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INVESTIGATION OF THE 4197 cm^{-1} ABSORPTION BAND OF POTASSIUM FERRICYANIDE UNDER HIGH PRESSURE

(Presented by Academician A. N. Terenin, 16 V 1964)

It is known that changes in the shape of the contour of a spectral band reflect changes in the interaction of a molecule (ion) with its surroundings, or changes within the molecule itself, occurring under the action of external factors. Pressure may be cited as one such factor. The influence of pressure on the shape of bands in the vibrational spectra of the simplest molecules, found predominantly in the gaseous state, has been investigated by Vodar (^{1}), P. A. Bazhulin and co-workers (^{2}), and a number of other specialists. The spectra of crystalline substances under pressure have been investigated only in electronic spectra; in this case, both under hydrostatic (^{3}) and uniaxial compression (^{4}), splitting of bands was observed, which was explained by a change in the symmetry of the centers responsible for the optical properties of the compounds. In the work of A. F. Prikhot' ko and co-workers (^{5}), deformation of crystals led to broadening of the electronic absorption bands, which the authors attributed to delocalization of the exciton excitation.

Infrared absorption spectra of solids under pressure have not been investigated, although they are of great interest, since they make it possible to study both the state of absorption centers (which may be ions or molecules in a crystal) and the state of the crystalline lattice surrounding them. In order to clarify some of these questions, we undertook an investigation of the infrared absorption spectrum of potassium ferricyanide, $K_3[\mathrm{Fe(CN)}_6]$, under pressure. This salt was chosen because the bands in its spectrum are comparatively narrow and sufficiently intense. On the other hand, it is also of interest to trace the effect of pressure on the spectrum of this complex salt in connection with the fact that the $3d$ electron shell of the iron coordination ion in it is incomplete.

Recording of the spectra under pressure was carried out on an apparatus previously developed by one of the authors (^{6}). In the region 4000–10 000 cm^{-1}, a strong band with a maximum at 4197 cm^{-1} under normal conditions and a weak band at 4228 cm^{-1} were found; on the latter is superposed an absorption band of atmospheric gases. The principal band apparently belongs to the first overtone of the vibration ν_4' in crystalline $K_3[\mathrm{Fe(CN)}_6]$, to which there corre-

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

sponds in the free anion the vibration ν_4 (F_{1u}) in Herzberg' s notation. In fact, from the point of view of symmetry, this vibration of all the CN ligands together with the central iron ion may be represented as a displacement of 4 ligands lying in the plane of a section of the octahedron parallel to the diagonal perpendicular to this plane, and a simultaneous antisymmetric vibration of the iron ion and the two remaining ligands relative to one another. In this case, owing to the intrinsic vibrations occurring in each CN group, the absorption band may split, as indeed may all other vibrational bands, into 2 components, according to the theory of Mathieu (^{7}). In the present case we are dealing with only one component, since the second falls in the KBr region. Assignment of the frequency was made on the basis of the theory of local groups proposed by Halford (^{8}) and Hornig (^{9}).

Upon compression of the specimen containing the salt, a shift of the 4197 cm^{-1} band toward higher frequencies was observed (Fig. 1). Within the limits of measurement accuracy, the shift may be characterized by a rectilinear dependence with slope $\Delta\nu/\Delta p = 1.0$ cm^{-1}/kbar. Beginning approximately at 5 kbar, a new band appears, which

shifts with increasing pressure at a rate $\Delta\nu/\Delta p = 1.45$ cm^{-1}/kbar. Recalculated to normal conditions, the frequency of its maximum is 4204 cm^{-1}. Its relative increase in intensity is caused by the superposition of a weak absorption band of atmospheric gases in the region of 4230 cm^{-1}. This is one of the reasons for the decrease in the resolution of both bands at pressures above 20 kbar.

Fig. 1. Change in the shape of the 4197 cm^{-1} absorption band of K_3[Fe(CN)$_6$] with pressure:
1 $-p = 1$ bar; 2 –12 kbar; 3 –8 kbar; 4 –21 kbar.

Fig. 2. Transmission spectra: 1 –[K_3Fe(CN)$_6$]; 2 –intermediate product, $p = 5$ kbar; 3 –final product, $p \simeq 23$ kbar. (The anomalous transmission on the high-frequency side of the absorption band is caused by the Christiansen effect.)

Another reason lies in the broadening of the bands upon compression of the salt. The 4228 cm^{-1} band shifts at a rate of 1.0–1.1 cm^{-1}/kbar. All changes in the spectrum are only partially reversible: after the pressure is released, the asymmetry of the band is more clearly expressed, and its width is increased compared with that observed before the start of the experiment. The substance removed from the high-pressure cell after maximum compression (the final product) has

Fig. 3. Transmission spectra of pure salts: 1—K_3[Fe(CN)$_6$] and 2—K_4[Fe(CN)$_6$]$3H_2O$.

Figure 3: Fig. 3. Transmission spectra of pure salts: 1—K_3[Fe(CN)$_6$] and 2—K_4[Fe(CN)$_6$]$3H_2O$.

a yellow-green coloration, whereas the initial substance is an orange-yellow powder.

The cause of such a change in the band shape is undoubtedly a lowering of the symmetry of the complex. Under compression conditions close to hydrostatic, it can occur only with asymmetry of the electron cloud of the complex. However, according to I. B. Bersuker $^{(10)}$, the ion [Fe(CN)$_6$]$^{3-}$ is an ideal octahedron, since the outer electron shell of the central iron ion is $3d^5$. In this case all covalent bonds of the Fe^{3+} ion with the ligands are identical, and a change in the symmetry of the complex under the action of pressure, without internal electronic transformations in it, is impossible. It remains to suppose that under compression Fe^{3+} is converted into Fe^{2+} with the formation of potassium ferrocyanide K_4[Fe(CN)$_6$]. In this process the symmetry of the initial anion O_h is replaced by D_{4h}, i.e., one of the diagonals of the octahedron becomes longer than the other two. This transformation should be accompanied by the appearance of new bands. Drickamer $^{(11)}$, who studied the same substance under conditions of simultaneous compression and shear, was the first to point out its possibility.

To verify the assumption about the transformation, spectra were studied of the initial salt K_3[Fe(CN)$_6$], of the intermediate product obtained as a result of several experiments at pressures not exceeding 5 kbar, and of the final product obtained at $\sim$ 23–25 kbar, in the region 1500–2200 cm^{-1} (Fig. 2). The spectra were recorded on a UR-10 spectrometer*. Samples were prepared by the paste method in vaseline oil. Analysis of the spectra showed that under pressure part of the salt K_3[Fe(CN)$_6$] is converted into K_4[Fe(CN)$_6$] $\cdot$ nH$_2$O. Indeed, the bands at 2045 and 1628 cm^{-1} belong to ferrocyanide, the second band being assigned to a deformation vibration of crystallization water. The band at 2117 cm^{-1} is characteristic only of the salt K_3[Fe(CN)$_6$], which is confirmed both by our own measurements of the spectra of the pure substances (Fig. 3) and by the data of other authors (12).

Fig. 3. Transmission spectra of pure salts: 1—K_3[Fe(CN)$_6$] and 2—K_4[Fe(CN)$_6$]$3H_2O$.

Thus, from the spectra of the final products in the region of the fundamental frequencies we have established that, in contrast to Drickamer (11), it is pressure that causes an irreversible transition of the complex with the Fe^{3+} ion into a

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complex with the Fe^{2+} ion. In addition, the comparative narrowness of the spectral bands indicates that the final product, like the initial one, remains in the crystalline state and not in the amorphous state.

In studies of pure $K_4[\mathrm{Fe(CN)}_6] \cdot 3\mathrm{H_2O}$ under pressure, a shift was found of the band at 4118 cm^{-1}, which also apparently belongs to the overtone $2\nu_4^1$ of the ferrocyanide complex, at a rate of 1.25 cm^{-1}/kbar. Consequently, the change in the shape of the 4197 cm^{-1} band of ferricyanide does not directly indicate the formation of ferrocyanide under pressure. In this case the component at 4204 cm^{-1} may be assigned to an unstable complex that is a transitional form between complexes of trivalent and divalent iron. The different value of $\Delta\nu/\Delta p$ for the studied bands is evidence of this. The absence of a larger number of components caused by lowering of the symmetry O_h of the initial substance is possibly due to insufficiently good resolution. Further studies are needed.

The identical dependence of the shift of the 4197 and 4228 cm^{-1} bands on pressure makes it possible to suppose their common origin. This is well explained by the theory of local groups. Indeed, the overtone $2\nu_4^1$ of the ferricyanide complex in the crystal has the vibration type $[(4A_g) + 2A_u]$, in which only the A_u components are allowed by the selection rules for infrared spectra, i.e., precisely two bands. The small relative strengthening of the 4228 cm^{-1} band under pressure probably characterizes an increase in the interaction of anions with one another in the crystal cell upon compression, which is responsible for the splitting of spectral bands in the crystalline state.

In conclusion, we express our gratitude for constant attention to the work to Academician A. N. Terenin and Corresponding Member L. F. Vereshchagin, and also to mechanic A. N. Yan for assistance in carrying out the experiments.

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