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The ν(CO) Vibrational Spectra of Planar Transition Metal Carbonyl Clusters

S. F. A. Kettle,*,† E. Boccaleri,‡ E. Diana,§ R. Rossetti,§ P. L. Stanghellini,*,‡ M. C. Iapalucci,‖ and G. Longoni‖

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K., Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", corso T. Borsalino 54, 15100 Alessandria, Italy, Dipartimento di Chimica IFM, Università di Torino, via P. Giuria 7, 10125 Torino, Italy, and Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy

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The ν(CO) vibrational spectra of planar transition cluster carbonyls containing $M(CO)_4$ groups are studied. It is possible to anticipate qualitatively, both for the infrared and Raman, the band intensity changes associated with increasing metallic nature of the cluster. These enable a unification of the band patterns shown by the species reported. As for (idealized) spherical clusters, the spherical harmonic model (SHM), suitably modified, becomes of more general applicability as cluster size increases, although for smaller species the tensor harmonic model (THM) makes a contribution.

Introduction

It seems that, on many fronts, inorganic chemistry is turning toward the study of molecules of increasing size.[1] One consequence of this is that some of the experimental methods that have been important in its development are becoming of less value. So, the vibrational spectra of large molecules are commonly so complicated that they can be regarded only as fingerprints and not as objects for analysis. Exceptions, of course, may be provided by resonance Raman and some localized, sharp and strong infrared features. However, it seems increasingly to be assumed that the way forward to an understanding of the spectra will lie in the use of theoretical methods, and DFT is currently popular, to predict them.[2] Behind this argument is the assumption that no new phenomena occur with increasing molecular size that may influence the appearance of the spectra. There is evidence that this assumption is invalid. The evidence comes from the transition metal carbonyls. The vibrational spectra of simple metal carbonyls are well understood.[3] Essentially, they are interpreted on the basis that every terminal CO group within a molecule may interact with every other terminal CO group (although the number of unknowns entailed may force simplifications). As the number of CO groups increases, and this means that as the molecular size increases, so the spectra should become increasingly complicated. In fact, large cluster carbonyls containing many CO groups have very simple spectra, often a single infrared peak, even when the molecular symmetry is low. Raman spectra, when available, commonly show two features, one on either side of the infrared, demonstrating that CO−CO vibrational coupling persists.[4] For a quarter of a century there was no interpretation of the spectra of these cluster carbonyls. Only recently, a quite new, spherical harmonic model (SHM) was suggested as explanation.[5] It seems that the metallic core of the clusters supports image dipoles, such as those that lead to simplifications in the vibrational spectra of species adsorbed on metals.[6]

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* Authors to whom correspondence should be addressed. E-mail: pierluigi.stanghellini@mfn.unipmn.it (P.L.S.); S.Kettle@uea.ac.uk (S.F.A.K.).

† University of East Anglia.

‡ Università del Piemonte Orientale "A. Avogadro".

§ Università di Torino.

‖ Università di Bologna.

(1) Tenne, R. *Prog. Inorg. Chem.* **2001**, *50*, 269. Shvartsburg, A. A.; Hudgins, R. R.; Dugourd, P.; Jarrold, M. F. *Chem. Soc. Rev.* **2001**, *30*, 26. Driess, M. *Adv. Inorg. Chem.* **2000**, *50*, 235. Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1.

(2) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391. Jang, J. H.; Lee, J. G.; Lee, H.; Xie, Y.; Schafer, H. F., III. *J. Phys. Chem. A* **1998**, *102*, 5298. Chermette, H. *Coord. Chem. Rev.* **1998**, *178−180*, 699. Schettino, V.; Pagliai, M.; Ciabini, L.; Cardini, G. *J. Phys. Chem. A* **2001**, *105*, 11192.

(3) Haines, L. H.; Stiddard, M. H. B. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 53. Kettle, S. F. A. *Top. Curr. Chem.* **1977**, *71*, 111.

(4) Kettle, S. F. A.; Diana, E.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chem.* **1998**, *37*, 6502.

(5) Kettle, S. F. A.; Diana, E.; Rossetti, R.; Stanghellini, P. L. *J. Am. Chem. Soc.* **1997**, *119*, 8228.

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For pseudospherical cluster carbonyls, in a spherical harmonic expansion of the CO modes, to give S + P + D + ..., only the P are infrared allowed, leading to a single infrared feature (with S + D Raman-allowed features on either side, frequencywise). The metal-like character of the cluster can be diminished by the incorporation of heteroatoms. Correspondingly, new features appear in the infrared, ultimately leading to the normal group theoretical predicted pattern. The link with the SHM is provided by its extension by the so-called tensor harmonic model (THM). For full details, the original publications should be consulted.[4,5,7−9]

The question at once arises as to whether effects similar to those found in cluster metal carbonyls are of more general occurrence. It is likely that the answer is positive. Consider a common molecular structure, that of two interpenetrating tetrahedra, one of metal atoms, one of ligands, M_4L_4. Fe_4S_4 systems of this type are of biological importance, for instance.[10] If there is strong M−M bonding, then one must expect that the M_4 tetrahedron will be capable of sustaining an image dipole and the SHM likely to be applicable. If, on the other hand, there is no M−M bonding, then the point group predictions would be appropriate. In between these two extremes one would expect that the SHM/THM combination would apply. In that the extension of inorganic chemistry to larger systems frequently involves ligands bridging metal atoms, the question posed for M_4L_4 would seem equally applicable. Given the diversity already available, it would be surprising if there were not those for which a harmonic analysis is the most appropriate approach. Evidence from areas as diverse as molecular magnets and long-range electron transfer points to metal−metal coupling of various sorts.[11] However, there is one serious problem connected with the more general application of the methodology. This is that, to date, it has only been applied to pseudospherical systems. Does it have a wider applicability? This is the topic that we explore in the present communication. We do so in the context of cluster transition metal carbonyls, where the work can be based on a secure foundation. Specifically, we move from a three-dimensional analysis to two dimensions, from spherical clusters to planar. First we predict the general form that the spectra should have, and then we compare these predictions with literature data, augmented wherever possible with additional measurements which we have made ourselves.

Experimental Section

The complexes $[Fe_4Au(CO)_{16}][NMe_3CH_2Ph]$ (**3**),[12] $[Fe_4Pt(CO)_{16}][NMe_3But]_2$ (**4**),[13] $[Ag_5Fe_4(CO)_{16}][NMe_3CH_2Ph]_3$ (**6**),[14] and $[CdFe(CO)_4]_4$ (**7**)[15] were prepared according to literature methods. The cluster $[Re_4(CO)_{16}][N(C_4H_9)_4]_2$ (**5**) was given us by Prof. D'Alfonso of the University of Milan.

Table 1. List of the Complexes Studied

no.	complex	reference data: infrared	reference data: Raman	structure
1	$Ru_3(CO)_{12}$	this paper and ref 16	this paper and ref 16	ref 17
2	$Os_3(CO)_{12}$	this paper and ref 16	this paper and ref 16	ref 18
3	$\{[Fe(CO)_4]_4Au\}^-$	this paper and ref 12	this paper	ref 12
4	$\{[Fe(CO)_4]_4Pt\}^{2-}$	this paper and ref 13	this paper	ref 13
5	$\{[Re(CO)_4]_4\}^{2-}$	this paper	this paper	ref 19
6	$\{[Fe(CO)_4]_4Ag_5\}^{3-}$	this paper and ref 14	this paper	ref 14
7	$[CdFe(CO)_4]_4$	this paper and ref 15	this paper	ref 15
8	$\{[Fe(CO)_4]_4Ag_4\}^{4-}$	ref 14		ref 14
9	$\{[Fe(CO)_4]_4Cu_5\}^{3-}$	ref 20		ref 20
10	$\{[Fe(CO)_4]_3Cu_3\}^{3-}$	ref 20		ref 20

The acetonitrile used as solvent for solution spectra was thoroughly degassed by a repeated freeze−pump−thaw cycle. Other solvents, including Nujol oil, were treated by a flow of nitrogen before use.

The infrared spectra were collected with a Bruker Equinox 55 FT-IR spectrophotometer, using a resolution of 2 cm^{-1} and averaging 32 scans.

The Raman spectra reported were collected using a Bruker RFS 100 FT Raman spectrophotometer, using NIR laser radiation at 1064 nm and a resolution of 4 cm^{-1}. To minimize decomposition of the sample, the cluster crystals were sealed in capillary glass tubes under nitrogen. Complex **3** showed some fluorescence, but a discrete spectrum was obtained with a power of 30 mW and an average of 2000 scans. Complex **4** needed 1000 scans at 30 mW power for the solid-state spectrum, while to obtain a good signal/noise ratio for a CH_3CN solution it was necessary to average 3000 scans using a laser power of 220 mW. The spectrum of complex **5** was easily obtained using a laser power of 70 mW and an accumulation over 200 scans. Complex **7** was analyzed with a power of 40 mW, and spectra were averaged over 1500 scans. Complex **6** showed a strong fluorescence with the NIR laser. Attempts to obtain a spectrum using a dispersive Raman instrument and a variety of different visible laser wavelengths failed. The spectrum we report was obtained on an ISA Instruments LABRAM micro Raman spectrophotometer. The spectrum was recorded using a red (633 nm) laser light and is the average of three measurements, each with an exposure time of 50 s. To obtain the maximum signal, avoiding problems due to optical dispersion caused by the cylindrical surface of the capillary tubes, the sample was put in a microscope slide with a concave slot and sealed with a cover under nitrogen in a glovebox.

Results

Table 1 lists the complexes included in the discussion of this paper; their schematic structures are illustrated in Figure 1.

They cover the majority of the planar carbonyl clusters that have been reported. A few of them have been selected on the basis of the availability in the literature of a figure

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(6) Pierce, N. A.; Sheppard, N. *Surf. Sci.* **1976**, *59*, 205. Sheppard, N.; Erkenlens, J. *Appl. Spectrosc.* **1984**, *38*, 471. Chabal, Y. J. *Surf. Sci. Rep.* **1988**, *8*, 211. Kettle, S. F. A. *THEOCHEM* **1995**, *341*, 25.

(7) Kettle, S. F. A. *Spectrochim. Acta A* **1998**, *54A*, 1639.

(8) Kettle, S. F. A.; Diana, E.; Boccaleri, E.; Stanghellini, P. L. *Eur. J. Inorg. Chem.* **1999**, 1957.

(9) Kettle, S. F. A.; Boccaleri, E.; Diana, E.; Rossetti, R.; Stanghellini, P. L.; Iapalucci, M. C.; Longoni, G. *J. Cluster Sci.* **2001**, *12*, 175.

(10) Malinek, S. M.; Coucouvanis, D. *Prog. Inorg. Chem.* **2001**, *49*, 599.

(11) Turner, J. W.; Schultz, F. A. *Coord. Chem. Rev.* **2001**, *219−221*, 81. Launay, J. P. *Chem. Soc. Rev.* **2001**, *30*, 386. Cornia, A.; Gatteschi, D.; Sessoli, R. *Coord Chem Rev.* **2001**, *219−221*, 573. Winpenny, R. E. P. *Adv. Inorg. Chem.* **2001**, *52*, 1.

(12) Albano, G. V.; Aureli, R.; Iapalucci, M. C.; Laschi, F.; Longoni, G.; Monari, M.; Zanello, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1501.

(13) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242.

(14) Albano, G. V.; Azzaroni, F.; Iapalucci, M. C.; Longoni, G.; Monari, M.; Mulley, S.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1994**, *33*, 5320.

(15) Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2090.

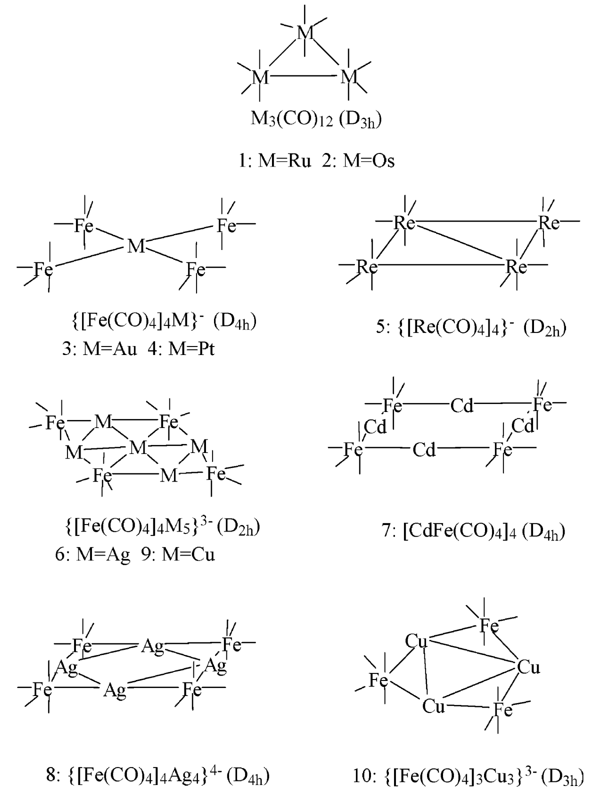

Figure 1. Schematic structures of the complexes.

showing an infrared spectrum; for these, of course, we have not been able to record the Raman spectra.

As Figure 1 clearly shows, the complexes in Table 1 span a variety of structures. All except three contain four $M(CO)_4$ units. The exceptions contain three (**1**, **2**, **10**); one of these also contains three hetero-metal atoms. Of the seven four-$M(CO)_4$ species, one contains no hetero-metal atom (**5**), two contain one hetero-metal atom (**3** and **4**), two contain four hetero-metal atoms (**7** and **8**), and the final two contain five hetero-metal atoms (**6** and **9**). Despite these many differences, the vibrational spectra of the compounds show clear similarities (Figures 4−10 and figures reported in the appropriate references). In particular, most conform to an infrared pattern of two strong bands, although in the simpler species these bands may be very close. In those cases (**5**, **6**, and **9**) in which there are structurally distinct $M(CO)_4$ groups, there is no overt evidence for this distinction in the spectra. Even in complexes where hetero-metal atoms are present, all of the indications are that all of the $M(CO)_4$ groups in a molecule are vibrationally coupled. The centrosymmetric complexes show an infrared−Raman exclusion although near-coincidences occur. The Raman spectra show more features than do the infrared and are more diverse. However, the diversity is more to be found in the intensities than in the general pattern of peaks. The general peak pattern is that there is a peak, usually of medium intensity, at high frequency. At anything up to 100 cm^{-1} to lower frequency occurs the strongest Raman peak; to the low-frequency side of this there is a series of smaller peaks. However, there are significant exceptions to this broad-brush pattern, and these merit detailed discussion.

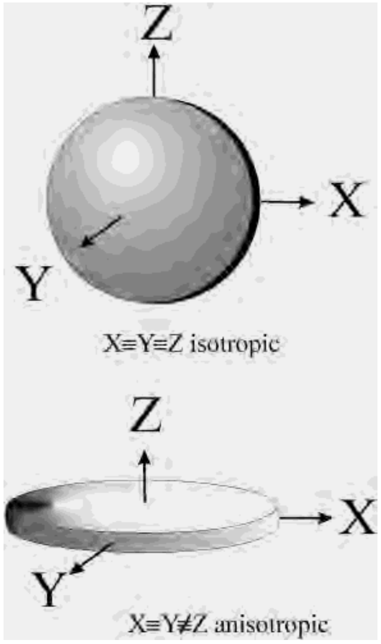

Figure 2. Compression of an isotropic sphere to give an anisotropic circular plane.

Discussion

(a) Theoretical Background. Considering only it for the moment, the SHM would be expected to be less applicable the smaller the cluster and the less spherical the cluster. The former points to tetrahedral clusters and we have elsewhere discussed these.[8] The extreme of nonspherical clusters is represented by planar clusters, whose behavior, we believe, can be understood with reference to spherical clusters. It is not difficult to see how the SHM might be expected to have to be modified to be adapted to planar clusters. If we take a sphere and compress it along the Z axis,[21] we eventually obtain a circle in which the properties in the X,Y plane derive from those of the sphere (Figure 2).

In the SHM, infrared activity is associated with the P mode. Anisotropy means that it will be split in a 1:2 [Z: (X,Y)] intensity ratio. However, the X,Y dipole moment changes can be doubled by the image dipole effect. This means that the intensity ratio [Z: (X,Y)] could increase to 1:8. The conclusion is clear: we expect two strongly allowed bands in the infrared, situated close together; of these, *the stronger will be that associated with the X,Y modes,* conveniently called the “planar” modes. Considering the Raman spectrum, the intensity predictions also enable unambiguous assignments to be made. In a planar complex there will be two totally symmetric modes, one derived from the S mode of the SHM (having the transformational

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(16) Battiston, G. A.; Bor, G.; Dietler, U.K.; Kettle, S. F. A.; Rossetti, R.; Sbrignadello, G.; Stanghellini, P. L. *Inorg. Chem.* **1980**, *19*, 1961.

(17) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(18) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(19) Bau, R.; Fontal, B.; Kaesz, A. D.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 6374.

(20) Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 445.

(21) We define the molecular axes as X, Y, and Z and the local axes of a CO group as x, y, and z.

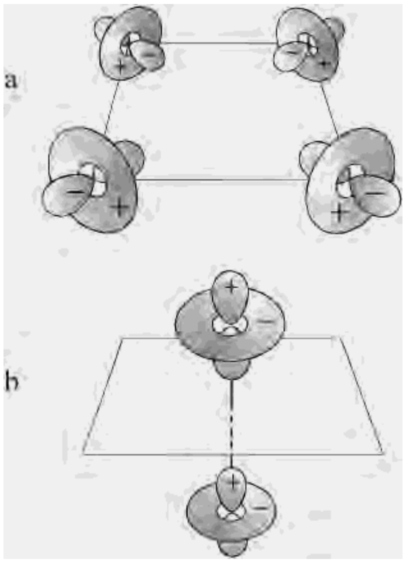

Figure 3. (a) The sum of CO derived-polarizability tensors of four coplanar CO groups is such that there is an approximate in-plane cancellation. (b) In contrast, for a pair of collinear CO groups the derived-polarizability tensors sum constructively in all directions.

properties of the function $X^2 + Y^2 + Z^2$) and one from one of the D modes (that having the transformational properties of the function $2Z^2 - X^2 - Y^2$). With increasing anisotropy there will be a separation of (X,Y) and Z contributions so that the two totally symmetric functions, in the limit, will assume the transformational properties of the functions ($X^2 + Y^2$) and Z^2. To better understand the effect this change will have on the relative intensities and relative frequencies of the two bands, we consider an octahedral metal carbonyl, $M(CO)_6$. This system has cubic symmetry and has been studied in detail.[22] The fact that it is not a polynuclear metal carbonyl is irrelevant; the model for the relative intensities of the Raman bands depends solely on the relative orientations of the CO groups and not on their bonding within the molecule. The observation that the Raman active e_g ν(CO) modes have a higher intensity than the a_{1g} in $M(CO)_6$ species leads to the conclusion that the derived-polarizability changes associated with CO bond stretching have, approximately, equal but opposite amplitudes along and transverse to the CO bond axis (z). That is, they are of the approximate form $z^2 - x^2 - y^2$. Figure 3a shows four such coplanar contributions, as is appropriate for a square planar cluster with four in-plane CO groups.

Summation of the four contributions shows a mutual cancellation and means that the resultant derived-polarizability is zero in the X,Y plane. For the ($X^2 + Y^2$) function the only contribution to the Raman intensity comes from the Z derived polarizability. This conclusion is not confined to the present example but is general, provided that the contributing CO groups are all C_n symmetry-related in the X,Y plane. Now consider the other two CO groups of the $M(CO)_6$ molecule, those lying along the Z axis (and corresponding to the Z^2 function of a planar cluster). These are shown in Figure 3b. It is evident that summation of the two contributions leads to a mutual reinforcement in all of the X,Y- and Z-directed derived-polarizability components. Again, this is a general conclusion. This discussion enables a prediction of the Raman intensity changes consequent on increasing anisotropy in a planar cluster. As the function $X^2 + Y^2 + Z^2$ becomes $X^2 + Y^2$, so its Raman intensity will decrease (but not become zero); as, at the same time, the function $2Z^2 - X^2 - Y^2$ becomes Z^2, so its Raman intensity will increase. In the spherical system the function $2Z^2 - X^2 - Y^2$ must have the same Raman intensity as all of the other D components, but as it becomes Z^2, it will become the strongest of the D. The above argument enables us to conclude that *the Z^2 function will be associated with the strongest Raman band in the spectrum*. Further, if the relative frequencies of the two totally symmetric bands are considered, we expect that the mixing causes them to move together in frequency.[23]

In summary, as anisotropy increases, so the highest frequency band in the Raman (the S-derived) will lose intensity; the intensity will reappear in the strongest band in the spectrum which, itself, will become the highest frequency of the set of D-derived peaks. The S peak will, correspondingly, drop in frequency, but this may not be evident unless it drops below the P-derived infrared features.

It is recognized that for metal surfaces the presence of an image dipole not only determines selection rules and influences band intensities but also modifies band frequencies.[24] One must assume that the same is true for planar clusters, in which case one must recognize that both the image dipole and anisotropy can cause frequency shifts. However, studies of metal surfaces have found that the image dipole effect is of the order of 10 cm^{-1} so that in the present work it is probably safe to attribute significantly larger separations of P- and D-mode derived features largely to anisotropy. Application of the above considerations gives hope of some considerable insights into the ν(CO) spectra of planar cluster carbonyls. However, because of the paucity of spectral bands, a paucity which is at the heart of the problem we address, it is not possible to carry out any worthwhile normal coordinate analysis, as we have already noted.

(b) Interpretation of the Spectra. Complexes 1 and 2. It is convenient to start the discussion with perhaps the simplest of the planar cluster carbonyls, species **1** and **2**.

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(22) Kettle, S. F. A.; Paul, I.; Stamper, P. *J. Chem. Soc., Dalton Trans.* **1972**, 2413. Kettle, S. F. A.; Paul, I.; Stamper, P. *Inorg. Chim. Acta* **1973**, *7*, 11. Kettle, S. F. A.; Luknar, N. *J. Chem. Phys.* **1978**, *68*, 2264.

(23) In the same way, mixing of s- and p-orbitals to give two sp hybrids involves the resultant function energies coming together.

(24) Shigeishi, R. A.; King, D. A. *Surf. Sci.* **1976**, *58*, 379. Nichols, H.; Hexter, R. M. *J. Chem. Phys.* **1980**, *73*, 965.

(25) Battiston, G. A.; Sbrignadello, G.; Bor, G. *Inorg. Chem.* **1980**, *19*, 1973.

(26) It has long been recognized that a simple vector addition of derived bond dipole moment derivatives is not always adequate to describe the relative infrared band intensities in simple carbonyl species.[27] The discrepancies are exacerbated as the number of metal atoms in the molecule increases, and so it is not surprising that Bor et al. include in their paper a review of the problem.[25] They only found it possible to account for the relative infrared band intensities in $M_3(CO)_{12}$ by introducing that which they called "an induced dipole moment". This may immediately be identified as equivalent to the image dipole moment of the SHM.

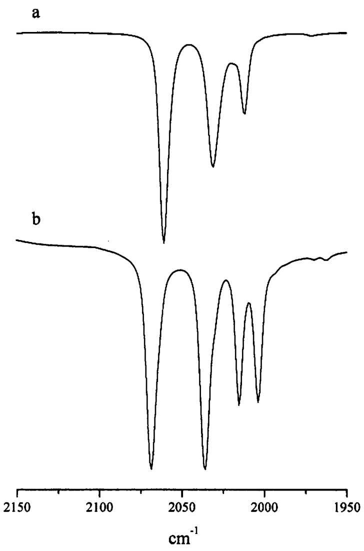

Figure 4. Infrared spectra (*n*-heptane) of complex **1** (a) and of complex **2** (b).

Not only have these been subjected to a detailed normal coordinate treatment[16] but the band intensities have been the subject of an equally thorough discussion.[25,26]

The solution infrared spectra of all four molecules in the $MM'_2(CO)_{12}$ (M and M′ = Ru, Os) series are well-known, but those of the homometallic species are given in Figure 4.

Working in D_{3h} symmetry[28] the highest frequency band is of E′ symmetry. This means that the vibration has *X*,*Y* degeneracy (although the axial vibrators make a major contribution). Next, there is a band, the intensity of which may approximate that of the E′, although sometimes weaker. This is the A_2'', with a dipole moment directed along the molecular 3-fold axis; it involves only the axial COs. Finally, at lowest frequency are two relatively weak E′ bands (only one has significant intensity in the Ru_3 complex). The Ru_3 species conforms rather well to the predictions above. The strongest infrared band is, indeed, the E′, and it is roughly twice the intensity of the A_2''. The weakest band, another E′, either steals intensity from the higher (the SHM model) or has some inherent intensity (the point group or THM model). In the Os_3 spectrum it seems that the two lower E′ bands steal intensity from the higher, so much so that they are themselves relatively strong and, correspondingly, the highest E′ little more intense than the A_2''. In neither spectrum is there any sign of any enhanced intensity in a band of E′ symmetry as a consequence of any induced dipole contribution. The (upper) $E'-A_2''$ splitting may therefore be taken as an indication of the magnitude of the asymmetry. The Raman spectra of these two species are given in Figure 5.

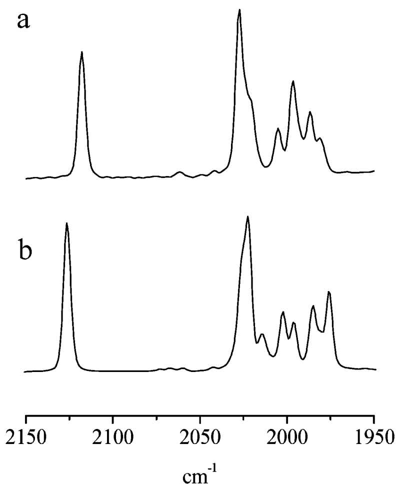

Figure 5. Raman spectra (crystals) of complex **1** (a) and of complex **2** (b).

They are of crystalline materials and so contain factor group effects; fortunately, these do not affect the main conclusions. As anticipated, the highest frequency peak and the strongest peak of the set at lower frequency are both totally symmetric. Further, the latter is the highest frequency of all the features which, in the SHM, are D in origin, an indication that mixing of the S- and D-derived totally symmetric modes is already occurring, a hypothesis confirmed by the extant normal coordinate analysis.[11] In summary, the SHM as applied to planar species provides a good broad-brush explanation of the ν(CO) spectra of $M_3(CO)_{12}$, M = Ru, Os, molecules although, of course, it cannot provide the same insights as a normal coordinate analysis. That it should be in agreement with such analyses in the present case becomes important for the many molecules for which such analyses are impossible and to which we now turn.

Complexes 3 and 4. Previous work, on relatively spherical clusters, has shown that when a hetero-metal atom bears a chemical resemblance to that carrying the CO ligands then there is little effect on the applicability of the SHM.[4,5] This statement probably indicates that when the valence band energies of the two different metals are comparable, they combine to give a common band structure. For planar species which contain hetero-metal atoms it is invariably the case that these hetero-metal atoms are, essentially, coplanar with the CO-carrying metal atoms. For these species, therefore, any such combined band structure will be in the plane of the metal atoms and thus such as to enable the creation of in-plane image dipoles. This leads us naturally to the two anions **3** and **4**, anions which, in particular, have similar Raman spectra (Figures 6 and 7 show both infrared and Raman).

They are spectra which show little asymmetry and find a ready interpretation as a high-energy S and split D, both Raman-allowed. The two totally symmetric Raman bands are the strongest in both spectra, just as for $M_3(CO)_{12}$, and that which is D-derived may well be the highest of the D set.

The interpretation of the infrared spectra leads to the conclusion that the P mode shows little splitting and is to be associated with the strong peak in **3** and the two proximate strong peaks in **4**. For the Au species it seems clear that the planar is at the higher frequency, as in the $M_3(CO)_{12}$. The

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(27) Kettle, S. F. A.; Paul, I. *Adv. Organomet. Chem.* **1972**, *10*, 199 and references therein.

(28) The Ru/Os distinction has no great effect on the appearance of the spectra of the mixed species,[16] a strong indication that the SHM should be relevant.

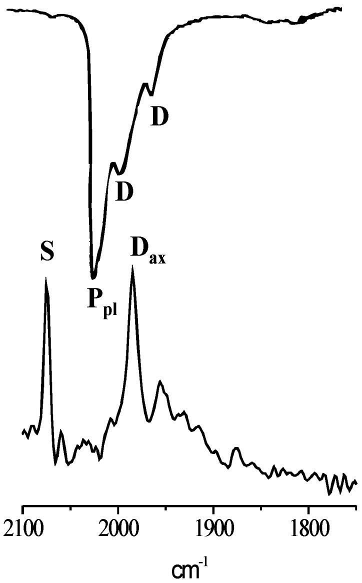

Figure 6. Infrared (upper, CH_2Cl_2) and Raman spectra (crystals) of complex **3**. In this and the following diagrams SHM assignments are given. The subscript "ax" indicates an out-of-plane mode while the subscript "pl" indicates an in-plane mode. Although the meaning is not quite the same as in the infrared, it is convenient to use these same labels for the Raman spectra.

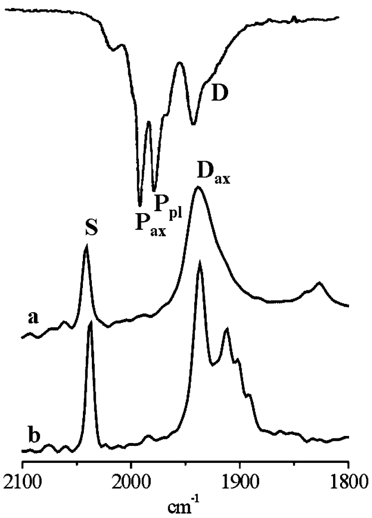

Figure 7. Infrared (upper, CH_3CN) and Raman spectra (a, CH_3CN; b, crystals) of complex **4**.

Pt is less clear, and we cannot unambiguously distinguish between the alternatives. However, a more consistent pattern for the entire set of compounds under study results when the lower-frequency mode is assigned as the planar. The lower-frequency peaks are seen because they gain intensity by a stealing mechanism, just as in $M_3(CO)_{12}$. In support of this assignment is the observation that all but one of the other species covered by the present work show such lower-frequency peaks.[29]

If the analysis is made with the molecular point group, and the THM to which it is closely related, the in-plane dipole moment changes which are tangential to the cluster plane would have to be included. These modes are derived from antisymmetric combinations of in-plane CO stretching vibrations at each Fe. We believe that it is these that are responsible for the reasonably strong band seen at ca. 1925 cm^{-1} in the spectrum of the Pt compound. That is, only a limited metallic band structure exists in this compound, and, indeed, in the Au compound. This conclusion is not surprising. It is these same antisymmetric modes which are responsible for the lower-frequency bands in the $M_3(CO)_{12}$ spectra, and it is difficult to believe that the structures of **3** and **4** are such as to lead to a significantly more extended band structure. However, a comparison of the discussions of **1** and **2** with that of **3** and **4** suggests that the relative frequencies of the two P-mode components (Z:X,Y) are very sensitive to the details of the cluster. For the molecules **1** and **2** the axial mode was the lower; for the anions **3** and **4** they were near-degenerate.

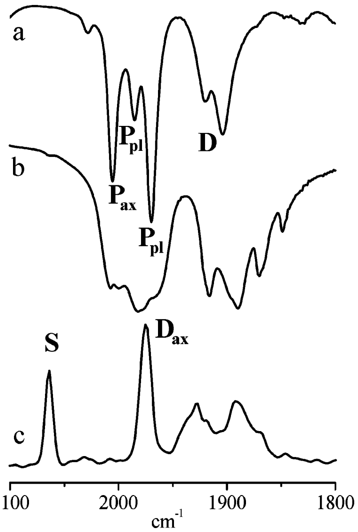

Figure 8. Infrared (a, acetone; b, KBr disk) and Raman (c, crystals) spectra of complex **5**.

Complex 5. The cluster **5** will surely have the most extended band structure of all of the species so far considered. Its infrared and Raman spectra are shown in Figure 8.

The two strong Raman bands entirely conform to the model presented above and will not be discussed further. The infrared spectrum presents a greater challenge. The strongest cluster of bands is, as expected, at the highest frequency. It is split into three. The number of bands is that expected using the SHM, recognizing that the molecular symmetry is D_{2h}. As there is no reason why the axial mode should be particularly weak in this case, one of the two strong peaks must be associated with this mode. Three pieces of evidence point us toward the higher frequency peak. First, we are struck by the profile similarity between the two lower pairs of bands. They seem to follow a pattern reasonable for two bands showing a loss of degeneracy as a consequence of the same asymmetry. Second, this assignment would mean that the (X,Y) pair are now located *below* the axial, for the first time in this series with confidence. We have already seen that the relative positions of these bands can vary considerably and this would be a continuation of that pattern.

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[29] An alternative interpretation, that the splitting on the strong infrared peak is attributed to splitting of the X,Y in-plane modes and the axial mode is assigned to a peak in near-coincidence with the lower-frequency strong Raman band, as for $M_3(CO)_{12}$, can immediately be excluded because the molecular symmetry of **3** and **4** is D_{4h}.

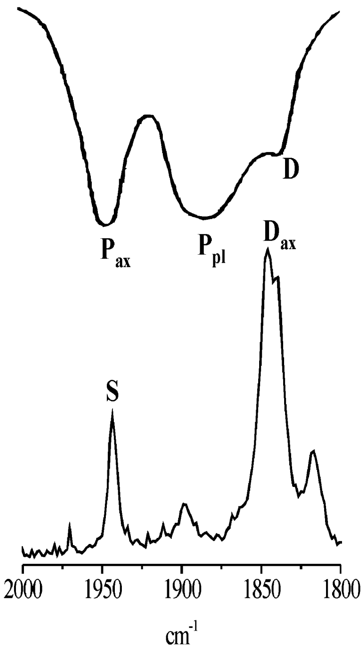

Figure 9. Infrared (upper, CH_3CN) and Raman spectra (crystals) of complex **6**.

Finally, this position is just that which we will find, rather unambiguously, for the next two species that we consider.

Complex 6. The anion **6** is, by far, the largest planar cluster that we have so far considered. The spectra (Figure 9) are the simplest so far encountered.

Spectral simplicity in the face of molecular complexity is the characteristic which led to the introduction of the SHM for spherical clusters. Many pieces of evidence in the spectra of **6** suggest that the corresponding situation holds for this planar cluster. First, in the infrared, this is the first species for which, unambiguously, a clear distinction can be made on intensity grounds between the axial (higher frequency) and planar components of the P mode of the SHM. The advent of in-plane metal-like behavior is, it will be recalled, expected to be made manifest by an enhanced intensity in the in-plane components. Second, in the Raman spectrum, this is the first species for which the axial totally symmetric mode gains considerable intensity at the expense of the highest frequency totally symmetric. Finally, the S peak is almost coincident with the P_{ax}, a situation which, it will be recalled, can occur as a consequence of S−D totally symmetric mixing. Both infrared and Raman spectra, then, are in conformity with the assertion that the spectra of this species show the presence of the effects of an image dipole in a metallic plane. Other minor peaks in both spectra are readily accounted for by the discussion above (albeit, as expected, with but a minor contribution from the THM) with one exception. This is a weak Raman peak at ca. 1900 cm^{-1}. We believe that this is a factor group component of the (*X*, *Y*) pair, gaining a small amount of Raman activity in the solid state.

Complex 7. The last species for which we have both infrared and Raman data is **7**, for which the infrared and Raman spectra are given in Figure 10.

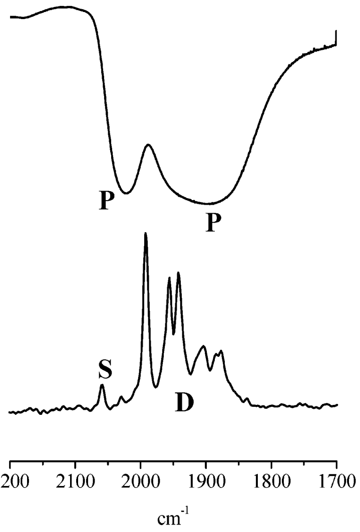

Figure 10. Infrared (upper, KBr disk) and Raman spectra (crystals) of complex **7**.

It is an eight metal atom species with a structure which is more extended than that of the nine metal atom **6**. Intuitively, one would expect a less developed band structure and so less evidence of image dipole effects. However, the important consideration here is the relative electronic compatibility of Ag (**6**) and Cd (**7**) with $Fe(CO)_4$. It seems that Cd is the superior. The infrared spectrum of the compound shows a clear P-mode splitting into axial and, much more intense, in-plane components. There is no hint of any THM contribution. The Raman follows the same pattern. The highest frequency peak is now very weak and, correspondingly, the (highest) D-mode component the strongest in the spectrum. Even so, its intensity seems to have been diminished by transfer to some of the lower-frequency D-mode components. While this transfer is forbidden in the D_{4h} molecule, the Raman is of the solid. Further, **7** is a neutral molecule so that the CO groups of one molecule will be in intimate contact with those of others in the crystal. Large factor group effects are entirely reasonable and with them both intra- and intermolecular intensity transfer. There is another aspect of the spectra of Figure 10 which we think may well be of significance. This is that the two highest frequency axial modes, one infrared and one Raman, are in the same frequency region, toward the higher frequency end of the spectral range. Correspondingly, the in-plane frequencies are clustered together some 100 cm^{-1} lower. A similarity between the frequencies of the axial modes was noted in $M_3(CO)_{12}$, where it was accidental, and in **5**, where it probably is accidental too. Here we believe that it is not. It is entirely reasonable that increasing anisotropy, coupled with increasing induced dipole effects, should lead to a separation of planar and axial modes. One aspect of this is the weakness of the highest frequency totally symmetric mode. However, unlike complex **6**, its frequency is not close to that of the highest infrared band. This is unlikely to result from solid state shifts; more probably it is a consequence of the separation of the axial and planar modes. The highest frequency D mode moves, relatively, to higher frequency, pushing the S mode to higher frequency ahead of it.

Complexes 8−10. The above discussion enables us to use just the infrared data to assess the importance of the in-plane anisotropy. It is helpful at this point to bring together the splitting on the two major infrared bands in the above spectra (that is $\nu_{ax} - \nu_{eq}$). These are: (**1**) −30 cm^{-1}; (**2**) −32 cm^{-1}; (**3**) ca. 0 cm^{-1}; (**4**) 15 cm^{-1}; (**5**) 35 cm^{-1}; (**6**) 70 cm^{-1}; (**7**) 125 cm^{-1}, where the signs reflect our assignments. For **8** the splitting of the infrared peaks is some 64 cm^{-1}, indicating a similarity to **6** although, structurally, of course, the resemblance is with **7**. That is, a similarity of chemical composition leads to a similarity of band structure and so of vibrational behavior. Complex **9**, where the splitting is 100 cm^{-1}, and complex **10**, where the splitting is 125 cm^{-1}, suggest a better electronic compatibility toward Fe or Cu with respect to Ag. For all of these examples the lower-frequency infrared peak is unambiguously that of greatest intensity. It is not always easy to assess relative intensities, particularly when (**9** and **10**) the spectra are of the solids and some putative factor group effects seem present. Even so, it is noteworthy that the species showing the greatest infrared splitting (**7**, **9**, **10**) are also the ones showing the greatest apparent low-frequency band intensity, since this is just what we would expect.

It is worthy of comment that these last four species (**7**−**10**) are those that, of all discussed in the present work, show the most extensive arrays of close-packed metal atoms in the metallic plane: again, just the pattern that the discussion in this paper would lead us to anticipate. We note that the conclusion that there exists a band structure common to the different metal atoms in these clusters is in accord with the conclusions of theoretical work.[30]

Conclusions

The subject area covered in the present work is made difficult by the frequent need to use literature data which were not optimal (data on solids when solution would have been preferred, for instance). Fortunately, the consequent adaptions are both small and reasonable and we are confident that the work described in this paper potentially provides significant insights into the ν(CO) vibrational spectra of planar transition metal clusters. In particular, where the spectral data were available, the model we introduced for the frequency and intensity patterns in the Raman proved a cornerstone of the work, so much so that the fact that it was applicable was usually only briefly commented on, attention being directed to other aspects of the spectra.

As expected from our studies of more spherical clusters, the larger the cluster the more applicable the SHM. For the smallest planar clusters either the point group approach or a mixed SHM/THM model may be used. It is interesting that the latter pair give insights into intensity patterns not revealed by the point group analysis. As the size/metallic nature of a planar cluster increases, so characteristic intensity patterns develop both in the infrared and Raman. In addition, it seems that new band frequency patterns also develop. First, for planar clusters it seems that there is a planar/axial anisotropy which increases with the size of the cluster. Second, it appears that the presence of the metallic layer can reduce the magnitude of the vibrational coupling between ligands on either side of this plane, evidenced by the approach in frequency of the axial modes in Figure 10.

We believe that, with the addition of the present work, a general understanding of the ν(CO) vibrational spectra of transition metal carbonyl clusters, which for long were a mystery, is now in place. Even so, the outcome is surprising. For simple metal carbonyls, attention is focused on the CO groups, their number, and their overall symmetry. The metal atoms are treated as simply supporting the CO groups; although ν(CO) force constants vary slightly with metal, this variation has scarcely merited attention. In contrast, for metal clusters, it is the metal atoms which are important. The number and overall symmetry of the CO groups are of no concern. For small metal clusters, some of which have been discussed above (and for others which we have reviewed elsewhere) and which stand between the two limits, both CO and metal influences are apparent. What is the origin of the difference? The present work enables us to begin to see a simple explanation. Within an isolated spherical metal atom a dipole can only be induced by an electronic transition to an excited dipolar state. An applied dipolar electric field can mix this excited state into the ground state, but the mixing is small. A vibrational transition dipole within a CO group will have little influence on the metal to which it is attached. In a cluster the situation is different. The possibility exists of dipoles of the type $M^{\delta+} - M^{\delta-}$ within the cluster, enabled by the band structure of the cluster. This, surely, is the origin of the “induced dipole” of the SHM and is the feature which causes the metallic core to dominate the spectral behavior. Such arguments add additional importance to the present work. Because only the first type of induced dipole can operate along the Z axis but the second in the X,Y plane, the ability of the SHM to explain the spectra of planar species provides a crucial test of the method itself. As we have seen, the method seems to perform well against this criterion. The next question is “why carbonyls?”. In that the ligands play a negligible determining role in the SHM, should not the method be more generally applicable? In practice, of course, it is the fact that so many more carbonyl clusters are available than clusters of any other simple ligand which led us to their study (along with the fact that these ligands have a very simple vibrational signature). Even so, the carbonyl clusters are not ideal. As we have commented, we have sometimes had to make use of literature data which were obtained more for characterization than for spectroscopic reasons. Only limited Raman data could be obtained or are available. Nonetheless, without accepting these limitations, the present study would not have been possible. Even so, real progress has been made and, in particular, nothing has emerged which might lead us to believe that the SHM is only applicable to carbonyl clusters. Indeed, we have studies in progress which suggest that it is much more general. In establishing the validity of the method, the present work is therefore of particular importance and, as we noted earlier, may well

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(30) Albert, K.; Neyman, K. M.; Pacchioni, G.; Rösch, N. *Inorg. Chem.* **1996**, *35*, 7370.

facilitate progress in understanding in some apparently remote subject areas. So, we have recently initiated a series of Gaussian ab initio studies aimed at the calculation of the vibrational spectra of cluster species; preliminary results on the Ru_3 species are in excellent accord with the present analysis.

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