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The vibrations of bridging carbonyl groups as more sensitive indicators of molecular geometry than terminal carbonyl groups in transition metal carbonyl cluster compounds ☆

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Abstract

The ν(CO) spectra of a series of transition metal cluster compounds are compared with their structures. Despite considerable structural differences, the spectra in the terminal region are surprisingly invariant. Rather more variation is shown in the bridging region spectra; it proves possible to understand these variations in terms of a qualitative model. A generalisation concerning bridging region spectra is presented.

Keywords: Clusters; Bridging carbonyl; Infrared Raman spectroscopy

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1. Introduction

The use of the terminal ν(CO) features as indicators of molecular geometry in simple transition metal carbonyl compounds has a long and successful history and is a structural tool regularly used to the present day. Not only does the general pattern, combined with a simple group theoretical analysis, rather reliably give the symmetry subtended by the groups but in favourable cases the relative intensities of the bands give bond angles with some precision. In contrast, there has been no similar application of ν(CO) features in the determination of the corresponding arrangement in transition metal carbonyl cluster compounds, although the fact that two compounds have similar (but not interpreted) ν(CO) band patterns has been adduced in evidence that they have similar structures. Even this apparently innocuous use of ν(CO) band paterns in transition metal cluster chemistry is not to be relied upon.

In the present communication we report on the use of the bridging ν(CO) features in the structural characterisation of a series of transition metal cluster compounds that have superficially similar terminal ν(CO) features but which, in fact, have rather different structures with symmetries ranging from T_d to C_1 and contain either five or six metal atoms which may or may not be identical.

2. Experimental

The compounds ($Rh_6(CO)_{16}$ [1], $Ir_6(CO)_{16}$ [2], $[FeIr_5(CO)_{16}]^-$ [3], $[Fe_2Ir_4(CO)_{16}]^{2-}$ [4], $[FeIr_5(CO)_{15}]^{3-}$ [3], $[Fe_2Ir_3(CO)_{14}]^-$ [5], $[FeIr_4(CO)_{13}]^{2-}$ [4]) were prepared according to literature methods; the cited references also report the molecular structures.

The IR spectra were recorded on a Perkin-Elmer 16PC FTIR at ~2 cm^{-1} resolution; reference subtraction and data manipulation were performed by the IR Data Manager software. CaF_2 cells of 0.1–0.5 thickness, previously purged with nitrogen or carbon monoxide, were used for solution spectra; the nujol mulls were prepared in a glove-box filled with dry nitrogen. The Raman spectra of microcrystalline samples were obtained using a Nicolet FT Raman model 910 with YAG laser excitation (power 40–100 mW) and resolution of ~4 cm^{-1}.

☆ This paper is dedicated to György Bor on the occasion of his 70th birthday.

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3. Results

The $\tilde{\nu}$(CO) IR spectra of five M_6 and two M_5 species, all containing only $M(CO)_2$ terminal CO groups, are detailed in Figs. 1–7, along with diagrams of their crystal structures. The wavenumber values of the bands belonging to the bridging CO modes are reported in Table 1. The first three spectra are those of isostructural $M_6(CO)_{16}$ molecules, all of T_d symmetry. In addition, the same structure is shared by $Co_6(CO)_{16}$ [6] of which the IR spectrum is given in Ref. [7]. The spectra are essentially identical, consisting of a strong peak with resolved low frequency shoulders (that of $Rh_6(CO)_{16}$ appears different but this is because of a concentration difference). Although $[FeIr_5(CO)_{16}]^-$ (Fig. 3) has a unique atom which reduces the symmetry to C_{2v}, if this is disregarded then it is isostructural with the uncharged clusters. Its terminal region spectrum is, indeed, indistinguishable although there is perhaps the merest hint of a splitting on the most intense peak;

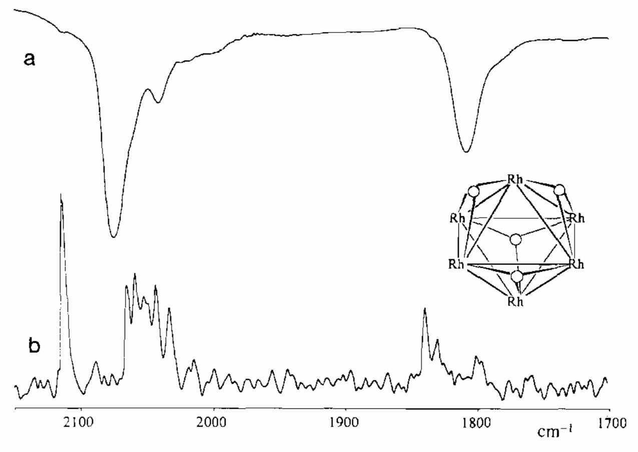

Fig. 1 (a) IR (THF solution) and (b) Raman (crystals) spectra of $Rh_6(CO)_{16}$ (the diagram of the structure shows only the bridging COs (open circles); the terminal COs, two on each metal atom, are omitted for clarity).

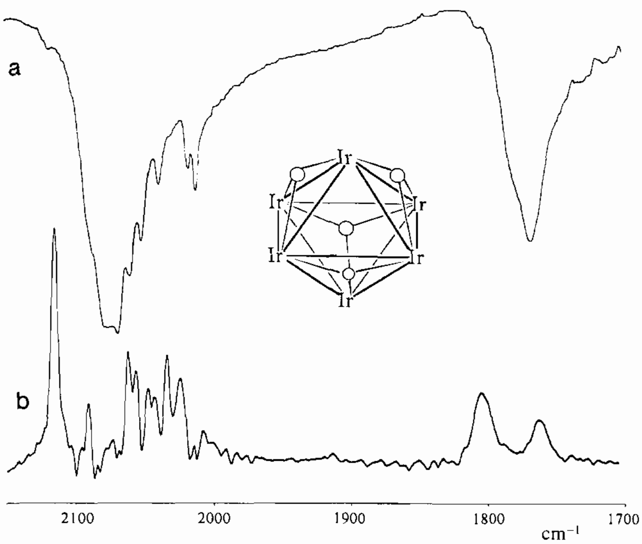

Fig. 2. (a) IR (nujol) and (b) Raman (crystals) spectra of $Ir_6(CO)_{16}$ (red isomer) (for the structure, see caption of Fig. 1).

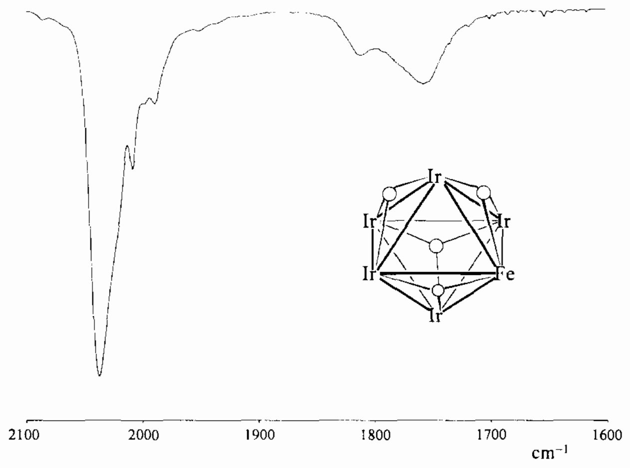

Fig. 3. IR spectrum (THF solution) of $[FeIr_5(CO)_{16}]^-$ (for the structure, see caption of Fig. 1).

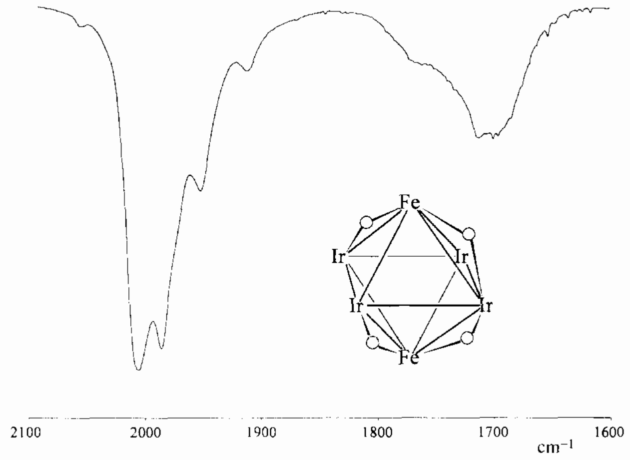

Fig. 4. IR spectrum (CH_3CN solution) of $[Fe_2Ir_4(CO)_{16}]^{2-}$ (for the structure, see caption of Fig. 1).

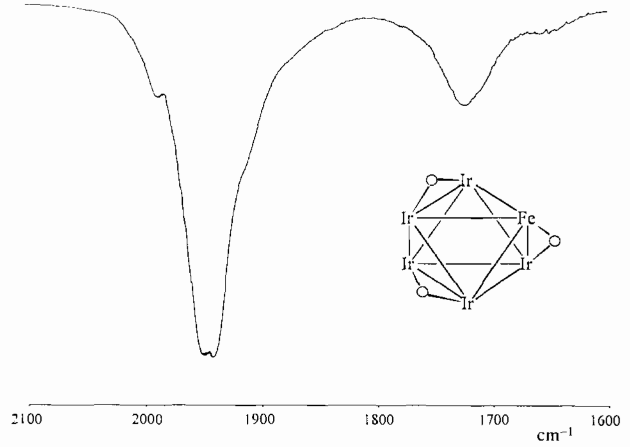

Fig. 5. IR spectrum (THF solution) of $[FeIr_5(CO)_{15}]^{3-}$ (for the structure, see caption of Fig. 1).

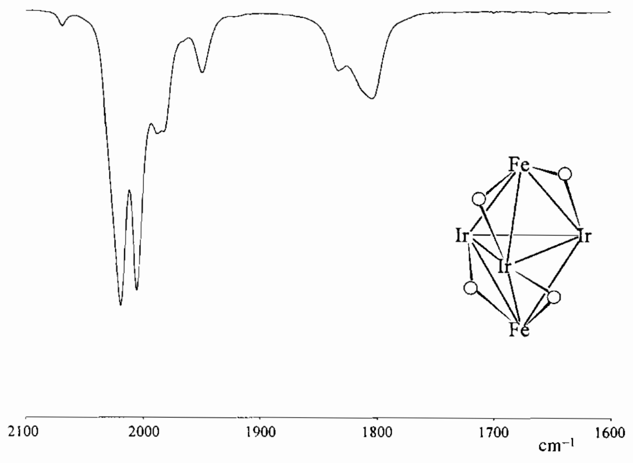

Fig. 6. IR spectrum (THF solution) of $[Fe_2Ir_3(CO)_{14}]^-$ (for the structure, see caption of Fig. 1).

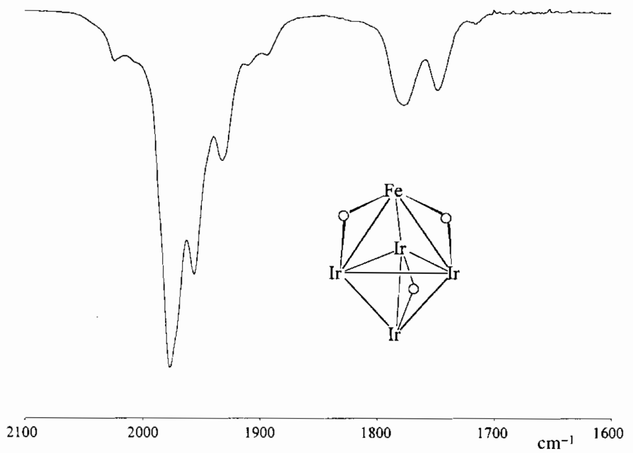

Fig. 7. IR spectrum (THF solution) of $[FeIr_4(CO)_{13}]^{2-}$ (for the structure, see caption of Fig. 1).

Table 1
IR and Raman wavenumber values (cm^{-1}) for the bridging carbonyl modes

Complex	ν values		
$Rh_6(CO)_{16}$	IR		1808s
	Raman	1838s (1829m)	1800m
$Ir_6(CO)_{16}$	IR		1766m
	Raman	1805s	1764m
$[FeIr_5(CO)_{16}]^-$	IR	1811w	1757m,br
$[Fe_2Ir_4(CO)_{16}]^{2-}$	IR	~1765w,sh	~1710/1700m,br
$[FeIr_5(CO)_{15}]^{3-}$	IR		1725m
$[Fe_2Ir_3(CO)_{14}]^-$	IR	1834w	1806m
$[FeIr_4(CO)_{13}]^{2-}$	IR	1778m	1749m

^{a} See text for details on the assignment.

however, such a splitting is more evident on the spectrum of $Ir_6(CO)_{16}$. It is clear that the terminal region spectra are insensitive to the change in metal atom and the reduction in symmetry (notwithstanding the bond length inequalities which also occur).

$Ir_6(CO)_{16}$ is particularly interesting because it occurs with two molecular structures [1]. The second form, whilst retaining an $(Ir(CO)_2)_6$ terminal structure, has an idealised molecular S_4 geometry with four edge bridged carbonyls (all the previous examples cited have four face bridged carbonyls). The effect of this change on the terminal region spectrum is minimal, an additional weak peak appearing and the splitting of the strongest band becoming more evident [2]. If differences in the metal atom are ignored, as it seems that they may be, then the anion $[Fe_2Ir_4(CO)_{16}]^{2-}$ is isostructural with this second form of $Ir_6(CO)_{16}$, although the idealised symmetry is now D_{2d}, with no symmetry-required degeneracies. The effect on the terminal region spectrum is again minimal (Fig. 4). The splitting on the strongest peak is clear but the number of shoulders drops to two.

$[FeIr_5(CO)_{15}]^{3-}$, with a unique metal atom, only three bridging carbonyls and C_1 symmetry has an essentially identical terminal region spectrum, albeit with broadened features (Fig. 5). Another C_1 species, $[Fe_2Ir_3(CO)_{14}]^-$ now with only five metal atoms, not six, but with four bridging carbonyls has a very similar terminal region spectrum, but lacking the broadening (Fig. 6).

This spectrum, in turn, resembles that of another M_5 species, $[FeIr_4(CO)_{13}]^{2-}$, which now has only three bridging carbonyls and is of C_s symmetry (Fig. 7). The general insensitivity of the terminal region spectra to the details of molecular structure and symmetry is quite amazing. All of the clusters listed are built of $M(CO)_2$ groups and this seems to be the unifying characteristic which dominates their terminal region IR spectra.

We have had limited success in obtaining the corresponding Raman spectra although FT Raman has produced some spectra of varying quality. Such as we have been able to obtain are given in the Figures. A similar transferability seems to exist. Because of the invariant use of large counter-ions, solid state effects will generally be small. We have, then, species with from T_d to C_1 symmetry, either five or six metal atoms and either twelve or ten terminal CO groups displaying terminal region spectra with superficial similarities. Although the origin of this pattern of uniformity is clearly worthy of further discussion, we shall not embark on this task here. Rather, our present concern is that of attempting an understanding of the ν(CO) bridging spectra, thus continuing a study set in train by Bor and co-workers [8–10].

Bridging region ν(CO) spectra have been little studied in the past [8–13]. By definition, they only appear in polynuclear species, for which the terminal region alone

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[1] Fig. 2. reports the IR spectrum of the first form (red isomer); a nujol mull was used because the solution spectra were complicated, presumably indicating equilibria.

often presents a sufficient problem. It would be in the spirit of the work of György Bor to carry out a detailed and precise analysis of spectra, aided by data on a series of isotopomers. For the bridging region, such work is in the future. It can only be mounted when the spectra are first understood in a general way. The object of the present paper is therefore that of attempting to provide the first steps in this general understanding. The Figures include data in the bridging $\tilde{\nu}$(CO) region (it does not prove necessary to distinguish between edge and face bridging carbonyls in the generalities of the vibrational discussion). Again, notwithstanding a general similarity of the bridging region spectra, this similarity is far less pronounced than that in the terminal region. The present work was stimulated by the recognition of these different characteristics of terminal and bridging regions. It is difficult to argue that the terminal region spectra show a structure sensitivity; could it be that the bridging region sensitivity is greater?

It is convenient first to consider the face-bridging carbonyls of the three tetrahedral clusters $Rh_6(CO)_{16}$ [1], $Co_6(CO)_{16}$ [7] and $Ir_6(CO)_{16}$ [2] (red form) which subtend the symmetry species A_1+T_2 in the group T_d, of which only the latter is IR active. Accordingly, only a single peak occurs in the bridging ν(CO) region in their IR spectra. However, a single peak would also be seen if there were four uncoupled CO groups and so the question arises of whether or not there exists coupling between them. Rather little work has been published on this problem, and that mostly by Bor and co-workers [8–10]. All extant work is in agreement; coupling occurs between bridging carbonyls [14] but none is evident between bridging and terminal carbonyls [8–13]. This conclusion is confirmed by the FT Raman of $Rh_6(CO)_{16}$, which shows a separation of ~40 cm^{-1} of two features in the bridging region, the lower wavenumber value approximately coinciding with that in the (solution) IR. The analysis presented in the present work assumes that this conclusion of the presence of bridging region coupling is of general validity, although we note that it leaves undetermined the question of whether coupling occurs between face and edge bridging carbonyls. To our knowledge, there is no information on this point; fortunately, it is not relevant to the present discussion since none of the compounds under study contains both types of bridge.

An immediate check on the question of the general applicability of a bridging-carbonyl coupling model is provided by the cluster anion $[FeIr_5(CO)_{16}]^-$ which is isostructural [3] with $Rh_6(CO)_{16}$, $Ir_6(CO)_{16}$ and $Co_6(CO)_{16}$ but with one metal atom unique. In comparison with the near-superimposability (apart from a gross wavenumber shift) of the terminal region spectra, a clear difference is evident in the bridging. In addition to the strong 'T_2' band, a band which has broadened, presumably reflecting an incipient splitting, the A_1 feature has become active at higher frequency (the wavenumber separation, of about 55 cm^{-1}, is far too great for the band to be the result of the loss of degeneracy within the T_2 mode). This A_1 activity, of course, is incompatible with T_d symmetry. It clearly confirms coupling; further, it seems that the bridging ν(CO) bands may show the greater sensitivity to the molecular symmetry. Is this a generally true statement? The evidence of the next species, $[Fe_2Ir_4(CO)_{16}]^{2-}$, is that it is. Although the idealised molecular symmetry is very low, C_s, the metal framework differs from that of the previous example by the reinstatement of a centre of symmetry. This reinstatement is evident in the bridging region by the weakening of the totally symmetric mode, a mode which is so weak that it would probably have been ignored had not the above correlation been traced. An alternative approach exists to the interpretation of this spectrum. In the anion $[Fe_2Ir_4(CO)_{16}]^{2-}$ the bridging CO groups are arranged approximately at the corners of a tetrahedron which is elongated along one twofold axis. In an idealised T_d geometry a single peak would be expected in the bridging region but in the actual molecule a splitting would be expected to result from the elongation. Again, the observed spectrum is in excellent accord with this, although it is to be noted – and it proves to be an important point – the splitting is rather small. Again, the model leads to the prediction of only weak activity in the 'A_1' mode. A subsidiary lesson of these examples seems to be that there can be a sensitivity of the bridging modes to the nature of the metal atoms but that any such sensitivity is rather small, although greater than that shown in the terminal region.

Consider next the anion $[FeIr_5(CO)_{15}]^{3-}$ which has three bridging groups (all the previous examples have four). The bridging groups in this anion have D_3 symmetry if the metal atoms are regarded as identical. However, unlike the case of $[FeIr_5(CO)_{16}]^-$, here the unique axis of distortion (C_3) does not pass through atomic centres and so may be less spectrally important. In D_3, the modes A_1+E are spanned by the bridging COs, of which only the latter is IR active. This is in excellent accord with the observed spectrum, which consists of a single band. In contrast, the number of IR allowed modes in the terminal region should increase from two (T_d) to seven (D_3) a number which, clearly, is not seen.

The last two examples are of M_5 species. In $[Fe_2Ir_3(CO)_{14}]^-$, of C_1 symmetry, the four bridging CO groups fall into two $(CO)_2$ sets, inter-related by a (hypothetical!) S_6 operation of the parent trigonal bipyramid. Although the angle subtended by the individual CO groups with the parent C_3 axis is not 90°, it is relatively large and the dipole projection along this axis small. Further, whilst the individual CO groups in the pair are not co-linear, they approximate this. Consider the symmetric vibration of the individual $(CO)_2$ unit. This can have little dipolar activity and that which there is will be largely 'C_3' directed. In the molecule, this will be a maximum in the out-of-phase combination (of the symmetric combinations) but can only give rise to a relatively weak band. In contrast, the asymmetric combination of COs in the individual $(CO)_2$ units will be very dipolar active. These transition dipoles will be perpendicular to the 'C_3' axis and will have the symmetry characteristics of x and x', where x and x' are coordinate axes rotated by 120°. The normal group theoretical procedure with such a pair would be to take linear combinations of them so as to generate an orthogonal degenerate pair, although in the present case the threefold symmetry required to make this a valid procedure is absent. Nonetheless, the bridge region spectrum is that which would be expected for one weak and one strong, the latter degenerate, modes. Unexpected although this explanation is, it has in common with a previous example the fact that the effects of molecular asymmetry on bridging region spectra are reduced unless there is a coincidence between distortion axis and metal atom coordinates. It should be noted that an alternative explanation for this spectrum is available if the two $(CO)_2$ sets do not couple with each other but this is inconsistent with the hypothesis of general coupling.

Support for the applicability of a coupled model when the bridging CO groups are well separated comes from the final species, shown in Fig. 7, $[FeIr_4(CO)_{13}]^{2-}$, a C_s molecule with three bridging CO groups. Two of these span edges of the 'top' of the parent trigonal bipyramid and the other spans the *trans* edge of the lower set. The argument follows that developed above, mutatis mutandis. Only the symmetric combination of the $(CO)_2$ may couple with the unique CO. The in-phase combination will have little activity but the out-of-phase will be strongly IR active. The antisymmetric combination of the $(CO)_2$ will also be strong. The spectrum observed is of two peaks of similar intensity, a spectrum inexplicable without coupling between the bridging groups.

The overall picture is one in which the geometrical disposition of the bridging CO groups is the dominant factor determining the spectrum that they present. Metal–atom asymmetries can be seen but only when the axis along which they occur is an important one for independent reasons. Degeneracies in bridging carbonyls seem to have a resilience, perhaps indicating mixing sufficient to influence IR intensities without causing observable splittings. This discussion admits some generalisation. In the terminal CO region the effects of the real molecular symmetry are almost, if not entirely, masked. In the bridging region they are reduced, but not to the point at which the disposition in space of the vibrators, and when fine details are considered, the details of their environment, is irrelevant to a discussion. The distinction may well be no more than a reflection of the fact that there are generally fewer bridging CO groups than terminal. As Johnson was the first to point out, the ensemble of CO groups in a cluster tend to span rather symmetrical arrangements. Within this symmetry, however, the *bridging* carbonyls, on their own, subtend a lower and more variable symmetry. It would not be surprising if these aspects are evident in the interpretations given in this paper. If this analysis is correct it indicates that the following general approach should be followed in the interpretation of the bridging region ν(CO) spectra of metal carbonyl clusters:

The bridging region ν(CO) spectra of transition metal cluster compounds show coupling between the individual CO groups. The form of the spectra is determined by the geometrical disposition of the bridging CO groups in space, possibly subject to minor distortions imposed by the metal atom framework to which they are bonded, more likely to be evident if the distortion axis passes through metal atoms supporting bridging carbonyls. They show little, if any, sensitivity to the geometry of terminal CO groups.

These generalizations serve to unify the interpretation of all of the spectra considered in this paper.

4. Discussion

In this paper we have presented a novel approach to the interpretation of the bridging carbonyl region of the vibrational spectra of transition metal carbonyl species. Its simplicity must in part arise from the fact that, in all of the species discussed, there are significantly fewer bridging carbonyls than terminal. This is a typical situation and so offers the prospect that the approach outlined above may prove to have a general applicability. Nonetheless, the approach is itself surprising. It depends on the existence of vibrational coupling between carbonyl groups which may be well separated in space, possibly with no attachment to a common metal atom. Clearly, the only coupling mechanism which is compatible with this requirement is one that operates through space, as opposed to through-bond. A dipole–dipole mechanism is clearly implicated. Indeed, the fact that for the well-studied mononuclear carbonyls it is invariably true that the coupling between CO groups attached to the same metal atom is greater than that between the corresponding M–C vibrators strongly suggests that here too a through-space mechanism may well dominate. We note, too, that this is the evident generating mechanism for the factor group splitting observed on many ν(CO) features of crystalline metal carbonyls.

Clearly, the attraction of a common mechanism to explain so many phenomena is considerable. It is true that calculations based on a transition dipole–transition dipole mechanism have not been uniformly successful but it has to be remembered that the remainder of the molecular system is not innocent. Indeed, Bor et al. have argued that some observed IR intensities can only be explained by invoking what they called an 'induced dipole', a dipole which represents the response of the molecular system to the CO transition dipole [15]. If this explanation is correct it suggests the existence of some interesting phenomena. Basically, it says that if two CO groups are close enough in space and have similar frequencies then coupling can occur between them. So, for example, it seems entirely possible that the bridging CO groups of a cationic carbonyl species might vibrationally couple with the terminal CO groups of an anionic carbonyl, either as an ion pair in solution or if crystallised together provided that a pair can be found with sufficiently similar frequencies. Such heteroionic vibrational coupling is a recognised and well characterised phenomenon [16]. In future work we plan to explore the possible existence of such phenomena in the metal carbonyl field.

Not too surprising, perhaps, is the fact that the above generalization relates to the symmetry subtended by the bridging carbonyl groups rather than the overall molecular symmetry. The vibrations of the bridging carbonyl groups in clusters are not the immediate counterpart of the vibrations of the terminal CO groups in mononuclear species, although it may reasonably be argued that it is the fortunate fact that the geometry of the latter carbonyls coincides with the molecular geometry which is responsible for the difference.

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