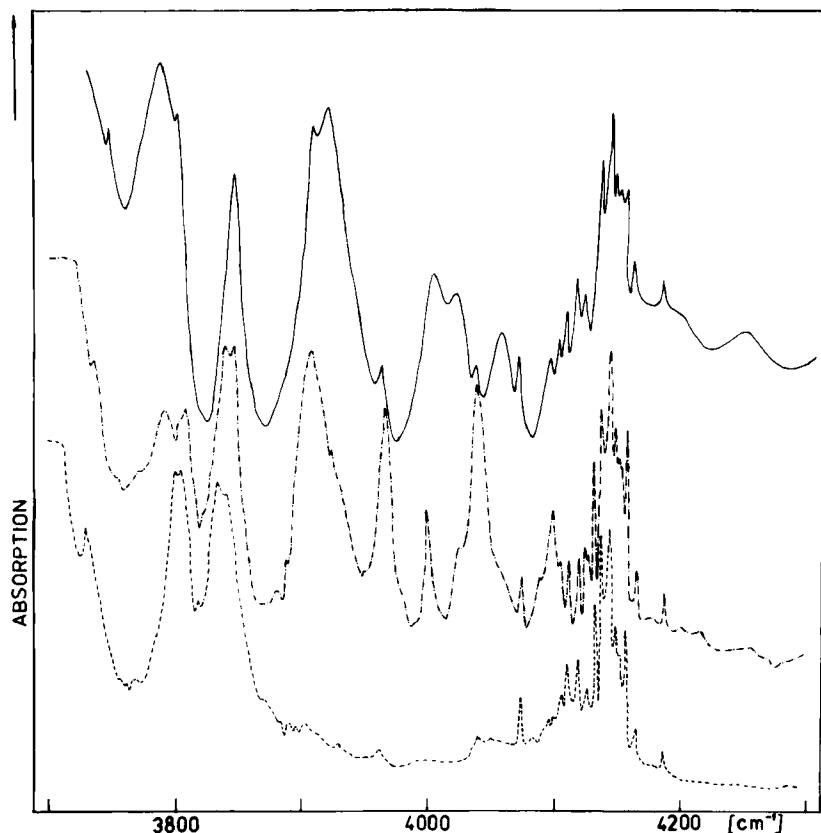


Fig. 1a. Infrared spectra at 90 K of KFCT (solid line), DKFCT (dashed line) and KFCT/DKFCT solution (dotted-dashed line). The record is obtained by a 2^x amplification.

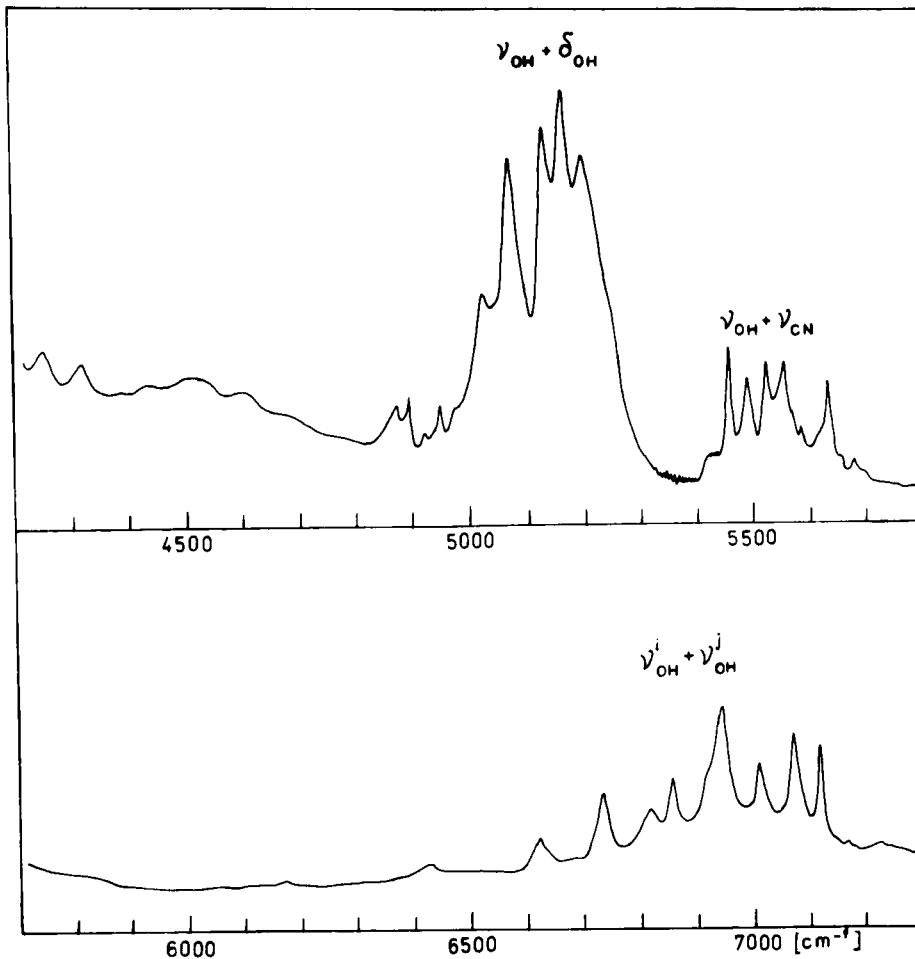


Fig.1b. Infrared spectrum of KFCT at 90 K in the region of 4200 - 7200 cm^{-1} obtained on a Specord 61 NIR.

the HDO and H_2O molecules in KFCT are nearly identical⁷. However, the HDO and H_2O libration frequencies are quite different and their combinations with ν_{OH} will be influenced by deuteration.

The system of extraordinary narrow bands located between 4070 - 4200 cm^{-1} , which are not affected by deuteration, are surely overtones and combinations of ν_{CN} stretching modes. The appearance of such narrow bands with a halfwidth of only $2 \pm 5 \text{ cm}^{-1}$ is a rare phenomenon in the IR-absorption, especially in the case of second order spectra. Moreover, it is rather strange that the overtone and combination bands at 90 K are better resolved than the corresponding fundamental bands at 28 K (Fig.2). A detailed assignment of the observed

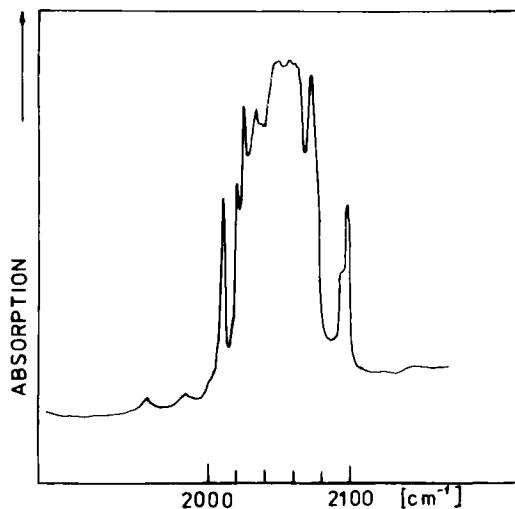


Fig.2. IR-absorption spectrum of $C\equiv N$ stretching fundamentals in KFCT crystal at 28 K, obtained on a Perkin-Elmer 180 spectrometer.

bands is difficult but not absolutely necessary. The strongest bands are concentrated in the frequency region of $4100 - 4150 \text{ cm}^{-1}$ and correspond to the overtones of the most intensive $\text{C}\equiv\text{N}$ lines at $2050-2070 \text{ cm}^{-1}$ in the first order spectra (Fig.2). The energy anharmonicity $2\chi_{\text{CN}}$ approximately evaluated from this correspondence has an average value of 10 cm^{-1} which is greater than the halfwidths of the fundamentals ($3 \pm 6 \text{ cm}^{-1}$). According to^{1,2,3}, we assume to observe bound ν_{CN} phonons.

The well separated bands with halfwidths of $8 \pm 15 \text{ cm}^{-1}$ in the region of $5400 - 5650 \text{ cm}^{-1}$ may be only combinations of water and cyanide stretching modes $\nu_{\text{OH}} + \nu_{\text{CN}}$. Their interpretation is also not easy if we take into consideration the complicated spectra of ν_{OH} and ν_{CN} fundamentals. As we have already mentioned, the infrared ν_{CN} bands are not well resolved even at 28 K. The corresponding Raman bands, however, are strongly polarized and can be identified more definitely⁶. Their wavenumbers are given in the Table 1.

The appearance of well resolved and relatively narrow bands, corresponding to $\nu_{\text{OH}} + \nu_{\text{CN}}$ combinations, shows that we observe discrete states due to a simultaneous excitations of these vibrations in the water molecules and in the $\text{Fe}(\text{CN})_6^{4-}$ ions. This fact can be explained by the existence of different bonds of the type $\text{O}-\text{H} \dots \text{N}$, which have been discussed by us in our previous papers^{7,9,10}. A tentative assignment of the observed combination bands to concrete frequency sums

TABLE 1

Wavenumbers of the Calculated and the Observed Combinations of the Type $\nu_{\text{OH}} + \nu_{\text{CN}}$ (cm^{-1}).

ν_{CN}	2100	2074	2062	2057	2045	2031	
ν_{OH}	calc	obs	calc	obs	calc	obs	calc
3370	5470	5465	5444	5436			
3442	5542	5533			5502	5499	5495
3496						5415	5415
3515	5615	5611	5589	5583			
3563					5572	5567	5560
3583	5683	5678	5657	5650	5625	5628	5608
							5608
							5614
							5611

$\nu_{OH} + \nu_{CN}$ is shown in Table 1. Of course, the interpretation of some bands, especially of those in the middle of the frequency region, cannot be completely unique but it accounts for the main experimental data. Some important conclusions can be drawn from this interpretation about the participation of the OH-oscillators in the different hydrogen bonds. For example, no such combination has been observed for the OH-oscillator with frequency of 3496 cm^{-1} . The band at 3496 cm^{-1} was earlier attached by us to the only OH-group (H_2O-I) engaged in H-bonding of the type O-H...O. Thus, there is no reason to expect considerable coupling between this group and the $Fe(CN)_6^{4-}$ ions. It is worth to notice that the more intensive the bands are in this region the greater are the anharmonic coupling constants.

The bands corresponding to overtones and combinations of internal water vibrations are the most interesting ones. The problems of hydrogen bond, water stretching vibrations and their anharmonicity are closely related. Extensive studies have been carried out in recent years on the overtones of the O-H stretching vibrations which demonstrated the difficulties in the interpretation of the observed spectra. It was found that a knowledge of the complete second order spectrum of water is necessary to understand the region of the stretching overtones and the combinations. Usually the authors consider only the OH stretching overtones because they are relatively well

isolated. In the case of KFCT one can see some well defined bands at 5000 - 5200 cm^{-1} (Fig.1b) corresponding mainly to intramolecular combinations of the type $\nu_{\text{OH}^+} + \delta_{\text{OH}}$ for the three kinds of water molecules. The mean energy anharmonicity has an approximate value of 5 cm^{-1} .

The ten bands in the region of 6500 - 7200 cm^{-1} are overtones, intra- and intermolecular combinations of OH stretchings. Additional investigations, e.g., by the help of isotope dilution technique, are necessary for their exact assignment. Without going into details, a preliminary estimate for the anharmonicity constants $2X_{\text{OH}}$ gives the value of about 200 cm^{-1} which increases with increasing the H-bond strength.

The data obtained in the present work are only a basis for further investigations of the second order vibrational spectrum of KFCT. An attempt will be made these qualitative considerations to be pursued more quantitatively.

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