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THE RAMAN SPECTRA OF MIXED CRYSTALS OF METAL CARBONYLS IN THE 2000 cm^{-1} REGION *

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Summary

The Raman spectra of mixed crystals of $M_xM'_{1-x}(CO)_6$, $0 < x < 1$ $M',M =$ Cr, Mo, W show an averaging of spectral features in the ν(CO) region for features associated with the molecular e_g modes but a superposition for the a_{1g} feature. This is correlated with the absence of factor group splitting in the latter case. The implication and generalisation of these observations are briefly discussed.

It is now recognised that the interpretation of the vibrational spectra of crystalline metal carbonyls in the 2000 cm^{-1} region requires the use of the so-called factor group approach. A closely related analysis (and one which gives identical spectra predictions) is the unit cell method. The fundamental result of either method is that the observed spectra may, to a good approximation, be predicted by taking as the fundamental vibrating unit the contents of the primitive unit cell. A particularly simple example is provided by the benzene-chromium tricarbonyl molecule which crystallises in the $P2_1/m$ space group. The orientation of the six carbonyl groups in the unit cell is shown in Fig. 1; their transformations under the operations of the appropriate factor group C_{2h}^2, which is isomorphic to the C_{2h} point group, are

$$\begin{array}{cccc} \{E/\tau\}, & \{2_1/\tau\}, & \{i/\tau\}, & \{m/\tau\} \\ 6 & 0 & 0 & 2 \end{array}$$

The irreducible components of this representation are $A_g + B_g + A_u + 2B_u$(using the C_{2h} character table). The spectral activities are also obtained from this table so we predict three peaks in the infrared and three, non-coincident, peaks in the Raman. This is entirely in accord with the spectral observations shown in Fig. 2,

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(apart from the observation of some weak additional peaks which are commonly supposed to result from these molecules, ca. 3% of the total, which contain ^{13}CO groups).

The applicability of this simple analysis rests on the assumption that the wavelength of the incident light used to study the spectra is large compared with typical intermolecular spacings in the crystal. If it is true that the incident light is, effectively, of infinite wavelength then the vibrations in all unit cells throughout the crystal will be excited in-phase (hence the behaviour of a single unit cell is representative of the whole crystal); the observed vibrations will be translationaly invariant. There are many studies in the literature which show that the assumption of translational invariance does not provide an adequate explanation for all spectra features but there is no evidence that it is not applicable to metal carbonyls, at least in the 2000 cm^{-1} region, and we shall assume its validity in this paper.

Observations, such as those given in Fig. 2, of non-coincident infrared and Raman spectra arising from coincident isolated molecule features, clearly indicate that intermolecular vibrational couplings are important. It must not be assumed that these couplings are limited to those occurring between the two $Cr(CO)_3$ groups shown in Fig. 1. There is no unique choice for the unit cell of any crystal, only, at most, a uniquely convenient one. Evidently, a large number of other, surrounding, $Cr(CO)_3$ units may couple with those shown in Fig. 1.

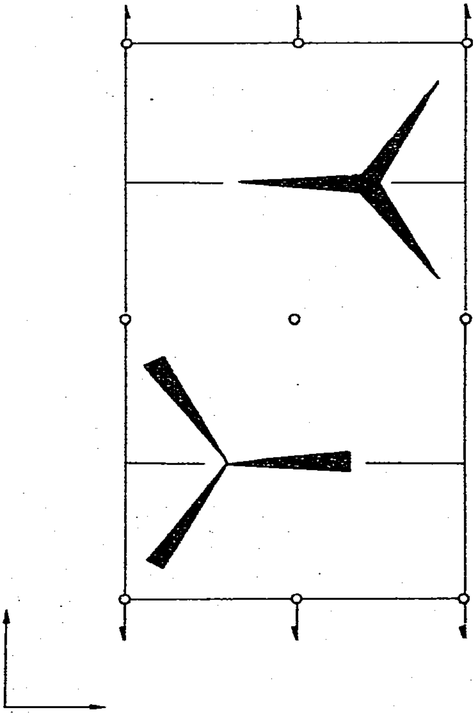


Fig. 1. Orientation of the six carbonyl groups in the unit cell of benzenechromium tricarbonyl (space group $P2_1/m$).

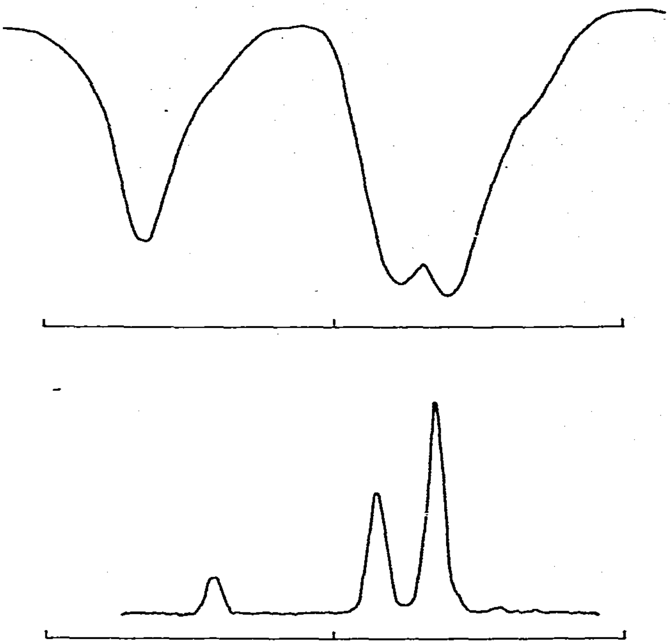
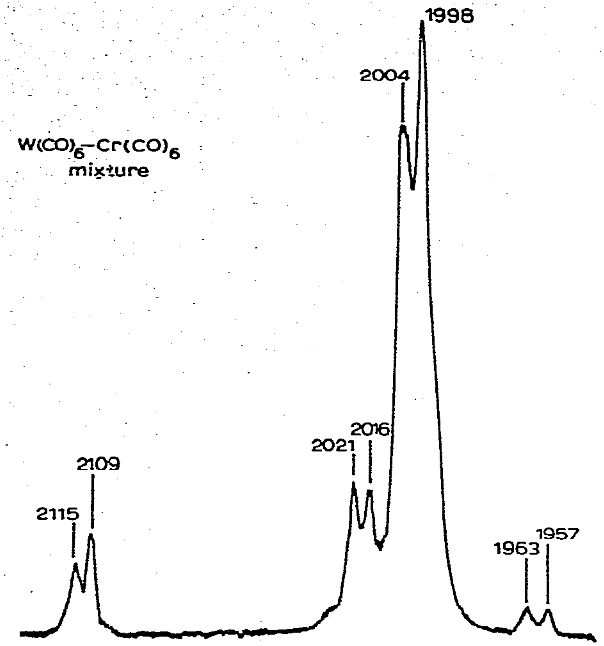


Fig. 2. IR and Raman spectra of benzenechromium tricarbonyl.

There is an apparent inconsistency in the above discussion. Whilst it is clear that the vibrations of the CO groups in different molecules couple with each other it has, nonetheless, been suggested that some of the minor spectral features in Fig. 2 are to be attributed to the presence of ^{13}CO. If this explanation is correct then the relatively small frequency shifts of the isotopic species is sufficient to almost entirely uncouple them from the vibrations of the CO groups of the rest of the lattice. Alternatively, if the ^{13}CO groups are not uncoupled then some other explanation for the weak peaks of Fig. 2 must be sought (probably in terms of anharmonicity or breakdown of the translational invariance approximation).

We have carried out studies on vibrational spectra of crystalline metal carbonyls enriched with ^{13}CO and found two distinct types of behaviour. In some cases the ^{13}CO groups are largely uncoupled from the ^{12}CO's whilst in other cases the ^{13}CO vibrations are sufficiently strongly coupled for it to be impossible to distinguish uniquely ^{13}CO modes. Evidently, a continuous range of intermediate cases also exists. These studies will be reported elsewhere. This work did, however, lead us to a study of the effect of the vibrational coupling which may exist in a mixed crystal between two chemically distinct but isomorphous compounds. In these studies we have relied almost entirely on Raman spectra. This is because the bands occuring in Raman spectra of metal carbonyls are usually very much narrower than the corresponding infrared bands so that it is possible to measure frequency changes more accurately and to observe band contour changes more readily.

In Fig. 3 we show the Raman spectra of a sample consisting of a coarsely ground mixture of $Cr(CO)_6$ and $W(CO)_6$, recorded with the sample at liquid ni-



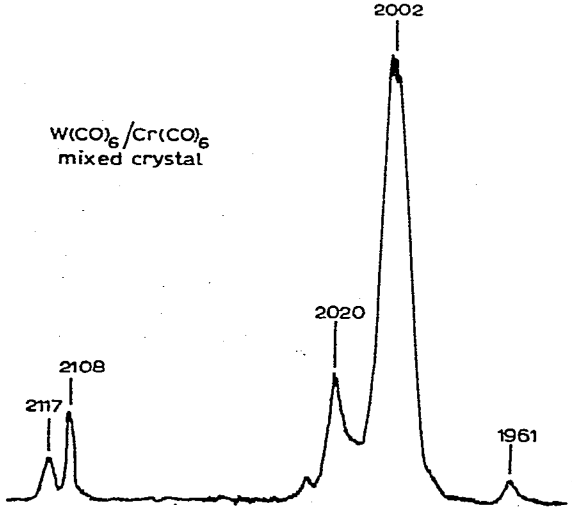


Fig. 3. Raman spectra of a mixture of $W(CO)_6$ and $Cr(CO)_6$ at liquid nitrogen temperature.

Fig. 4. Raman spectra of mixed crystals of $W(CO)_6$ and $Cr(CO)_6$ obtained after sublimation in an approximate 1 : 1 ratio.

trogen temperature. The large number of peaks arising from the E_g vibrations (in O_h) of each of the two species clearly indicates the existence of intermolecular vibrational coupling and thus the applicability of the factor group approach. It is interesting to note that this coupling is unlikely to originate in a dipole—dipole mechanism as the molecules retain octahedral symmetry in the crystal, to good approximation, and there is no evidence for significant infrared activity. It is not possible to comment on the presence of a factor group splitting in the peaks derived from the parent A_{1g} modes. Although two Raman active factor group components are predicted it is very easy to demonstrate that one of these is expected to have a very low intensity (it arises as a non-totally symmetric sum of components of, essentially, isotropic molecular contributions). The spectral observation of only one peak therefore leaves unanswered the question of whether the (unobserved) band is coincident with or separated from the observed feature. Only if the two bands were non-coincident would there be evidence for intermolecular vibrational coupling. A further feature to be noted in Fig. 3 is the occurrence of two distinct "^{13}CO" peaks at 1963 and 1957 cm^{-1}.

Figure 4 shows the Raman spectrum of the crystals obtained when a mixture of chromium and tungsten hexacarbonyl were sublimed together in an approximately 1 : 1 ratio. Whilst separate peaks are observed for each species in the high frequency region a single pattern (similar in band contour and distribution to those of either component but intermediate in frequency) is observed in the lower frequency region. Equally interesting is the observation of a single "^{13}CO" feature at ca. 1962 cm^{-1}.

We interpret these observations, qualitatively, as follows. The observation of factor group splitting in the 2035-1950 cm^{-1} region of pure carbonyl species indicates the existence of intermolecular vibrational coupling. This vibrational coupling is quite large relative to the frequency separation between corresponding chromium and tungsten spectral features so that each species contribute approximately equally to the vibrations which give rise to the observed spectral features, leading to frequencies which are intermediate between those of either pure component. The averaging of the "^{13}CO" features strongly suggests that, if indeed this is their origin, then these modes are not entirely uncoupled from

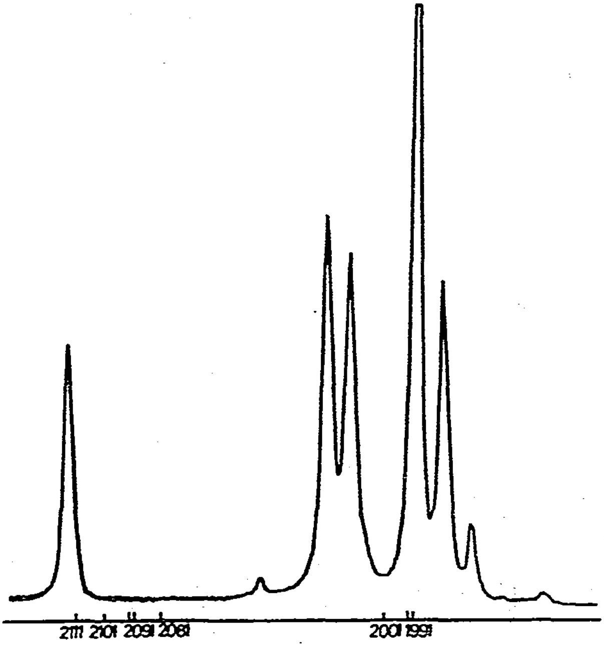


Fig. 5. Raman spectrum of a polycrystalline sample of $Mn_2(CO)_{10}$.

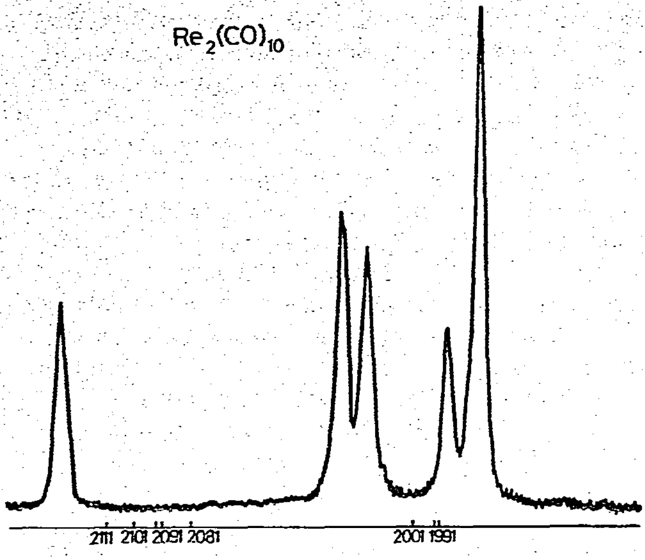


Fig. 6. Raman spectrum of a polycrystalline sample of $Re_2(CO)_{10}$.

those of the ^{12}CO containing-units. These features apart, all other spectral features in the entire Raman spectrum (not just the section shown in Fig. 3) of the mixed crystal are, essentially, a superposition of the spectra of components (the small frequency shifts observed probably arising from relatively small changes in the static field contribution). In particular, we interpret the observation of two peaks at ca. 2110 and 2118 cm^{-1} as indicating the absence of intermolecular coupling between the molecular A_{1g} vibrations, (indeed, for perfectly octahedral species the first non-vanishing term in the coupling would be hexadecapole—hexadecapole). We conclude that factor group splitting is very small for these peaks and so the factor group method inappropriate (in par-

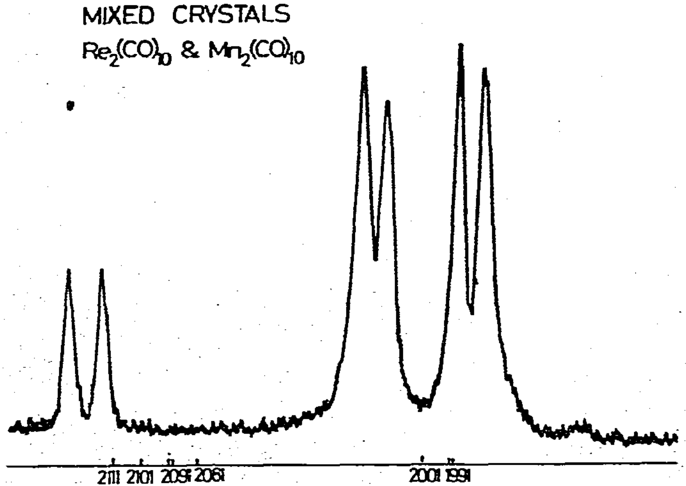


Fig. 7. Raman spectrum of a co-sublimed crystal of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$.

ticular, we are led to expect that the low-intensity peak, discussed earlier, is essentially coincident with the observed peak).

We have carried out similar studies on a wide variety of carbonyl species; these results will be reported elsewhere. As an illustration of the other phenomena which we have observed we present in Fig. 5 and 6 the Raman spectra of polycrystalline samples of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in the 2000 cm^{-1} region. The Raman spectrum of the co-sublimed crystal is shown in Fig. 7 and demonstrates, inter alia, that intensity sharing is, as expected, an additional phenomena associated with vibrational coupling between dissimilar molecules.

Experimental

Spectra were recorded using an argon krypton ion gas laser (Spectra Physics 165) using the 6471 Å red line, with the sample at —190° C. In all cases a number of mixed crystals was studied, covering a range of concentrations. Averaging, when it occurs, occurs at all concentration ratios but the frequencies of the "averaged" peaks vary with mole ratio of the components, and are more intermediate than "average", as also do peak heights when these differ in the spectra of the pure components. Powder X-ray photographs were obtained for all samples studied and a smooth variation of unit cell parameters with composition observed.

Acknowledgement

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