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VI. CALCULATION OF FORCE CONSTANTS IN THE CO STRETCHING REGION OF *cis*-DISUBSTITUTED GROUP VI METAL CARBONYLS AND IRON CARBONYL COMPLEXES WITH C_{2v} SYMMETRY

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SUMMARY

For complexes of the type *cis*-$L_2M(CO)_4$ (M = Mo, W, Cr; L = a phosphine, arsine or amine), $(RHg)_2Fe(CO)_4$ (R = Me, Bu) and $(R_3M)_2Fe(CO)_4$ (M = Pb, Sn, Si or Ge) all the CO stretching force constants are calculated using a rigorous algebraic procedure based on the Cotton and Kraihanzel force field.

SYMMETRY AND CALCULATION OF FORCE CONSTANTS

In recent papers[1-3] a new method for the calculation of all the CO stretching force constants of substituted metal carbonyls was developed. The compounds treated in this work belong to the C_{2v} (or local C_{2v}) symmetry class, and therefore show four IR- and Raman-active stretching frequencies in the CO region ($2A_1+B_1+B_2$). The calculations for the force constants in the CO stretching region for complexes of this type as well as for other substituted metal carbonyls have been carried out previously using the C–K approximation method[4]. As reported earlier[1-3], this method could be improved using some interaction force constant relations which were found using orbital overlap theories outlined by Jones[5]. Strict mathematical combination of these relationships with the Cotton and Kraihanzel secular equations in their exact formulation directly yields the values of force constants in perfect accordance with the spectroscopic data.

For some compounds listed in Tables 1 and 2 the carbonyl stretching force constants have already been evaluated using either the C–K approximation method ($k_{t/2}=k_c=k_{c'}$), or the simplification[7] $k_c=k_{c'}$.

The calculations were mainly carried out in double precision using an IBM 360 type 30 computer of the Computing Laboratory of the University of Ghent.

RESULTS AND DISCUSSION

The complete set of five CO stretching force constants for the compounds treated in this paper are calculated for the first time.

TABLE I

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS OF *cis*-$L_2M(CO)_4$ COMPOUNDS (METHOD A)

No.	Compound	Ref.	Frequencies (cm⁻¹)				Force constants (mdynes/Å)				
			$A_1(1)$	$A_1(2)$	B_2	B_1	k_1	k_2	$k_{c'}$	k_c	k_t
1	$[(C_4H_9)_2P(C_6H_5)]_2Cr(CO)_4$[a]	6	2002	1906	1893	1874	14.62_9	15.14_2	0.3313_4	0.4394_0	0.6626_7
2	$[(C_4H_9)_3P]_2Mo(CO)_4$[a]	6	2015	1913	1899	1886	14.78_8	15.27_9	0.3541_8	0.4161_0	0.7083_6
3	$[(C_4H_9)_2P(C_6H_5)]_2Mo(CO)_4$[a]	6	2016	1917	1902	1888	14.83_4	15.31_1	0.3470_5	0.4311_7	0.6941_0
4	$[(C_4H_9)P(C_6H_5)_2]_2Mo(CO)_4$[a]	6	2021	1924	1904	1892	14.93_5	15.35_0	0.3512_6	0.4719_1	0.7025_3
5	$[(C_4H_9)_3P]_2W(CO)_4$[a]	6	2012	1908	1889	1882	14.74_0	15.15_7	0.3695_9	0.4292_5	0.7391_8
6	$[(C_6H_5)P(C_4H_9)_2]_2W(CO)_4$[a]	6	2016	1911	1894	1886	14.78_8	15.23_3	0.3696_0	0.4162_6	0.7392_1
7	$[(C_6H_5)_2P(C_4H_9)]_2W(CO)_4$[a]	6	2018	1918	1898	1890	14.87_8	15.27_6	0.3601_2	0.4445_1	0.7202_4
8	$(PF_3)_2Mo(CO)_4$[b]	7	2091	2022	2022	2003	16.48_0	16.97_8	0.2293_4	0.2691_7	0.4586_7
9	$(CF_3PF_2)_2Mo(CO)_4$[b]		2094	2036	2036	2013	16.65_8	17.13_6	0.1935_7	0.2849_2	0.3871_4
		7	2094	2036	2013	2036	16.94_6	16.84_8	0.2376_9	0.1966_9	0.4753_8
10	$[(CF_3)_2PF]_2Mo(CO)_4$[b]		2093	2033	2033	2013	16.63_6	17.10_0	0.2000_5	0.2635_0	0.4001_0
		7	2093	2033	2013	2033	16.88_2	16.85_4	0.2406_9	0.1822_3	0.4813_8
11	$(CCl_3PF_2)_2Mo(CO)_4$[c]		2079	2015	2010	1990	16.32_6	16.77_1	0.2235_2	0.3252_2	0.4470_5
		7	2079	2015	1990	2010	16.57_7	16.52_0	0.2595_0	0.2532_7	0.5190_0
12	$(Et_2NPF_2)_2Mo(CO)_4$[c]		2055	1974	1950	1942	15.71_6	15.98_9	0.3124_7	0.4777_8	0.6249_4
		7	2055	1974	1942	1950	15.82_0	15.88_5	0.3233_9	0.4559_5	0.6467_7
13	$(C_5H_{10}NPF_2)_2Mo(CO)_4$[c]		2053	1977	1952	1942	15.73_8	15.99_0	0.2970_8	0.5001_3	0.5941_7
		7	2053	1977	1942	1952	15.87_4	15.85_4	0.3079_7	0.4783_6	0.6159_5
14	$(PH_3)_2Mo(CO)_4$[a]	8	2036	1946	1932	1923	15.31_4	15.72_2	0.3202_4	0.3729_8	0.6404_9
15	$(NH_3)_2Mo(CO)_4$[d]	8	2010	1837	1915	1780	13.30_6	15.48_3	0.3326_2	0.5045_6	0.6652_4
16	$(PMe_3)_2Cr(CO)_4$[e]	9	2001	1901	1873	1866	14.59_5	14.91_6	0.3707_3	0.5266_8	0.7414_6
			2001	1901	1866	1873	14.68_1	14.83_1	0.3809_1	0.5063_2	0.7618_1
17	$(PMe_2Ph)_2Cr(CO)_4$[c]	9	2003	1905	1880	1866	14.61_1	15.00_1	0.3599_3	0.5421_5	0.7198_5
18	$(AsMe_2Ph)_2Cr(CO)_4$[c]	9	2008	1904	1893	1873	14.61_2	15.18_5	0.3529_4	0.4369_7	0.7058_8
19	$(PMe_3)_2Mo(CO)_4$[e]	9	2016	1910	1896	1874	14.68_0	15.25_8	0.3667_4	0.4901_1	0.7334_7
			2016	1910	1874	1896	14.93_9	14.99_9	0.4046_8	0.4142_3	0.8093_5
20	$(PMe_2Ph)_2Mo(CO)_4$[e]	9	2011	1912	1895	1878	14.72_6	15.21_0	0.3500_7	0.4755_6	0.7001_4
			2011	1912	1878	1895	14.92_9	15.00_7	0.3782_9	0.4191_2	0.7565_8
21	$(AsMe_2Ph)_2Mo(CO)_4$[e]	9	2016	1912	1898	1869	14.65_4	15.27_7	0.3605_5	0.5404_1	0.7211_0
22	$(PMe_3)_2W(CO)_4$[c]	9	2008	1898	1880	1862	14.51_7	15.05_2	0.3854_4	0.5079_8	0.7708_9
			2008	1898	1862	1880	14.72_8	14.84_0	0.4158_5	0.4471_6	0.8317_0
23	$(PMe_2Ph)_2W(CO)_4$[e]	9	2008	1901	1883	1873	14.61_8	15.07_9	0.3762_0	0.4436_8	0.7524_0
			2008	1901	1873	1883	14.73_4	14.96_3	0.3941_1	0.4078_5	0.7882_2
24	$(AsMe_2Ph)_2W(CO)_4$[e]	9	2012	1908	1887	1862	14.59_7	15.13_4	0.3733_2	0.5883_3	0.7466_4
25	$[EtN(PF_2)_2]Mo(CO)_4$[f]		2066	1991	1973	1963	15.98_4	16.29_7	0.2842_3	0.4140_6	0.5684_6
		10	2066	1991	1963	1973	16.11_2	16.16_9	0.2996_7	0.3831_9	0.5993_3
26	$[EtN(PPh_2)_2]Mo(CO)_4$		2023	1924	1907	1887	14.88_9	15.39_8	0.3522_2	0.5014_2	0.7044_3
		11	2023	1924	1887	1907	15.13_1	15.15_6	0.3844_6	0.4369_3	0.7689_2
27	$(HgMe)_2Fe(CO)_4$[g]	12	2048	1978	1989	1956	15.71_5	16.38_5	0.1997_0	0.2566_4	0.3993_9
28	$(HgBu)_2Fe(CO)_4$[g]	12	2042	1970	1983	1950	15.60_2	16.28_9	0.2001_5	0.2378_5	0.4002_9
29	$(PbEt_3)_2Fe(CO)_4$[g]	12	2040	1976	1985	1958	15.71_1	16.29_0	0.1849_2	0.2204_5	0.3698_3
30	$(SnMe_3)_2Fe(CO)_4$[g]	12	2057	1987	1998	1968	15.88_3	16.53_1	0.2005_9	0.2339_7	0.4011_8
31	$(SiCl_3)_2Fe(CO)_4$[g]	12	2125	2078	2070	2061	17.41_5	17.66_9	0.1781_9	0.2518_9	0.3563_8
32	$(SiEt_3)_2Fe(CO)_4$[g]	12	2064	2000	2025	1989	16.11_4	16.85_0	0.1406_7	0.1294_8	0.2813_4
33	$(GeEt_3)_2Fe(CO)_4$[g]	12	2058	1990	1999	1971	15.93_3	16.54_5	0.1995_7	0.2364_8	0.3991_3
34	$(SnMe_3)_2Fe(CO)_4$[g]	12	2057	1987	1998	1963	15.84_3	16.53_1	0.2005_9	0.2736_8	0.4011_7
35	$(PbEt_3)_2Fe(CO)_4$[g]	12	2040	1976	1985	1958	15.71_1	16.29_0	0.1849_2	0.2204_5	0.3698_4

[a] In cyclohexane. [b] Vapour. [c] In hexane. [d] In nujol mull. [e] In $CHCl_3$. [f] In CCl_4. [g] In n-hexadecane.

TABLE 2

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS OF *cis*-$L_2M(CO)_4$ COMPOUNDS (METHOD B)
For references see Table 1.

No.	Compound	Frequencies (cm^{-1})				Force constants (mdynes/Å)				
		$A_1(1)$	$A_1(2)$	B_2	B_1	k_1	k_2	$k_{c'}$	k_c	k_t
1	$[(C_4H_9)_2P(C_6H_5)]_2Cr(CO)_4$	2002	1906	1893	1874	14.76_5	15.00_5	0.3759_6	0.5757_2	0.5263_5
2	$[(C_4H_9)_3P]_2Mo(CO)_4$	2015	1913	1899	1886	14.93_4	15.13_3	0.4016_4	0.5621_7	0.5622_9
3	$[(C_4H_9)_2P(C_6H_5)]_2Mo(CO)_4$	2016	1917	1902	1888	14.78_0	15.16_5	0.3913_8	0.5773_4	0.5479_3
4	$[(C_4H_9)P(C_6H_5)_2]_2Mo(CO)_4$	2021	1924	1904	1892	15.09_7	15.18_9	0.3865_4	0.6332_9	0.5411_5
5	$[(C_4H_9)_3P]_2W(CO)_4$	2012	1908	1889	1882	14.90_4	14.99_4	0.4113_9	0.5924_8	0.5759_5
6	$[(C_4H_9)_2P(C_6H_5)]_2W(CO)_4$	2016	1911	1894	1886	14.94_6	15.07_5	0.4151_2	0.5743_0	0.5811_7
7	$[(C_4H_9)P(C_6H_5)_2]_2W(CO)_4$	2018	1918	1898	1890	15.04_1	15.11_2	0.3975_5	0.6081_8	0.5565_8
8	$(PF_3)_2Mo(CO)_4$	2091	2022	2022	2003	16.55_9	16.89_9	0.2711_7	0.3481_9	0.3796_4
9	$(CF_3PF_2)_2Mo(CO)_4$	2094	2036	2036	2013	16.72_4	17.06_9	0.2288_9	0.3516_3	0.3204_4
10	$[(CF_3)_2PF]_2Mo(CO)_4$	2093	2033	2033	2013	16.70_5	17.03_1	0.2365_5	0.3324_4	0.3311_7
		2093	2033	2013	2033	17.03_3	16.70_3	0.2356_8	0.3336_6	0.3299_5
11	$(CCl_3PF_2)_2Mo(CO)_4$	2079	2015	2010	1990	16.41_1	16.68_6	0.2585_4	0.4103_2	0.3619_5
12	$(Et_2NPF_2)_2Mo(CO)_4$	2055	1974	1942	1950	Negative *y* values				
13	$(C_5H_{10}NPF_2)_2Mo(CO)_4$	2053	1977	1952	1942	Negative *y* values				
14	$(PH_3)_2Mo(CO)_4$	2036	1946	1932	1923	15.45_0	15.58_6	0.3605_9	0.5087_7	0.5047_0
15	$(NH_3)_2Mo(CO)_4$	2010	1837	1915	1780	13.37_2	15.41_7	0.4281_1	0.5704_5	0.5993_6
16	$(PMe_3)_2Cr(CO)_4$	2001	1801	1873	1866	Negative *y* values				
17	$(PMe_2Ph)_2Cr(CO)_4$	2003	1905	1880	1866	Negative *y* values				
18	$(AsMe_2Ph)_2Cr(CO)_4$	2008	1904	1893	1873	14.75_1	15.04_5	0.4047_4	0.5762_2	0.5666_3
19	$(PMe_3)_2Mo(CO)_4$	2016	1910	1896	1874	14.83_0	15.10_8	0.4167_0	0.6402_0	0.5833_9
20	$(PMe_2Ph)_2Mo(CO)_4$	2011	1912	1895	1878	14.87_8	15.05_8	0.3915_1	0.6275_8	0.5481_1
21	$(AsMe_2Ph)_2Mo(CO)_4$	2016	1912	1898	1869	14.80_3	15.12_8	0.4092_8	0.6885_1	0.5729_9
22	$(PMe_3)_2W(CO)_4$	2008	1898	1880	1862	14.68_2	14.88_6	0.4326_5	0.6731_5	0.6057_1
23	$(PMe_2Ph)_2W(CO)_4$	2008	1901	1883	1873	14.78_1	14.91_6	0.4214_4	0.6060_7	0.5900_1
24	$(AsMe_2Ph)_2W(CO)_4$	2012	1908	1887	1862	14.76_7	14.96_4	0.4117_9	0.7584_6	0.5765_0
25	$[EtN(PF_2)_2]Mo(CO)_4$	2066	1991	1963	1973	Negative *y* values				
26	$[EtN(PPh_2)_2]Mo(CO)_4$	2023	1924	1907	1887	15.04_2	15.24_5	0.3939_0	0.6543_9	0.5514_6
27	$(HgMe)_2Fe(CO)_4$	2048	1978	1989	1956	15.77_2	16.32_7	0.2445_1	0.3137_3	0.3423_1
28	$(HgBu)_2Fe(CO)_4$	2042	1970	1983	1950	15.65_7	16.23_3	0.2461_6	0.2935_1	0.3446_3
29	$(PbEt_3)_2Fe(CO)_4$	2040	1976	1985	1958	15.76_5	16.23_6	0.2256_8	0.2743_3	0.3159_5
30	$(SnMe_3)_2Fe(CO)_4$	2057	1987	1998	1968	15.94_0	16.47_3	0.2456_0	0.2913_1	0.3438_3
31	$(SiCl_3)_2Fe(CO)_4$	2125	2078	2070	2061	17.49_2	17.59_2	0.1991_6	0.3294_4	0.2788_3
32	$(SiEt_3)_2Fe(CO)_4$	2064	2000	2025	1989	16.14_4	16.82_0	0.1795_0	0.1595_2	0.2512_9
33	$(GeEt_3)_2Fe(CO)_4$	2058	1990	1999	1971	15.99_2	16.48_6	0.2431_4	0.2952_1	0.3404_0
34	$(SnMe_3)_2Fe(CO)_4$	2057	1987	1998	1963	15.90_0	16.47_3	0.2456_0	0.3310_2	0.3438_3
35	$(PbEt_3)_2Fe(CO)_4$	2040	1976	1985	1958	15.76_5	16.23_6	0.2256_8	0.2743_3	0.3159_5

Again two methods of evaluation were tried, namely A and B. Both these methods were already outlined in a previous paper[2]. The values listed in Table 1 are found using method A, whereas the physically acceptable force constants resulting from method B are presented in Table 2. All corresponding *y* values are positive[2].

For some of the compounds of Table 1 (compds. 12, 16, 19, 20, 22, 23, 25, 26) there are two assignments which result in sets of force constants to both of which the sequence $k_1 < k_2$ applies. Since a rigorous assignment should be based upon arguments other than band positions and intensities only, a choice between the two assignments could not be made and therefore both of them are presented.

For other complexes of Table 1 (compds, 9, 10, 11, 13) there are also two possible assignments, but one of them results in $k_1 < k_2$, the other in $k_1 > k_2$.

As Cotton and Kraihanzel developed their secular equations on the explicit assumption that the substituent ligands in metal carbonyl complexes have poorer π-acceptor properties than CO, resulting in the criterion $k_1 < k_2$, and since the calculations presented in this series of papers are mainly based on the CK force field, the assignment resulting in the sequence $k_1 < k_2$ for the radial and axial CO stretching force constants is preferred.

However, inspection of some fluorophosphine carbonyl complexes of Table 1 indicates that for one of the assignments listed, k_1 and k_2 are of similar magnitude. Since it is well known that some fluorophosphine compounds [CF_3PF_2, $(CF_3)_2PF$, PF_3] are strong π-acceptor ligands with acceptor characteristics similar to those of CO, the spectra could also agree with $k_1 \leqslant k_2$ or even $k_1 \geqslant k_2$ for these complexes.

It is also very important to stress that the magnitude of k_1 and k_2 depends strongly on the relative frequencies of the B_1 and B_2 modes. Only an exact assignment of these frequencies could allow conclusions about $k_1 > k_2$ or $k_1 < k_2$.

The force constants for some compounds presented in Table 2 (compds. 12. 13, 16, 17, 25) yield negative y values. Since y is a factor related to the change in π-overlap integral occurring on the substitution of a CO group by a ligand in a metal carbonyl, it cannot be negative[1,2,3].

It is also important to note that to the interaction force constants obtained by method B, the sequence $k_{c'} < k_t < k_c$ applies whereas method A results into a pattern of force constants given by the general sequence[1-3] $k_{c'} < k_c < k_{t'}$ which has also been found for other metal carbonyl substitution products by Kaesz *et al.*[13] using isotopic substitution methods. For these two reasons we must conclude that the inclusion of angular correction terms in the calculation of interaction force constants[14] does not improve the results.

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