# Solid State Studies. Part VII. A Single-crystal Raman Study of the Vibration of the $Cr(CO)_3$ Unit in Hexa- and Penta-methylbenzenetricarbonylchromium

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Single-crystal Raman studies of the isomorphous title compounds have shown that, whilst a vibrational factor-group method offers the simplest explanation of the 2000 cm$^{-1}$ region, some features remain unexplained by it.

IN a recent study of the solid-state vibrational spectra of the isomorphous compounds hexamethyl- and pentamethyl-benzenetricarbonylchromium it was suggested that, although the correct factor group is $D_{2h}^{15}$, an analysis of the spectra in the 2000 cm$^{-1}$ region is more appropriately carried out in $D_{2h}^{11}$, the size of the unit cell being halved.[1] The latter is preferable, as a first approximation, because it recognises that in the hexamethyl compound (and, presumably, the pentamethyl also) each $Cr(CO)_3$ lies on a local, but not (quite) crystallographic, mirror plane, all these local mirror planes being parallel. Even this approach does not recognise the full pseudo-symmetry of the $Cr(CO)_3$ units. Each of these retains, to a good approximation, the threefold rotation axis of the isolated molecule. In the crystal structure, although $z = 8$, the $Cr(CO)_3$ units are packed so that these pseudo-three-fold axes are almost parallel. Although it does not seem possible to exploit this observation by a simple transposition to a factor group appropriate to a trigonal system, the arrangement undoubtedly has an important effect on the vibrational spectra. For instance, it provides an explanation for the observation of a single intense band derived from the (molecular) totally symmetric CO stretching vibration whilst the full factor group predicts three bands in this region and the modified factor group predicts two.

The crystal structure of the hexamethyl compound has been determined and we have shown that the pentamethyl is isomorphous. This observation implies a disorder in the crystal packing of the latter compound to accommodate the $CH_2$-group difference between the two compounds.

It is to be expected that, as resolution increases, the analysis of the 2000 cm$^{-1}$ region in terms of a vibrational factor group will break down since its use implies degeneracy between modes which are distinct in the full factor group. Only if appropriate symmetry non-related interaction constants are precisely equal can such a degeneracy persist. A test of the applicability of the vibrational factor-group model can be made in two ways. First, the spectral resolution may be increased. Secondly, the symmetry characteristics associated with individual spectral features may be determined. The room-temperature i.r. spectra are relatively broad and, although some narrowing occurs on cooling to −196 °C, no new features emerge. The Raman peaks in a polycrystalline sample are also narrower but, again, no new features appear on cooling. In all these cases the resolution in the spectra was band-width limited (the instrumental resolution being 1 cm$^{-1}$ or better). We have therefore directed our attention to single-crystal Raman studies. Ideally, these should be carried out at −196 °C. Although such studies have been attempted the decreased collection angle, resulting from the large cryostat needed, resulted in a poor signal-to-noise ratio. Further, the difficulty of crystal alignment resulted in increased breakthrough. The low-temperature spectra are, consequently, clearly inferior to those obtained at room temperature. We therefore report only the latter.

## RESULTS AND DISCUSSION

Tricarbonylpentamethylbenzenechromium crystallises in the orthorhombic *Pbca* space group with eight molecules in a unit cell of dimensions $a = 13{\cdot}65$, $b = 13{\cdot}45$, and $c = 15{\cdot}24$ Å. Crystals were easily obtained from 1 : 1 diethyl ether : di-isopropyl ether solutions as rectangular blocks of dimensions *ca.* 10 × 3 × 1 mm bounded by {100} and with well developed (010) faces. The crystal shape is therefore ideal for a single-crystal Raman study. In particular, breakthrough would be expected to be small. This proved to be the case for all the several crystals studied. The preparation and analysis of the compound have been detailed elsewhere.[1]

Tricarbonylhexamethylbenzenechromium also crystallises in the orthorhombic space group *Pbca* ($D_{2h}^{15}$) with $Z = 8$ and has a unit cell of dimensions $a = 13{\cdot}67$, $b = 13{\cdot}53$, and $c = 15{\cdot}27$ Å.[2] In contrast to the pentamethyl compound, it proved very difficult to obtain good quality crystals of tricarbonylhexamethylbenzenechromium. The compound is only moderately soluble in di-isopropyl ether (a solvent we have found it advantageous to use for crystal-growing purposes). It is slightly more soluble in benzene, but the crystals obtained were inferior in quality to those from di-isopropyl ether. Crystals were eventually obtained from di-isopropyl ether as essentially rectangular plates, of varying dimensions. The largest, *ca.* 3 × 1 × 0·2 mm, was used for the spectra reported in this paper. The crystals were commonly of hexagonal cross-section, a few with developed (102) faces, but the majority with well developed (001) faces. As for the pentamethyl compound, the crystal studied

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[1] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc.* (*A*), 1969, 2224.

[2] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.

was oriented from its conoscopic interference figures and the axes identified by $X$-ray techniques (see Figure 1). The small size of the crystal prevented cutting to a rigorous rectangular shape, so some breakthrough effects are to be expected in the spectra.

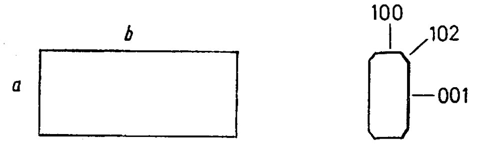
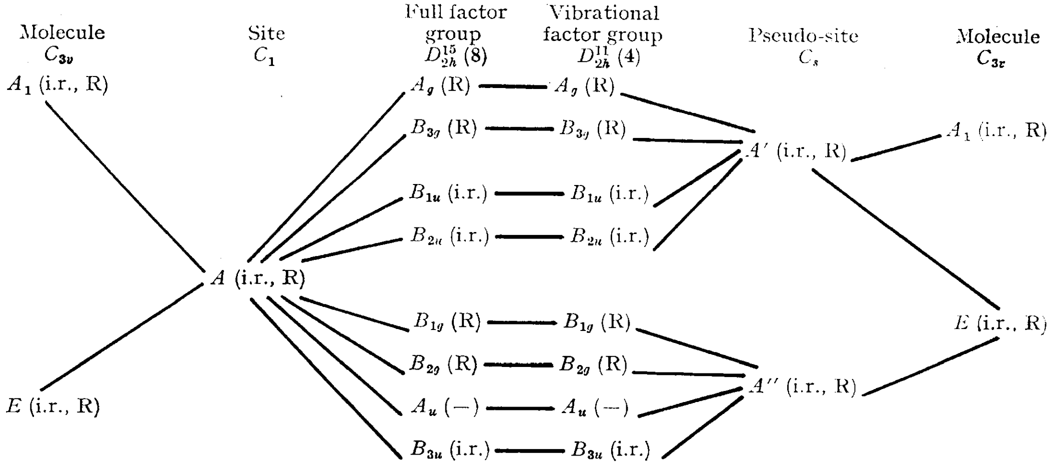


**Figure 1** The morphology of tricarbonylhexamethylbenzenechromium

We have found that the expectation of less breakthrough in the case of the pentamethyl compound was realised. This species, then, provides the more incisive test of the applicability of the alternative factor groups. Because the symmetry elements whose existence is implied by a $D_{2h}^{11}$ factor group are not crystallographic the breakdown of the vibrational factor-group model would most probably be manifested by spectral observations which are intermediate between those appropriate to $D_{2h}^{11}$ and $D_{2h}^{15}$. That is, the degeneracies implied by $D_{2h}^{11}$ would be relieved.

Table 1

Correlation table for tricarbonylhexamethylbenzenechromium



In changing from $D_{2h}^{15}$ to $D_{2h}^{11}$ there is, in standard setting, a permutation of co-ordinate axes: $z(D_{2h}^{15}) \longrightarrow y \longrightarrow x$. We avoid the problems arising from this by using the inverse permutation to refer $D_{2h}^{11}$ factor-group predictions to the same co-ordinate system as $D_{2h}^{15}$. Using this notation, the two groups are related by what is, in $D_{2h}^{11}$, the factor-group coset isomorphic to $\sigma(yz)$ in $D_{2h}$ becoming the $y$ axial glide coset in $D_{2h}^{15}$. Physically, the distinction between the two space groups is that the two 'half' unit cells in $D_{2h}^{15}$ are required to vibrate in-phase in $D_{2h}^{11}$ (being related by a pure translation) but in $D_{2h}^{15}$ the out-of-phase vibration is also allowed. Evidently, the two cases may be distinguished by the $\sigma_h(yz)$ operation in the isomorphic point group. The correlation is given in Table 1, from which the spectral predictions follow directly (note that $A_u$ vibrations are the only inactive species).

$$\begin{array}{ccc}
D_{2h}^{11} & & D_{2h}^{15} \\
A_g & \longrightarrow & A_g + B_{3u} \\
B_{1g} & \longrightarrow & B_{1g} + B_{2u} \\
B_{2g} & \longrightarrow & B_{2g} + B_{1u} \\
B_{3g} & \longrightarrow & B_{3g} + A_u \\
A_u & \longrightarrow & A_u + B_{3g} \\
B_{1u} & \longrightarrow & B_{1u} + B_{2g} \\
B_{2u} & \longrightarrow & B_{2u} + B_{1g} \\
B_{3u} & \longrightarrow & B_{3u} + A_g
\end{array}$$

The simplest distinction between the vibrational and full factor-group analyses is that the latter predicts twice as many Raman peaks as the former. It was on this basis that the applicability of a vibrational factor-group approach was first suggested. The transition $D_{2h}^{11} \longrightarrow D_{2h}^{15}$ would be expected to be characterised by weak peaks occurring in the Raman at positions approximating to those of i.r. absorptions (Table 1). Further, the symmetry species of these weak peaks is clear. Thus, in those vibrations arising from molecular $A_1(C_{3v})$ modes, $D_{2h}^{11}$ predicts Raman features of $A_g$ and $B_{3g}$ symmetry, whilst the applicability of $D_{2h}^{15}$ will be indicated by the presence of additional peaks associated with vibrations of $B_{1g}$ and $B_{2g}$ species. Analogous arguments apply to the i.r. spectrum but the peaks are too broad to permit the observation of additional features unless these are themselves rather intense.

The arrangement of the $Cr(CO)_3$ units in the unit cell in *ab* projection is shown in Figure 2 for the hexamethyl compound.[2] The orientation of the pseudo-mirror planes and pseudo-three-fold axes discussed earlier is evident from this Figure.

The correlations between the molecular, vibrational, and full factor groups are shown in Table 2 together with the predicted Raman activities. The single-crystal Raman spectra of the pentamethyl derivative are shown in Figure 3 and those of the hexamethyl in Figure 4, the corresponding data being detailed in Tables 3 and 4.

TABLE 2

Factor and point group correlations

| Full factor group ($D_{2h}^{15}$) | Molecular mode ($C_{3v}$) | Vibrational factor group[1] ($D_{2h}^{11}$) |
|---|---|---|
| $A_g$ $(xx, yy, zz)$ | $A_1$ | $A_g$ $(xx, yy, zz)$ |
| $B_{1g}$ $(xy)$ | | $B_{3g}$ $(yz)$ |
| $B_{2g}$ $(xz)$ | | |
| $B_{3g}$ $(yz)$ | | |
| $2A_u$ $(xx, yy, zz)$ | $E$ | $A_g$ $(xx, yy, zz)$ |
| $2B_{1g}$ $(xy)$ | | $B_{1g}$ $(xy)$ |
| $2B_{2g}$ $(xz)$ | | $B_{2g}$ $(xz)$ |
| $2B_{3g}$ $(yz)$ | | $B_{3g}$ $(yz)$ |

TABLE 3

Infrared and single-crystal Raman frequencies (cm$^{-1}$) for the carbonyl stretching vibrations of tricarbonylpentamethylbenzenechromium

| Infrared | | | Raman intensities ‡ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Solid state † | | Solution | | | | | | | | |
| I | II | (CCl$_4$) | $\Delta\nu$ | $Z(XX)Y$ | $Z(YY)X$ | $Y(ZZ)X$ | $Z(YX)Y$ | $Z(XZ)Y$ | $Z(YZ)Y$ | Assignment |
| 1947 | 1948 | 1957 | *ca.* 1934 | | | | | | 4 | $B_{3g}$ |
| *ca.* 1939sh | *ca.* 1940sh | | 1933 | 25 | 48 | 20 | | | | $A_g$ |
| 1929 * | 1929 * | | *ca.* 1928 | 9 | 22 | 9 | | | | $(A_g)$ |
| 1876 | 1877 | | 1879 | | | (4) | | 47 | | $B_{2g}$ |
| *ca.* 1866sh | 1867 | | *ca.* 1873 | | | | | 11? | | $(B_{2g})$ |
| *ca.* 1858 | 1859 | 1883 | 1868 | | | | | | 10 | $(B_{3g})$ |
| 1853 | 1849 | | 1859 | | | | | | 100 | $B_{3g}$ |
| 1822 * | 1821 * | | 1857 | 39 | 11 | 19 | (11) | (3) | | $A_g$ |
| | | | 1851 | 5 | 6 | 7 | | | | $(A_g)$ |
| | | | 1849 | | | (3) | 69 | | | $B_{1g}$ |

* $^{13}$CO. † I, Room temperature; II, low temperature. ‡ Peak heights (arbitrary units).

TABLE 4

Infrared and single-crystal Raman frequencies (cm$^{-1}$) for the carbonyl stretching vibrations of tricarbonylhexamethylbenzenechromium

| Infrared | | Intensities ‡ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Solid state | Solution (CCl$_4$) | $\Delta\nu$ | $Z(XX)Y$ | $X(YY)Z$ | $X(ZZ)Y$ | $X(YX)Z$ | $X(ZX)Z$ | $X(ZY)Z$ | Assignment |
| 1945 | | 1928 | 24 | 46 | 16 | | | (3) | $A_g$ |
| *ca.* 1938sh | 1953 | 1924sh | 12 | 20 | 6 | | | | $(A_g)$ |
| 1926 * | | | | | | | | | |
| 1869 | | 1872 | (6) | | (16) | | 35 | | $B_{2g}$ |
| *ca.* 1854sh | | 1864 | | | | | | 12 | $(B_{3g})$ |
| 1849 | 1879 | 1851 | | | | | | 100 | $B_{3g}$ |
| 1819 * | | 1850 | 46 | 8 | 30 | (13) | (4) | | $A_g$ |
| | | 1845 † | (14) | (4) | (5) | 60 | (2) | (4) | $B_{1g}$ |

* $^{13}$CO. † There is possibly a coincident peak. ‡ Peak heights (arbitrary units).

*$A_g$ Modes* [$z(xx)y$, $z(yy)x$, $y(zz)x$].—It is clear from both Figures 3 and 4 that only two strong peaks are common to all the above spectra [because $x^2$, $y^2$, and $z^2$ transform independently as $A_g$, identical relative band intensities are not expected for $(xx)$, $(yy)$, and $(zz)$ observations, only a correspondence between frequencies]. An additional feature in the $(zz)$ spectra is undoubtedly breakthrough of a $B_{2g}$ mode which is seen strongly in $(xz)$ polarisation. This peak is also seen in the $(xx)$ spectrum of the hexamethyl compound. Although not evident from Figures 3 and 4, it is clear from Tables 3 and 4 that there is also some breakthrough from a $B_{1g}$ mode. An unexpected observation is the appearance of a second $A_g$ peak some 5 cm$^{-1}$ to low energy of the main $A_g$ peaks in all the spectra. Although no such peak is shown associated with the 1850 cm$^{-1}$ $A_g$ mode in Table 4 it seems probable that one occurs, unresolved from the 1845 cm$^{-1}$ $B_{1g}$ peak (the separation between the two peaks in the pentamethyl spectra is only 2 cm$^{-1}$). In the case of the higher energy $A_g$ mode the additional feature cannot be associated with a breakdown in the vibrational factor-group model since the full factor group does not predict an additional $A_g$ mode. We incline to the view that this peak is a hot band involving a low-frequency lattice mode. It would not be expected that cooling to −196 °C would significantly alter the intensity of this peak and, indeed, we were unable to detect any change (although the poor signal-to-noise ratio of our low temperature spectrum might well have obscured any variation). The status of the $A_g$ peaks at 1845(9) cm$^{-1}$ is also unclear. Their presence could be taken as evidence against the applicability of the vibrational factor-group approach. However, before accepting this viewpoint we would seek similar evidence relating to modes of different symmetry. In the absence of such confirmatory data we incline to the view that these peaks have a similar origin to those at 1924(8) cm$^{-1}$.

*$B_{1g}$ and $B_{2g}$ Modes* [$x(yx)z$, $z(yx)y$, $z(xz)y$), $x(zx)z$].—These modes are considered together because in each case the vibrational factor group predicts a single peak whilst the full factor group predicts two. As is evident from Figures 3 and 4, to a first approximation the

vibrational factor-group method is applicable. In no spectrum is there any evidence for a second peak of $B_{1g}$ symmetry. In the pentamethyl compound there is probably a second $B_{2g}$ peak, some 6 cm$^{-1}$ lower in energy than the main peak. This additional peak is reminiscent of the additional peaks found in the $A_g$ spectra and could have a similar origin. Equally, it could indicate the approximate nature of the vibrational factor-group approach.

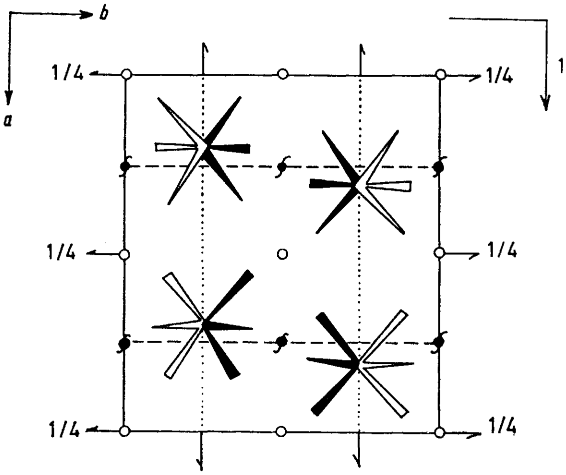


FIGURE 2 The projection of the Cr(CO)$_3$ units, symbolically represented, in the unit cell of tricarbonylhexamethylbenzenechromium onto the *ab* plane

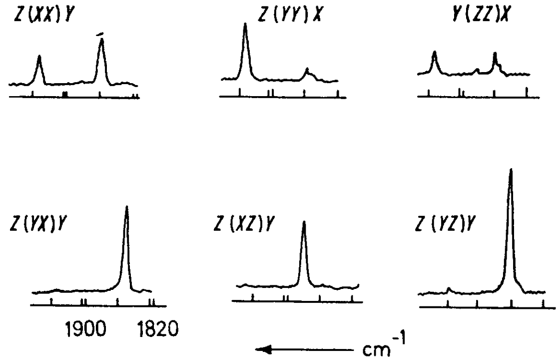


FIGURE 3 Single-crystal Raman spectra of tricarbonylpentamethylbenzenechromium

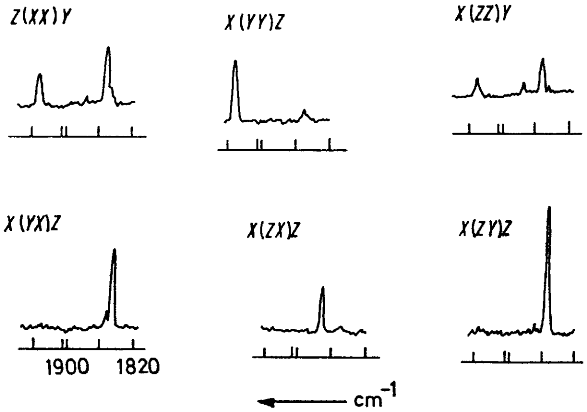


FIGURE 4 Single-crystal Raman spectra of tricarbonylhexamethylbenzenechromium

*$B_{3g}$ Modes* [$x(zy)z$, $z(yz)y$].—In contrast to the prediction of two and three peaks, respectively, from the vibrational and full factor-group methods, it is clear from Figures 3 and 4 that only a single strong $B_{3g}$ peak occurs (some breakthrough of the *ca.* 1930 cm$^{-1}$ $A_g$ peak is seen). The 'missing' peak should also appear in the *ca.* 1930 cm$^{-1}$ region. However the reason for its absence seems clear; it lies in the near-parallel nature of the local threefold axes of the individual molecules discussed at the beginning of this paper. This alignment means that in forming the crystallographic derived-polarisability tensors appropriate to the various Raman-active species derived from the local $A_1$ (in $C_{3v}$) modes, only the totally symmetric combination (++++) of molecular derived-polarisability tensors will not vanish (using a Wolkenstein approach). A zero, or, at least, very low intensity for the Raman peak associated with the $B_{3g}$ mode is therefore predicted. Similar arguments (in $D_{2h}^{15}$) apply to the $B_{1g}$ and $B_{2g}$ peaks in this region and indicate the importance of the *ca.* 1850 cm$^{-1}$ region in distinguishing between the alternative factor groups.

The $B_{3g}$ species are of particular importance in this respect because, as Tables 3 and 4 indicate, there is a peak of this species *ca.* 10 cm$^{-1}$ to *high* energy of the strong $B_{3g}$ peak in this region in both penta- and hexamethyl spectra. Although a two-quantum explanation cannot be excluded, the most probable explanation for this observation seems to be the approximate nature of the vibrational factor-group method.

*The Low Frequency Region.*—The interpretation of the low frequency spectra of metal carbonyl species in the solid state is, like the corresponding molecular spectra, made difficult by the extensive mixing of M–C stretching vibrations with M–C–O deformations. Additionally, further complications are introduced by the appearance of lattice modes together with corresponding overtone and combination bands. That there is some considerable lack of concordance between the two sets of data below *ca.* 300 cm$^{-1}$ may well be associated with the disorder which is presumably present in the pentamethyl compound. The data are similar to those found by Adams and Squire [3] in their work on polycrystalline forms.

A common observation is that a particular peak occurs in more than one polarisation. The magnitude of the effect is such that it cannot be attributed to breakthrough. Rather, we believe, it originates in the small extent of factor groups splitting in the low-frequency internal modes. In this situation, the information which can be obtained from single-crystal studies is small. We shall therefore not discuss our data further. Detailed data have been treated as a Supplementary publication (No. SUP 21293, 5 pp.).*

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* For details of the Supplementary publication scheme, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[3] D. M. Adams and A. Squire, *J. Chem. Soc.* (*A*), 1970, 814.

*Conclusion.*—Although the vibrational factor group offers the simplest explanation for the main features observed in both the polycrystalline and single-crystal Raman spectra of penta- and hexa-methylbenzenetricarbonylchromium in the 2000 $cm^{-1}$ region, it cannot account for all the additional features revealed by single-crystal studies. It is clear that the explanation of some of these features lies outside any simple harmonic oscillator/factor-group approach. However, an additional peak observed in ($yz$) polarisation can most readily be explained by the full-factor group. Some of the present ambiguities could only be resolved by a single-crystal study at 4 K.

## EXPERIMENTAL

Spectra were recorded on a Spex 1401 instrument using 632·8 nm excitation and photon counting. Incident power was usually in the range 10—20 mW. Spectral slit width was 1 $cm^{-1}$ or better.

[4/264 *Received, 11th February,* 1974]