

Relative Intensities in the Raman Spectra of Metal Carbonyl Derivatives in the 2000 cm⁻¹ Region

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Summary The relative Raman intensities and the depolarisation behaviour for the A_1 and E $\nu(\text{CO})$ modes in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ differ considerably; this observation is interpreted in terms of a bond-derived polarisability model.

STUDIES of the variation in the physical properties of terminal carbonyl groups as functions of other ligands bonded to transition metals include the effects of the systematic variation of a phosphine ligand^{1,2} or of substituents in a benzene ring.^{3,4} There appears to have been no study, however, of the electronic effects caused by the enlargement of a symmetrically bonded C_n^- to a C_{n+1}^- membered ring. We report here the surprising differences in kind between the carbonyl groups in the species $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$.

The crystal structures of each of the above compounds have been determined^{5,6} and it has been found that in both the terminal CO groups closely approximate to local C_{3v} symmetry, the angle between pairs of carbonyl groups being very close to 90°. In this situation the relative intensities of the A_1 and E carbonyl stretching modes in the Raman spectra are given by the expressions (1) and (2) where b is the bond derived polarisability tensor element along the CO bond axis whilst a and c are those transverse to this bond. The Cartesian axis corresponding to c is symmetrical and that corresponding to a is antisymmetrical in the local mirror plane.

The observed Raman spectra of these two species recorded in dichloromethane solution with 632.8 nm radiation are

is essentially cylindrically symmetric for $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, but there is a considerable asymmetry in the case of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$.

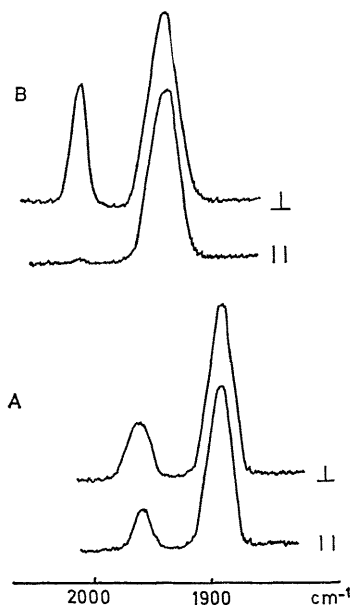


FIGURE. Solution Raman Spectra. A: $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ in CH_2Cl_2 , B: $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ in CH_2Cl_2 . \perp and \parallel refer to direction of observation in relation to electric vector of incident laser beam.

$$\frac{I_p(E)}{I_p(A_1)} (\perp) \sim \frac{[3.5(a^2 + c^2) + 4.7(b^2 - ab - bc) - 2.3ac]}{[4.5(a^2 + c^2) + 6.7(ab + bc) + 4.3ac + 3.3b^2]} \quad (1)$$

$$\frac{I_p(E)}{I_p(A_1)} (\parallel) \sim \frac{[3.0(a^2 + c^2) + 4.0(b^2 - ab - bc) - 2.0ac]}{(a - c)^2} \quad (2)$$

shown in the Figure. It is evident that the intensity pattern given by the manganese compound requires that $a \simeq c$. In this case the expression for $I_p(E)/I_p(A_1) (\perp)$ reduces to that given elsewhere for a carbonyl of O_h symmetry.⁷ We conclude that the change in bond polarisability consequent upon an alteration in the CO bond length

From the observed intensities (Table) it may be concluded that $\frac{b}{a}$ (or $\frac{b}{c}$) for $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ is ca. -6.66 or -0.86 .

For $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, $\frac{b}{a}$ is ca. $+9.10$ or -1.28 whilst the

TABLE

Compound	ν_E	ν_{A_1}	$\frac{I_p(E)}{I_p(A_1)} (\perp)$	$\frac{I_p(E)}{I_p(A_1)} (\parallel)$	$\rho(E)$	$\rho(A_1)$	Solvent
$\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$..	1893	1970	8.3	11.4	0.85	0.60	CH_2Cl_2
$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$..	1934	2016	3.7	67.0	0.86	0.05	CH_2Cl_2
$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$..	1936	2022	3.7	∞	0.86	ca. 0	C_6H_6

corresponding values of $\frac{b}{c}$ are -1.28 and $+9.10$, respectively [expressions (1) and (2) being symmetric in a and c]. The derived CO bond polarisability tensor elements commonly differ in sign in the metal carbonyls.⁷ The present work shows that their relative ratios may also vary considerably. This is endorsed by the observation that, for $C_6H_6Cr(CO)_3$,

a and c differ in sign [*cf.* $C_5H_5Mn(CO)_3$]. For the manganese compound the O_h -like behaviour of the Raman intensities is also reflected in the $\rho(A_1)$ value.

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