

## Vibrational Spectra of Bridging Carbonyl Groups in Transition Metal Carbonyl Clusters

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Received January 23, 2002

The spherical harmonic model (SHM), previously used for the analysis of the terminal  $\nu(\text{CO})$  vibrations of transition metal carbonyl clusters, is applied to the corresponding bridging CO modes. The model is applicable, although the spectra show a greater sensitivity to the molecular geometry than is the case for their terminal counterparts. The reasons for this sensitivity are discussed. When both  $\mu_2$  and  $\mu_3$  CO groups are present in a molecule, a spectral distinction may not be apparent.

### Introduction

The vibrational spectra of the terminal  $\nu(\text{CO})$  modes of simple transition metal carbonyls containing  $(\text{CO})_n$  units have long been used to provide simple, quick, convenient, and accurate indications of both the  $(\text{CO})_n$  symmetry and the bond angle that they subtend at the metal atom.<sup>1</sup> It was initially expected that the same techniques could be applied to transition metal cluster carbonyls, but they proved a disappointment in this respect. Instead of the wealth of spectral features usually predicted by group theory, very simple infrared spectra, frequently consisting of a single strong band, were observed. Even today, obtaining Raman spectra for these clusters is far from trivial; the few that exist seem to consist of two bands of any intensity, one on either side of that in the infrared.<sup>2</sup> This pattern has only recently been explained,<sup>3</sup> and then only by a model which differs greatly from the traditional approach.

If a cluster is treated as spherical with the attached CO groups radiating radially from it, then a spherical harmonic

model (SHM) predicts a spectral pattern in which a strong infrared band (corresponding to the P spherical harmonic) is sandwiched between two Raman (corresponding to the S and D spherical harmonics) bands. The degenerate (P and D) bands may be split by descent into the real molecular symmetry, yielding up to three and five proximate bands, respectively. The apparent physical unreality of the model has been addressed by recognizing that it reflects and extends the existence of a selection rule in clusters akin to the surface selection rule of metal surface spectroscopy.<sup>4</sup> The presence of image dipoles within the cluster modifies both selection rules, intensities and frequencies, notwithstanding the fact that the band structure of a cluster is but a poor imitation of that in the bulk metal.

Such an explanation immediately raises the question of why this behavior should be limited to the vibrations of terminal carbonyl groups. It therefore becomes relevant that it has been suggested that the vibrations of *bridging* carbonyl groups provide more useful geometric information than do the terminal ones in metal cluster carbonyls.<sup>5</sup> Why should terminal and bridge groups apparently differ? Part of the answer to this question may be that there are often fewer bridge carbonyls than terminal. The cluster selection rule permits up to three spectrally active infrared features to be seen (one for each coordinate axis) in first order (in second

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Table 1. List of the Clusters Containing  $\mu_2(\text{CO})$  Only

no.	complex	no. $\mu_2(\text{CO})$	point group	no. IR bands predicted	no. IR bands obsd	ref	no.	complex	no. $\mu_2(\text{CO})$	point group	no. IR bands predicted	no. IR bands obsd	ref
1	$[\text{Os}_8(\text{CO})_{22}]^{2-}$	2	$C_2$	2	vw, w	8	43	$[\text{Co}_9\text{C}_2(\text{CO})_{19}]^{2-}$	10	$C_{2v}$	8	m, w(sh)	42
2	$[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$	3	$C_s$	3	m	9	44	$[\text{Rh}_9\text{Pt}_2(\text{CO})_{22}]^{3-}$	11	$C_1$	11	ms(br)	43
3	$[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$	3	$C_1$	3	m, m	10	45	$[\text{Co}_{11}(\text{CO})_{25}\text{C}_2]^{3-}$	11	$C_1$	11	w, mw, m	44
4	$[\text{Pt}_3(\text{CO})_6]^{2-}$	3	$D_{3h}$	1	s	11	46	$[\text{Rh}_9(\text{CO})_{21}\text{P}]^{2-}$	12	$C_4$	6	s	45
5	$\text{Ir}_6(\text{CO})_{15}(\text{AuPPH}_3)_2$	3	$C_s$	3	m	12	47	$[\text{Co}_{14}\text{N}_3(\text{CO})_{26}]^{3-}$	12	$D_3$	6	ms, m	46
6	$[\text{Ir}_4\text{Fe}_2(\text{CO})_{16}]^{2-}$	4	$C_1$	4	w(sh), s, s	13	48	$[\text{Rh}_{10}(\text{CO})_{22}\text{As}]^{2-}$	12	$D_4$	4	m(br)	47
7	$\text{Ir}_6(\text{CO})_{16}$ black isomer	4	$S_4$	2	s, s	14	49	$[\text{Rh}_{10}(\text{CO})_{22}\text{S}]^{2-}$	12	$D_4$	4	ms	48
8	$[\text{Co}_6\text{N}(\text{CO})_{13}]^-$	4	$C_s$	4	m	15	50	$[\text{Rh}_{10}(\text{CO})_{22}\text{P}]^{2-}$	12	$D_4$	4	ms	49
9	$[\text{Ir}_6(\text{CO})_{15}\text{CO}_2\text{R}]^-$	4	$C_1$	4	m	16	51	$[\text{Ni}_{12}(\text{CO})_{21}\text{H}_2]^{2-}$	12	$D_{3h}$	4	s	50
10	$[\text{Ir}_{10}(\text{CO})_{21}]^{2-}$	4	$C_1$	4	m	17	52	$[\text{Ni}_{12}(\text{CO})_{21}\text{H}]^{3-}$	12	$D_{3h}$	4	s	50
11	$[\text{Ru}_{10}(\text{CO})_{24}\text{C}_2]^{2-}$	4	$D_2$	4	m	18	53	$[\text{Ni}_{12}(\text{CO})_{21}]^{4-}$	12	$D_{3h}$	4	s	50
12	$[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$	5	$C_1$	5	m	19	54	$[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$	12	$D_{3h}$	4	m, s, m	11
13	$[\text{Co}_6\text{H}(\text{CO})_{15}]^-$	5	$C_{2v}$	4	ms	20	55	$[\text{Ni}_9\text{Pt}_3(\text{CO})_{21}\text{H}_2]^{2-}$	12	$D_{3h}$	4	m	51
14	$[\text{Ru}_8\text{H}_2(\text{CO})_{21}]^{2-}$	5	$C_1$	5	w(sh), m	21	56	$[\text{Ni}_9\text{Pt}_3(\text{CO})_{21}\text{H}]^{3-}$	12	$D_{3h}$	4	m	51
15	$[\text{Ir}_{12}(\text{CO})_{24}]^{2-}$	5	$C_s$	5	w(sh), m(br)	22	57	$[\text{Ni}_9\text{Pt}_3(\text{CO})_{21}]^{4-}$	12	$D_{3h}$	4	m	51
16	$[\text{Ni}_6(\text{CO})_{12}]^{2-}$	6	$D_{3d}$	2	m, s	6	58	$[\text{Co}_{13}(\text{CO})_{24}\text{C}_2]^{4-}$	12	$C_2$	12	ms, mw	52
17	$\text{Pd}_4(\text{CO})_6(\text{PBu}_3)_4$	6	$T_d$	1	w, m(sh), m(sh), s	23	59	$[\text{Co}_{13}(\text{CO})_{24}\text{H}_2]^{3-}$	12	$C_s$	12	ms, mw	53
18	$[\text{Pt}_6(\text{CO})_{12}]^{2-}$	6	$D_{3h}$	2	m, s	11	60	$[\text{Rh}_{13}(\text{CO})_{24}\text{H}_4]^-$	12	$C_s$	12	ms	54
19	$[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$	6	$C_s$	6	m, w(sh)	24	61	$[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$	12	$C_s$	12	ms	54
20	$[\text{Ir}_9(\text{CO})_{20}]^{3-}$	7	$C_1$	7	m	25	62	$[\text{Rh}_{13}(\text{CO})_{24}\text{H}_2]^{3-}$	12	$C_s$	12	ms	54
21	$[\text{Ir}_9\text{H}(\text{CO})_{19}]^{4-}$	7	$C_1$	7	m	17	63	$[\text{Rh}_{13}(\text{CO})_{24}\text{H}]^{4-}$	12	$C_s$	12	ms	54
22	$[\text{Co}_7\text{N}(\text{CO})_{15}]^{2-}$	7	$C_1$	7	m, w(sh), w(sh)	26	64	$[\text{Rh}_{12}\text{Pt}(\text{CO})_{24}]^{4-}$	12	$C_s$	12	mw, ms	55
23	$[\text{Ni}_8\text{C}(\text{CO})_{16}]^{2-}$	8	$D_{4d}$	2	s	27	65	$[\text{Rh}_{11}\text{Pt}_2(\text{CO})_{24}]^{3-}$	12	$C_s$	12	ms	55
24	$[\text{Co}_6\text{Ni}_2\text{C}_2(\text{CO})_{16}]^{2-}$	8	$C_{2h}$	4	m, w	28	66	$[\text{Rh}_{12}(\text{CO})_{27}\text{Sb}]^{3-}$	15	$C_1$	15	s(sh)	56
25	$[\text{Ir}_{12}(\text{CO})_{26}]^{2-}$	8	$C_s$	8	m	29	67	$[\text{Rh}_{14}(\text{CO})_{26}]^{2-}$	15	$C_1$	15	w, m(sh), m, w(sh)	57
26	$[\text{Rh}_{12}(\text{CO})_{24}\text{C}_2]^{2-}$	8	$C_1$	8	w, m, w	30	68	$[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$	15	$D_{3h}$	5	m, s, m	11
27	$[\text{Co}_9(\text{CO})_{21}\text{Si}]^{2-}$	8	$C_4$	4	m, w(br)	31	69	$[\text{Rh}_{14}(\text{CO})_{25}\text{H}]^{3-}$	15	$C_1$	15	m, w(sh)	58
28	$[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$	9	$D_{3h}$	3	s, m	32	70	$[\text{Ni}_9\text{Co}_3(\text{CO})_{20}\text{C}]^{3-}$	16	$C_1$	16	m, m, s, w	59
29	$[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$	9	$D_{3h}$	3	s	33	71	$[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$	16	$C_s$	16	ms	60
30	$\text{Rh}_6\text{C}(\text{CO})_{15}(\text{Ag}(\text{PPh}_3))_2$	9	$D_{3h}$	3	s, m	34	72	$[\text{Rh}_{17}(\text{CO})_{32}\text{S}_2]^{3-}$	16	$C_1$	16	m, m	61
31	$[\text{Rh}_6\text{C}(\text{CO})_{15}(\text{Au}(\text{PPh}_3))]^-$	9	$C_{3v}$	6	s, m	34	73	$[\text{Rh}_{12}(\text{CO})_{30}\text{C}_2\text{Ag}]^{3-}$	18	$D_{3d}$	6	s, m, m	62
32	$[\text{Co}_6\text{N}(\text{CO})_{15}]^-$	9	$D_{3h}$	3	m(sh), vs, w	35	74	$[\text{Pt}_{18}(\text{CO})_{36}]^{2-}$	18	$D_{3h}$	6	w(sh), s, m(sh), m(sh)	11
33	$[\text{Rh}_6\text{N}(\text{CO})_{15}]^-$	9	$D_{3h}$	3	m(sh), vs, w	35	75	$[\text{Rh}_{14}(\text{CO})_{33}\text{C}_2]^{2-}$	21	$D_{3h}$	7	w, vs, s	63
34	$[\text{Ni}_9(\text{CO})_{18}]^{2-}$	9	$D_{3h}$	3	s	7	76	$[\text{Rh}_{15}(\text{CO})_{30}]^{3-}$	24	$C_1$	24	vs(br), m(sh)	64
35	$[\text{Pt}_9(\text{CO})_{18}]^{2-}$	9	$D_{3h}$	3	w(sh), s, m	11	77	$[\text{Rh}_{28}\text{N}_4(\text{CO})_{41}\text{H}_x]^{4-}$	26	$C_s$	26	m, m, w	65
36	$[\text{Ir}_{11}(\text{CO})_{23}]^{3-}$	9	$C_1$	9	w, m	36	78	$[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{5-}$	36	$O_h$	3	s	66
37	$[\text{Co}_{10}\text{N}_2(\text{CO})_{19}]^{4-}$	10	$C_1$	10	m, ms, w	37	79	$[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{6-}$	36	$O_h$	3	s	66
38	$[\text{Ni}_{10}(\text{CO})_{20}\text{Ge}]^{2-}$	10	$D_{5d}$	2	ms, m	37	80	$[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{7-}$	36	$O_h$	3	s	66
39	$[\text{Ni}_{10}(\text{CO})_{16}\text{C}_2]^{2-}$	10	$C_{2h}$	5	m, m	38	81	$[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{8-}$	36	$O_h$	3	s	66
40	$[\text{PtRh}_{10}(\text{CO})_{21}\text{N}]^{3-}$	10	$C_2$	10	m, w(sh), w(sh)	39	82	$[\text{HNi}_{32}(\text{CO})_{36}\text{C}_6]^{5-}$	36	$O_h$	3	s	66
41	$[\text{Rh}_{12}(\text{CO})_{23}\text{C}_2]^{4-}$	10	$C_s$	10	s, m(sh), w	40	83	$[\text{HNi}_{38}(\text{CO})_{42}\text{C}_6]^{5-}$	36	$D_{3d}$	12	s, s	67
42	$[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$	10	$D_{5h}$	2	s	41							

order there is intensity transfer to features inactive in zeroth order but with the same symmetry as an active species in the real molecular geometry). For all of the bridge carbonyl-containing molecules that have been studied in detail to date, this is no problem: no more than three bands are group theoretically predicted. But there exist in the literature examples in which more than this number of bridge carbonyl frequencies have been reported. Does this indicate that the cluster selection rule does not apply to bridge carbonyls? Of course, an alternative is that a complicated bridge region spectrum could be an indication of multiple species in solution (bridge carbonyls are often rather mobile). The present work addresses the general problem by a rather detailed survey of the bridge region  $\nu(\text{CO})$  spectra of carbonyl clusters, often with a large number of  $\mu_2$  and/or  $\mu_3$  bridging CO groups.

## Experimental Section

The complexes  $[\text{Ni}_6(\text{CO})_6(\mu_2\text{CO})_6]^{2-}$  and  $[\text{Ni}_9(\text{CO})_9(\mu_2\text{CO})_9]^{2-}$  were synthesized according to literature methods. The samples for

the Raman spectra were prepared by sealing crystals of the complexes in a glass capillary under argon. The spectra were recorded by a Bruker RFS 100 with  $\text{Nd}^{3+}/\text{YAG}$  laser and Ge-diode detector (laser power 65 mW, resolution 4  $\text{cm}^{-1}$ , 300 scans for  $[\text{Ni}_6(\text{CO})_6(\mu_2\text{CO})_6]^{2-}$ ; laser power 40 mW, resolution 4  $\text{cm}^{-1}$ , 750 scans for  $[\text{Ni}_9(\text{CO})_9(\mu_2\text{CO})_9]^{2-}$ ).

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

## Results

The spectral data of more than 100 transition metal carbonyl clusters are collected in Tables 1–3, which separately list the clusters containing  $\mu_2$  CO,  $\mu_3$  CO, and both  $\mu_2$  and  $\mu_3$  CO, respectively. The collection is not exhaustive but includes a significant selection of clusters with

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**Table 2.** List of the Clusters Containing  $\mu_3(\text{CO})$  Only

no.	complex	no. $\mu_3(\text{CO})$	point group	no. IR bands predicted	no. IR bands obsd	ref
84	$[\text{Ir}_6(\text{CO})_{14}(\text{HgCl})_2]^{2-}$	2	$C_{2v}$	2	m(br)	12
85	$\text{Rh}_6(\text{CO})_{16}$	4	$T_d$	1	w, s	68
86	$\text{Co}_6(\text{CO})_{16}$	4	$T_d$	1	w, s	69
87	$\text{Ir}_6(\text{CO})_{16}$ red isomer	4	$T_d$	1	s(br)	14
88	$[\text{PtRh}_5(\text{CO})_{15}]^-$	4	$C_{2v}$	4	s	70

bridging COs. In particular, we have addressed our attention to the clusters whose relevant paper reports a figure with the infrared spectra, thus allowing a better analysis of the

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frequency/intensity behavior (in the tables, they are reported in bold characters). Details of the experimental spectra are summarized in a list where each band is classified on the basis of its approximate intensity (vs = very strong, s = strong, ms = medium-strong, m = medium, mw = medium-weak, w = weak) and, in parentheses, of its shape (sh = shoulder, br = broad). Together, the number of the IR allowed modes, calculated on the basis of the molecular symmetry, is indicated. We usually discarded complexes where only infrared solid-state spectra (in a Nujol mull or KBr disk) are reported. Almost invariably, these IR spectra show much more structure than those reported for species studied in solution. Clearly, factor group/site group effects provide the explanation of this additional structure; as a consequence, such spectra cannot immediately be related to

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**Table 3.** List of the Clusters Containing Both  $\mu_2(\text{CO})$  and  $\mu_3(\text{CO})$ 

no.	complex	no. bridging CO			point group	no. IR bands predicted $\mu_2/\mu_3$	no. IR bands obsd	ref
		$\mu_2$	$\mu_3$	total				
89	[Ru <sub>6</sub> (CO) <sub>18</sub> ] <sup>2-</sup>	2	2	4	C <sub>2v</sub>	2/3	m(br)	71
90	[Rh <sub>7</sub> N(CO) <sub>15</sub> ] <sup>2-</sup>	4	1	5	C <sub>s</sub>	4/1	m, mw, m	72
91	[Rh <sub>6</sub> CoN(CO) <sub>15</sub> ] <sup>2-</sup>	4	1	5	C <sub>s</sub>	4/1	m, mw, w	72
92	[Rh <sub>6</sub> IrN(CO) <sub>15</sub> ] <sup>2-</sup>	4	1	5	C <sub>s</sub>	4/1	m, mw, w	72
93	[Ru <sub>10</sub> H <sub>2</sub> (CO) <sub>25</sub> ] <sup>2-</sup>	4	1	5	C <sub>1</sub>	4/1	m(br)	73
94	[Co <sub>6</sub> (CO) <sub>15</sub> ] <sup>2-</sup>	3	3	6	C <sub>3v</sub>	2/2	s, s, w	74
95	[Ru <sub>11</sub> H(CO) <sub>27</sub> ] <sup>3-</sup>	6	1	7	C <sub>1</sub>	6/1	m(br)	73
96	[Ni <sub>9</sub> C(CO) <sub>17</sub> ] <sup>2-</sup>	4	4	8	C <sub>4v</sub>	2/2	ms, m(br)	27
97	Ni <sub>13</sub> Sb <sub>2</sub> (CO) <sub>24</sub> ] <sup>2-</sup>	4	4	8	C <sub>2h</sub>	2/2	m(br), w(sh)	75
98	Ni <sub>13</sub> Sb <sub>2</sub> (CO) <sub>24</sub> ] <sup>3-</sup>	4	4	8	C <sub>2h</sub>	2/2	m(br), w(sh)	75
99	Pd <sub>8</sub> (CO) <sub>8</sub> (PMe <sub>3</sub> ) <sub>7</sub>	6	2	8	C <sub>s</sub>	6/2	m, s	76
100	[Ni <sub>11</sub> Bi <sub>2</sub> (CO) <sub>18</sub> ] <sup>2-</sup>	6	2	8	C <sub>2h</sub>	3/1	m, w(sh)	77
101	[Ni <sub>11</sub> Bi <sub>2</sub> (CO) <sub>18</sub> ] <sup>3-</sup>	6	2	8	C <sub>2h</sub>	3/1	m, w(sh)	77
102	[Ni <sub>11</sub> Bi <sub>2</sub> (CO) <sub>18</sub> ] <sup>4-</sup>	6	2	8	C <sub>2h</sub>	3/1	m, w(sh)	77
103	[Rh <sub>6</sub> Ni(CO) <sub>16</sub> ] <sup>2-</sup>	6	3	9	C <sub>3v</sub>	4/2	m, m, m(sh)	78
104	[Ni <sub>12</sub> (CO) <sub>22</sub> Ge] <sup>2-</sup>	6	4	10	C <sub>1</sub>	6/4	m, mw	79
105	[Ni <sub>12</sub> (CO) <sub>22</sub> Sn] <sup>2-</sup>	6	4	10	C <sub>1</sub>	6/4	ms(sh), mw	79
106	[Rh <sub>9</sub> Cu(CO) <sub>19</sub> (NCMe) <sub>3</sub> ]	8	3	11	C <sub>s</sub>	8/3	m, w(br)	80
107	[Fe <sub>6</sub> Pd <sub>6</sub> H(CO) <sub>24</sub> ] <sup>3-</sup>	6	6	12	D <sub>3d</sub>	2/2	w(sh), m	81
108	[Fe <sub>6</sub> Pd <sub>6</sub> (CO) <sub>24</sub> ] <sup>4-</sup>	6	6	12	D <sub>3d</sub>	2/2	w(sh), m	81
109	Pd <sub>10</sub> (CO) <sub>12</sub> (Pbu <sub>3</sub> n) <sub>6</sub>	8	4	12	S <sub>4</sub>	4/2	s, s, m	82
110	[Rh <sub>9</sub> (CO) <sub>19</sub> ] <sup>3-</sup>	9	3	12	C <sub>1</sub>	9/3	ms, m(sh), m(sh)	83
111	[PtRh <sub>8</sub> (CO) <sub>19</sub> ] <sup>2-</sup>	9	3	12	C <sub>1</sub>	9/3	s(br)	84
112	[Rh <sub>10</sub> (CO) <sub>21</sub> ] <sup>2-</sup>	12	2	14	C <sub>1</sub>	12/2	sh, m, m, m, sh,	85
113	[Rh <sub>22</sub> (CO) <sub>35</sub> H <sub>x</sub> ] <sup>5-</sup>	21	2	23	C <sub>1</sub>	21/2	m, m(br)	86
114	[Rh <sub>22</sub> (CO) <sub>37</sub> ] <sup>4-</sup>	18	7	25	C <sub>3</sub>	12/5	m(br), m(sh), ms, w	87
115	[HNi <sub>34</sub> (CO) <sub>38</sub> C <sub>4</sub> ] <sup>5-</sup>	26	2	28	C <sub>i</sub>	13/1	s	88
116	[Ni <sub>35</sub> (CO) <sub>39</sub> C <sub>4</sub> ] <sup>5-</sup>	27	2	29	C <sub>1</sub>	27/2	ms, m(sh)	88
117	[Ni <sub>38</sub> Pt <sub>6</sub> (CO) <sub>48</sub> H <sub>3</sub> ] <sup>3-</sup>	12	18	30	D <sub>3d</sub>	3/5	ms, m(sh)	89
118	[Ni <sub>38</sub> Pt <sub>6</sub> (CO) <sub>48</sub> H <sub>2</sub> ] <sup>4-</sup>	12	18	30	D <sub>3d</sub>	3/5	ms, m(sh)	89
119	[Ni <sub>38</sub> Pt <sub>6</sub> (CO) <sub>48</sub> H] <sup>5-</sup>	12	18	30	D <sub>3d</sub>	3/5	ms, m(sh)	89
120	[Ni <sub>38</sub> Pt <sub>6</sub> (CO) <sub>48</sub> ] <sup>6-</sup>	12	18	30	D <sub>3d</sub>	3/5	ms, m(sh)	89
121	[Au <sub>6</sub> Pd <sub>6</sub> (Pd <sub>6-x</sub> Ni <sub>x</sub> )Ni <sub>20</sub> (CO) <sub>44</sub> ] <sup>6-</sup>	30	6	36	D <sub>3d</sub>	7/2	vs	90
122	[Au <sub>6</sub> Ni <sub>32</sub> (CO) <sub>44</sub> ] <sup>6-</sup>	30	6	36	D <sub>3d</sub>	7/2	vs, m(sh)	90
123	[Pd <sub>33</sub> Ni <sub>9</sub> (CO) <sub>41</sub> (PPH <sub>3</sub> ) <sub>6</sub> ] <sup>4-</sup>	24	12	36	D <sub>3h</sub>	6/3	s	91
124	[Ni <sub>36</sub> Pt <sub>4</sub> (CO) <sub>45</sub> ] <sup>6-</sup>	24	12	38	C <sub>3v</sub>	16/8	s	92
125	[Ni <sub>37</sub> Pt <sub>4</sub> (CO) <sub>46</sub> ] <sup>6-</sup>	27	12	39	C <sub>3v</sub>	18/8	s	92

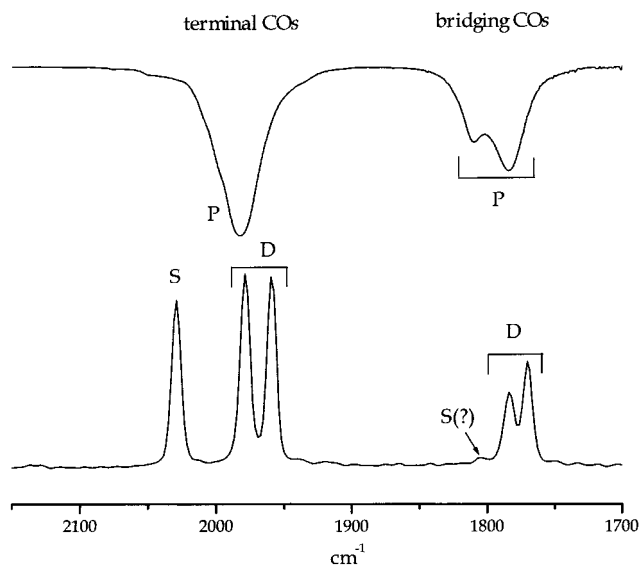
the molecular symmetry. Another potential problem is that more than one isomeric species may exist in solution. In this paper, we have included cases showing such complications, indicating what we believe to be their origin. We believe that this is preferable to excluding data which apparently do

not agree with our model, even if such exclusion could be justified.

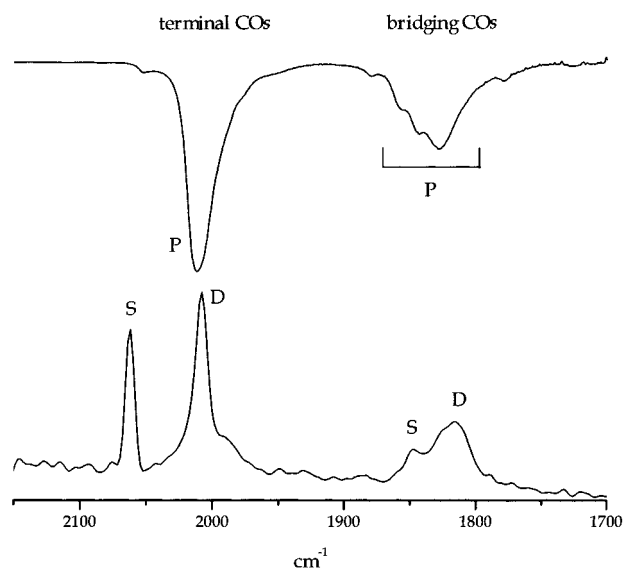
Raman spectra are usually not available in the literature. We have recorded the Raman spectra of two species, [Ni<sub>6</sub>(CO)<sub>6</sub>( $\mu_2$ CO)<sub>6</sub>]<sup>2-</sup> and [Ni<sub>9</sub>(CO)<sub>9</sub>( $\mu_2$ CO)<sub>9</sub>]<sup>2-</sup> (**16** and **34** in the Table 1), which are illustrated in Figures 1 and 2. Even if the spectra are recorded in different means (infrared, solution; Raman, crystals), we are confident that they can be strictly related. We demonstrated<sup>93</sup> that, when a large

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**Figure 1.** Infrared (upper curve, CH<sub>3</sub>CN solution) and Raman (lower curve, crystals) spectra of the complex [Ni<sub>6</sub>(CO)<sub>6</sub>(μ<sub>2</sub>CO)<sub>6</sub>][Ph<sub>4</sub>As]<sub>2</sub>.



**Figure 2.** Infrared (upper curve, CH<sub>3</sub>CN solution) and Raman (lower curve, crystals) spectra of the complex [Ni<sub>9</sub>(CO)<sub>9</sub>(μ<sub>2</sub>CO)<sub>9</sub>][Et<sub>4</sub>N]<sub>2</sub>.

counteraction exists in the crystal, it dilutes the cluster species and prevents any intermolecular coupling of the Raman vibrations (unlike the IR, they are not dipolar), and so, the Raman spectrum can be confidently treated as molecular.

Finally, Figure 3 illustrates the structural sketches of selected examples of the species listed in the tables.

## Discussion

First of all, we give a brief comment concerning the vibrations of the terminal CO groups. We have already discussed their behavior by a survey of a large list of species,<sup>2</sup> including the majority of the complexes presented here. It is appropriate to comment that the terminal ν(CO)s, for all of the species that we consider, follow the simple SHM; a cluster selection rule operates. That is, they show a single strong band in the infrared, the P mode, rarely with additional structure as weak/shoulder bands on the long wavelength

edge of the main band. We do not want to anticipate our conclusions, but the previous statement that the bridging carbonyl groups of a cluster are more sensitive to the cluster geometry than are the terminal groups<sup>5</sup> can be easily demonstrated. The present data can be compared with those reported in ref 2 (there are many entries common to the two papers) where it will be found that the spectra in the bridging region are more structured than the corresponding spectra in the terminal region. As an example, consider the case when the number of terminal carbonyls is the same as the number of bridging ones: all the bridging COs are symmetry-related, but the molecular symmetry is lower than cubic. Such a complex is the anion {[Ni(CO)<sub>10</sub>(μ<sub>2</sub>CO)<sub>10</sub>Ge]<sup>2-</sup> (**38**), of *D*<sub>5d</sub> symmetry. In the bridging region, this shows two bands some 20 cm<sup>-1</sup> apart, the higher in frequency giving the stronger band. The spectrum can be interpreted on either the point group model or the SHM, the former predicting an A<sub>2u</sub> + E<sub>u</sub> pattern whilst the latter, reflecting the sensitivity to metal atom asymmetry, predicts a split P band, again into A<sub>2u</sub> + E<sub>u</sub>. In this case, the group theoretical and spherical harmonic predictions are identical, but we note that only the bridging region shows evidence for the molecular asymmetry; the terminal region shows only one strong band.

If the bridging carbonyl groups obey the SHM, a strong infrared band is expected, possibly split into its components. So, splitting into three bands is understandable, but it seems that other reasons must be adduced to explain why some species have more than three infrared bands in the bridging region. This is the second point to be considered, and it is appropriate to anticipate the following discussion by highlighting one such example, that of Pd<sub>4</sub>(μ<sub>2</sub>CO)<sub>6</sub>(PBu<sub>3</sub>)<sub>4</sub>, (**17**), of *T*<sub>d</sub> symmetry. Like all of the others that we initially consider, it contains only μ<sub>2</sub> bridging CO groups. Group theory predicts one infrared band. Four are reported, spanning over 150 cm<sup>-1</sup>, stretching from the terminal to bridge regions. The presence of multiple species in solution seems clear.<sup>23</sup> An inherent problem with the present study is that of attempting to distinguish between examples exhibiting solution equilibria and those genuinely not conforming to the SHM.

We consider first the species listed in Table 1. Perhaps the most evident point is that the observed infrared spectra are usually simple, only for 3 examples have as many as 4 bands been reported, compared with group theoretical predictions of up to 26 bands. For complexes **1–11**, with between two and four bridging groups (so that in the SHM only S and P are spanned), a maximum of two infrared bands in the bridging region is observed. The simple SHM predicts one; for **6** and **7**, the two bands observed are very close and can be interpreted as a split P mode. However, for **1** and **3** there are splittings of some 40 cm<sup>-1</sup>, more than can reasonably be accounted for as a P-mode splitting. Both species have structures that are derived from octahedra and so could well be fluxional; the reported spectra are for solutions. We suspect that more than one isomer is present in these solutions.

Species **12–36**, with from five to nine bridging CO groups, are such that in the SHM S, P, and D harmonics are

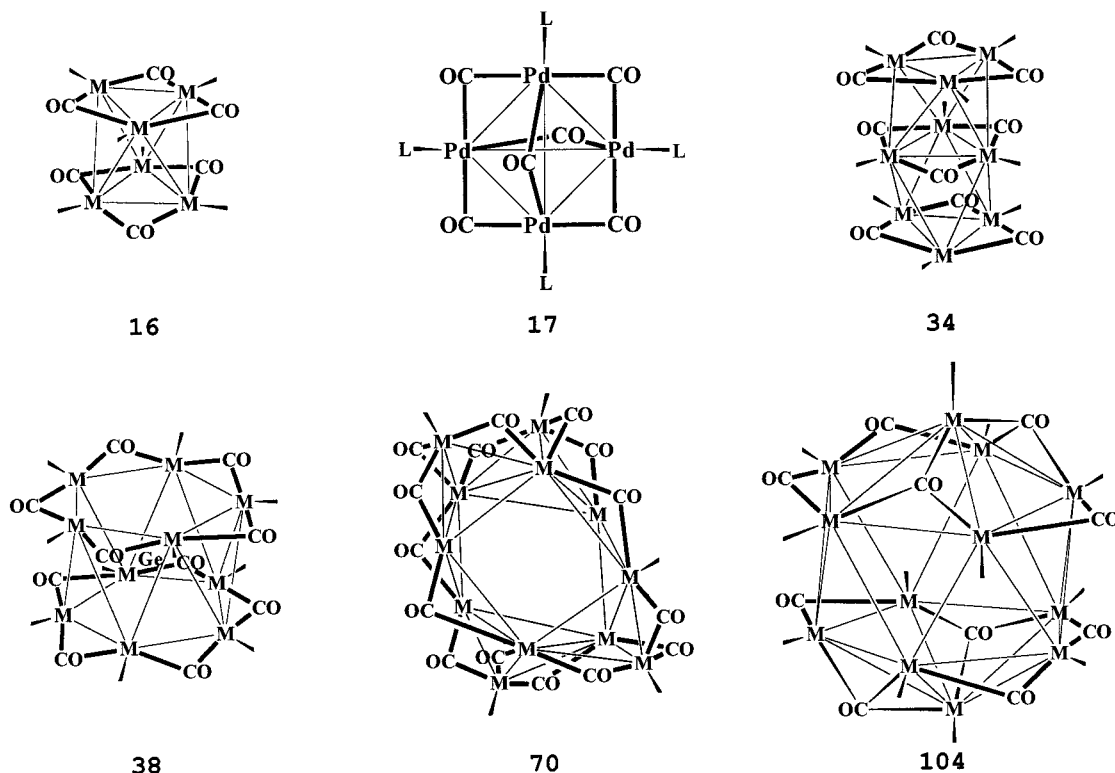


Figure 3. Sketches of selected examples of metal clusters.

spanned. That is, for them, the possibility of some weak intensity transfer from P to D harmonics exists, when allowed by the molecular symmetry.<sup>94</sup> Of these 25 examples, 1 example, number 17 already discussed, shows more infrared bands than predicted from the molecular point group. Five examples (16, 18, 32, 33, 35) conform to the point group predictions; the rest all have simpler spectra than predicted, eight having but a single infrared band.

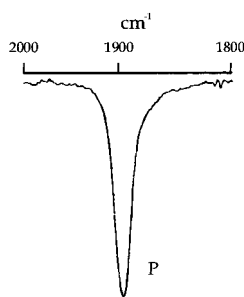
For two of those species, the infrared and Raman spectra are illustrated in Figures 1 and 2. These complexes are structurally related and consist of two or three triangular  $[\text{Ni}_3(\text{CO})_3(\mu_2\text{CO})_3]$  units, piled one on top of the other. Both species clearly follow the SHM, both in the terminal and in the bridging CO stretching regions. In each region, the spectra consist of an infrared band (P mode) between two Raman bands (S and D modes). In the  $\text{Ni}_6$  species, the D mode is clearly split into two components, something which does not occur with the larger (more spherical)  $\text{Ni}_9$  cluster, where some broadening but no splitting is apparent. It is noticeable, too, that in the former species the S mode of the bridging CO has quite low Raman intensity.

In the  $\text{Ni}_6$  species, that which has been assigned as the S mode appears some  $26\text{ cm}^{-1}$  above that assigned as P. For the  $\text{Ni}_9$  compound, the separation is  $34\text{ cm}^{-1}$ . For three of

the five complexes which are indicated previously as following the point group predictions, a similar pattern is followed, a shoulder appearing some  $30\text{ cm}^{-1}$  above a strong infrared band. Further, a weak band occurs below the strong infrared, consistent with a D mode intensity stealing from the P. The spectrum of the remaining compound,  $[\text{Pt}_9(\text{CO})_9(\mu_2\text{CO})_9]^{2-}$  (35), is entirely consistent with those just described but, in addition, looks rather like a better-resolved version of that of  $[\text{Ni}_9(\text{CO})_9(\mu_2\text{CO})_9]^{2-}$  (34). Overall, it is clear that for this group, even when there is more detail than predicted by the simple SHM, a refined SHM is applicable. When the point group predictions are valid, the SHM adds information by indicating qualitative relative band intensities. Finally, within this group there is one species,  $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$  (28), for which the spectra are clearly solvent dependent.<sup>32</sup> The problem of equilibria in solution is omnipresent.

The remaining entries of Table 1, all with 10 or more bridging carbonyls, do not follow the point group infrared predictions, except for one case (38). There are 24 that show a single infrared band, as predicted by the SHM, while 3 (67, 70, 74) show 4 (the largest number reported, although point group analyses predict up to 24). Not many spectra have themselves been given in the literature, but those available give a hint of broadened structure at the lower frequency end, not always detailed. This structure could well be associated with some weak activity of F spherical harmonic features; for 67 and 74, this seems clearly the explanation of the four reported bands. However, this does not seem to be the explanation for the spectrum of  $[\text{Ni}_9\text{Co}_3(\text{CO})_{20}\text{C}]^{3-}$  (70), which is unique. For this species, the terminal  $\nu(\text{CO})$  spectrum consists of a single band, but

(94) This argument may be clarified by reference to a parallel situation. The p and d orbitals of a transition metal complex can be regarded as associated with P and D spherical harmonics; the p orbitals are dipolar, the d, quadrupolar. For transition metal complexes, transitions involving the p orbitals are often strongly electric dipole allowed, whereas transitions within the d shell are not. Tetrahedral complexes are usually much more intensely colored than their octahedral counterparts because, although both are cubic, p-d mixing is symmetry-allowed in the former, leading to a dipolar component in the "forbidden" transitions and more intense "d-d" bands.



**Figure 4.** Infrared spectrum (DMF solution) of the complex  $[\text{HNi}_{32}\text{C}_6(\text{CO})_{36}][\text{MePh}_3\text{P}]_5$ .

the bridging  $\nu(\text{CO})$  spectrum consists of four. The crystal structure shows that the complex contains a near-random distribution of Co and Ni and, moreover, some semibridging CO groups.<sup>59</sup> It is reasonable to suspect the presence of several isomers in solution, but nevertheless, the different terminal/bridging  $\nu(\text{CO})$  patterns reinforce the conclusion that the bridging region is more molecular geometry-sensitive than is the terminal.

At the end of the list are reported the largest clusters of all, with the greatest number of bridging carbonyls. As we have found for terminal COs, the larger the cluster, the more strictly the SHM is followed. The complex  $[\text{HNi}_{38}\text{C}_6(\text{CO})_{42}]^{5-}$  (**83**), with  $D_{3d}$  symmetry, provides a good example. In this molecule, the crystal structure shows that 36 of the carbonyl groups are bridging; they fall into 3 sets, each with 12 members. It follows, since each spans the regular representation of  $D_{3d}$ , that six infrared features are group theoretically predicted. Experimentally, two bands, one with a shoulder, are observed split by less than  $20\text{ cm}^{-1}$ . A very similar pattern has been reported for  $[\text{Ni}_{38}\text{C}_6(\text{CO})_{42}]^{6-}$ ,<sup>67</sup> giving some confidence that the system is free of isomer complications. In  $D_{3d}$ , of course, the triply degenerate P mode of spherical symmetry splits into singly degenerate and doubly degenerate components with a 1:2 intensity ratio. That is, the spectra are in accord with the predictions of the SHM provided that allowance is made for the real molecular symmetry. Even clearer is the series  $[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{n-}$  (**78–81**), an extreme example, that of clusters containing only bridging carbonyl groups. In these  $O_h$  molecules, the crystal structure shows that the bridging carbonyl groups fall into a set of 12 and a set of 24.<sup>66</sup> Group theoretically, three infrared active bands are predicted. Figure 4 shows that there is only a single infrared band. Interestingly, and significantly, there is no evidence of any isotopic structure, notwithstanding the fact that  $\sim 40\%$  of the molecules contain  $^{13}\text{C}$ . This observation excludes the possibility that there is a single band because the bridge COs are vibrationally uncoupled from one another; the species provides the clearest example of a species obeying the SHM.

The few complexes containing only  $\mu_3$  bridging CO groups (in addition to terminal), for which infrared data are available, are listed in Table 2. They contain no more than four bridging COs, and so, rich spectra are not to be expected. When group theory predicts infrared active bands, only one is seen, consistent with the simple SHM. However, for two examples with  $T_d$  symmetry (**85** and **86**), where both group theory and

the SHM predict a single band, two are reported. Unfortunately, these are mull spectra, and we therefore place no great significance on the discrepancy with our predictions, attributing them to factor group effects. As mentioned earlier, in this paper we have generally not considered data obtained from mull spectra. Unfortunately, the spectra of all- $\mu_3$  species are so scarce that we had to relax this rule.

We now turn to a discussion of species with both  $\mu_2$  and  $\mu_3$  carbonyl bridges. Table 3 lists some 37 examples. It seems quite obvious that the spectra of all the species can only be interpreted on the basis of the SHM. Owing to the low symmetry generally exhibited, point group theory predicts many more infrared bands than those shown by the real spectra. An interesting problem is whether the (structurally very different)  $\mu_2$  and  $\mu_3$  bridging groups give rise to separate spectral features or are coupled together. It is reasonable to focus the attention to the species which have similar numbers of COs belonging to the two sets in order that the intensities of the bands are comparable. An example is provided by  $[\text{Ni}_9\text{C}(\text{CO})_{17}]^{2-}$  (**96**) with four  $\mu_2$  COs and four  $\mu_3$  COs. The presence of two bands separated by more than  $50\text{ cm}^{-1}$  clearly points to two separate P modes of the two sets. Similar is the spectral behavior of the complexes  $[\text{Ni}_{12}(\text{CO})_{23}\text{E}]^{2-}$  (**104**, E = Ge; **105**, E = Sn). Note that the terminal  $\nu(\text{CO})$  perfectly agree with the SHM predictions. On the other hand, the series formed by  $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{30}\text{H}_{6-n}]^{n-}$  (**117–120**) must be considered. These all have  $D_{3d}$  symmetry with 12  $\mu_2$  and 18  $\mu_3$ . Just two bands have been reported with frequencies which fall with formal anionic charge and are separated by not more than  $15\text{ cm}^{-1}$ . Here, it seems that there is no distinction between  $\mu_2$  and  $\mu_3$  features, the bands being due to the splitting of the unique P mode. The final entries in Table 3, corresponding to clusters with more than 40 metal atoms, show just a single band. The conclusion seems straightforward; the two sets of bridging carbonyls give rise to separate vibrational features when the clusters are not too large and the relevant frequencies lie in well-separated spectral regions. As the clusters become larger, the two features tend to collapse into a single spectral pattern, which eventually becomes a single band. The SHM is the only model in any way applicable and is the only one that can be blind to the distinction between  $\mu_2$  and  $\mu_3$  carbonyls.

## Conclusions

The present work has demonstrated the existence of remarkable simplifications in the vibrational spectra of bridging metal carbonyls. In general, the spectra are understandable on the basis of the SHM; we have not found a single example for which it was necessary to invoke the more complicated THM. Moreover, it is clear that the spectra of the smaller bridged species more often show splittings than do the spectra of their terminal counterparts, the splittings being understandable in terms of the molecular symmetry. This in accord with the observation that the spectra of bridge carbonyls are more sensitive to molecular geometry than are those of the terminal ones. The reason could be that the bridge carbonyls are attached to at least two metal atoms and so are more sensitive to the metal atom arrangement.

Equally, it could be that the bridge carbonyls are in closer proximity to the region of high electronic density of the cluster and thus more sensitive to its shape.

When there are several structurally different bridging COs, their spectral differences are only evident for smaller molecules, even if the difference is between  $\mu_2$  and  $\mu_3$  bridging carbonyls. So, the recent report<sup>95</sup> that a Pd<sub>145</sub> cluster shows but a single sharp band in the  $\mu_2(\text{CO})$  region cannot be taken as an indication that all of the CO groups are equivalent (the X-ray study does not locate them). One is tempted also to speculate that for extremely large clusters the spectral distinction between terminal and bridging carbonyls may become less evident.

However, this fact points to an additional problem area. The vibrational characteristics of small clusters have been used as models for the characterization of the vibrational spectra of species adsorbed on metal surfaces.<sup>96</sup> In this way,

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(95) Tran, N. T.; Powell, D. R.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4121.

“edge” and “face” bridging carbonyls have been distinguished. But we have found that this distinction is lost for large clusters. There are two possibilities evident to us. First, that the frequency separation observed for adsorbed carbonyls may reflect not the bonding of carbonyl groups but the electronic characteristics of the surface under study. Second, that the carbonyl groups studied on surfaces occur in small islands and so are better modeled by small clusters than by large. Of course, it is also possible that large clusters are not good models for surfaces, but we can see no obvious reason this should be the case.

**Acknowledgment.** This work has been supported by the Università di Torino through a Cooperation Agreement with the University of East Anglia (R.R. and S.F.A.K.) and by MURST through Cofin2000 (M.C.I. and P.L.S.).

IC020068A

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