CHEMISTRY LETTERS, pp. 239-242, 1981.

ELECTRONIC RAMAN BANDS IN POTASSIUM FERRICYANIDE

Atsuko OHATA, Yoshiyuki MORIOKA, and Ichiro NAKAGAWA
Department of Chemistry, Faculty of Science,
Tohoku University, Aoba, Aramaki, Sendai 980

In the Raman spectrum of potassium ferricyanide several new bands were found at low temperatures. The Raman bands at 665 cm^{-1} and 840 cm^{-1} are assigned to the electronic transitions within a ground state manifold of a low-spin Fe^{3+} ion and that at 935 cm^{-1} is attributed to a vibronic transition.

Raman and infrared studies on potassium ferricyanide, $K_3Fe(CN)_6$ have been done extensively.$^{1-7)}$ In the present study on the Raman and infrared spectra at low temperatures, several new bands were found. In this letter, we describe the nature of these bands and present an interpretation that these bands are related to the electronic transitions within a ground state manifold of a low-spin ferric ion.

Raman spectra of polycrystalline samples and single crystals were recorded using a JRS-400 T Raman spectrometer and a 632.8 nm line from a He-Ne laser as a source. Low temperature measurements were carried out using a closed cycle helium refrigerator down to 30 K. Infrared spectra were measured in a form of KBr disk using a Hitachi 285 infrared spectrometer and a home-made cryostat in the temperature range from 295 to 85 K.

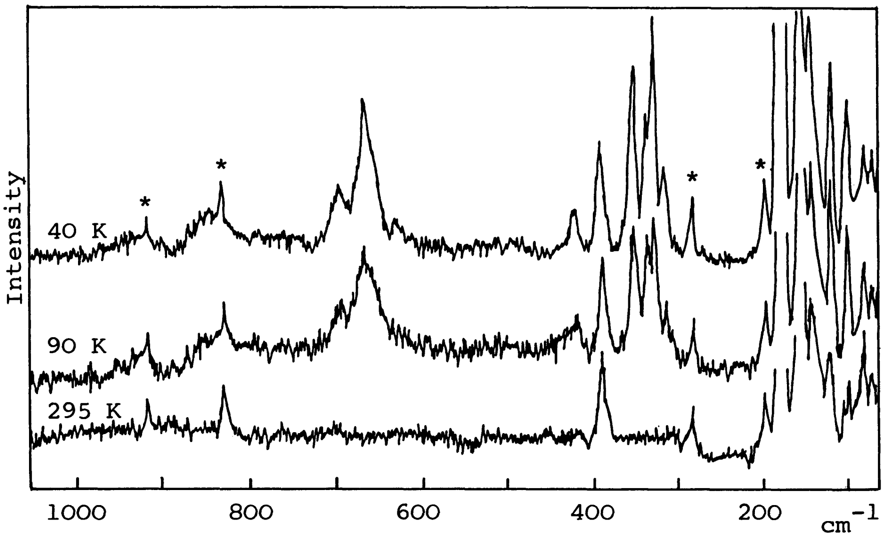

Fig. 1. Raman spectra of polycrystalline $K_3Fe(CN)_6$.
* denotets emission lines from a He-Ne laser.

Raman spectra of polycrystalline samples from 295 to 40 K are shown in Fig. 1. On cooling the samples, five bands around 350 cm^{-1} and four bands in the region 650-1000 cm^{-1} appear, and their intensities increase with lowering the temperature. The bands around 350 cm^{-1} have been observed by Iqbal$^{7)}$ and assigned to the components of $\nu_4(e_g$, FeC str.) and $\nu_5(f_{1g}$, FeCN bend.) of $[Fe(CN)_6]^{3-}$, on the basis of the normal coordinate analysis of Nakagawa and Shimanouchi$^{4)}$. The appearance of these bands and their intensity at low temperatures have been explained in connection with the Jahn-Teller effect in $^2T_{2g}$ ground term$^{7)}$. The remaining four bands at 665, 695, 840 and 935 cm^{-1} have not been reported by previous researchers. In this region no fundamental vibrations are expected$^{4)}$. The temperature dependence of these Raman bands suggests that they arise from electronic transitions, since electronic Raman bands for low-lying electronic states of transition metal ions so far investigated strengthen their intensities remarkably on lowering the temperature. The Fe^{3+} ion in a low-spin state has $^2T_{2g}$ ground term, which splits into three levels due to the spin-orbit interaction and the tetragonal distortion as shown schematically in Fig. 2. Kamimura has derived a formula for the energy levels within a $^2T_{2g}$ ground term$^{8)}$, and obtained two parameters in this formula, on the basis of the data of magnetic susceptibility and electron spin resonance. By using Kamimura's formula and parameters, the energies of low-lying electronic states are calculated to be 758 cm^{-1} and 705 cm^{-1} from the lowest level. Thus it is very likely that two of the above four Raman bands correspond to these two electronic transitions.

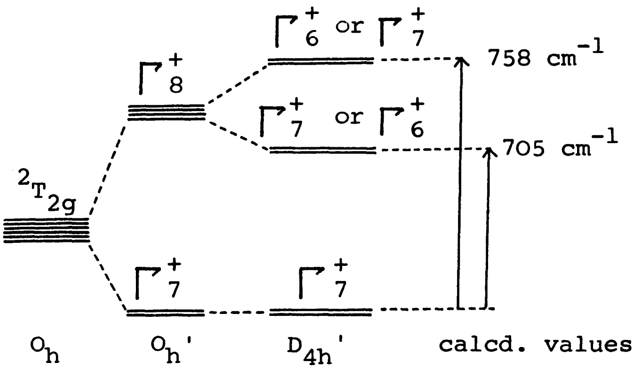

Fig. 2. Energy levels of $^2T_{2g}$ ground state of low spin ferric ion. (Calculated values are based on the Kamimura's formula$^{8)}$.)

As an alternative interpretation, these four Raman bands might be the overtones and combination bands of the ν_4 and ν_5, since a similar behavior on the temperature dependence is revealed for the Raman bands in the region 650-1000 cm^{-1} and those around 350 cm^{-1}. However, the 665 cm^{-1} band is too strong to be assigned to the overtone or combination band, on considering that a resonance Raman effect is not operative under this experimental condition. The 840 cm^{-1} band is also too strong to be interpreted as an overtone of the $\nu_{10}(f_{2g}$, FeCN bend.) at 420 cm^{-1}. A weak band at 695 cm^{-1} may be assigned to the combination band $(\nu_4 + \nu_5)$. A binary combination of the f_{1u} and f_{2u} modes of $[Fe(CN)_6]^{3-}$ may appear in Raman spectra. The $\nu_7(f_{1u}$, FeC str.) is observed around 510 cm^{-1} and the ν_8(f_{1u}, FeCN bend.) and ν_{12}(f_{2u}, FeCN bend.) are observed in the region 380-410 cm^{-1} (see Fig. 4). An appropriate binary combination of ν_7, ν_8 and ν_{12} could not be obtained to explain the above Raman bands.

In relation to the interpretation of the temperature-dependent Raman bands, infrared side bands provide useful information. In Fig. 3, infrared spectra in the region 3300-1900 cm^{-1} are shown. In this region the ν_6 fundamental band(f_{1u}, CN str.) is observed, accompanied by several side bands designated as ν_a, ν_b, ν_c, ν_d, ν_e and ν_f. The ν_a(ν_6 + 334) and ν_b(ν_6 + 357) are interpreted as the combination bands ν_6 + ν_5 and ν_6 + ν_4, respectively. The ν_c(ν_6 + 390) is definitely assigned to ν_6 + ν_2(a_{1g}). The ν_d(ν_6 + 660) band is stronger than ν_a and ν_b bands and thus it is unlikely that the ν_d band arises from a ternary combination such as ν_6 + 2ν_4, ν_6 + 2ν_5 and ν_6 + ν_4 + ν_5. Furthermore, at room temperature the ν_d band as well as the ν_e and ν_f bands is observed, while the ν_a and ν_b bands are not observed. Accordingly the appearance of the ν_d, ν_e and ν_f bands is caused by the different origin from that of the ν_a and ν_b phonon combination bands and is associated

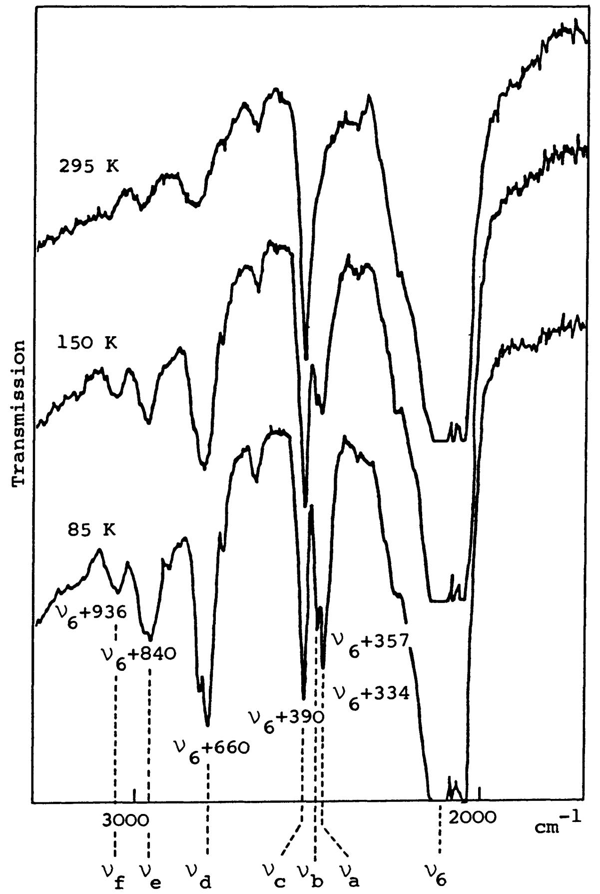

Fig. 3. Infrared spectra of $K_3Fe(CN)_6$. (3300 cm^{-1} - 1900 cm^{-1})

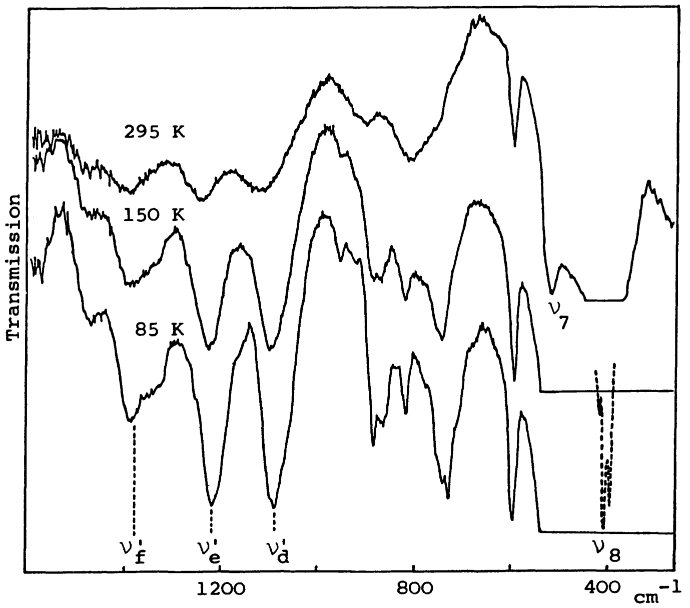

Fig. 4. Infrared spectra of $K_3Fe(CN)_6$ in the region 1550-300 cm^{-1}. (Dotted line shows ν_8 and ν_{12} bands at 85 K.)

with the vibronic transition. The ν_d band is interpreted as the transition to the ν_6 vibrational level in the electronic excited state, related to the Raman band at 665 cm^{-1}. Similarly the $\nu_e(\nu_6 + 840)$ band arises from the vibronic transition to the ν_6 vibrational level in the electronic excited state, related to the Raman band at 840 cm^{-1}. The Raman band at 935 cm^{-1} is considered to be a vibronic Raman band in which the electronic state at 840 cm^{-1} and $\nu_{11}(f_{2g}$, CFeC def.) around 100 cm^{-1} participate, and the $\nu_f(\nu_6 + 936)$ infrared band corresponds to the transition to the $\nu_6 + \nu_{11}$ vibrational level in the electronic state at 840 cm^{-1}.

Figure 4 shows the infrared spectra in the region 1550-300 cm^{-1}. Dunsmuir and Lane$^{5)}$ reported the broad bands at 1100, 1225 and 1375 cm^{-1} in the single crystal transmission spectrum at room temperature, but no interpretation was given for these bands. The ν_d', ν_e' and ν_f' in Fig. 4 correspond to these three bands, and as in the case of ν_d, ν_e and ν_f in Fig. 3, they are assigned to the vibronic side bands in which the ν_8 vibrational level participates.

In conclusion, the Raman bands at 665 cm^{-1} and 840 cm^{-1} are interpreted as arising from the electronic transitions within a ground state manifold of a low-spin Fe^{3+} ion, and that at 935 cm^{-1} is attributed to a vibronic transition. This interpretation is also verified from the analysis of the infrared side bands accompanying the ν_6 and ν_8.

A part of this study is supported by Yamada Science Foundation.

REFERENCES

1) I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, 18, 101 (1962).
2) V. Lorenzelli and P. Delorme, Spectrochim. Acta, 19, 2033 (1963).
3) D. Bloor, J. Chem. Phys., 41, 2573 (1964).
4) I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, 26A, 131 (1970).
5) J. T. R. Dunsmuir and A. P. Lane, J. Chem. Soc. (A), 776 (1971).
6) D. M. Adams and M. A. Hooper, J. Chem. Soc. (A), 160 (1972).
7) Z. Iqbal, J. Phys. C, 10, 3533 (1977).
8) H. Kamimura, J. Phys. Soc. Jpn, 11, 1171 (1956).

(Received December 18, 1980)