# The Raman Spectrum of $[(C_5H_5)Fe(CO)]_4$: a Resonance Effect

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*Summary* The deep-green colour of $[(C_5H_5)Fe(CO)]_4$ suppresses Raman scattering with available light sources, but an intense polarized band has been observed at 214 $cm^{-1}$, and is attributed to the symmetric Fe–Fe stretching mode, enhanced by a resonance Raman effect: the Fe–Fe force constant is estimated at 1·3 mdyn/Å.

METAL–METAL stretching frequencies have been identified in the Raman and i.r. spectra of a variety of binuclear and polynuclear complexes.[1] The associated force constants, calculated with reasonable allowance for mixing with metal–ligand vibrations, agree well with other measures of metal–metal bond strengths, such as dissociation energies, bond lengths, and m.s. fragmentation patterns.[1] A particularly interesting cluster compound is the cyclopentadienyl iron carbonyl tetramer, whose structure[2] is shown in Figure 1. It contains a regular tetrahedron of iron atoms, with triply bridging carbonyl ligands over the tetrahedral faces, and $\pi$-cyclopentadienyl ligands bound terminally. Formally the molecule contains $Fe^{I}$, isoelectronic with $Mn^{0}$, but the Fe–Fe distances, 2·52 Å, are 0·40 Å shorter than the Mn–Mn distance[3] in $Mn_2(CO)_{10}$.

The deep-green colour of $[(C_5H_5)Fe(CO)]_4$ makes it a difficult candidate for Raman spectroscopy. Its molar extinction coefficient ranges between 1000 and 3000 throughout the visible region. There is a weak minimum in the spectrum at *ca.* 5400 Å and two very broad bands extending into the red and blue regions, the latter terminating in a sharp rise to a peak at 3950 Å ($\epsilon_{max} = 19,000$). No Raman scattering could be observed for solid samples or for a saturated chloroform solution, using a variety of exciting frequencies of an $Ar^+/Kr^+$ mixed-gas laser. An attempt was then made to optimize the concentration[4] and light path. A 0·3 mm diameter *X*-ray capillary tube was filled with a $7 \times 10^{-3}$M-solution of the compound in chloroform. Transverse excitation of the sample with a focussed 5682 Å laser beam gave a spectrum with a totally polarized band at 214 cm$^{-1}$, shown in Figure 2. Apart from solvent bands no other Raman emissions could be detected.

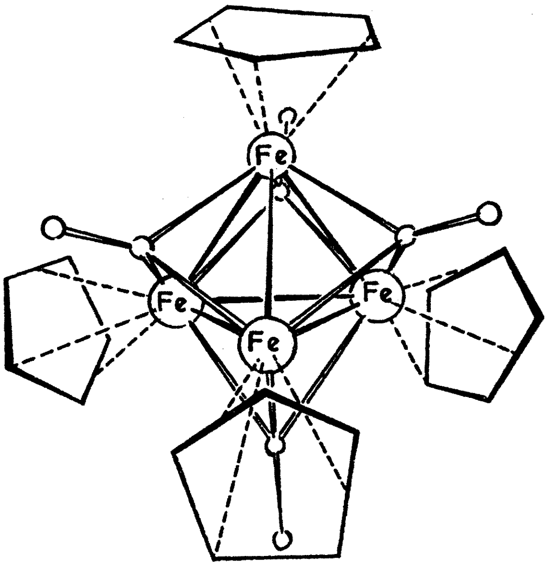

FIGURE 1. *The structure of* $[(C_5H_5)Fe(CO)]_4$ (*taken from ref.* 2).

We assign the 214 cm$^{-1}$ band to the totally symmetric ($A_1$) Fe–Fe stretching mode, and suggest that its observation rests on intensity enhancement through a resonance Raman effect.[4] Comparison of its intensity with that of the adjacent 260 cm$^{-1}$ band of chloroform leads to an estimate of the Fe–Fe bond polarizability derivative,[5] $\bar{\alpha}'$Fe–Fe, of 9 Å$^2$, on the assumption that the mode is pure Fe–Fe stretching. Mixing with other co-ordinates can only result in an increase in this value. In comparison, $\bar{\alpha}'$Mn–Mn is 5·4 Å$^2$ in $Mn_2(CO)_{10}$ (corrected for resonance enhancement)[6] and $\bar{\alpha}'$Ge–Ge is 1·9 Å$^2$ in $Ge_2(CH_3)_6$.[7] Furthermore, the 214 cm$^{-1}$ band was not observed with 6471 Å excitation, although the 260 cm$^{-1}$ chloroform band appeared clearly. We estimate that the relative intensity, $I_{214}/I_{260}$, at 6471 Å is less than 20% of its value at 5682 Å. The 214 cm$^{-1}$ band was observed with shorter wavelength excitation, 5308 and 4880 Å, but bubble formation from localised heating prevented intensity measurements.

If the 214 cm$^{-1}$ band were pure Fe–Fe stretching, the symmetry $A_1$ Fe–Fe force constant would be 0·38mdyn/Å, an unreasonably low value. Interaction with the $A_1$ metal–carbonyl stretching mode (there is no $A_1$ bending mode) is expected to be slight, since the Fe–Fe and Fe–C symmetry co-ordinates are nearly orthogonal. On the other hand, interaction with terminal ligands may be significant,[8] especially when they have high effective mass, as in the present case. An estimate of this effect was obtained as follows. An effective Fe–($C_5H_5$) stretching force constant of 3·47 mdyn/Å was obtained from the $A_1$ Fe–($C_5H_5$) frequency, 301 cm$^{-1}$, of ferrocene,[9] on the assumption of point mass 65 for ($C_5H_5$). This assumption is reasonable since the vibration involves all of the atoms of ($C_5H_5$) moving in phase. A $2 \times 2$ secular determinant, involving only the $A_1$ Fe–Fe and Fe–($C_5H_5$) modes of $[(C_5H_5)Fe(CO)]_4$, was then solved, using $F_{\text{Fe-(C}_5\text{H}_5)} = 3{\cdot}47$ mdyn/Å and $\nu_{\text{Fe-Fe}} = 214$ cm$^{-1}$. The result gave $\nu_{\text{Fe-(C}_5\text{H}_5)} = 550$ cm$^{-1}$ and $F_{\text{Fe-Fe}} = 1{\cdot}3$ mdyn/Å, reflecting a very substantial interaction of the co-ordinates. Similar calculations with the Fe–CO co-ordinate confirmed that its mixing is unimportant. While the present value for $F_{\text{Fe-Fe}}$ must be viewed as provisional, it is clearly much higher than $F_{\text{Mn-Mn}}$ (0·59 mdyn/Å)[10] in $Mn_2(CO)_{10}$, in accord with the pronounced shortening in bond length.

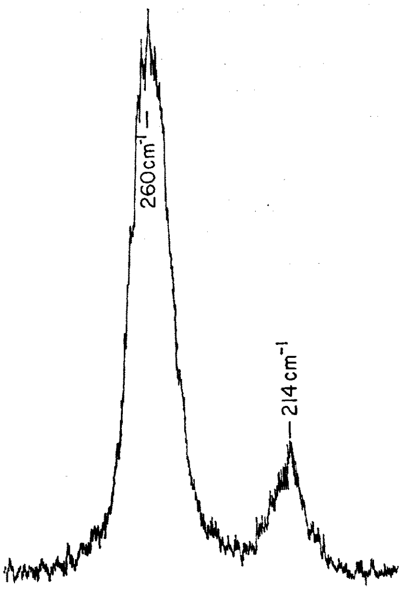

FIGURE 2. *The* 214 cm$^{-1}$ *Raman band* (*totally polarized*) *of* $7 \times 10^{-3}$M-$[(C_5H_5)Fe(CO)]_4$ *in* $CHCl_3$, *contained in a* 0·3 *mm* X-*ray capillary.*

*Transverse excitation with a* 5682 Å $Ar^+/Kr$ *laser beam. Instrument conditions: slit width* 2·5 *cm*$^{-1}$, *scan rate* 22 *cm*$^{-1}$/*min, time constant,* 1 *s.*

The Raman spectrometer used in this work is equipped with a Coherent Radiation Model 52 $Ar^+/Kr^+$ mixed gas laser, and has been described elsewhere.[6]

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