The Use of Luminescence Spectroscopy to Determine Infrared and Raman Inactive Fundamentals: The τ_{2u} Vibrational Frequencies of the $Cr(CN)_6^{3-}$ Ion

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Summary The 5K luminescence spectrum of $Cr(CN)_6^{3-}$ in $K_3Co(CN)_6$ has enabled the i.r. and Raman inactive τ_{2u} Cr–C–N and C–Cr–C bending modes to be located.

THE octahedral hexacyanide complexes of transition metals are important compounds for the study of π-bonding in co-ordination compounds. Although there have been numerous studies of the i.r. and Raman spectra of these compounds, several assignments are still uncertain and therefore reliable values of the force field potential constants are not available. Jones[1-3] has assigned the lower of the two i.r. active fundamentals in the 300—600 cm^{-1} region as the T_{1u} M–C stretch and the upper as the T_{1u} M–C–N bend, whereas Nakagawa and Shimanouchi[4,5] have reversed these assignments.

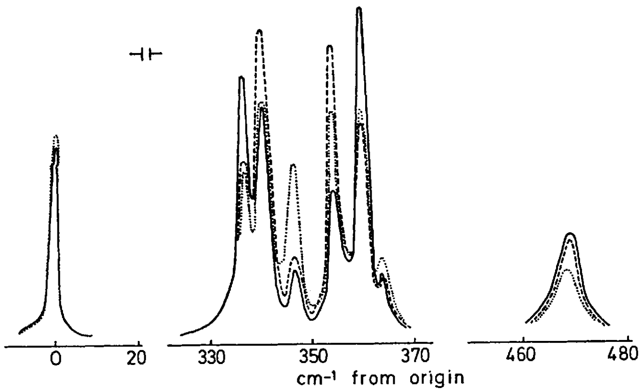

FIGURE. *Part of the 5K luminescence spectrum of the* 4 Or *form of* K_3 (Co:Cr)(CN)$_6$ · · · · · · · *electric vector* ||a *on* ac; – – – ||b(bc), ——— ||c(bc). *Note abscissa discontinuities, there are no strong features in the regions* 230—330 cm^{-1}, 370—460 cm^{-1} *or* 475—700 cm^{-1} *from the origin* (12,373 cm^{-1}).

Of the thirteen vibrational modes of the O_h M(CN)$_6^{3-}$ anion,[6] three (the T_{2u} C–M–C deformation and the T_{2u} and T_{1g} M–C–N bending modes) are inactive in both the i.r. and Raman spectra. The use of a physically realistic force field requires the observation of the largest possible number of fundamental vibrational modes so that it has been necessary to estimate the frequencies of these inactive modes by the measurement of combination bands[1,2] or by relying on a site symmetry of less than O_h to make the transition weakly allowed.[2,4] The possibility of splittings due to different crystallographic sites,[7,8] or correlation field effects[9] or of the failure of the k = O selection rules,[9] makes these methods unreliable. A much more direct method of locating the ground state T_{2u} vibrations of the Cr(CN)$_6^{3-}$ ions is to measure the $^2E_g \rightarrow {}^4A_g$ luminescence spectrum of the Cr(CN)$_6^{3-}$ ion in a dilute crystal since the internal T_{1u} and T_{2u} vibrations are then allowed even in O_h symmetry[10] and first-order correlation field splittings cannot occur. The measurement of electronic transitions is often of use in determining i.r. and Raman inactive vibrational frequencies.[11]

We have measured the 366 nm excited 5K polarised luminescence spectrum of a single crystal of the four layer orthorhombic modification[7] of K_3Co(CN)$_6$ containing 0·073% of chromium. The ^2E–^4A luminescence spectrum of the Cr(CN)$_6^{3-}$ in this lattice is exceptionally strong and well resolved and more than 100 vibronic lines can be observed (a full report and analysis will be published later). The ^2E state is split by 49 cm^{-1} due to spin–orbit coupling and the low site symmetry but at 5K only the lower state is populated. The spectrum at about 350 cm^{-1} and 470 cm^{-1} from the lower origin is of particular interest (Figure). Although the eight Co(CN)$_6^{3-}$ ions in the unit cell of the four layer orthorhombic modification of K_3Co(CN)$_6$ are at three crystallographically distinct sites of symmetry C_2, C_2, and C_1, they have essentially identical geometry. Neither the electronic origins nor any of the other vibrations show splittings that can be attributed to differences between the sites. It is most unlikely therefore that any of the structure near 350 cm^{-1} can be attributed to this cause. The six bands between 330 and 370 cm^{-1} must represent the six components of two triply degenerate (in O_h) vibronically active[10] internal modes of the Cr(CN)$_6^{3-}$ ion. The emission bands near 340 cm^{-1} and 468 cm^{-1} are almost coincident with strong absorption bands in the 80K i.r. spectrum[5] of K_3Cr(CN)$_6$ and must be assigned as T_{1u} vibrations. There is only weak i.r. absorption at about 360 cm^{-1}, so that this vibration must be the T_{2u} Cr–C–N bending mode. The assignment of the C–Cr–C deformation modes is complicated by strong coupling to lattice modes but a similar argument shows that bands in the luminescence spectrum at 86 and 96 cm^{-1} have mainly T_{2u}C–Cr–C bending character and that bands are 143, 152, 162, and 166 cm^{-1}, have considerable T_{1u} C–Cr–C bending character.

The vibrational modes observed in this work are in fair agreement with the earlier normal co-ordinate analysis of Nakagawa and Shimanouchi[4] and support their assignments, but further work is required to establish whether a physically reasonable F-matrix can be found which reproduces the position and splitting of the T_{1u} and T_{2u} modes using the assignments of Jones.

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