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SOLID STATE STUDIES

XXVIII *. RAMAN INTENSITY ANOMALIES AND INTERMEDIATE MODE BEHAVIOUR IN THE ν(CO) REGION IN MIXED CRYSTALS OF $M(CO)_5X$ ($M = Mn, Re; X = Cl, Br$) **

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Summary

The Raman spectra of mixed crystals containing $Mn(CO)_5X$ ($X = Cl, Br$) and $Re(CO)_5X'$ ($X' = Br, Cl$) show band broadening and both band weakening and enhancement in the ca. 1975 cm^{-1} region. These phenomena are associated with weak vibrational coupling between micro-domains of the pure components in the crystal and, thus, with so-called intermediate-mode coupling.

The ν(CO) vibrational spectra of the manganese and rhenium pentacarbonyl halides have been the subject of extensive study. Whilst their vibrational spectra in the ν(CO) region in solution are well understood [1–16], the spectra of the crystalline materials present new problems. It is clear that in the crystal the ν(CO) vibrations of different molecules may be coupled together [17], a phenomenon found for many metal carbonyl species. This coupling is both mode and structure sensitive. Thus, some ν(CO) molecular normal vibrations may be inter-molecularly coupled whilst

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* For Part XXVII see Ref. 24.

** Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983. S.F.A.K. had the privilege of obtaining his PhD under the supervision of Professor Emeléus. That work was concerned with the tin hydrides, and, as a sideline, some preliminary studies were made of the reactions between SnH_4 and some transition metal carbonyls. The work was not carried to a stage at which it could be published, but it did serve as an introduction to metal carbonyls, the subject of the present communication.

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others are not. Generally, one would expect those vibrations which are strongly infrared active to show the greatest intermolecular coupling (because of strong dipole-dipole coupling). However, if the appropriate vibrators are physically well separated in the lattice, *mutatis mutandis*, a smaller coupling is expected. There is, then, the possibility that vibrational data can provide crystal structure data, in much the same way that solution vibrational data may provide molecular structural data for metal carbonyls. In practice, the search for structural data has revealed a wealth of information on intermolecular vibrational coupling, and it is this that has tended to take over as the immediate object of the study.

In the case of $M(CO)_5X$ species ($M = Mn, Re$; $X = Cl, Br$) it has been found that the highest frequency (molecular A_1) peak is two mode (i.e. not vibrationally intermolecularly coupled) in character whereas all other $\nu(CO)$ features are either one- or intermediate-mode (i.e. coupled to some extent) [17]. Detailed studies have revealed the existence of an intensity-stealing phenomenon in the Raman spectrum such that one factor group component of the molecular B_1 mode is mixed with a molecular E-mode-derived component of the same factor group symmetry (factor groups are derived from space groups; the need to use factor groups implies the existence of intermolecular vibrational coupling). Finally, the lowest frequency $\nu(CO)$ feature of A_1 symmetry, whilst subject to clear factor group splitting in the solid state commonly shows intermediate mode behaviour in mixed crystals. Associated with this intermediate mode behaviour there are intensity asymmetries and it is these asymmetries which are the subject of the present paper.

Before proceeding to these problems it is convenient to enumerate pertinent features of the $\nu(CO)$ spectra of $M(CO)_5X$ species and of their crystals.

(a) X-ray diffraction measurements indicate that all of these species are isomorphous and form mixed crystals over the complete span of concentrations.

(b) They crystallise in the *Pnma* (D_{2h}^{16}) space group with $Z = 4$ [18].

(c) In the crystal the unique, axial, CO groups all lie in parallel planes; projected onto a common plane, the axial CO groups are either parallel or subtend an angle of ca. 74°.

(d) The splitting of ca. 5 cm^{-1} observed in the Raman spectra of the $\nu(CO)$ axial band in the pure compounds at ca. 1955 cm^{-1} is established as factor group in origin because:

(i) A splitting into two components (of A_g and B_{2g} symmetries) is predicted by a factor group analysis.

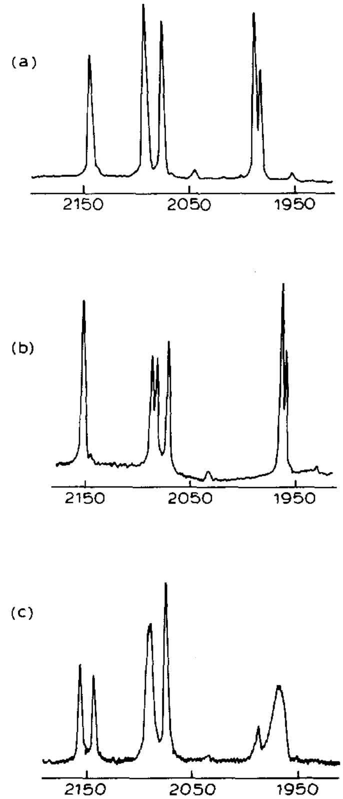
(ii) The corresponding infrared spectra also show two components which are non-coincident with the Raman, as predicted by a factor group analysis (B_{1u} and B_{3u} modes are predicted).

(iii) A single crystal Raman study has shown that the two Raman bands have different polarization characteristics [19].

(iv) In mixed crystals the Raman peaks broaden and show an intermediate mode behaviour, albeit with the complications which are the subject of the present paper. Such behaviour indicates the presence of intermolecular vibrational coupling.

(v) The molecular $\nu(CO)$ axial vibration is strongly dipole active so that intermolecular dipole-dipole coupling would be expected and would manifest itself in factor group splitting.

We turn now to the specific problems which are the concern of this paper. The central problem is demonstrated in Fig. 1(a)–1(c). Figure 1(a) shows the Raman



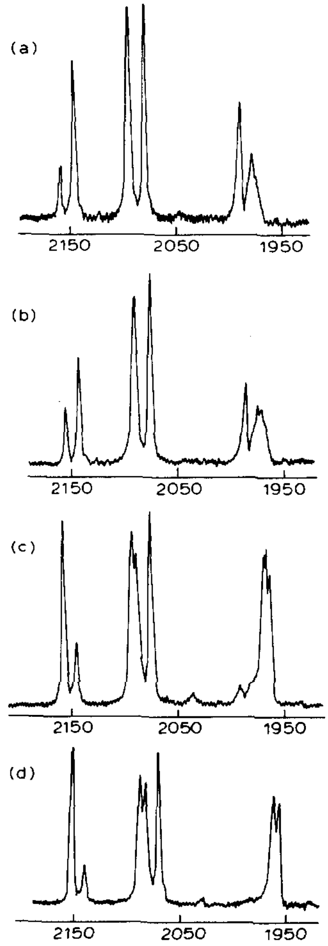


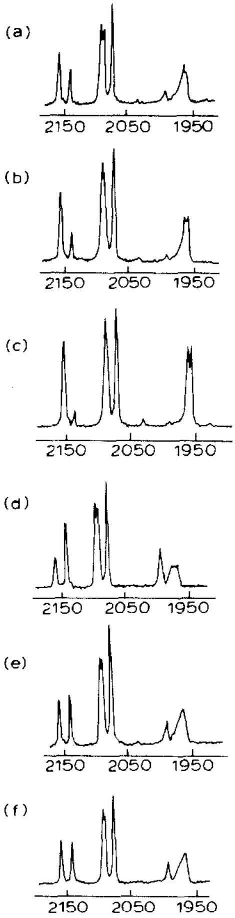
Fig. 1. The Raman spectra in the 2000 cm^{-1} region of (a) $Mn(CO)_5Cl$; (b) $Re(CO)_5Br$ and (c) a 1 : 1 co-crystallised mixture of $Mn(CO)_5Cl$ and $Re(CO)_5Br$.

Fig. 2. The Raman spectra in the 2000 cm^{-1} region of $[Mn(CO)_5Cl]_x[Re(CO)_5Br]_{1-x}$: (a) $x = 0.80$; (b) $x = 0.65$; (c) $x = 0.35$; (d) $x = 0.20$. Note that the $x = 0.5$ case is given in Fig. 1(c).

spectra of polycrystalline $Mn(CO)_5Cl$ in the 2000 cm^{-1} region and Fig. 1(b) that of $Re(CO)_5Br$. The Raman spectrum of a co-crystallised 1 : 1 mixture of these components is shown in Fig. 1(c). Whereas the A_1 (equatorial) region in Fig. 1(c) is clearly a sum of those of Figs. 1(a) and 1(b), in the A_1 (axial) region there have been clear changes in peak structure, position and relative intensity. The variation of these as a function of the composition of the mixed crystal is shown in Fig. 2.

These phenomena are not confined to the $Mn(CO)_5Cl/Re(CO)_5Br$ case; in Fig. 3 we show the Raman spectra in the $\nu(CO)$ region of mixed crystals containing $Mn(CO)_5Br$ and $Re(CO)_5Cl$. Very similar behaviour to that shown in Fig. 2 is evident in the $\nu(CO)$ axial region at ca. 1975 cm^{-1}.

In the examples shown in Figs. 2 and 3 the crystal components differed both in metal and halogen. Figure 4 shows that it is the former which is significant. This



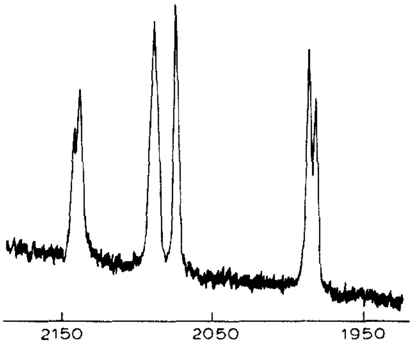


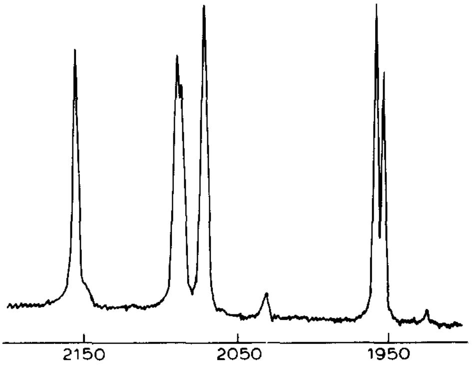
Fig. 3. The Raman spectra in the 2000 cm^{-1} region of $[Mn(CO)_5Br]_y[Re(CO)_5Cl]_{1-y}$: (a) $y = 0.76$; (b) $y = 0.64$; (c) $y = 0.56$; (d) $y = 0.50$; (e) $y = 0.35$; (f) $y = 0.20$.

Fig. 4. The Raman spectrum in the 2000 cm^{-1} region of a 1 : 1 co-crystallised mixture of $Mn(CO)_5Br$ and $Mn(CO)_5Cl$.

figure shows the Raman spectrum in the $\nu(CO)$ region of crystals containing a 1 : 1 co-crystallised mixture of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$. The spectrum is very similar to that of pure $Mn(CO)_5Cl$; that of $Mn(CO)_5Br$ (Fig. 5) is also very similar, the major difference being the splitting seen on the ca. 2090 cm^{-1} peak. This may be compared with the similar splitting seen for $Re(CO)_5Br$ in Fig. 1(b); $Re(CO)_5Cl$ is intermediate in this respect, as is evident from Fig. 6.

A comparison between the frequencies of the $\nu(CO)$ A_1-axial-derived features of Figs. 1 and 6 make clear the origin of the different intensity patterns seen in the 1975 cm^{-1} region in Figs. 1(c), 2 and 3 compared with Fig. 4. The pattern of Fig. 4 is the typical one-mode behaviour of two vibrations at very similar frequencies. In contrast, when Mn- and Re-species are mixed the $\nu(CO)$-axial features are ca. 25 cm^{-1} apart and intermediate mode behaviour is observed.

Although this explanation is, we believe, correct, it is clear that it is also



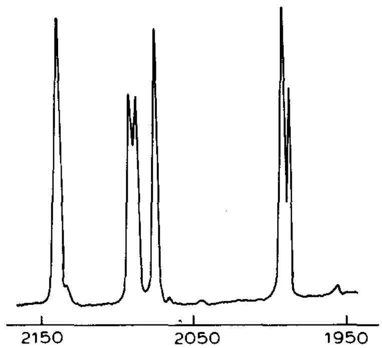


Fig. 5. The Raman spectrum in the 2000 cm^{-1} region of polycrystalline Mn(CO)$_5$Br.

Fig. 6. The Raman spectrum in the 2000 cm^{-1} region of polycrystalline Re(CO)$_5$Cl.

incomplete because it fails to account for the intensity anomalies seen in the 1975 cm^{-1} region in Figs. 1(c), 2 and 3. Thus, Figs. 1(a) and 1(b) show that the relative intensities of ν(CO)-equatorial to ν(CO)-axial features (at ca. 2150 and 1975 cm^{-1}) are very similar in Mn(CO)$_5$Cl and Re(CO)$_5$Br. In the 1 : 1 mixed crystal (Fig. 1(c)), where the ca. 2150 cm^{-1} peaks are of comparable intensities, there is a gross difference in intensities in the ca. 2975 cm^{-1} region.

We believe that the explanation for the intensity anomaly is to be found in a paper by Decius [20] in which he discussed the origin of a similar phenomenon in crystalline nitrates and carbonates. In his case he was able to consider a linear chain of anions and, for this pseudo-one-dimensional case, was able to carry out a detailed analysis. The present example is clearly three-dimensional and a similar unambiguous analysis is not possible. However, the physical picture is clear enough. Consider a 1 : 1 mixed crystal such as those of Fig. 1(c) and 3(d). The mixed crystal is envisaged as containing a random mixture of the two components distributed over the lattice sites. There will, then, be micro-domains of each pure component, each domain bounded by a domain of the alternant component. Each domain will, then, contain a few molecules, the size and shape of these domains being statistically determined. Within each domain the ν(CO) axial vibrators are coupled in-phase (until the domain becomes large enough for putative factor group-type splitting to occur), the amplitude of vibration decreasing towards the edges of the domain. Immediately outside the domain there will be a weak coupling of the ν(CO) axial vibrators of the other component (Re(CO)$_5$Cl, if the domain were of Mn(CO)$_5$Br, for example) which will vibrate either in-phase or out-of-phase with the domain vibration. Decius was able to show that, for his case, the in-phase case occurred for the lower frequency domain vibrator and the out-of-phase case for the higher frequency [20]. In his case, where infrared activity was under consideration, this meant a reinforcement of the dipole strength of the lower frequency mode and a diminution of dipole strength and thus a weakening of the higher. He thus explained the observed intensity anomaly [20]. In our case, too, it is the lower frequency band which enjoys an intensity enhancement relative to the higher frequency. However, it does not follow that the Decius model is immediately applicable. Firstly, the nitrate/carbonate case could be dealt with by a single intermolecular interaction constant (that between adjacent anions in the chain). In our, three dimensional, case more interaction constants would be needed and all need not be of the same sign. Secondly, we are concerned with Raman rather than infrared intensities (the infrared spectra of the crystalline mixed pentacarbonyl halides in the 1975 cm^{-1} region are too broad to make realistic analysis possible). Although Raman intensities may be analytically derived by addition of appropriately orientated molecular derived polarizability tensor elements, these tensor elements, referred to a diagonal tensor, need not – and probably are not – of the same sign [21–23]. This means that Raman intensity enhancement may arise from out-of-phase coupled vibrators, suitably oriented, because the opposite phase may cancel opposite signs of the derived polarizability tensor elements which have to be added.

Conclusions

The intensity anomalies associated with the ca. 1975 cm^{-1} Raman active features in mixed crystals of $M(CO)_5X$ ($M = Mn, Re$; $X = Cl, Br$) is entirely consistent with their description as showing 'intermediate-mode behaviour'. Both originate in the limited effective extent of the intermolecular vibrational coupling of the $\nu(CO)$ axial modes. However, although the qualitative explanation is clear, an unambiguous quantitative analysis is not yet possible.

Experimental

Compounds were prepared and purified by literature methods and mixed crystals formed by rapid crystallisation. The composition of the mixed crystals was determined by comparison of intensities of all features showing two-mode behaviour in the spectra and by comparison with the spectra of physical (non-co-crystallised) mixtures of the same components.

Spectra were run on samples at room temperature on a Spex 1401 double monochromator using photon-counting and an incident laser power of ca. 20 mW at the sample (Spectra-Physics 165 Ar/Kr operating at 6471 Å). Resolution was 2 cm^{-1} and scanning 5 cm^{-1} min^{-1}.

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