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Application of the Spherical Harmonic Model to the Study of the Terminal ν(CO) Spectra of Transition Metal Carbonyl Clusters

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The application of the spherical harmonic model to the interpretation of the terminal ν(CO) spectra of transition metal carbonyl clusters is explored. Unless there is strong spectral evidence to the contrary (when the tensor harmonic model is applicable), the coupling between CO vibrators at each metal atom is to be ignored when these vibrators are symmetry-related. The overwhelming majority of carbonyl clusters conform to the spherical harmonic model, either in its simplest form—in which only a single infrared band is observed in the solution infrared spectrum—or in its more elaborate form. In the latter, bands of lower intensity are observed on the low-frequency side of the intense band. The greater the separation from the intense band, the weaker the additional band, indicating an intensity stealing mechanism. The observations have been interpreted in terms of a "cluster selection rule" analogous to the "surface selection rule" of metal surface spectroscopy and the implications of this rule are discussed.

Introduction

Although they have long been the subject of detailed study there are unresolved problems in the field of the vibrational spectra of simple transition metal carbonyls. One example, which to our knowledge has nowhere been generally discussed, is that posed by the study of these carbonyls in the crystalline state. Such studies show that vibrational coupling occurs between CO vibrators in different molecules (factor group splittings are commonly observed).[1] It follows, then, that there is a through-space mechanism by which carbonyl vibrators may couple. There is no evident reason such mechanisms can only occur between different molecules and we must conclude that they may contribute to the intramolecular vibrational couplings observed in simple carbonyl species. If this is so, attempts to place a purely intramolecular interpretation on quantities such as the interaction constants of a vibrational analysis must be of uncertain validity. This highlights a second problem; that of the relative magnitudes of interaction constants. To our knowledge, there is no example in the literature of the ab initio calculation of force and interaction constants in which the absolute magnitudes of bond−bond interaction constants fail to diminish with increase in separation between the coupled bonds.[2] This pattern, of course, is that expected; separation increases damping. However, it is not that always found for those simple transition metal carbonyls for which a complete vibrational analysis has been performed.[3] Both of the above points, which may well be related, indicate that there are hidden complexities in the interpretation of the normal coordinate analyses that are available in the literature of simple transition metal carbonyls.

The above comments also have considerable implications for a normal coordinate analysis of the C═O modes of transition metal cluster carbonyls. On one hand, the complexity of these species is such that a considerable number of different force and interaction constants is needed for a complete analysis. On the other hand, the arguments just presented indicate that the most obvious solution—that of setting the majority of the interaction constants equal to zero—is surely invalid. In cluster carbonyls, the intramolecular separations between CO vibrators may well be comparable to those between the intermolecular CO groups for which through-space coupling is observed in simple species. In that the factor groups splittings observed in such simple species are commonly of the order of 10 cm^{-1}, one is faced with a potentially extremely difficult problem for transition metal carbonyl clusters. Both intramolecular and through-space vibrational couplings of significant magnitude are to be expected, and so complicated vibrational spectra should result. If it were possible to analyze these spectra using a normal coordinate approach, the resulting interaction constants would have little physical meaning, being the resultant of two distinct

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[1] An extreme example is provided by the observation that the E_g ν(CO) modes of mixed crystals of $M(CO)_6$, M = Cr, Mo, W, are indistinguishable from the modes of the pure components except that the observed frequencies are a function of the composition of the crystal (Kariuki, D. N.; Kettle, S. F. A. *Inorg. Chem.* **1978**, *17*, 141). For this particular example the lowest multipolar coupling is quadrupolar−quadrupolar; the corresponding dipolar−dipolar coupling must be expected to be stronger (but is not directly observable because of the broad bands found in the infrared of the crystals).

[2] See, for example: *Spectrochim. Acta A* **1997**, *53*, 1039−1364 (Special Issue devoted to ab initio calculation of force fields).

[3] Of particular note are the octahedral hexacarbonyls, for which the spectral data available (which includes data from isotopomers) are more than adequate to enable a complete and unambiguous normal coordinate analysis (Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349). Here, it is invariably found that the absolute magnitude of the cis coupling between two C═O vibrators is greater than that between the two C−M in the intervening C−M-C unit, although the expected attenuation with separation would lead to the opposite inequality. A through-space contribution to the cis coupling of the two C═O vibrators is indicated. It may well occur for the *trans* coupling too. In any case, it is to be noted that the coupling between cis C═O's (largely through empty space) is greater than that between trans (where there is a high intervening electron density, the effect of which is metal dependent).

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Table 1. List of Representative Clusters with Only M−CO Units

cluster	no. of units	no. of μ_n(CO)		ideal sym-metry	no. of IR peaks		ref
		μ_2	μ_3		pred	obs[a]	
$[Rh_4(CO)_{11}]^{2-}$	4	7		C_s	4	vs*	6
$[Co_6(CO)_{14}]^{4-}$	6		8	O_h	1	vs*	7
$[Rh_6(CO)_{14}]^{4-}$	6		8	O_h	1	vs	8
$Co_6(CO)_6S_8$	6			O_h	1	vs* [b]	9
$[Pt_3(CO)_6]_2{}^{2-}$	6	6		D_{3h}	2	vs*	10
$[Co_6(CO)_{15}N]^-$	6	9		D_{3h}	2	vs	11
$[Rh_6(CO)_{15}N]^-$	6	9		D_{3h}	2	vs	11
$[Co_6(CO)_{15}C]^{2-}$	6	9		D_{3h}	2	vs*	12
$[Rh_6(CO)_{15}C]^{2-}$	6	9		D_{3h}	2	vs	13
$[Ni_6(CO)_{12}]^{2-}$	6	6		D_{3d}	2	vs	14
$[Rh_6(CO)_{15}(AuPPh_3)N]^-$	6	9		C_{3v}	4	vs*	15
$[Rh_6(CO)_{14}(H)N]^{2-}$	6	8		C_s	6	vs(sh)*	16
$[Rh_6(CO)_{14}PPh_3C]^{2-}$	5	9		C_s	5	vs*	17
$[Rh_6Ni(CO)_{16}]^{2-}$	7	6	3	C_{3v}	5	vs*	18
$Ni_8(CO)_8(PPh)_4$	8			O_h	1	vs	19
$[Ni_8(CO)_{16}C]^{2-}$	8	8		D_{4d}	2	vs	20
$[Co_6Ni_2(CO)_{16}C_2]^{2-}$	8	8		C_{2h}	4	vs, s(sh), m	21
$[Ni_9(CO)_{18}]^{2-}$	9	9		D_{3h}	3	vs*	22
$[Pt_3(CO)_6]_3{}^{2-}$	9	9		D_{3h}	3	vs*	10
$[Ni_9(CO)_{17}C]^{2-}$	9	4	4	C_{4v}	5	vs	20
$[Rh_9(CO)_{21}P]^{2-}$	9	12		C_4	5	vs*	23
$[Rh_8Pt(CO)_{17}]^{2-}$	7	9	1	C_1	7	vs*	24
$Rh_9Cu(CO)_{19}(NCMe)_3$	8	8	3	C_s	8	vs(sh)	25
$[Ni_{10}(CO)_{20}Ge]^{2-}$	10	10		D_{5d}	4	vs	26
$[Rh_{10}(CO)_{22}P]^{2-}$	10	12		D_4	4	vs*	27
$[Rh_{10}(CO)_{22}As]^{2-}$	10	12		D_4	4	vs*	28
$[Rh_{10}(CO)_{22}S]^{2-}$	10	12		D_4	4	vs*	29
$[Ni_{10}(CO)_{16}C_2]^{2-}$	6	10		C_{2h}	3	vs(sp)	30
$[Rh_{10}Pt(CO)_{21}N]^{3-}$	11	10		C_{2v}	9	vs, m	31
$[Rh_9Pt_2(CO)_{22}]^{3-}$	11	11		C_1	11	vs	32
$[Co_{11}(CO)_{22}(C)_2]^{3-}$	11	11		C_1	11	vs	33
$[Ni_{12}(CO)_{21}]^{4-}$	9	12		D_{3h}	3	vs	34
$[Ni_{12}(CO)_{21}H]^{3-}$	9	12		D_{3h}	3	vs	34
$[Ni_{12}(CO)_{21}H_2]^{2-}$	9	12		D_{3h}	3	vs(sh)	34
$[Ni_{12}(CO)_{21}H_3]^-$	9	12		D_{3h}	3	vs(sh)	34
$[Ni_9Pt_3(CO_{21})]^{4-}$	9	12		D_{3h}	3	vs	35
$[Ni_9Pt_3(CO_{21})H]^{3-}$	9	12		D_{3h}	3	vs	35
$[Ni_9Pt_3(CO_{21})H_2]^{2-}$	9	12		D_{3h}	3	vs	35
$[Pt_3(CO)_6]_4{}^{2-}$	12	12		D_{3h}	4	vs*	10
$[Rh_{12}(CO)_{30}(C)_2Ag]^{3-}$	12	18		D_{3d}	3	vs	36
$[Ni_9Co_3(CO)_{20}C]^{3-}$	4	16		D_2	4	vs*	37
$[Rh_{12}(CO)_{27}Sb]^{3-}$	12	15		C_1	12	vs(sh)	38
$[Ni_{12}(CO)_{22}Ge]^{2-}$	12	6	4	C_1	12	vs	26
$[Ni_{12}(CO)_{22}Sn]^{2-}$	12	6	4	C_1	12	vs	26
$[Rh_{12}Pt(CO)_{24}]^{4-}$	12	12		D_{3h}	4	vs, m	15
$[Rh_{11}Pt_2(CO)_{24}]^{3-}$	12	12		C_s	12	vs(sh)	15
$[Rh_{13}(CO)_{24}H]^{4-}$	12	12		D_{3h}	4	vs	39−41
$[Rh_{13}(CO)_{24}H_2]^{3-}$	12	12		D_{3h}	4	vs*	39−41
$[Rh_{13}(CO)_{24}H_3]^{2-}$	12	12		D_{3h}	4	vs	39−41
$[Rh_{13}(CO)_{24}H_4]^-$	12	12		D_{3h}	4	vs	39−41
$[Co_{13}(CO)_{24}(C)_2]^{4-}$	12	12		C_2	12	vs(sh)	42
$[Co_{13}(CO)_{24}(C)_2]^{3-}$	12	12		C_s	12	vs(sh)*	43
$[Rh_{14}(CO)_{33}(C)_2]^{2-}$	12	21		D_{3h}	4	vs(sh)*	44, 45
$[Rh_{14}(CO)_{25}]^{4-}$	9	16		C_s	10	vs(sh)*	46
$[Rh_{14}(CO)_{25}H]^{3-}$	10	15		C_1	10	vs(sh)	47
$[Rh_{14}(CO)_{26}]^{2-}$	11	15		C_1	11	vs*	41, 48
$[Rh_{15}(CO)_{30}]^{3-}$	6	24		D_{4h}	2	vs*	6
$[Pt_3(CO)_6]_5{}^{2-}$	15	15		D_{3h}	5	vs*	10
$[Rh_{15}(CO)_{27}]^{3-}$	13	14		C_1	13	vs	49
$[Rh_{17}(CO)_{32}(S)_2]^{3-}$	16	16		D_{4d}	4	vs(sh)*	50
$[Pt_3(CO)_6]_6{}^{2-}$	18	18		D_{3h}	6	vs*	10
$[Pt_{19}(CO)_{22}]^{4-}$	12	10		D_{5h}	3	vs(sh), m	51
$[Rh_{22}(CO)_{37}]^{4-}$	12	6	1	C_3	6	vs*	52
$[Rh_{22}(CO)_{35}H_x]^{5-}$	12	21	2	C_1	12	vs*	53
$[Pt_{24}(CO)_{30}]^{2-}$	22	8		C_{2v}	18	vs*	54
$[Pt_{26}(CO)_{32}]^{2-}$	23	9		C_s	23	vs*	54
$[Ni_{34}(CO)_{38}H(C)_4]^{5-}$	10	26	2	C_i	5	vs	55
$[Ni_{35}(CO)_{39}(C)_4]^{6-}$	10	27	2	C_1	10	vs	55
$[Ni_{38}(CO)_{42}(H)(C)_6]^{5-}$	6	36		D_{3d}	2	vs	56
$[Ni_{38}Pt_6(CO)_{48}]^{6-}$	18	12	18	D_{3d}	5	vs	57
$[Ni_{38}Pt_6(CO)_{48}H]^{5-}$	18	12	18	D_{3d}	5	vs	57
$[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$	18	12	18	D_{3d}	5	vs	57
$[Ni_{38}Pt_6(CO)_{48}H_3]^{3-}$	18	12	18	D_{3d}	5	vs	57

[a] The asterisk indicates that spectra were used. [b] Two Raman peaks not coincident with the infrared.

contributions, through-bond and through-space, questioning the value of such analyses. Another problem with the vibrational analysis of cluster carbonyls is the absence of data on isotopomers.[4] It is perhaps not surprising that all of the extant normal coordinate analyses of the C═O modes of cluster carbonyls are for relatively simple clusters in which each metal atom is linked to all of the other metal atoms. Neither is it surprising that there has been no such analysis reported for almost twenty years (the most recent concerned $M_3(CO)_{12}$ species, M = Ru, Os).[5]

Although the above considerations lead to the expectation that C═O vibrational analyses of metal carbonyl clusters will be difficult and their interpretation even more so, they also indicate that there should be a wealth of spectral data available: more nonzero interaction constants lead to richer spectra. While we are aware of no reason to question the arguments we have adduced, the last conclusion has no contact with reality. A general characteristic of transition metal carbonyl cluster compounds is the simplicity of their terminal ν(CO) infrared spectra. If the arguments that we have presented are not invalid, they must be incomplete; some major phenomenon must have been overlooked—and we believe this to be the case. If this is so, then the meaning of a conventional normal coordinate analysis is placed yet further in question, although this is a rather academic point because the general simplicity of the observed spectra is such that there are not enough data to enable such analyses. The situation finds focus in the observation that a cluster commonly shows a much simpler spectrum than the species from which it is made, even though it contains many times the number of terminal CO groups in the latter.

Results

The focus of the present work is a survey of the ν(CO) vibrational spectra of transition metal carbonyl clusters. There are so many of these in the literature that we are forced to be selective. Table 1 contains a list of representative clusters containing solely M(CO) groups. Table 2 lists species with only

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(4) For a cluster with 20 CO groups, about a quarter of the molecules in a normal sample will be enriched with ^{13}CO. There will not be a single enriched species but several, differing in the position of the enrichment and therefore in spectroscopic characteristics. It will not be possible to enrich one position selectively. Further, in that each molecular vibration may involve all of the terminal CO groups in a molecule, it is far from clear that the displacements of the frequencies of the singly enriched species from those of the nonenriched will be sufficient to enable their resolution. Increasing the enrichment will lead to a plethora of species, the data from which would surely be incapable of deconvolution. Isotopomeric studies are not expected to be of value.

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Table 2. List of Representative Clusters with Only $M(CO)_2$ Units

cluster	no. of units	no. of μ_n(CO) μ_2	μ_3	ideal symmetry	no. of IR peaks pred	obs[a]	ref
$Co_6(CO)_{16}$	6	4		T_d	2	vs(sh)	58
$Rh_6(CO)_{16}$	6	4		T_d	2	vs(sh)*	58
$Ir_6(CO)_{16}$ (red)	6	4		T_d	2	vs(sh)*	59, 60
$Ir_6(CO)_{16}$ (black)	6		4	S_4	4	vs*	59, 60
$[Ru_6(CO)_{16}C]^{2-}$	6	4		C_s	13	vs(sh)	61, 62
$Co_6(CO)_{12}C(S)_2$	6			D_{3h}	3	vs, m*	63
$Co_6(CO)_{12}C(Se)_2$	6			D_{3h}	3	vs, m*	64
$Co_6(CO)_{12}C(Te)_2$	6			D_{3h}	3	vs, m*	65
$[Ru_{10}(CO)_{24}C_2]^{2-}$	10	4		D_2	15	vs(sh,sh)	66
$[Fe_6Pd_6(CO)_{24}]^{4-}$	6	6	6	D_{3d}	4	vs(sh,sh)	67
$[Fe_6Pd_6(CO)_{24}H]^{3-}$	6	6	6	D_{3d}	4	vs(sh,sh)	67

[a] The asterisk indicates that spectra were used.

Table 3. List of Representative Clusters with Only $M(CO)_3$ Units

cluster	no. of units	ideal symmetry	no. of IR peaks pred	obs[a]	ref
$Ir_4(CO)_{12}$	4	T_d	2	vs, m*	60
$Co_4(CO)_{12}Sb_4$	4	T_d	2	vs, s	68
$Fe_4(CO)_{12}(AsMe)$	4	T_d	2	s, m	69
$Fe_5(CO)_{15}C$	5	C_s	15	vs, s, m, w	70
$Ru_5(CO)_{15}C$	5	C_s	15	vs, s, m	70
$Os_5(CO)_{15}C$	5	C_s	15	vs, s, m	70
$Ru_5(CO)_{15}$(Pbut)	5	C_s	15	vs, m, w	71
$[Os_6(CO)_{18}P]^-$	6	D_{3h}	5	vs(sp), m(sh)*	72
$Ru_6(CO)_{18}(H)_2$	6	D_{3d}	5	vs(sp), m	73
$[Ru_6(CO)_{18}(H)]^-$	6	D_3	9	vs, w	74
$[Os_6(CO)_{18}]^{2-}$	6	D_3	9	vs, w*	74, 75
$[Os_6(CO)_{18}H]^-$	6	C_{3v}	10	vs(sp,sh)	76, 77
$Os_6(CO)_{18}$	6	C_{2v}	15	vs(sp), s(sh), 2w	75
$Os_6(CO)_{18}(H)_2$	6	C_s	18	vs(sp), m(sp), w(sp)	76, 78
$[Re_7(CO)_{21}C]^{3-}$	7	C_{3v}	12	vs(sp), m(sp), m, w*	79
$[Re_8(CO)_{24}C]^{2-}$	8	D_{3d}	7	s, m(sp), w*	80

[a] The asterisk indicates that spectra were used.

$M(CO)_2$ groups, Table 3 those with $M(CO)_3$ groups, and Table 4 those with a mixture of different $M(CO)_n$ units. Each of the tables gives the idealized symmetry of the CO arrangement and the consequent group theoretical predictions for infrared activity. This is to be compared with the pattern of peaks reported in the infrared spectra, also given in the tables. The spectral data available to us are of variable quality. When spectra are given in the literature, we have been able to make our own assessment in terms of the present model. Tables of frequencies are more

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Table 4. List of Representative Clusters with Different $M(CO)_n$ Units

cluster	no. of $M(CO)_n$ units			no. of μ_n(CO)		ideal symmetry	no. of IR peaks		ref
	$n = 1$	$n = 2$	$n = 3$	μ_2	μ_3		pred	obs[a]	
$[CoFe_3(CO)_{13}]^-$	1		3	3		C_{3v}	6	vs, m(sh)	115
$[CoRu_3(CO)_{13}]^-$	1		3	3		C_{3v}	6	vs, m	115
$[Fe_4(CO)_{13}]^{2-}$		3	1	3	1	C_{3v}	5	vs(sh)	81
$[CoFe_2Ru(CO)_{13}]^-$	1		3	3		C_s	10	vs(sp,sh)	115
$[CoFeRu_2(CO)_{13}]^-$	1		3	3		C_s	10	vs(sp,sh)	115
$[Co_4(CO)_{11}I]^-$	1	2	1	3		C_s	8	vs(sh)*	82, 83
$[Ni_5(CO)_{12}]^{2-}$	3		2	3		D_{3h}	3	vs, m	84
$[Fe_5(CO)_{14}N]^-$		2	3	1		C_s	13	vs(sh)	85
$[Ru_5(CO)_{14}N]^-$		2	3	1		C_s	13	vs, s, m	86
$Fe_5(CO)_{14}(H)N$		4	1	3		C_s	11	vs, s, s	85
$[Co_6(CO)_{15}H]^-$	2	4		5		C_{2v}	9	s, m	87
$[Co_6(CO)_{13}N]^-$	3	3		4		C_s	9	vs	88
$[Fe_6(CO)_{16}C]^{2-}$		5	1	3		C_s	13	vs(sh,sh)	89
$[Rh_6(CO)_{13}C]^{2-}$	5	1		6		C_s	7	vs	90
$Ru_6(CO)_{17}C$		2	4	1		C_s	16	vs(sp)*	91
$[Ru_6(CO)_{18}]^{2-}$		4	2	2	2	C_{2v}	12	vs(sp,sh)*	74, 92
$[Ru_6(CO)_{16}N]^-$		4	2	2		C_s	14	vs(sh)	86
$[Co_6(CO)_{13}C]^{2-}$	4	2		5		C_1	8	vs(sh)*	93
$[Rh_6(CO)_{12}PPh_3C]^{2-}$	5	1		5		C_1	7	vs*	116
$[Ir_6(CO)_{15}(COOCH_3)]^-$	1	5		4		C_1	11	vs(sp)*	94
$[Rh_7(CO)_{15}N]^{2-}$	4	3		4	1	C_s	10	vs, vw	116
$[Rh_6Co(CO)_{15}N]^{2-}$	4	3		4	1	C_1	10	vs	116
$[Rh_6Ir(CO)_{15}N]^{2-}$	4	3		4	1	C_1	10	vs, vw	116
$[Co_9(CO)_{21}Si]^{2-}$	5	4		8		C_4	7	vs(sh)	95
$[Rh_9(CO)_{19}]^{3-}$	5	1		9	3	C_1	7	vs(sp)	96
$[Os_{10}(CO)_{24}C]^{2-}$		6	4			T_d	4	vs, s*	97
$[Os_{10}(CO)_{24}C(H)_4]^{2-}$		6	4			T_d	4	vs, s(sh)*	97
$[Os_{10}(CO)_{24}(AuBr)C]^-$		6	4			C_1	24	vs, s	98
$[Rh_{12}(CO)_{25}(C)_2]^-$	10	2	10	1		C_1	14	vs[b]	99
$[Rh_{12}(CO)_{24}(C)_2]^{2-}$	8	4		8		D_{4h}	4	vs(sh)	100
$[Rh_{12}(CO)_{23}(C)_2]^{4-}$	11	1		10		C_s	13	vs*	101
$[Ru_8Cu_7(CO)_{24}(H)_2(Cl)_7]^{2-}$		2	6	2		C_{2v}	17	vs, vs, s, s	102
$[Ru_{12}Cu_6(CO)_{34}(H)_2(Cl)_2]^{2-}$		8	4	6		D_{2h}	7	vs,vs(sh), m	102
$[Os_{20}(CO)_{40}]^{2-}$	4	12	4			T_d	6	s, s, w	103

[a] The asterisk indicates that spectra were used. [b] Shows solid-state splitting.

difficult to interpret; quite often two different but close frequencies are reported which, in the light of our own experience and the solvent used, we have interpreted as a single but split peak. In addition, we have our own collection of original spectra and those of other workers which have kindly been made available to us (we have also quoted the literature references). Those examples for which we have been able to work from spectra are indicated by an asterisk. In the tables

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the spectral data are reported using the following notation. When a strong peak is observed but which shows a splitting and, say, a shoulder, this is given as s(sp,sh). The s indicates a strong band, qualified by the quantities in parentheses (split, shoulder). When there are several bands, say three, they are reported in order of decreasing frequency using a pattern like vs(sp), m, w(sh), where vs = very strong, m = medium, and w = weak. For a few, but important, cases solution Raman data are available and these are given in footnotes. In a few others, Raman data on crystalline solids are available but these we have not generally reported. The reason is that such spectra can show factor group effects (the fact that intermolecular vibrational coupling occurs indicates the basic "normality" of these clusters—here, they behave just like simple carbonyls). In favorable cases one can argue that factor groups effects are negligible or, where the spectra of several closely related isomorphic species are available, it has proved possible to argue back from solid-state Raman spectra to give solution data but the arguments are long and detailed—and it is not always evident which are favorable cases.[5,104] In this uncertain situation we have preferred to confine ourselves to solution data, which are unambiguous. The entries in each table are listed in order of increasing nuclearity of the metal cluster core.

In viewing the tables the following points are relevant. Whenever there is an $M(CO)_n$, $n \geq 2$, group in a mononuclear transition metal carbonyl there is coupling between the n ν(CO) vibrations. It must be assumed that this coupling also occurs in polynuclear species, notwithstanding the common lack of overt evidence for it. Such coupling invariably leads to some modes which have dipole moment changes tangential to the surface of a spherical cluster. If these modes were spectrally active it would be necessary to invoke the tensor harmonic model (vide infra). Appropriate examples exist and they will be reviewed later.

Discussion

The problem detailed in the Introduction has recently been explained by a model which, at the simplest level, ignores the details of the structure of the cluster and considers the CO groups as radially attached to a spherical cluster surface.[105] A spherical harmonic analysis of the vibrational problem then shows that of the harmonics subtended (S + P + D + ...) only the P modes are dipolar and therefore infrared active. Similarly, only the S and D are Raman active. The basic picture which emerges is of a single strong infrared peak sandwiched between two Raman features (it is assumed that data from dissolved species are being discussed and that the number of carbonyl groups present is such as to span into the D set). The transition to real molecules is made by noting that the molecular symmetry will be less than spherical, so that some splitting of the predicted single but degenerate features must be expected. Further, in the reduced symmetry some spectral activity transfer into modes of the same symmetry as the predicted active species is also to be expected. However, any transfer will be such that the greater the frequency separation between the "allowed" mode and the "stealing" mode, the less will be the transfer (in a perturbation treatment) and so the lower the stolen intensity. That is, the highest frequency infrared band will be the strongest and any other infrared bands seen will progressively become weaker to lower frequency. With these developments, the model seems to be applicable to most nonplanar cluster carbonyl species. The few to which it does not apply have strong tangential (to the surface of the sphere), as well as radial, dipolar-active modes. Such tangential modes arise, for example, from the E mode of a $M(CO)_3$ unit (the CO vibrators within a $M(CO)_n$ unit are always vibrationally coupled). For such molecules, an extension of the model to incorporate the essentials of Stone's tensor harmonic approach to the bonding in clusters[106] has been described. It is important to recognize, however, that what has just been said does *not* mean that all clusters with $M(CO)_n$ groups, in which all of the n carbonyls are symmetry related, are to be treated by the tensor harmonic formalism. The need to invoke the tensor harmonic approach is infrequent for such species.

Although a general approach to the interpretation of the ν(CO) spectra of the terminal carbonyl groups of clusters is thus in place, it leaves unanswered important questions. In particular, why should it be necessary to regard all CO groups as radiating from the surface of a sphere when, manifestly, they radiate from the metal atom to which they are attached? One of us has recently provided an answer to this question in suggesting that there is a cluster equivalent of the so-called "surface selection rule" of metals.[107] The fact that a dipole moment change in an adsorbed molecule induces an image dipole moment change in a metal surface is well-known in metal surface spectroscopy.[108] 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 suggestion that there is a related "metal cluster selection rule" is intriguing, for it divides metal carbonyl clusters into two classes. The first, the vast majority, behave as conductors and so are able to sustain image dipoles. They thus follow the more generally applicable model described above and which, for simplicity, may be called the "spherical harmonic model" (SHM). The second set are those that are not able to sustain an image dipole and so approximate to insulators. These, the minority, are those that require Stone's tensor harmonic treatment, a treatment that may conveniently be called the "tensor harmonic model" (THM).

The statement that the metal atoms in a cluster behave as a fragment of a conductor has immediate implications for the electronic band structure of the cluster—filled bands neither conduct electricity nor sustain image dipoles. The implication, then, is that the majority of transition metal carbonyl clusters are materials with, effectively, incompletely filled bands. Calculations[109] on bare metal clusters, indeed, commonly lead

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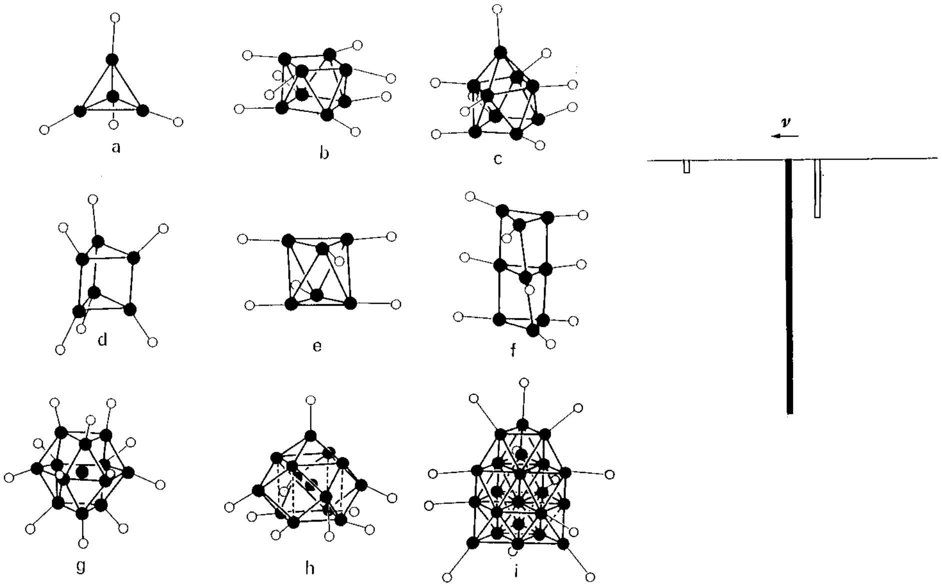

Figure 1. Selected examples of metal carbonyl clusters with M$-$CO units only: (a) $[Rh_4(CO)_{11}]^-$, (b) $[Ni_8(CO)_{16}C]^{2-}$, (c) $[Ni_9(CO)_{17}C]^{2-}$, (d) $[Co_6(CO)_{15}N]^-$, (e) $[Ni_6(CO)_{12}]^{2-}$, (f) $[Pt_9(CO)_{18}]^{2-}$, (g) $[Rh_{13}(CO)_{24}H_3]^{2-}$, (h) $[Rh_{14}(CO)_{25}]$,$^{4-}$ (i) $[Rh_{22}(CO)_{37}]^{4-}$ (bridging CO's are omitted for clarity). The common infrared spectral pattern is shown on the right. The features are associated with the spherical harmonics S, P, and D (high to low frequency) in order; only the P (full bar) is infrared-allowed in zeroth order, and S and D (open bars) are sometimes present (see text).

to the conclusion that they have incompletely filled band structures but it is usually found that the addition of ligands such as carbonyls change the situation; filled bands now result, in contrast to the discussion above. The simplest way out of this dilemma is to recognize that the (transition) dipole moment associated with carbonyl stretching modes can induce a mixing with low-lying empty bands. A parallel with phenomena such as the temperature-independent paramagnetism of, say, the permanganate anion can be drawn.[110] A very similar suggestion has been made to account for the paramagnetism of the even-electron cluster $[Os_{10}C(CO)_{24}H_2]$ (except that here the mixing occurs in zeroth order).[111] Relevant is the fact that although the contribution of infrared spectra to the study of metal$-$metal vibrations is small, there seems no evidence that clusters behave as reflectors in this spectral region. Such reflectivity would be expected if the clusters were true metallic fragments.

The above paragraphs serve to define a general approach to the interpretation of the terminal ν(CO) spectra of transition metal carbonyl clusters. However, there are several questions to be addressed about its application in specific cases. It is the object of the present paper to cover this aspect. In it, different possible strategies for the application of the model will be applied. In the simplest form of the SHM the cluster is assumed to be spherical, although we have indicated above the modifications which might be needed to accommodate the real structure geometry.[105] In practice, the molecular symmetry of the cluster seems of little importance. Further, clusters containing a variety of different metal atoms can usually be treated on a par with clusters containing only one type of metal atom. This seems to be a further way in which the model stands up to testing; since experimentally, the vibrational spectra of the two types of clusters show no great qualitative difference even though the molecular symmetries must differ considerably.[112−116] It would be reasonable to expect that, when a mixed-metal cluster has a lower symmetry than its homometallic counterpart, this will be manifest in more evident band splittings and more evident intensity transfer. Even though reasonable and expected, these characteristics commonly do not serve to distinguish corresponding homo- and heterometallic clusters; effective conductor properties dominate.

In the discussion of specific spectra we will ignore the very weak peak that commonly occurs at highest frequency in the infrared spectra. This is associated with the S mode and, in many symmetries, remains Raman-only active. It seems to be a characteristic of almost all terminal ν(CO) spectra that this highest frequency, totally symmetric, mode appears as a very weak peak, even when it is symmetry forbidden. Asymmetric solvent cages may offer one explanation, isotopic species another.

The Spherical Harmonic Model. Table 1 contains a review of M(CO)-containing species and Figure 1 shows some of the metal core arrangements covered, along with a schematic spectrum common to all. We note that since all of the CO groups will be orientated essentially perpendicular to the surface of the cluster, the THM will never be applicable to such clusters. In agreement with the SHM, the essential invariance of the spectra with number of M(CO) units and molecular symmetry is quite remarkable. It is as if there were no vibrational coupling between the M(CO) units, although it is clear (vide infra) that this cannot be the explanation. Rather, the species must be regarded as conforming to the SHM very closely; that is, there is an effective incomplete electronic band structure associated with the metal clusters in all of them. We note that if the CO groups were vibrationally uncoupled then a clear ^{13}CO feature

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should invariably be seen; not only is its absence evidence for coupling but the weak shoulders/peak reported for particular examples do not have the frequencies appropriate for this explanation. Examples of such additional features are so few that it is tempting to wonder whether their occasional presence indicates the coexistence of other complexes in solution. There is one M(CO) species for which useful Raman data are available $Co_6(CO)_6S_8$[9] although they are of crystalline samples. Two Raman peaks are reported, the infrared frequency falling between the two Raman. This, of course, is just the pattern predicted by the SHM and is also a pattern which confirms the presence of vibrational coupling.

It is clear from Tables 2−4 that as soon as a cluster contains $M(CO)_n$, $n \geq 2$, a cluster may exhibit more than a single infrared feature, although the spectra are almost invariably simpler than predicted group theoretically. In accord with the expectation of the SHM, the additional peaks occur as a small splitting and/or shoulder on a main peak. The absence of such additional features for molecules containing only M(CO) groups indicates that they cannot arise simply because of low symmetry or intensity stealing, even though they behave as if these are the explanations and may be interpreted as such. The putative involvement of tangential components is indicated; reasonably enough, there exists a continuity between the SHM and THM.

Two alternative procedures exist for the application of the SHM. It is helpful to demonstrate the difference explicitly and so we consider the case of a molecule which contains only $M(CO)_2$ groups, exemplified by a T_d species, $Rh_6(CO)_{16}$, which has six $M(CO)_2$ groups. This species has been briefly examined in ref 105, where the representation of the spectra and the assignment of the modes are illustrated. First, however, the simple group theoretical approach to the vibrations of the twelve CO groups. The predictions ($A_1 + E + T_1 + 2T_2$) are for there to be two infrared active and four Raman active features, two of which will coincide with the infrared peaks. This is in accord with the observed spectra,[58,112] and, while gratifying, it is to be noted that there is no account given of the relative band intensities.

In the SHM applied to $Rh_6(CO)_{16}$, one might consider just the six totally symmetric (in the local C_{2v} symmetry) $Rh(CO)_2$ modes. These transform as $A_1 + T_2 + E$ in the molecular T_d symmetry (the corresponding antisymmetric modes give rise to $T_1 + T_2$ symmetry coordinates). Adding the spherical harmonic parentage of each feature, $S(A_1) + P(T_2) + D(E)$, we see that all modes are predicted to be spectrally active there being two Raman peaks, sandwiched between which is an infrared. While this correctly accounts for the presence and general pattern of three strongest peaks in the two spectra, it neither explains the infrared−Raman coincidences observed nor the additional peaks. Extending the discussion to include the antisymmetric modes in the discussion could explain the latter but not the former. Mixing between symmetric and antisymmetric modes could be added to give the required intensity redistribution but would have to be considerable and thus negate the starting hypothesis of separate symmetric and antisymmetric modes.

The second approach is to apply the SHM to the full set of twelve terminal carbonyl groups. The twelve now span $S(A_1) + P(T_2) + D(E + T_2) + F(T_1)$ spherical harmonics. Again, S and D originating modes are Raman active and the P infrared. Now, however, in contradistinction to the previous model—where they were kept apart by the symmetric-antisymmetric separation—mixing between the T_2 functions originating in the P and D harmonics can occur. Further, it is predicted that the strong Raman peak will split into two, $D(T_2 + E)$, and that these will be at lower frequency than the strong infrared peak $P(T_2)$. Mixing between the T_2 functions will give Raman-infrared coincident bands with, for the infrared (higher frequency first), a strong−weak pattern. For the Raman it will be a weak−strong. The splitting of the D will be such that the T_2 is the *higher* frequency component.[117] This prediction is in excellent accord with the experimental observations and makes it clear that in the application of the SHM the full set of vibrators should be considered. Even in a high-symmetry example such as this, the spectral predictions from the SHM go well beyond those from simple group theory. Such agreement gives confidence in the ability of the model to make meaningful predictions in other cases where group theory itself is inadequate. This confidence is supported by the data in Table 2, where for every example reported the spectra are simpler than group theoretically predicted. The common observation of a high frequency infrared strong peak (often showing fine structure), sometimes accompanied by a weaker peak to longer wavelength, is entirely understandable in terms of the SHM model.

As the above discussion shows, the simple SHM can provide a good starting point for a discussion of the infrared (and, where available, Raman) spectra of cluster carbonyls. This remains true for the potentially more complicated case of clusters containing $M(CO)_3$ groups (Table 3). Generally speaking, they show evidence of more spectral bands than do species with only $M(CO)_2$ groups but far fewer than the number predicted group theoretically. The common pattern, again, is for there to be a strong high frequency peak, sometimes showing structure, accompanied by two or three progressively weaker peaks to lower frequency, which may also show fine structure. Again, this is a pattern which is entirely understandable in terms of the SHM. Table 4 contains examples of clusters which contain $M(CO)_n$ groups with more than one value of n. However, as the table shows, they are in no way significantly distinguished from the entries in Tables 2 and 3. In that the SHM does not distinguish between different origins of the CO vibrators, this indifference of the spectra to the existence of disparate vibrator sets is in accord with the model. Akin to this is the presence in the tables of clusters which contain different metal atoms. As is particularly evident when they have counterparts with only one type of metal atom, the presence of mixed metal cores has no evident significant effect on the observed spectra. Again, this indifference is inherent in the SHM.

The Tensor Harmonic Model. In Table 5 are given examples of species for which the tensor harmonic formalism seems that which is appropriate as a first approximation for an interpretation of their spectra. The characteristics of this model can be seen by a consideration of the case of a hypothetical $[M(CO)_3]_6$ molecule of essentially octahedral structure, assumed to follow it. The local A_1 modes will transform as $A_{1g} + E_g + T_{1u}$ and the discussion of these (radial) modes is covered by the SHM. The local E modes (which are tangential) transform as $T_{1g} + T_{1u} + T_{2g} + T_{2u}$. These have the potential for spectral activity and so the basic pattern characteristic of the THM would be the appearance of two strong well separated peaks in the infrared, both T_{1u}. The relative intensities of these peaks is a more difficult matter. At one extreme, that in which there were no vibrational coupling between the $M(CO)_3$ units, the above

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[117] The reason for this pattern of energies is that the T_2 functions mixed, the P and (three of the) D, are *orthogonal*. When orthogonal functions mix, the mixed functions have energies intermediate between those of the pure components—compare s and p orbitals mixing to give two, identical except for orientation in space, sp hybrids. So here, the two T_2 features seem remarkably close together.

Table 5. List of Representative Clusters Following the Tensor Harmonic Model

cluster	no. of M(CO)$_n$ units $n = 1$	$n = 2$	$n = 3$	no. of μ_2(CO)	ideal symmetry	no. of IR peaks pred	obs[a]	ref
$Os_4(CO)_{12}O_4$			4		T_d	2	s, vs*	118, 119
$Re_4(CO)_{12}F_4$			4		T_d	2	ms, s	120
$Re_4(CO)_{12}(SMe)_4$			4		T_d	2	m, s[b]	121
$Re_4(CO)_{12}(SeC_6H_5)_4$			4		T_d	2	m, s[b,c]	121
$Ru_4(CO)_{12}F_8$			4		D_{4d}	5	m, s(sh)	122
$Mn_4(CO)_{12}F_2(OH)_2$			4		C_{2v}	8	s, vs[b]	123
$Mn_4(CO)_{12}F(OH)_3$			4		C_s	12	s, vs[b]	123

[a] The asterisk indicates that spectra were used. [b] Intensity not specifically reported but inferred from the discussion in the text. [c] Raman data available.

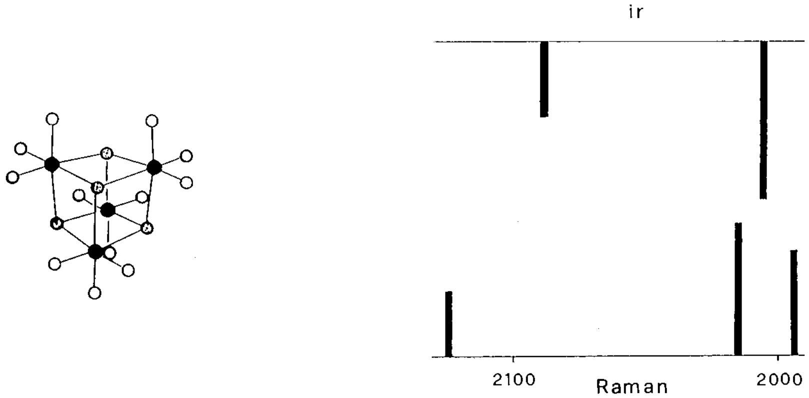

Figure 2. Sketch of the structure of $M_4(CO)_{12}(\mu_3E)_4$ complexes and schematic infrared and Raman patterns of $Os_4(CO)_{12}(\mu_3O)_4$ (ref 119). The pattern is that typical of the above species for which the TSH model is applicable. The infrared spectrum can be interpreted in terms of uncoupled $M(CO)_3$ groups but the Raman spectrum shows that this explanation is invalid (see text).

analysis would only be applicable in a formal sense and the band intensities would be ca. 1:2, as in an isolated $M(CO)_3$ unit. Away from this case, the situation depends on the assumptions made in the dipolar expansion but the other limiting case is that in which the band intensity ratio is ca. 1:1, although even this is dependent on the bond angles at the $M(CO)_3$ group. As working model, we have taken the THM to be applicable whenever there occur two strong well separated bands in the terminal ν(CO) region in which the lower in frequency is stronger than that at higher. For all of the species reported in this table, the general pattern is of two peaks, of which the lower in frequency is approximately twice as intense as the higher. This pattern has lead several authors, usually when reporting the preparation of the compounds, to interpret the pattern as indicating uncoupled $M(CO)_3$ groups. This interpretation is best discussed in the context of an example to which the THM seems applicable, the T_d molecule $Os_4O_4(CO)_{12}$.[118] The infrared and Raman spectra are available for this compound;[119] the Raman is important as the noncoincidence of the Raman bands with the infrared clearly demonstrates that there is coupling between the $Os(CO)_3$ units. The treatment on the basis of the THM has been detailed in a previous paper[105] and consists of $A_1 > T_2$ and $T_2 > E > T_1$ energy patterns derived from the local $Os(CO)_3$ A_1 and E modes, respectively. The reported data, both infrared and Raman, are in good accord with these predictions, as illustrated in the schematic spectral representation shown in Figure 2.

The distinctive feature of $Os_4O_4(CO)_{12}$ compared with earlier examples is the presence of O bridges spanning the $Os(CO)_3$ units. It seems entirely reasonable that these bridges should disrupt the electronic band structure of a compact Os_4 unit and lead to effective insulator properties. It is a characteristic of several of the species listed in Table 5 that they contain rather electronegative atoms as bridges and so could also lead to effective insulators. However, it seems that it can be a delicate matter. So, although a sulfur bridged Re species is listed, the data in the literature indicate that the corresponding iron compound should not be.[124] Finally, it is to be noted that the examples in Table 5 are all of relatively small clusters. This is suggestive. It hints that for small clusters it is marginal whether the cluster band structure is such that the "cluster selection rule" is operative and that molecular features which tend to disrupt this band structure may be sufficient to lead to the applicability of the THM.

Conclusions

The present work has explored the application of the SHM and THM models to the interpretation of the ν(CO) vibrational spectra of transition metal carbonyl clusters. For clusters containing just M(CO) groups it works remarkably well in its simplest form. It is also applicable to more complicated species and the observations that the vibrational spectra are almost insensitive to the cluster geometry, to the metal atom composition and to the CO group distribution are explained. Even when it would seem a natural first step, the coupling together of carbonyl groups at one metal is to be ignored unless the observed infrared spectrum contains several strong bands with significant separations, indicative of the applicability of the THM.

It must be recognized that the general thrust of the present work is very different from that indicated by attempts to extend

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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—at best, they are an output, not an input—and so it is often not 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 force field subject to a self-consistent iterative convergence. In the present work band intensity patterns and band position patterns have been the focus of 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. About 80% of the examples that we cite conform reasonably well to the simplest form of the SHM—the prediction of a single infrared peak. None of these cases could be the subject of a normal coordinate analysis.

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