Why Are the Terminal ν(CO) Infrared Spectra of Metal Cluster Carbonyls So Often So Simple?

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Abstract: Two spherical tensor harmonic models for the spectral intensities of infrared and Raman bands of large, and particularly spherical, molecules are presented and applied to the terminal ν(CO) modes of homonuclear metal carbonyl clusters. The first is applicable when it appears that the coupling between CO groups on different metals effectively competes with that on one metal. It predicts that the closer the arrangement of carbonyl groups approaches spherical, the closer will the spectral pattern be to a single infrared band and two Raman bands, one on either side of the infrared band. When it appears that coupling between CO groups on one metal dominates that between CO groups on different metals, a different intensity pattern is expected, although simplifications compared to the results of a point-group analysis are again predicted.

Introduction

The formalism to be adopted toward the analysis of the vibrational characteristics of molecules is both well-known and well-developed.[1] However, it has an unfortunate property: it is particularly appropriate to small molecules (so that, for instance, vibrators are sufficiently proximate that the presence of a center of symmetry has a profound effect not only on the predictions but also on the observed spectra). As molecules become larger, the predictions are almost invariably much richer than the observed spectra. The reason is clear: some couplings become so weak that predicted separations are less than the experimental resolution. There is no evidently reliable extension of classical vibrational analysis evident to us that addresses this dilemma. A new approach is needed. In the present paper we present a novel approach to the analysis of the vibrational spectra of large, and particularly pseudospherical, molecules. For some considerable time we have had a particular interest in the vibrational spectra of transition metal cluster carbonyls[2] and these will be our particular concern in the present paper. However, it seems that the methodology is of wider applicability—fullerenes and boranes are just two evident potential extensions. The approach is one common in the physical sciences, particularly when symmetric, or near-symmetric species are involved—a spherical harmonic expansion.

In recent work we have found that the terminal ν(CO) infrared spectra of a variety of transition metal cluster carbonyl species were relatively invariant with respect to the number of CO groups and to the molecular geometry.[3] The terminal ν(CO) infrared spectra of the species in solution could all be regarded as derived from a basic pattern consisting of a single strong peak. This invariably had a weak high-frequency feature, associated with the nodeless totally symmetric vibrational mode. The low-frequency side of the strong peak showed more structure, structure which varied from unresolved shoulders through to well-resolved low frequency features. The closer a peak is to the strong peak, the greater is its intensity. The overall picture was very much that of a single allowed mode, which might exhibit splitting, but, perhaps more important, from which other features gained intensity by a stealing mechanism. A detailed survey of the literature, which we shall present elsewhere, shows that this pattern is typical of the entire field. The present paper offers an explanation of these observations, although it must be accepted at the start that some of the conclusions reached are counterintuitive, in that no extension of the discussions in the literature lead to them. On the other hand, the two spherical-harmonic based models which we present are simple, something that is surely an attractive feature.

Discussion

In the present paper we throughout make the assumption that the species under consideration are isolated. That is, solution spectra are the subject of discussion. For Raman, in particular, such spectra are not always readily available and care may be needed. When carbonyl cluster molecules are effectively separated from each other by large counterions, our models should be appropriate. In the absence of this simplification, the possible existence of a factor group and/or more specific local intermolecular coupling should not be overlooked; suitable modifications are readily made.[4]

The Spherical Harmonic Model. The discussion of the bonding in metal cluster compounds poses many problems. In this situation, it is natural that a wide variety of approximate approaches be explored—particularly when there are well-known and effective models that apply. The 18-electron rule and Wade's rules are two obvious examples of the latter. Of the other simple methods there is one that is of particular concern to the present work. This is Stone's tensor harmonic approach[5]

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(or the Hoffmann and Gouterman model for boron hydrides[6] —the two are effectively the same when discussion is confined to radially-directed orbitals). The communality of the Stone and the Hoffmann−Gouterman models is reflected in the first of the two that we shall develop, that appropriate to the case in which the vibrational coupling between CO groups on different metal atoms appears to be more important than that between CO groups on one metal atom. This particular model seems to be the more generally applicable of the two, despite the fact that it is by no means evident that it should be so from the literature on the analysis of the v(CO) vibrational spectra of the simplest of clusters, dimeric species.

The Interunit Coupling Dominant Model. In the Stone, Hoffmann, and Gouterman model the bonding between identical atoms distributed over the surface of a sphere involves a nodeless combination (S), followed in energy by a triply degenerate set of one-node functions[7] (P), then a 5-fold degenerate set (D), then a 7-fold degenerate set (F), and so on. In any particular molecule, the orbital degeneracies implicit in this spherical model are split by the potential field of the nuclei. This general approach is not surprising. It is well-known that in high-symmetry arrangements it almost invariably proves advantageous to carry out a spherical harmonic expansion of the problem under consideration; commonly only a few terms of the expansion are non-zero. Descent in symmetry to the real structure then leads to useful predictions. In theoretical inorganic chemistry this approach is perhaps best known as a fundamental part of the crystal field theory.[8] Its extension is key to Stone's tensor harmonic model of the bonding in cluster compounds[5,9] and will be that followed in the present paper but applied to the problem of the vibrational spectroscopy of cluster carbonyls. Our basis set in the first model is therefore taken as the complete set of terminal v(CO) vectors attached to the cluster metal atoms, directed radially outward. In a spherical or pseudospherical arrangement the v(CO) modes will follow the pattern outlined above, with the energy pattern inverted because of the sign of the v(CO)−v(CO) interaction constant. The nodeless totally symmetric S mode is therefore expected at the highest energy. Next in energy will be the three degenerate one-node P vibrations, then the 5-fold degenerate two-node D, then the 7-fold degenerate three node F, and so on (higher nodalities need only be invoked for cases with more than 16 CO groups). Of these, the S and D will be Raman allowed (note that the S are not necessarily the most intense) and the P infrared allowed, the P having a frequency intermediate between those of the S and D. As far as the infrared is concerned, the prediction is clear: for pseudospherical species one strong peak is to be expected in the solution infrared. This, of course, is close to the general observation reported at the beginning of this paper and is what prompted the present line of analysis.

Although some of the species in the work which led to the present study contained two chemically different metal atoms, implicit in the present model is the assumption that all v(CO) force constants are identical. We shall therefore exemplify the applicability of the present model by considering only species containing a single type of metal atom although; in fact, the model seems applicable to many species containing more than
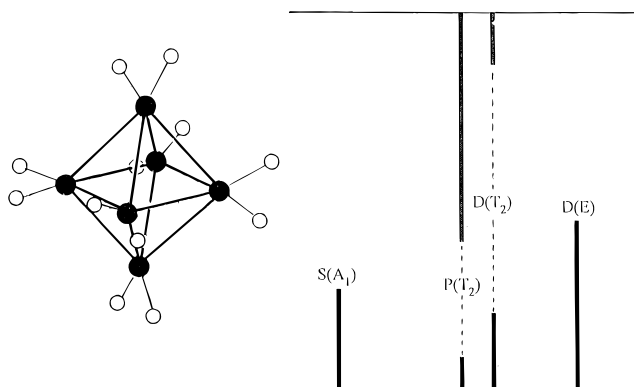
Figure 1. Sketch of the structure of $M_6(CO)_{12}(\mu_4CO)_4$ complexes (bridging CO's are omitted for clarity) and predicted patterns of the infrared and Raman spectra.

one chemically different metal atom. We shall normally ignore the very weak peak that commonly occurs at the highest frequency in the infrared spectra.

$Rh_6(CO)_{16}$ both approximates to spherical symmetry and demonstrates the essentials of our first model. It has 12 terminal CO groups in T_d symmetry. In the spherical harmonic model the vibrations of these groups span S + P + D + F(3), or adding the appropriate T_d symbols $S(A_1)$ + $P(T_2)$ + $D(E + T_2)$ + $F(T_1)$. Of these, only $P(T_2)$ is inherently dipolar, although the symmetry-allowed mixing with the other, D-originating, T_2 mode will transfer some intensity to the latter. We expect that the higher frequency T_2 mode will be the more intense of the two infrared active modes. The reported solution spectrum has an intense peak at high frequency and a much weaker one at lower frequency,[3,10] as predicted by the model. The structure (without bridging carbonyls) and infrared and Raman spectra are detailed in Figure 1. We note that the presence of the bridging carbonyl groups does not seem in any way to weaken the applicability of the model. The spectrum of the isostructural, red, isomer of $Ir_6(CO)_{16}$ is also very similar to that of $Rh_6(CO)_{16}$, notwithstanding the fact that it was recorded in the solid state;[11] that of the black isomer, of S_4 symmetry, shows marginally more low-frequency structure. Again, this spectrum was recorded in the solid state and the crystal structure is such that additional, factor group, splittings are expected to be manifest in the infrared spectrum[11] so the overall agreement with our model must be regarded as excellent. Although it has fewer metal atoms than any of the above examples, $Ir_4(CO)_{12}$ also has T_d symmetry and the v(CO) vibrations span the same irreducible representations: $S(A_1)$ + $P(T_2)$ + $D(E + T_2)$ + $F(T_1)$. It too has an infrared spectrum characterized by a strong high-frequency peak and a much weaker one at longer wavelength.[12] For these species, the Raman predictions are the reverse of the infrared: $T_2(D)$ strong and $T_2(P)$ weak, along with an $A_1(S)$ at highest frequency. The lowest frequency modes, originating in $T_1(F)$, will be silent. The Raman spectra of all of these species are available, although only recorded on crystalline materials. Those of $Ir_6(CO)_{16}$ and $Rh_6(CO)_{16}$, although noisy, clearly are in accord with predictions of the present model.[3] Similarly, that of $Ir_4(CO)_{12}$ has been reported but is complicated by solid state effects.[13] Even so, it is clear that the predictions of the present work are essentially obeyed, and it is clear that the spherical harmonic model can provide insights into the relative band

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(6) Hoffmann, R.; Gouterman, M. *J. Chem. Phys.* **1962**, *36*, 2189.

(7) This statement refers to the nodes inherent in the combination and says nothing about the inherent nodal characteristics of the orbital involved on a particular atom.

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intensities in the terminal ν(CO) infrared spectra, and also the Raman where available, of metal carbonyl clusters. The fact that the first spherical harmonic model works so well, together with the absence of the spectroscopic signatures that normally characterize $M(CO)_n$ units, may be interpreted in terms of an effective competition between intra- and interunit coupling. The former may be the weaker, but there are more contributions to be included.

The Intraunit Coupling Dominant Model. The model just presented is that appropriate to the case where the molecule behaves as if there is exclusively interunit coupling (where a unit is a group such as $M(CO)_3$, from which the cluster may be regarded as "built up"). In it, the members of the basis set contain no nodal planes perpendicular to the surface of the enveloping sphere, even when such planes appear "natural" for, say, each $M(CO)_3$ group. The other limiting case is that in which spectral interpretation is based on the assumption of dominant intraunit coupling (but with enough interunit coupling to make its inclusion necessary). In this model it is appropriate first to couple the individual vibrators at any one center together, so that for the transition metal carbonyl clusters, for each $M(CO)_n$ unit n orthogonal vibrational functions arise, most probably with some symmetry-enforced degeneracies. These functions can be classified by the number of nodal planes that they contain perpendicular to the surface of the cluster sphere (it is these nodes that ensure their mutual orthogonality). A clear distinction between this and our first model is at once evident. The present model is based on the existence of such nodal planes (and these nodal planes pass through the metal atoms, as is evident from the way that they were derived). There will be one function with 0 nodes, the totally symmetric combination. There will be two with 1 node, two with 2 nodes (all passing through the particular metal atom and perpendicular to the surface of the cluster), and so on until the complete set of local $M(CO)_n$ functions is exhausted (in practice, the total number of functions will seldom be greater than 3). The function with 0 nodes will be associated with a dipolar vector directed essentially radially from the center of the cluster. It follows that the argument developed for our first, no node basis set, model is applicable to the complete set of functions; they give rise to the spherical harmonics S + P + ... as appropriate. As before, of these only the P will be infrared active (and S and D Raman active). For the set of noded one-center functions, where the nodes all pass through the local metal atom and are perpendicular to the surface of the cluster, this model has to be extended. The extension is that given by Stone[5,9] in his seminal work on the bonding in cluster compounds. We shall confine our discussion to the one-center 1 node functions. Stone has shown that in spherical symmetry these transform as two, related, sets. Considering the $M(CO)_3$ case, the two 1 node functions (those that transform together as E in the local C_{3v} symmetry) are related to each other by a 90° rotation about the center-of-cluster to the M axis. It is convenient to proceed by a detailed study of a familiar example that covers almost all of the situations which arise in practice (the extension to examples with more than 18 terminal CO groups presents no problems; the data in Stone's papers are immediately applicable). In an octahedral M_6 system, $M_6(CO)_{18}$ for instance, the six pairs of 1 node functions, together, transform as $T_{1g} + T_{1u} + T_{2g} + T_{2u}$. Here, the 90° rotation relationship reappears in that this rotation interconverts members of the T_{1g} and T_{1u} sets; the T_{2g} and T_{2u} sets are similarly interconverted. The vibrational modes fall into two sets, each with a pair of triply degenerate modes. As

in the bonding case,[5] in the vibrational case, if one member of a pair is at low energy, the other is at a corresponding high energy (to aid reference to the original work, these are the V_{1m}, $\bar{V}_{1m}$ and (three members of) the V_{2m}, $\bar{V}_{2m}$ sets of Stone's papers[5,9]). For an octahedral species, taking in-phase combinations of adjacent vibrators to be at the higher energy (and σ-type coupling to be stronger than π), the sequence is:

$$T_{2g} > T_{1u} > T_{1g} > T_{2u}$$

It is illuminating to add to this the sequence arising from the 0 node combinations. This is:

$$A_{1g} > T_{1u} > E_g$$

The vibrational levels arising from the 0 and the 1 node combinations will have a zeroth-order energy level separation which is that between the A_1 and E of the local $M(CO)_3$ modes. So, the resulting pattern is:

$$A_{1g} > T_{1u} > E_g$$
$$T_{2g} > T_{1u} > T_{1g} > T_{2u}$$

where the two sets have been deliberately staggered to indicate that their relative positions is not firmly established. The prediction is of two sets of T_{1u} modes in which that at the lower energy is associated with a band in the infrared which is approximately twice as intense as that at higher energy (this being the approximate situation for the A_1 and E modes in C_{3v}—the model as developed above has no place for intensity transfer). A rare example to which the intraunit dominant model seems approximately applicable is that of $Os_4O_4(CO)_{12}$. This species has T_d symmetry and 12 terminal CO groups so that the spectral predictions for the strong intergroup coupling model is that given earlier for other molecules of T_d symmetry. For the present, strong intraunit coupling model the predictions are for a C_{3v} basic A_1 + E splitting and for these to follow the discussion of this paragraph with T_d substituting for O_h. The local A_1 modes are therefore expected to follow a $A_1(S)$ + $T_2(P)$ pattern (D and F harmonics are not spanned). The local E are expected to follow a $T_2 > E > T_1$ energy pattern (this has been discussed by Stone;[9] the T_1 and T_2 are interconverted by the 90° rotation; the E are rotated onto themselves, and this fact serves to establish that they are sandwiched between the other two). The reported data are in good accord with these predictions.[14] In particular, the lower frequency infrared peak is about twice the intensity of the higher peak and is almost coincident with the more intense and higher frequency of a pair of proximate Raman features (here, solution infrared and solid state Raman are being compared).

An example which serves to some extent to link the two models of this paper is provided by the $[\{Co(CO)_4\}_4Bi]^-$ anion. In this T_d species, three COs at each Co lie essentially on the surface of a common sphere and are related to each other by the local C_3; at each Co one CO group is radially directed. The most obvious approach is to treat the two sets separately. We follow this line of reasoning to see what conclusions result and how they are related to the observations. The radially-directed COs are simplest and lead to a prediction of $A_1(S)$ + $T_2(P)$. The other three are most simply treated as (local C_{3v}) A_1 + E. Of these, the A_1 is again radially directed (although orthogonal to the first discussed) and again gives rise to $A_1(S)$ + $T_2(P)$. The E set are perfectly orientated to invoke the use of the tensor set formalism; as discussed above, T_2 + E + T_1 are generated.

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The prediction, therefore, is for three infrared active modes—and this is precisely what is found.[15] The same prediction arises from a normal group theoretical treatment, showing that the present approach is not necessarily at variance with this. However, one point at which the present model has an advantage is in that it would lead one to expect that one infrared band (that arising from the second set of radially-directed vectors) will be weak (because of its required orthogonality to that coming from the, clearly, highly dipolar first set). Indeed, one band is reported as being weak. Clearly, the present model enables a simple general discussion of the spectra of this particular species, a molecule that would otherwise be beyond any present theoretical approach.

Conclusions

The present work offers, for the first time, an explanation of the unexpected simplicity of the terminal ν(CO) spectra of many cluster species. In the limit, it does so by invoking a model in which, effectively, no account is taken of the metal atoms to which the CO groups are bonded. This model of "CO groups on the surface of a sphere" should be equally applicable to CO groups on the surface of small metal particles and so may well provide an interface between vibrational spectroscopic studies on them and parallel studies on clusters. A fascinating possibility is that it may prove possible to effect a union between the present, symmetry based, spherical harmonic model and a recent, also symmetry based, restatement[16] of the surface selection rule (appropriate to metal surfaces). When the assumption of effective spherical symmetry no longer holds, the spherical harmonic model ceases to be applicable and, in the limit, the molecular point group predictions become appropriate. There is an alternative situation covered by the model and this is that in which there is an effective spherical symmetry but the coupling between CO units bonded to individual metal atoms dominates. For such cases, it is not the molecular symmetry that is of importance but, rather, the local symmetry at the metal atoms (at its present stage of development the model assumes that these are all identical). For such cases it is necessary to recognize the full tensorial aspects of the spherical harmonic model. One way or another (and it is usually one way) the spherical harmonic model presented in this paper seems applicable to the vast majority of transition metal carbonyl cluster species. However, it must be recognized that the general thrust of the present work is very different from that indicated by attempts to extend studies of simple carbonyls into the cluster area. Such attempts are largely frequency based. That is, force constant data are used to predict frequencies. Intensities are afforded a much lower priority and so it is rarely clear whether the predicted band intensities (and these are almost unknown for the Raman) are in such good accord with the data as a set of frequencies and a force field subject to a self-consistent iterative convergence. Could such apparent agreement be misleading? This is a key question posed by the present work in which, rather, band intensity patterns and band position patterns have been used as the method of analysis rather than the precise numbers of a force field analysis. What is abundantly clear is that the present method offers the prospect of real progress in the understanding of the ν(CO) features of transition metal cluster carbonyls far too complicated for there to be any hope of a normal coordinate analysis treatment. One very likely answer to the problem posed above is found in the suggestion that the coupling between CO vibrators, be they molecular or cluster, is through-space rather than through-bond. There are several indicators that this is the case; two very convincing pieces of evidence are the following. The first is the coupling between the CO groups of different carbonyl-containing molecules in a crystal which gives rise to the phenomenon of factor group splitting and which is surely through-space. The second piece of evidence concerns mononuclear carbonyls for which a full vibrational analysis has been carried out. In these it is found that the coupling between two cis CO groups is always greater than that between the two M–C vibrators to which they are attached and through which, on a through-bond model, the coupling between them is mediated, although, in the hexacarbonyls, for the trans couplings this pattern is reversed. For the cis case, the inequality is in the wrong direction, through-bond couplings are expected to become smaller with an increase in the number of intervening bonds, not larger; each additional intervening bond exerts a damping influence. In that the trans M–C,M–C interaction constant is greater than the cis, the through-bond model would lead one to expect that the trans C–O,C–O interaction constant should be much greater than the cis. In fact, it is much smaller. If, then, the conventional vibrational analysis associates with an intramolecular feature (an interaction constant) that is in some measure, if not entirely, through-space, it is only to be expected that the limitations of a conventional vibrational analysis will become evident as the volume, the space, which it attempts to treat becomes sufficiently great. It will no longer be reasonable to project onto an intramolecular coupling constant that which is, at least in some measure, an extramolecular effect. The coupling between two CO groups in a cluster, which may be spatially proximate but well-separated chemically, is a case in point. When this coupling, which clearly may be large, is represented as a coupling through bonds it may involve so many bonds that the intramolecular model becomes ridiculous. We believe that the approach and models presented in this paper provide a more acceptable alternative.

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