The Interpretation of the Terminal ν(CO) Spectra of Some Tetranuclear Carbonyl Clusters

Sidney F. A. Kettle,*[a] Eliano Diana,[b] Enrico Boccaleri,[b] and Pier Luigi Stanghellini*[c]

Keywords: Cluster compounds / Vibrational spectroscopy / Spherical harmonics / Carbonyl complexes

The recently suggested spherical (SHM) and tensor (THM) harmonic models are applied to the interpretation of the terminal ν(CO) spectra of twenty six tetrahedral transition metal clusters containing between four and twelve terminal carbonyl groups. Although the SHM is perhaps the more generally relevant, there are species for which the THM is appropriate as a first approximation. The distinction between the two appears to be associated with a disruption of the band structure of the cluster either by the introduction of heterometal atoms or by the presence of a group – acetate ester, halide or hydride – presumably acting as an electronegative substituent.

Introduction

In a recent communication we explored the application of a novel, spherical harmonic, model (SHM) to the interpretation of the terminal ν(CO) vibrational spectra of transition metal cluster carbonyls.[1] The model, which in its simplest form ignores the cluster structure and geometry, was found to be of general applicability. It is the only extant model which successfully explains how a large, low-symmetry molecule with a large number of terminal CO groups can show only a single peak in the solution infrared. The model in its simplest form carries out a spherical harmonic expansion of the ν(CO) modes, considering the CO groups as radially attached to the spherical cluster surface. The spherical harmonic analysis of the vibrational problem shows that, of the harmonic subtended (S + P + D + F +....), only the P mode is infrared active and only the S and D modes are Raman active. So the simple model predicts two Raman bands, noncoincident with the single infrared. When the model is extended to take account of the molecular symmetry, splitting of the single degenerate feature is expected, together with intensity transfer between the spherical harmonic descendants of the same symmetry. More complex spectra can arise, yet there are very few clusters containing a three-dimensional array of metal atoms for which the SHM fails to give a convincing spectral interpretation.[2]

A limited group of clusters, all with a tetrahedral metal core, was found to exhibit a different spectral pattern. This pattern was susceptible to interpretation by a tensor harmonic formalism (the tensor harmonic model, THM), which requires the introduction of strong tangential (to the surface of the sphere) dipolar-active modes. This model predicts several strong and well-separated peaks. This point is illustrated in Figure 1, where we give the expected qualitative diagrammatic spectra for C_{3v} tetranuclear clusters with nine terminal CO groups (the most common structure − vide infra), following the SHM or THM, respectively.

The two models can be related to the recently proposed "metal cluster selection rule",[3] which is a cluster-equivalent to the well-known "surface selection rule" of metals.[4] A dipole moment change in an adsorbed molecule (or in a CO bonded to a cluster) induces an image dipole moment change in the metal bulk (or in the metal cluster). The dipole moment changes perpendicular to the metal surface reinforce and those parallel to it cancel, leading to the rule "only dipole moment changes perpendicular to the surface are spectrally dipole active". The clusters following the SHM are able to sustain image dipole and so behave as metals. The clusters following the THM are not able to do this and so approximate to insulators.

Some tetrahedral clusters required the SHM for the interpretation of their spectra and others the THM. Those that required the latter model were those in which the metal atoms were separated by electronegative bridging ligands.[5] The interpretation placed on this observation is that the presence of these ligands gave clusters which lacked the transition-dipole induced metallic conductivity. However, it was recognised that the matter was not so simple: "...it can be a delicate matter. So, although a sulfur bridged Re_4 species is [one that follows the THM] the reported data indicate that corresponding iron compound [does not]".[2] Related to this is the fact that it appears to be the case that it is only for tetrahedral species that the duality of model applicability occurs with such clarity. In that the tetrahedron is the simplest of all three-dimensional arrangements of metal atoms, this itself is perhaps not too surprising − the larger the metal cluster the more applicable the SHM, or so it seems.

Given the "delicate" nature of the choice of applicability of the SHM or the THM to tetrahedral clusters we felt the matter worthy of a more detailed study. All the evidence indicates that, in reality, there is continuity between the SHM and the THM, an aspect which, as the above dis-

---

[a] School of Chemical Sciences, University of East Anglia,
Norwich NR4 7TJ, Great Britain
[b] Dipartimento di Chimica IFM, Università di Torino,
via Pietro Giuria 7, I-10125 Torino, Italy
[c] Dipartimento di Scienze e Tecnologie avanzate,
Università del Piemonte Orientale "A. Avogadro",
Corso T. Borsalino 54, I-15100 Alessandria, Italy

1434−1948/99/1111−1957 $ 17.50+.50/0

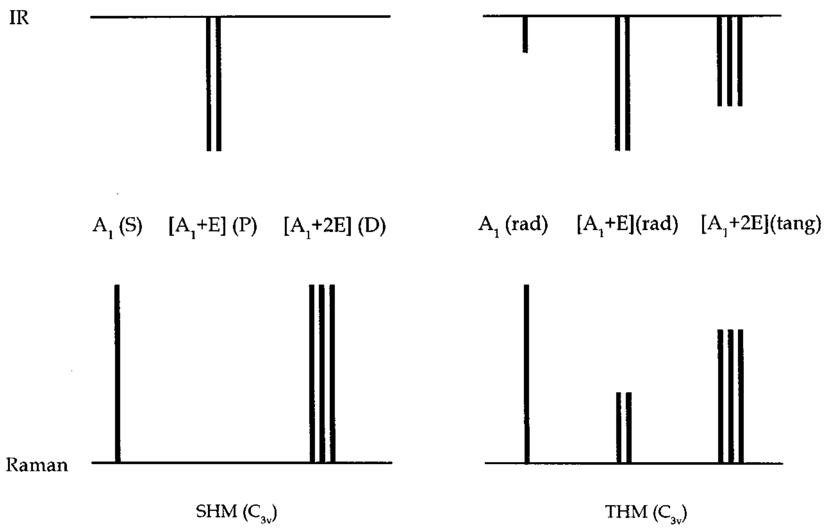

Figure 1. Schematic representation of the prediction of the SHM and of the THM for a $M_4(CO)_9$ system in C_{3v} symmetry; the order of the splitting within any one harmonic is molecule-dependent and so no indication of relative intensities within a set is given

cussion shows, seems particularly important for tetrahedral clusters. What of tetrahedral clusters which have no electronegative bridge atoms? Is there evidence that they may show at least putative THM behaviour? The present work is devoted to a study of this question and does so by a review of the infrared and, wherever data are available, the Raman spectra of some tetrahedral transition metal cluster carbonyls.

Results

Table 1 details the tetrahedral metal carbonyl clusters that we have reviewed. They were selected from those references that include figures which show the infrared spectra and do not merely give frequency data.

The Raman spectra were recorded by us whenever possible. It is convenient to start by a study of the spectra of

Table 1. The spectral behaviour of the (CO) features of some tetrahedral metal carbonyl clusters

N[a]	Complex	Symmetry[b]		P splitting[c] (cm^{-1})	Vibr. Model	Spectra	
		CO′s	molecule			infrared	Raman
1a	$Co_4(CO)_{12}$	C_{3v}	C_{3v}	8	SHM	this paper and ref.[6]	this paper
1b	$Rh_4(CO)_{12}$	C_{3v}	C_{3v}	5	SHM	this paper and ref.[6]	this paper
1c	$Co_3FeH(CO)_{12}$	C_{3v}	C_{3v}	9	borderline	this paper and ref.[6]	this paper
1d	$[Fe_3RhH(CO)_{12}]^{2-}$	C_{3v}	C_s	22	THM	this paper and ref.[7]	this paper
1e	$[Fe_2Ir_2(CO)_{12}]^{2-}$	C_{3v}	C_s	ca. 28	THM	ref.[8]	ref.[9]
1f	$[FeIr_3(CO)_{12}]^-$	C_{3v}	C_s	ca. 35	THM	ref.[8]	ref.[9]
1g	$[Fe_2Ir_2(-CO)_{12}AuPPh_3]^-$	C_{3v}	C_s	35	THM	this paper and ref.[8]	this paper
1h	$[Ir_4(CO)_{11}H]^-$	C_{3v}	C_s	10	SHM	ref.[10]	n.a.
1i	$[Ru_2Rh_2(CO)_{12}H]^-$	C_{3v}	C_s	20	borderline	ref.[11]	n.a.
1j	$Co_3Rh(CO)_{12}$	C_{3v}	C_s	ca. 10	SHM	ref.[12]	n.a.
1k	$Rh_3Ir(CO)_{12}$	C_{3v}	C_{3v}	3	SHM	ref.[12]	n.a.
1l	$Co_2Rh_2(CO)_{12}$	C_{3v}	C_s	15	borderline	ref.[12]	n.a.
1m	$Rh_2Ir_2(CO)_{12}$	C_{3v}	C_s	0	SHM	ref.[12]	n.a.
1n	$Co_2Ir_2(CO)_{12}$	C_{3v}	C_s	17	borderline	ref.[12][13]	n.a.
2a	$Co_4(CO)_{11}PPh_3$	C_s	C_s	ca. 15	SHM	this paper and ref.[14]	this paper
2b	$[Ir_4(CO)_{11}COOMe]^-$	C_s	C_s	ca. 30	THM	ref.[15]	n.a.
2c	$[Co_4(CO)_{11}COOMe]^-$	C_s	C_s	20	borderline	ref.[16][17]	n.a.
2d	$[Rh_4(CO)_{11}COOMe]^-$	C_s	C_s	35	THM	ref.[16][17]	n.a.
2e	$[Co_4(CO)_{11}I]^-$	C_s	C_s	20	borderline	ref.[17][18]	n.a.
3a	$[Rh_3Ru(CO)_{12}]^{2-}$	C_s	C_s	ca. 20	borderline	ref.[19]	n.a.
3b	$[Ir_4(CO)_{10}H_2]^{2-}$	C_s	C_s	20	borderline	ref.[20]	n.a.
3c	$[Ru_2Rh_2(CO)_{12}]^{2-}$	C_s	C_s	ca. 30	THM	ref.[11]	n.a.
3d	$[Ru_2Rh_2(-CO)_{12}AuPPh_3]^-$	C_s	C_s	18	borderline	ref.[11]	n.a.
4a	$[RhRu_3(CO)_{13}]^-$	C_3	C_3	0	SHM	ref.[19]	n.a.
5a	$Ir_4(CO)_{12}$	T_d	T_d	0	SHM	ref.[21]	ref.[22]
6a	$[Rh_4(CO)_{12}]^-$	C_s	C_s	0	SHM	ref.[16]	n.a.

[a] The numbers refer to the number and to the arrangement of the terminal CO′s, irrespective of the presence of bridging CO′s, other ligands or different metal atoms; **1**: (9 CO′s), $[M(CO)_3][M(CO)_2]_3$; **2**: (8 CO′s), $[M(CO)_3][M(CO)_2]_2[M(CO)]$ (**2e** is $[M(CO)_2]_4$); **3**: (7 CO′s), $[M(CO)_3][M(CO)_2][M(CO)]_2$; **4**: (10 CO′s), $[M(CO)_3]_3[M(CO)]$; **5**: (12 CO′s), $[M(CO)_3]_4$; **6**: (4 CO′s), $[M(CO)]_4$. – [b] The symmetry relates to the terminal CO groups and to the whole molecule, respectively. – [c] Applicable as a first approximation.

three structurally closely related species, **1a, 1b** and **1c**, all of C_{3v} symmetry, symmetry shared, of course, by the arrangement of the terminal CO groups. The group-theoretically predicted features are $3A_1 + 3E$, all modes being both infrared and Raman active. Their infrared and Raman spectra are shown in Figures 2, 3 and 4.

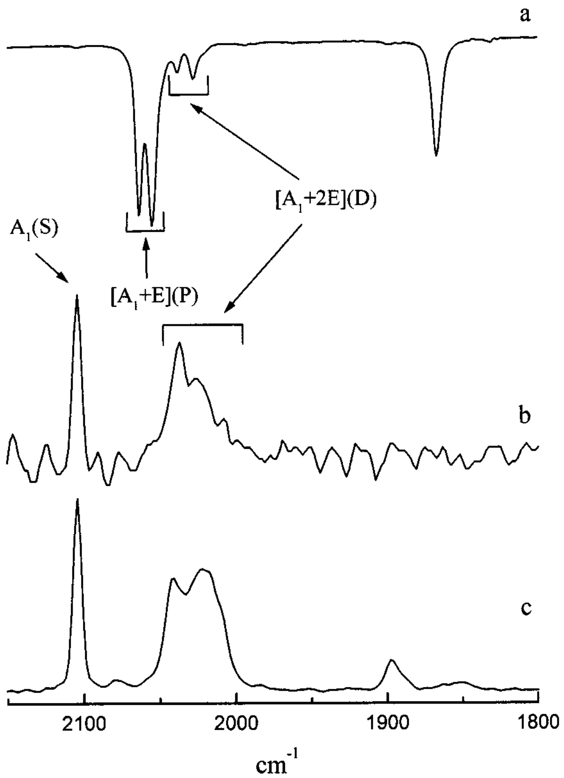

Figure 2. Solution infrared (a) and Raman (b: solution; c: crystals) spectra in the CO stretching region; complex: $Co_4(CO)_{12}$ (**1a**); solvents: (a) *n*-hexane, (b) CCl_4.

In these figures we also give the Raman spectra of crystalline samples; comparison of these with those from solutions gives confidence that the Raman spectrum of a crystalline compound, where this is the only one available, is not far removed from that of the dissolved species. All species show a high frequency A_1 mode, strong in the Raman spectrum and weak but coincident in the infrared spectrum; we shall have little to say concerning this mode beyond noting that it is the S mode of the SHM.

The complex $Co_4(CO)_{12}$ provides a good starting point for the study of the other modes because its spectra conform to the SHM predictions rather well. Consider the infrared spectrum, with two intense peaks, one approximately twice the intensity of the other, separated by ca. 8 cm^{-1}. Assignment as an A_1 + E splitting of the P mode of the SHM by the molecular C_{3v} symmetry is clear. Equally clear is that very little mixing occurs between functions originating in the P and D harmonics; the 2E + A_1 peaks at lower frequency, D in origin, are relatively weak in the infrared. The absence of any significant Raman intensity at the positions of the two strong infrared peaks is in accordance with the occurrence of little mixing. Conversely, the Raman D-originating peaks are split into a strong Raman peak, corre-

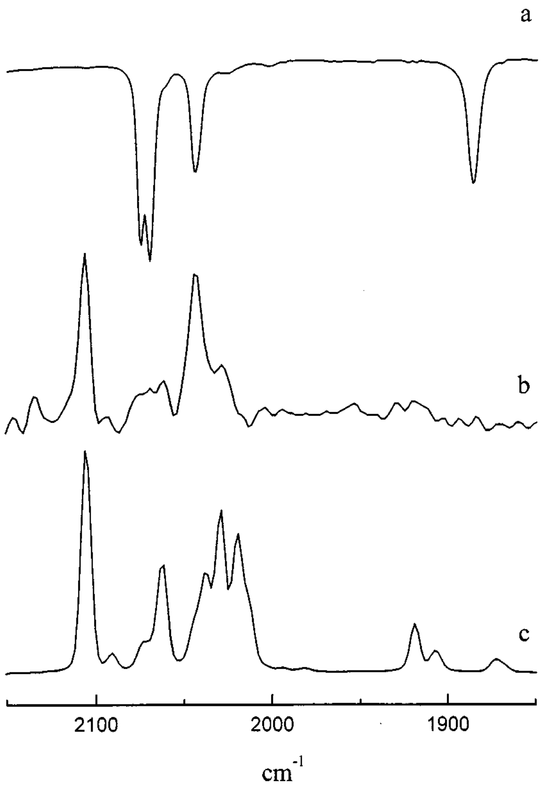

Figure 3. (see Figure 2); complex: $Rh_4(CO)_{12}$ (**1b**); solvents: (a) *n*-hexane, (b) CCl_4.

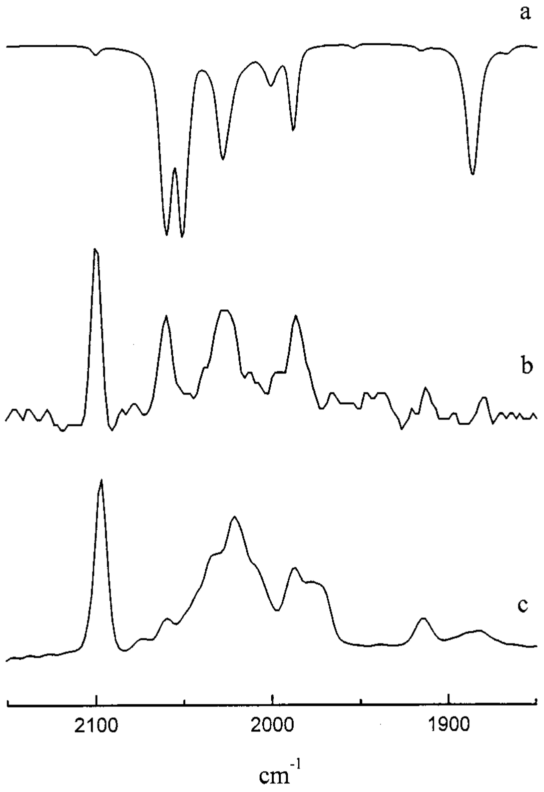

Figure 4. (see Figure 2); complex: $Co_3FeH(CO)_{12}$ (**1c**); solvents: (a) *n*-hexane, (b) CCl_4.

sponding to a weak infrared band, and a medium-broad peak largely coincident with another weak infrared absorption. There is another very weak and broad infrared peak at longest wavelength. As we shall see, a consistent pattern emerges if it is the lower frequency E modes which are most effective at stealing infrared intensity from the higher E mode. The Raman intensities, therefore, suggest that the assignment of these three infrared peaks is E, E and A_1 in that order, rather than E, A_1, E as previously suggested on the basis of the infrared spectrum alone.[4] The general explanation of the spectra seems clear, as is the conclusion arising from them: the SHM provides a convincing interpretation of the vibrational spectra. With this interpretation established, that of **1b** is also clear; it is basically the same. However, there is one significant difference: although the splitting of the individual spherical harmonics is less, the mixing between P and D functions is greater. The evidence for this assertion is that in the infrared the higher of the two E (D) is (relatively) stronger than in the cobalt species. Conversely, and as required by the SHM, the Raman E (P) is (relatively) stronger than in **1a** (the solid state spectra help to remove any ambiguity on this point). The spectra of **1c**, although significantly different, are related to the pattern set by **1a** and **1b**. However, the splitting of the (infrared active) P mode seems reversed. The E mode infrared intensity is distributed amongst all of the infrared-active E modes so that the E (P) is now weakened such that it is of about the same intensity as the A_1 (P), a considerable intensity having been transferred to both of the E (D) s, this transfer serving to identify them. The A_1/E (P) interchange is indicated by the infrared-Raman coincidence, which for this species occurs for the higher frequency P-derived mode (cf. **1b**). The infrared intensities indicate clearly that the zeroth-order SHM functions are significantly mixed in this species. The Raman is in complete agreement with this, the correspondences being just those expected. However, the reversed pattern of splitting in the P mode of the SHM (and, probably, changes in the D mode splitting too, vide infra), show that the substitution of a Co by FeH has had a significant disruptive effect and induced a significant move towards THM behaviour. A limiting THM behaviour would be characterised by an A_1 (S) and $[A_1 + E]$(P) splitting of the radial modes and a $[A_1 + 2E]$ splitting of the tangential modes. In particular, the tangential modes will have significant infrared intensity, a feature that serves to characterise the THM; it is to be noted that a P mode splitting occurs in both the SHM and the THM, although it seems to be larger in the latter.

In summary, through the series **1a−c** we see a progression from almost pure SHM behaviour through to something that shows characteristics which surely indicate a transition to something closer to the THM limit. For this reason we do not regard the evident E, A_1, E splitting of the lower infrared set in **1c** as requiring the same pattern for **1a**.

The effect of metal-atom substitution in tetrahedral clusters can be further explored in the complex **1d**. It has a (solid state) Raman spectrum which very closely resembles that of **1b** and which surely must be interpreted similarly (Figure 5).

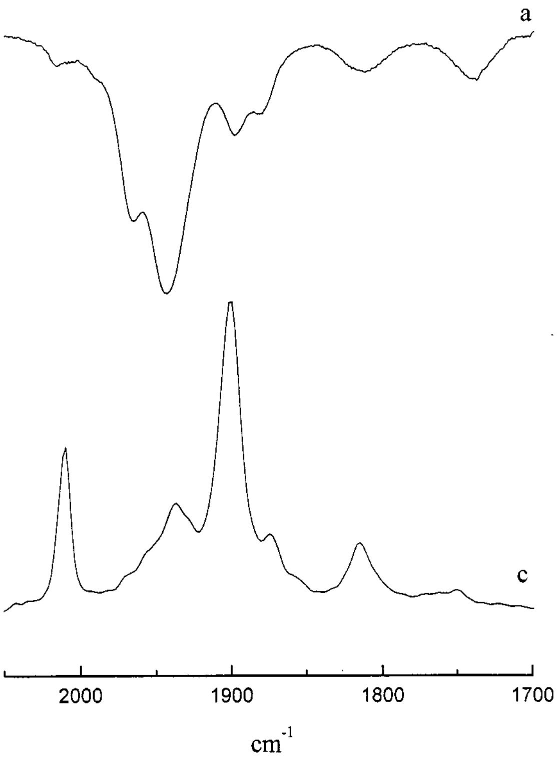

Figure 5. (see Figure 2); complex: $[Fe_3RhH(CO)_{12}]^{2-}$ (**1d**); solvents: (a) CH_3CN.

The intermolecular CO coupling (factor group effects) in anionic metal carbonyl clusters is minimised by the dilution effect caused by the presence of a large counterion. This is relevant to complex **1d** which has C_s symmetry, as the rhodium atom lies in the basal triangle.[7] Notwithstanding its lower symmetry and the presence of a “hetero” metal atom, the similarity of its spectra with those of **1b** is remarkable. As we have pointed out, such an indifference to metal atom heterogeneity is not unusual in clusters and the fact that the indifference is implicit within the SHM has been claimed[2] as a strength of the model. Other complexes sustain this assessment. Consider the pair **1e** and **1f**, whose spectra have already been reported.[8] The similarity of the spectra of **1e** with those of the C_{3v} complexes is clearly evident. The spectra of **1f** suffer from the poor quality of the Raman spectrum and of the broadness of the infrared; however, the patterns seem similar and so too, presumably, are the explanations. Moreover, the complex **1g**, structurally derived from **1e** with an $AuPPh_3$ unit bridging the basal $FeIr_2$ triangle,[8] does not show any significant changes in the spectra (Figure 6) − the splitting of the P and D modes is simply more evident.

Finally, we have considered seven other species, **1h−1n**. Like all of the molecules considered so far, they have nine terminal CO groups and C_s symmetry. Immediately evident is the overall similarity between comparable spectra, both

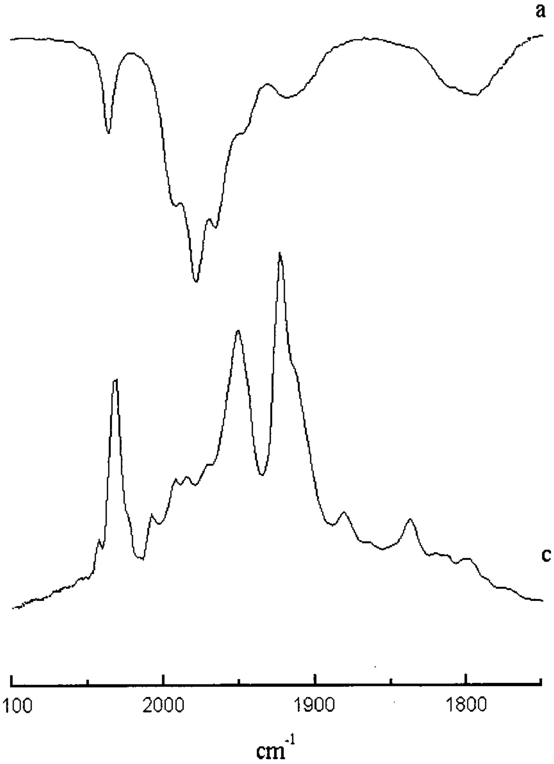

Figure 6. (see Figure 2); complex: $[Fe_2Ir_2(CO)_{12}AuPPh_3]^-$ (**1g**); solvents: (a) CH_2Cl_2.

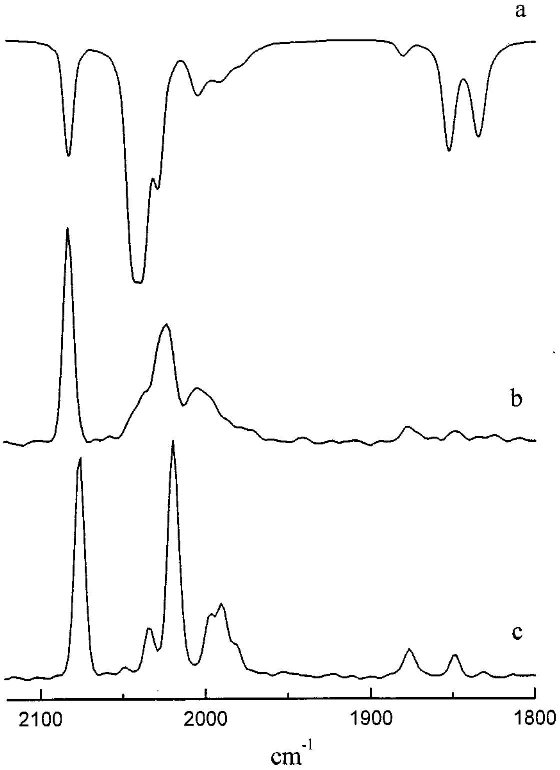

Figure 7. (see Figure 2); complex: $Co_4(CO)_{11}PPh_3$ (**2a**); solvents: (a) CCl_4, (b) CCl_4.

between these species and those of Figures 2−6, notwithstanding the fact that two of these species contain H as a bridging ligand and that one has a M_4, two a MM'_3 and the other four a $M_2M'_2$ core. It is clear that the general pattern established for the first three molecules, of C_{3v} symmetry, is applicable to others of C_s. This is helpful because the low symmetry of the latter means that group theory, unaided, offers few insights.

Figure 7 shows the ir and Raman spectra of **2a**, a species derived from **1a** by substitution of a basal CO by a phosphane.[14] Consequently, it has eight terminal carbonyl groups with the structural form $M(CO)_3[M(CO)_2]_2M(CO)$. Like the molecules **1d−1n**, the molecular symmetry is C_s, but whereas for these latter the idealised CO group arrangements are all C_{3v}, this arrangement now has only C_s symmetry. Despite this change, and that of the number of terminal CO ligands, the spectra of Figure 7 are qualitatively very similar to those of Figures 2−6; the S + P + D pattern is clearly recognisable. The only change that seems evident is that the highest frequency, totally symmetric, A′ mode has an increased infrared activity. This is not surprising in view of the reduction in CO group symmetry. The literature reports a set of $[M_4(CO)_{11}COOR]^-$ (M = Co, Rh, Ir) complexes,[15−17] all having the same number and arrangement of the CO groups. Raman spectra are not available but the infrared spectra exhibit a behaviour very close to that just discussed. A general comment which may be made at this point is that, as Table 1 shows, neither metal atom nor terminal carbonyl symmetries have any apparent influence on the spectral behaviour observed.

The compounds **2b−2d** are very interesting in that they all contain a single acetate-derived substituent. As a first approximation, the second and third row transition element examples conform to the THM whilst the first row example lies somewhere between the two extremes. Whilst they conform to the pattern that the introduction of electronegative substituents leads to near THM behaviour, they provide the first examples in which the presence of a single electronegative substituent is sufficient to bring about this transition. The compound **2e**, with a single iodide anion, is borderline, as are a number of other species with H as a ligand. It should be recognised that the species which have been the subject of the present paragraph serve to remove a possible ambiguity concerning the THM. This concerns the matter of Mν(CO)−M′ν(CO) coupling. In that it does not invoke the (additional) coupling via an induced-dipole mechanism of the SHM, could it be that the THM is only appropriate to species in which Mν(CO)−M′ν(CO), or perhaps just $[M\nu(CO)_n]-[M'\nu(CO)_m]$, (with no constraints on M, M′, n or m as long as they refer to different units) coupling is negligible? The present series seem to make it quite clear that the existence of coupling is entirely consistent with the applicability of the THM.

The final set which we review is a series of four tetranuclear species (**3a−d**) containing just seven terminal carbonyl groups. They comprise one M_4, one M_3M' and two $M_2M'_2$ compounds. Their infrared spectra, again of variable quality, are illustrated in the Figures of the relevant papers (Table 1). Yet again, the general impression is one of similarity with the other spectra given in this paper. The essential indifference of the spectra to the number of terminal carbonyl groups is an indicator of the applicability of a common model and this seems to be that of a borderline between the SHM and THM, with a bias towards the latter.

Finally, we group together three more complexes with different numbers of CO groups and different symmetries. The anion **4a**, of C_3 symmetry but now with ten terminal CO groups has recently bee reported. The carbonyl groups in this complex are arranged as $[M(CO)][M(CO)_3]_3$.[19] In this discussion, this is grouped with the well-known $Ir_4(CO)_{12}$ (**5a**) and $[Rh_4(CO)_{12}]^-$ (**6a**) complexes, with $[M(CO)_3]_4$ and $[M(CO)]_4$ carbonyl arrangements, respectively. What is remarkable is the fact that their infrared spectra differ very little from each other and are even simpler than those reported in Figures 1 and 2, despite the considerable difference in number of terminal CO groups in, and different symmetries of, the relevant molecules. The SHM is applicable to all of them, explaining the spectral observations.

Discussion

The most evident conclusion to be drawn from the spectra discussed above is that they are all related and show little sensitivity to the detailed molecular geometry or, indeed, to the number of terminal carbonyl groups in the molecule. The formal charge on the carbonyl species affects the mean frequency of the band pattern but not its general characteristics. As a starting point, the SHM is clearly appropriate. However, as we suspected when the present work commenced, there seem to be some species that show at least some aspects of a move towards the applicability of the THM. Although we recognise that distinctions are arbitrary − there can be conflicting indications − we incline to the view that when the (commonly observed) splitting of the P mode is less than, say, 10 cm^{-1}, then the SHM is applicable. This applicability is also manifest in the fact that whilst there is infrared intensity in the Raman-active D modes and Raman intensity in the infrared-active P modes, this transfer is less than in the species about to be discussed. When the splitting of the P mode features is greater than, say, 25 cm^{-1}, there is a significant movement towards the applicability of the THM (although the limiting characteristics of this model are rarely encountered). Another indicator of the move towards THM behaviour is an increase in infrared-Raman intensity transfer. So, clusters **1a**, **1b**, **1h**, **1j**, **1k**, **1m**, **2a**, **4a**, **5a** and **6a** show SHM-type behaviour whilst clusters **1d**, **1e**, **1f**, **1g**, **2b**, **2d** and **3c** show a significant move towards THM-type behaviour. Others, **1c**, **1i**, **1l**, **1n**, **2c**, **2e**, **3a**, **3b** and **3d** are rather borderline, emphasising the existence of continuity between the SHM and THM. To further explore this point, we can go back to Figure 1.

The pattern can be reinterpreted in terms of the basic model behind the SHM/THM distinction. Pure SHM has been interpreted as the metal cluster core behaving as a perfect conductor; it can sustain an image dipole, presumably because of a dipole-induced mixing with low-lying excited states. Conversely, pure THM behaviour is associated with the cluster behaving like a perfect insulator. So, the data that we have presented above indicate that the Co_4 cluster is more "metallic" than is the Rh_4. Further, the replacement of a Co by an FeH in the Co_3Fe unit is sufficient to disrupt the band pattern of Co_4 and to give a much less metallic unit. At the present it only seems possible to make such comments post hoc. We have previously commented on the fact that, very often, replacement of a metal atom with a quite different one in a cluster has little, if any, effect on the vibrational spectra. Given the discussion at the beginning of this paper, we would expect that any metal-atom substitutional effect would be particularly evident for tetrahedral clusters and this expectation seem justified, although it does not mean that all tetrahedral mixed-metal species conform to the THM.

In the present work we have reviewed the terminal ν(CO) vibrational spectra of some twenty six tetrahedral cluster carbonyls. The details of the reviews have decreased throughout the paper, for two reasons. First, the spectral similarities observed means that there would otherwise have been much repetition. Second, for many of the later species either no Raman data were available or only relatively poor quality spectra. For the examples discussed at the beginning of the paper, good quality Raman data provided important corroborative evidence for conclusions reached from the infrared. Nonetheless, the general conclusion to be reached is clear. Tetrahedral cluster carbonyls seem to show sensitivity to the molecular composition greater than that revealed for comparable species of a higher nuclearity in a recent survey. In retrospect, this is not a surprising conclusion since the "cluster selection rule" that seems to control cluster spectral activities is related to the surface selection rule of metal surfaces. Tetrahedral clusters are those clusters most removed from the surface of bulk metal. Not surprisingly, therefore, some of the tetrahedral clusters reviewed in the present work seem to show a significant tendency to exhibit vibrational spectroscopic characteristics indicative of a move towards the THM. That the presence of electronegative ligands can make the THM that which is applicable is therefore entirely consistent. Overall, this suggests that other examples of THM applicability will only be found in low-nuclearity clusters.

Conclusions

In the present paper we have addressed the problem of the relative applicability of the SHM and the THM to the terminal ν(CO) vibrations of tetrahedral transition metal carbonyl clusters. For the species, which we surveyed − which were as broadly based as the data available in the literature would allow − they were found to be roughly equally applicable. This pattern explains a confusion apparent in the literature, that there are some tetrahedral species for which the available data are such as to make a normal coordinate analysis possible and others for which the data are not. The former are those that follow the THM. Overall, the pattern revealed is one that strongly supports the interpretation of the SHM in terms of a cluster selection rule, akin to the surface selection rule. Substitution of a metal atom of a homometallic cluster by a different metal or the addition of a highly electronegative group or atom to a molecule both have the effect of making the THM more applicable. Equally, they will have the effect of disrupting, at least to some extent, the band structure associated with the metal atoms in the cluster. This connection between band-structure disruption and THM applicability is just that expected on the basis of the cluster selection rule. This conclusion leads to a useful prediction, that THM behaviour should become increasingly rare as the cluster size increases and, as our recent survey has shown, this seems to be the case. In the other direction, there are trimetallic clusters (and, indeed, a whole family of clusters in which all of the metal atoms are located in the same plane) but these clearly merit a separate discussion concerning the applicability of the SHM and THM (vibrations located in the molecular plane may well behave rather differently from displacements perpendicular to it)

Experimental Section

$Co_4(CO)_{12}$[23] (**1a**), $Co_3FeH(CO)_{12}$[24] (**1c**) and $Co_4(CO)_{11}PPh_3$[14] (**2a**) were prepared as previously reported. $Rh_4(CO)_{12}$ (**1b**) was purchased from Sigma Aldrich and used after recrystallisation from *n*-hexane under CO. $[Fe_3RhH(CO)_{12}]^{2-}$ (**1d**) and $[Fe_2Ir_2(CO)_{12}AuPPh_3]^-$ (**1g**) were kindly donated by Professor R. Dalla Pergola, University of Milan.

IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrophotometer at a resolution of 2 cm^{-1} in *n*-hexane for neutral complexes, and in CH_2Cl_2 for anionic systems, both in a NaCl cell. Raman spectra were recorded on a Bruker RFS 100 spectrophotometer equipped with an Nd^{3+}:YAG laser and Ge-diode detector at a resolution of 4 cm^{-1}. Measurements on crystalline samples were performed in capillary vials sealed under inert gas. Due to the risk of heating and decomposition, low laser powers (10−30 mW) were used and several scan-packets (of 50−100 scans each), interleaved by a recovery time and then averaged, were made. Solution spectra were recorded in CCl_4, a solvent that proved to have a very low background in the carbonyl stretching spectral region. Solutions were prepared by stirring the sample in a flask under a nitrogen flow and then filtering off the insoluble excess (highly concentrated solutions are required). Solutions were put into a quartz cuvette, which was sealed under inert gas. Laser powers of about 200 mW and about 3000 scans were used.

Acknowledgments

We are indebted to the Italian MURST (Ministero della Università e della Ricerca Scientifica e Tecnologica) for financial support (40% funding).

---

[1] S. F. A. Kettle, E. Diana, R. Rossetti, P. L. Stanghellini, *J. Am. Chem. Soc*. **1997,** *119*, 8228.

[2] S. F. A. Kettle, E. Diana, R. Rossetti, P. L. Stanghellini, *Inorg. Chem*. **1998**, *37*, 6502.

[3] S. F. A. Kettle, *Spectrochimica Acta A*, **1998,** *54A*, 1639.

[4] N. A. Pierce, N. Sheppard *Surf. Sci.* **1976**, *59*, 205; N. Sheppard, J. Erkelens *Appl. Spectrosc.* **1984**, *38,* 471;Y. J. Chabal *Surf. Sci. Rep.* **1988**, *8,* 214; S. F. A. Kettle *Theochem* **1995,** *341,* 25.

[5] D. Bright, *J. Chem. Soc., Chem. Commun.* **1970** 1169; U. A. Jayasooria, C.E. Anson, *J. Am. Chem. Soc.* **1986,** *108,* 2894; E. Horn, M. R. Snow, *Aust. J. Chem.* **1981**, *34*, 737; E. W. Abel, P. J. Hendra, R. A. N. McLean, M. M. Qurashi, *Inorg. Chim. Acta* **1969**, *3*, 77; C. Marshall, R. D. Peacock, D. R. Russel, I. L. Wilson, *J. Chem. Soc., Chem. Comm.* **1970,** 1643; E. Horn, M. R. Snow, P. C. Zeleny, *Aust. J. Chem.* **1980**, *33*, 1659; D. J. Darensbourg, K. K. Klausmeyer, J. D. Draper, J. A. Chojnacki, J. H. Reibenspies, *Inorg. Chim. Acta* **1998**, *270*, 405.

[6] G. Bor, G. Sbrignadello, K. Noack, *Helv. Chim. Acta* **1975**, *58*, 815.

[7] R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi, G. Longoni, *J. Organomet. Chem.* **1988**, *352*, C59.

[8] R. Della Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi, M. Sansoni, *J. Chem. Soc., Dalton Trans.* **1990**, 127.

[9] S. F. A. Kettle, E. Diana, P. L. Stanghellini, R. Della Pergola,. *Inorg. Chim. Acta* **1993**, *212*, 75.

[10] R. Bau, M. Y. Chiang, C. Y. Wei, L. Garlaschelli, S. Martinengo, T. F. Koetzle, *Inorg. Chem.* **1984**, *23*, 4758.

[11] A. Fumagalli, D. Italia, M. C. Malatesta, G. Ciani, M. Moret, A. Sironi, *Inorg. Chem.* **1996**, *35*, 1765.

[12] S. Martinengo, P. Chini, V. G. Albano, F. Cariati, T. Salvatori, *J. Organomet. Chem.* **1973**, *59*, 379.

[13] V. G. Albano, G. Ciani, S. Martinengo, *J. Organomet. Chem.* **1974**, *78*, 265.

[14] G. Cetini, O. Gambino, R. Rossetti, P. L. Stanghellini, *Inorg. Chem.*, **1968**, *7*, 609; D.J. Darensbourg, B. Scott Peterson, R. E. Schmidt, *Organometallics* **1982**, *1*, 306

[15] L. Garlaschelli, S. Martinengo, P. Chini, F. Canziani, R. Bau, *J. Organomet. Chem.* **1981**, *213*, 379.

[16] S. Martinengo, A. Fumagalli, P. Chini, V. G. Albano, G. Ciani *J. Organomet. Chem.* **1976**, *116*, 333.

[17] G. Longoni, S. Campanella, A. Ceriotti, P. Chini, V. G. Albano, D. Braga, *J. Chem. Soc., Dalton Trans.* **1980,** 1816.

[18] V. G. Albano, D. Braga, G. Longoni, S. Campanella, A. Ceriotti, P. Chini, *J. Chem. Soc., Dalton Trans.* **1980,** 1820.

[19] A. Fumagalli, M. Bianchi, M. C. Malatesta, G. Ciani, M. Moret, A. Sironi, *Inorg. Chem.* **1998**, *37*, 1324.

[20] G. Ciani, M. Manassero, V. G. Albano, F. Canziani, G. Giordano, S. Martinengo, P. Chini, *J. Organomet. Chem.* **1978**, *150*, C17.

[21] D. Roberto, L. Garlaschelli, M. Pizzotti, *Inorg. Chem.*, **1995**, *34*, 3555.

[22] F. Cariati, V. Valenti, G. Zerbi, *Inorg. Chim. Acta* **1969**, *3*, 378.

[23] R. A. Friedel, I. Wender, S. L. Shufler, H. W. Sternberg, *J. Am. Chem. Soc.* **1955,** *77,* 3951.

[24] P. Chini, L. Colli, M. Peraldo, *Gazz. Chim. Ital.* **1960**, *90*, 1005.

Received May 21, 1999
[I99180]