Relative Intensities in the Raman Spectra of Metal Carbonyls in the 2000 cm^{-1} Region

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Summary The relative intensities of bands in the Raman spectra of transition-metal carbonyls in the 2000 cm^{-1} region are anomalous and indicate that the bond derived polarisability tensor elements are of opposite sign along and transverse to the CO bond axis.

A GENERALISATION frequently made is that the bands corresponding to totally symmetric molecular vibrations are the most intense in Raman spectra.[1] Here we report our observation that for transition-metal carbonyls, $M(CO)_n; n > 1$, in the 2000 cm^{-1} region, these bands are relatively weak, and our interpretation of this phenomenon. Although the phenomenon and explanation are general we confine our discussion to octahedral metal carbonyls and, in particular, to $Cr(CO)_6$. The Raman spectrum of a methylene dichloride solution recorded with a He–Ne gas laser (6328 Å) source is shown in the Figure. Since the compound is colourless the resonant Raman effect can be expected to be absent and this was confirmed by argon ion laser studies.

Species	Solvent	$I_p(A_{1g})/I_p(E_g)$	
$[Re(CO)_6]^+$	MeCN	0·44	Ref. 6
$Cr(CO)_6$	CH_2Cl_2	0·14	This work
$Mo(CO)_6$	CH_2Cl_2	0·14	This work
$W(CO)_6$	CH_2Cl_2	0·16	This work
$[V(CO)_6]^-$	MeCN	0·08	Ref. 6

The Wolkenstein[2] approach to Raman intensities is applicable in the present case.[3] If the component of the derived polarisability tensor along the CO bond axis is denoted b and that perpendicular to it a, then it may readily be shown that, for polarised incident light, the relative intensities of the bands corresponding to vibrations of A_{1g} and E_g symmetry are given by equation (1)[4] to a good level of approximation.

$$I_p(A_{1g})/I_p(E_g) = 5/7 \times (b + 2a)^2/(b - a)^2 \qquad (1)$$

The observation that $I_p(A_{1g})/I_p(E_g)$ is *ca.* 0·14 is consistent with b/a being either *ca.* −1·1 or −4·5. In either case, it is evident that the derived polarisability tensor elements a and b must be of opposite sign. This is in contrast with the common case in which longitudinal and transverse bond polarisability derivatives are believed to be of the same sign, leading to intense bands corresponding to totally symmetric vibrations.[5] Of the two possible values of b/a, that of −4·5 seems the more probable because of its relationships to the solutions of equation (1) corresponding to $I_p(A_{1g}) > I_p(E_g)$ (for which it is believed that b/a is positive). The unusual behaviour of the carbonyl ligand may well be a reflection of the different response of CO σ and π electron-densities to bond-length changes. For octahedral species the ratio $I_p(A_{1g})/I_p(E_g)$ increases with increase of formal positive charge in the carbonyl species, as shown in the Table. This phenomenon may well be general—it also occurs for the isoelectronic species $[Fe(CO)_4]^{2-}$, $[Co(CO)_4]^-$, and $Ni(CO)_4$.[7]

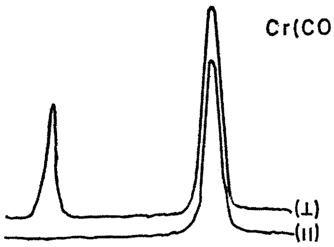

FIGURE. *Raman spectrum of a methylene dichloride solution of* $Cr(CO)_6$ *recorded with a* He–Ne *gas laser* (6328 Å) *source.*

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