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# Interpretation of the ν(CO) vibrational spectra of cluster compounds: tetrahedral anions $[Fe_2Ir_2(CO)_{12}]^{2-}$, $[HFe_2Ir_2(CO)_{12}]^-$ and $[FeIr_3(CO)_{12}]^-$

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## Abstract

The analysis of the ν(CO) infrared and Raman spectra of the title compounds demonstrates the feasibility of using reliable force constant data from a model species in the interpretation of the vibrational spectra of another. This parameter transferability, similar to that used in the Extended Huckel method, should lead to a progress in understanding the vibrational CO spectra of more complex, low symmetry metal carbonyl cluster compounds.

## Introduction

In a previous communication we demonstrated the feasibility of using reliable force constant data from one species in the interpretation of the vibrational spectra of another [1]. In general, this would not be regarded as a particularly significant event. However, the context in which we used it was in a study of the ν(CO) vibrational spectra of transition metal cluster compounds. These compounds have proven particularly difficult to analyse, and any procedure which makes such an analysis possible could be of considerable importance, not only giving insights into the way that carbonyl groups on one atom interact with those on another but also insights into the way that these interactions are modified by changes in the other ligands present. There is currently a real need for such information. For instance, in the field of molecular mechanics, applications of which to metal carbonyl clusters are just beginning to appear [2].

In the particular case studied in the previous communication, that of $Ru_3(CO)_9(\mu_3C_6H_6)$, the relationship with the reference molecule, $Ru_3(CO)_{12}$, was simply that of the removal of three axial carbonyl groups and their replacement by a benzene molecule. The consequent geometrical changes in the remaining CO groups were not great and so it was not surprising that simply taking the data for $Ru_3(CO)_{12}$, unchanged, and substituting them into the relevant force constant equations gave a predicted spectrum which approximated to the pattern observed [1].

In this particular case there were sufficient spectral data to enable an independent spectral assignment with relatively little ambiguity and, again not too surprisingly, this pattern also agreed with that observed. We use the phrase 'not too surprisingly' because the 'independent assignment' actually relied on some of the concepts which find mathematical expression in the force constant data – that the interaction between carbonyl groups on the same metal atom will be greater than that between carbonyl groups on different metal atoms, for instance. However, the 'independent assignment' also used data which are not normally included in a normal coordinate analysis – relative band intensities and a discussion of the consequences of solid state effects. So, whilst the 'independent assignment' is not entirely independent, it is sufficiently so for the concurrence of the two approaches to be gratifying.

This success has encouraged us to apply the force constant transferability approach to molecules for which

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the 'independent assessment' method led to more ambiguous conclusions, it proving impossible to distinguish between several alternatives. Three such compounds, the anions $FeIr_3(CO)_{12}^-$, $HFe_2Ir_2(CO)_{12}^-$ and $Fe_2Ir_2(CO)_{12}^{2-}$, are the subject of the present communication.

## Experimental

The compounds $[N(P(C_6H_5)_3)_2)]_2[Fe_2Ir_2(CO)_{12}]$ and $[N(P(C_6H_5)_3)_2)][FeIr_3(CO)_{12}]$ were prepared and crystallised as described in the literature [3]. The cluster $[As(C_6H_5)_4][HFe_2Ir_2(CO)_{12}]$ was obtained by addition of 85% $H_3PO_4$ to an acetone solution of $[As(C_6H_5)_4]_2[Fe_2Ir_2(CO)_{12}]$ and precipitated from $CH_3OH$/water.

IR spectra in $CH_2Cl_2$ solutions or in KBr discs were obtained on a Perkin-Elmer PE 580 IR spectrophotometer. Raman spectra were recorded in crystalline samples with the Bruker FRA 106 FT-Raman module, attached to the IPS 66 FT-IR spectrometer (laser power 130 mW, resolution 4 $cm^{-1}$).

Normal coordinate calculations were performed by means of the program CLIMAX written by Dr G.J. Kearley (Institut Laue-Langevin, Grenoble).

## Results and discussion

The structures of the three clusters consist of a tetrahedron of metal atoms, one face of which is surrounded by bridging carbonyl groups and has $M(CO)_2$ groups at its corners. The opposite apex is a $M(CO)_3$ group [3] (Fig. 1). The structure is that found in $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$ [4].

These three latter species have been the subject of detailed normal coordinate analyses [5], and so the object of the present work is to investigate whether it is possible to extend these analyses to the title compounds. The fact that there is a superficial similarity between the spectra reported in ref. 5 and those of the above three species gives hope that enquiry along the present lines could reasonably expect to be successful.

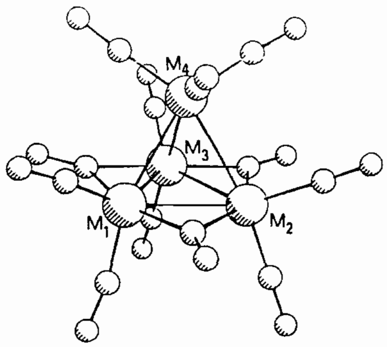

Fig. 1. Structure of the complexes: $M_1 = M_4 = Ir$, $M_2 = M_3 = Fe$ for $[Fe_2Ir_2(CO)_{12}]^{2-}$ and, presumably, for $[HFe_2Ir_2(CO)_2]^-$, $M_1 = M_3 = M_4 = Ir$, $M_2 = Fe$ for $[FeIr_3(CO)_{12}]^-$.

We shall concern ourselves only with the terminal carbonyl groups but before doing so it is perhaps relevant to comment that no case is known in which spectrally significant coupling exists between terminal and bridging carbonyls [6]. In the present case, for all three compounds, the bridging carbonyls display two peaks of equal intensity in the IR in all phases. They are undoubtedly to be assigned as the components of a split E mode (E in the parent $C_{3v}$ symmetry) – the associated $A_1$ mode is expected to have negligible intensity for three coplanar carbonyls. The $A_1$ mode actually appears, weakly, in the spectrum of the solid and, much more strongly, in the Raman. The lesson from this is that we cannot expect pseudo-$C_{3v}$ symmetry in the terminal region either and it is this aspect which, potentially, makes a qualitative analysis of the spectra so difficult. Not only must we expect 'E' modes to be split but, because there are three of them which may mix – and one component of each may also mix with '$A_1$' modes – we cannot expect split E modes to be identified by the components having similar intensities. However, our analysis indicates that this is a too pessimistic attitude and that both in IR and Raman intensity criteria remain useful. This is an important conclusion for it opens the way to a study of species of which the symmetry might be though to be too low for an analysis to have any hope of a unique solution.

The $\nu$(CO) vibrational spectra of $FeIr_3(CO)_9^-$ (IR and Raman), $HFe_2Ir_2(CO)_9^-$ and $Fe_2Ir_2(CO)_9^{2-}$ (the last two, IR only – the Raman could not be obtained) are shown in Fig. 2. Note that from this point on we shall only include in the formulae those carbonyls included in our analysis.

The values for the force and interaction constants are given in Table 1 (see Fig. 3).

As we have indicated, we have based our analysis on the work on $Co_4(CO)_{12}$ and related species [5]. However, there was no iridium species amongst those that have been analysed and the only iron compound is a tricarbonyl*. This situation is probably much less serious than it seems. The reason lies in the approximate nature of any parameter transferability. Thus, Bor *et*

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*A normal coordinate calculation of $Ir_4(CO)_{12}$ has been reported in ref. 7 and it might seem reasonable to include these parameters in the present work. However, in order to avoid an underdetermined problem, they had to set two interaction constants to zero. The work of Bor *et al.* [5] avoids this problem by the use of data on isotopic species and, in the present work, we regard it as most important that the parameters used be of uniform basic quality.

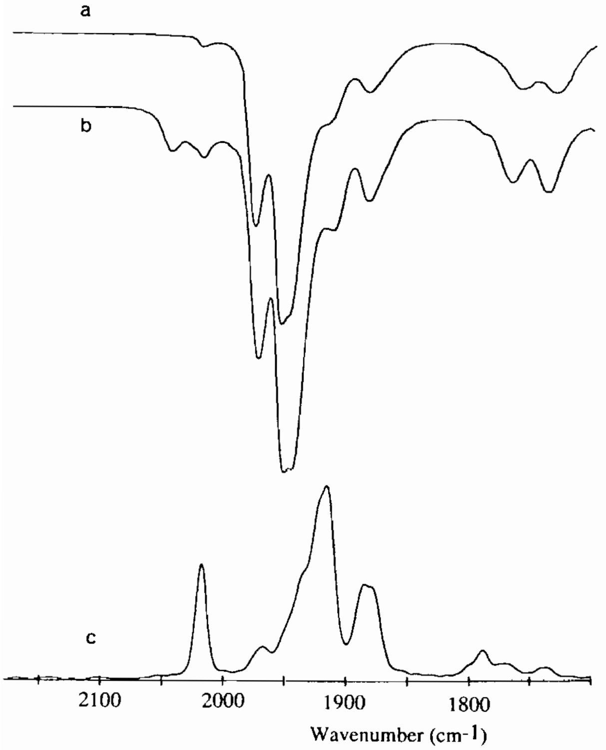

Fig 2. Infrared (a: $CH_2Cl_2$ solution, b KBr disc) and Raman (c: crystals) spectra of $[Fe_2Ir_2(CO)_{12}]^{2-}$ in the $\nu$(CO) region.

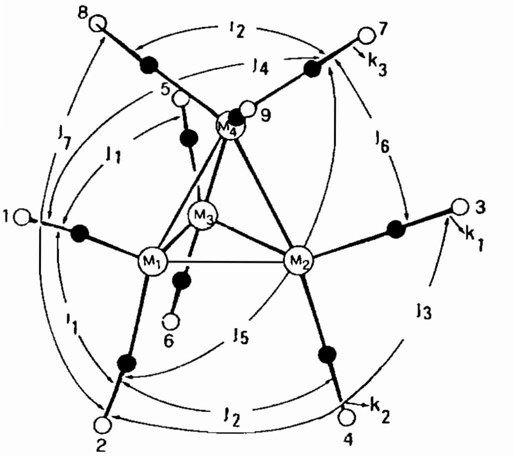

Fig 3. Definition of the force and interaction constants (see ref. 5). For sake of clarity, labels are referred to a $C_{3v}$ symmetry.

TABLE 1. The force field parameter values used for the normal coordinate calculation[a]

| | Ir–Ir | Ir–Fe | Fe–Fe |
|---|---|---|---|
| $k_1$ | 17.102 | | 16.343 |
| $k_2$ | 17.133 | | 16.343 |
| $k_3$ | 17.097 | | 16.343 |
| $i_1$ | 0.279 | | 0.270 |
| $i_2$ | 0.293 | | 0.306 |
| $j_1$ | 0 066 | 0.071 | 0.075 |
| $j_2$ | 0.085 | 0.092 | 0.097 |
| $j_3$ | 0.030 | 0.037 | 0.044 |
| $j_4$ | 0.033 | 0.033 | 0.033 |
| $j_5$ | 0.018 | −0.005 | −0.029 |
| $j_6$ | 0.133 | 0.142 | 0.150 |
| $j_7$ | 0.037 | 0.021 | 0.005 |

[a] For the notation, see Fig. 3 and ref. 5.

*al.* [5] analysed two molecules containing a $Co_3(CO)_6$ basal plane (counting only the terminal carbonyls). If a genuine parameter transferability exists, it might reasonably be manifest here (although the presence of a hydrogen in one compound introduces a doubt). In fact, transferability exists, to better than 1%, for the bond stretching force constants. For geminal interactions the agreement is better than 10% while for indirect interactions it is better than 100%. This latter figure might be sufficient to stop the enquiry immediately — although the fact that the numbers involved are rather small should not be overlooked — but this would be to miss an important point. This is that the *relative* order of the magnitudes of these quantities remains unchanged and that, as a result, within any one set of comparable data the *relative*, as opposed to the absolute, values change by almost an order of magnitude less than the figures just quoted. What this means is actually most comforting. We can make significant errors in the parameter choice and yet obtain the correct sequence of energy levels. The separations may be wrong but the order will be correct. We should be able to reduce the separation errors by scaling the overall calculated splitting to the experimental. Indeed, it is inevitable that some sort of scaling should be needed for we are using data from neutral species to predict the spectra of anions. If we are fortunate in choosing the parameters reasonably ‘correctly’ — we recognise that the problem is undetermined — then we will be rewarded by reproducing the observed frequencies reasonably closely.

In a situation such as this it is necessary to choose the parameter values in a simple, consistent and logical way. Force constant and geminal interaction constant values for the (Fe)–CO groups were taken directly from ref. 5; indirect interaction constant values were calculated as the arithmetic means of those appropriate to the connected atoms and so were dependent on the approximation used for (Ir)–CO values. Three approximations were used for the latter. First, they were set equal to the corresponding (Rh)–CO data. Second, the sequence Co–Rh–Ir was taken to have equal parameter increments at each step (using tetracarbonyl data for Co and Rh to avoid the problem of the hydrogen-containing species). Finally, we took the arithmetic mean of the two. Not surprisingly, since these three approximations are linearly related, the consequent energy calculated levels vary smoothly. No energy level crossings occur. In view of this invariance we felt it

TABLE 2. Observed (A) and calculated/predicted (B) values of the frequencies and intensities of the CO stretching bands for $[Fe_2Ir_2(CO)_{12}]^{2-}$, $[HFe_2Ir_2(CO)_{12}]^-$ and $[FeIr_3(CO)_{12}]^-$

| $[Fe_2Ir_2(CO)_{12}]^{2-}$ | | | | $[HFe_2Ir_2(CO)_{12}]^-$ | | | | $[FeIr_3(CO)_{12}]^-$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Frequency | | Intensity | | Frequency | | Intensity | | Frequency | | Intensity | |
| A | B[a] | A | B | A | B[a] | A | B | A | B[a] | A | B |
| 2023 | 2023 | w | mw | 2068 | 2068 | m | mw | 2069 | 2069 | w | m |
| 1977 | 1986 | s | s | 2029 | 2035 | s | s | 2028 | 2034<br>2028 | vs | m<br>vs |
| 1953 | 1951<br>1946 | vs | s<br>s | 2009 | 2003<br>1999 | vs | s<br>s | 1997 | 1997<br>1996<br>1992 | vs | m<br>m<br>m |
| 1946 | 1942<br>1933 | vs | s<br>m | 1996 | 1955<br>1987 | vs | s<br>m | | | | |
| 1916 | 1919 | m | ms | 1982 | 1974 | s | ms | 1985 | 1985<br>1973 | m | mw<br>mw |
| 1886 | 1891<br>1886 | m | m<br>w | 1944 | 1949<br>1944 | m | m<br>w | 1937 | 1937 | m | m |

[a]All fittings were done by forcing highest and lowest frequencies to agree with experiments.

TABLE 3. Infrared (solution: $CH_2Cl_2$, solid state: KBr disc) and Raman (crystals) $\nu$(CO) values of $[Fe_2Ir_2(CO)_{12}]^{2-}$

| | Ir | | Raman |
|---|---|---|---|
| | Solution | Solid state | |
| Terminal | | 2046vw | |
| CO | 2023w | 2020w | 2018m |
| | 1977s | 1971s | 1966w |
| | 1953vs | 1948vs | |
| | ~1946vs, sh | 1941vs | ~1935m, sh |
| | ~1916m, sh | 1912m | 1916s |
| | 1886m | 1884m | 1885m |
| | | | ~1878m, sh |
| Bridging | | ~1788w, sh | 1788mw |
| CO | 1761m | 1766m | 1769w |
| | 1733m | 1736m | 1735w |

For the notation, see Fig. 3 and ref. 5

acceptable to concentrate on that parameter set which gave the best fit to the experimental data. This was the set in which the iridium parameters were set equal to the corresponding rhodium ones and we report only these. In the case of the $Fe_2Ir_2$ species this parameter set was only marginally 'better' than the arithmetic mean set; however, for the $FeIr_3$ set the difference was much more significant. In Table 1 we give the parameter set and in Table 2 the results obtained for the three species, comparing them with the experimental values.

As an additional check on the reasonableness of our model we have used the normal coordinates obtained to make qualitative predictions of the relative intensities of the IR bands. These are also given in Table 2, along with the qualitative experimental values. It is evident that, overall, the agreement in Table 2 is good and leaves little doubt that the consequent spectral assignment is correct. The only significant and evident error is in the relative intensities of the two highest-frequency bands, accompanied in the $Fe_2Ir_2$ case by a frequency error. The two bands are of the same symmetry and have dipole moment changes along, essentially, the pseudo-threefold axis. Clearly, our calculations do not depict these modes correctly; although only a small change is needed to remove the error we did not regard it in the spirit of the enquiry so to do.

In the above we have depended solely on solution IR data. In addition, there are solid state IR, in some cases at low temperature, and, in one case, Raman data. In the case of two of the compounds crystal structures are known [3], information which could be of importance in interpreting the spectral data from solid state species. The most complete data set is for the $Fe_2Ir_2$ species and we concentrate on this (Table 3). The room temperature IR of the solid is very similar to that of the compound in solution. This indicates that solid state intermolecular vibrational coupling is not large. We conclude that the Raman may also be interpreted as essentially molecular in origin. The shift in IR frequencies is rather uniform on passing to the solid state – about 5 $\mathrm{cm}^{-1}$ – and we could apply the same correction to the Raman data to obtain pseudo-solution frequencies. However, there are other points arising from the Raman. The first is that the lowest frequency band is clearly a doublet in the Raman, the higher component essentially being at the position predicted. Second, a shoulder at *c*. 1916 $\mathrm{cm}^{-1}$ in the solution IR is seen at 1921 $\mathrm{cm}^{-1}$ (corrected value) as the strongest band in the Raman and corresponding to one of our predicted peaks. Other peaks show a general IR–Raman coincidence.

## Conclusions

We believe that the results presented above demonstrate that progress can be made in understanding the vibrational spectra of low symmetry metal carbonyl cluster compounds by using force constant data from related molecules. The patterns of vibrational symmetry species obtained seem rather insensitive to the fine details of the actual numbers used. One may perhaps see a parallel with the widespread use of the Extended Huckel method in electronic structure calculations, where an analogous sort of parameter transferability is used. It this analogy is pursued one may perhaps envisage the development of preferred parameter sets for use in models such as that which we have presented. In this context it is noteworthy that the Fe–(CO) parameters which we have used were taken [5] from the work on a HFe system. It is therefore probably not without significance that our fit to data on a HFe system was better than to that of the corresponding species without the H.

Another point worthy of comment relates to the expectation of parameter transferability. This is that it is highly likely that there is a large measure of topological control of the outcome of calculations such as those that we have carried out. The actual parameters then serve as a refinement of this model. In support of this assertion we note that if the related $Ir_4(CO)_{12}$ terminal CO problem is approximated by all bond stretching force constants being set equal and all bond interaction constants separately being set equal then the energy level problem, essentially a topological one, is determined by the ratio of these quantities and the problem admits of a unique solution. The actual energy level splittings are all multiples of the band interaction constant. It is surely significant that, in the present case, the solution gives, with only one inversion, the qualitative energy level pattern previously obtained.

## Acknowledgements

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