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V*. CALCULATION OF CO STRETCHING FORCE CONSTANTS OF *cis*-DISUBSTITUTED GROUP VI METAL CARBONYLS AND (ORGANO) GROUP IV METAL IRON CARBONYL COMPLEXES WITH LOCAL C_{2v} SYMMETRY

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SUMMARY

Using the Cotton and Kraihanzel force field, a more exact direct method is applied for calculating the CO stretching force constants of substituted metal carbonyls of general formula *cis*-$L_2M(CO)_4$ (M = Mo, W, Cr; L = phosphine or amine) and of complexes of formula $[R_2MFe(CO)_4]_2$ (M = Si, Ge, Sn or Pb), $(R_3Sn)_2Fe(CO)_4$, $R_4M_3[Fe(CO)_4]_4$ (M = Sn or Pb) and $M[Fe(CO)_4]_4$ (M = Ge, Sn or Pb).

SYMMETRY AND CALCULATION OF FORCE CONSTANTS

In a previous paper[1] we have described a rigorous algebraic method for direct evaluation of CO stretching force constants in substituted transition metal carbonyls of formula $[LM(CO)_4]_2$ where M is a Group VIIA metal. This method is based upon the Cotton and Kraihanzel force field[2] and orbital overlap theories outlined by Jones[3] and further developed by Abel *et al.*[4]. As stated, the molecular point group for these compounds is D_{2h}, but this could be reduced to a local C_{2v} carbonyl environment.

The (organo) Group IV metal iron carbonyl complexes listed in Table 1 belong to the point group C_{2v}, D_{2h} or D_{2d}. However, even for the latter two classes the analysis could also be done according to a local C_{2v} symmetry to each octahedron moiety of the molecule. Although the calculation of CO stretching force constants for the organometal Group IV (carbonyl) iron compounds have already been done by Dalton *et al.*[5], their procedure could be modified yielding more acceptable results as was mentioned in an earlier paper[6].

The compounds of the type *cis*-$L_2M(CO)_4$ (M = Mo, W, Cr) listed in Tables 2 and 3 belong to the C_{2v} point group. The IR and Raman active CO bands are $2A_1 + B_1 + B_2$. The CO stretching force constants have been evaluated previously, but only within the frame of the Cotton and Kraihanzel's approximation $k_c = k_{c'} = k_t/2 = k_i$.

Using the interaction force constant relations and the secular equations

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*For Part IV see ref. 1.

TABLE 1

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS OF GROUP IV METAL IRON CARBONYL COMPLEXES

Compound	Ref.	Frequencies (cm^{-1})				Force constants (mdyne/Å)				
		$A_1(1)$	$A_1(2)$	B_2	B_1	k_1	k_2	$k_{c'}$	k_c	k_t
$Me_4Sn_3[Fe(CO)_4]_4$[a]	8	2054	1989	2026	1980	15.93_4	16.79_4	0.1046_5	0.0936_6	0.2092_9
						Negative y-values				
$Et_4Sn_3[Fe(CO)_4]_4$[a]	8	2054	1988	2026	1978	15.91_0	16.79_4	0.1047_9	0.1013_3	0.2095_8
						Negative y-values				
$Bu_4Sn_3[Fe(CO)_4]_4$[a]	8	2050	1987	2023	1976	15.88_5	16.73_7	0.1007_9	0.1086_6	0.2015_6
						15.90_1	16.72_1	0.1324_2	0.1248_3	0.1854_0
$Me_4Pb_3[Fe(CO)_4]_4$[a]	8	2048	1986	2021	1977	15.88_5	16.70_4	0.1005_4	0.0929_2	0.2010_8
						Negative y-values				
$Ge[Fe(CO)_4]_4$[a]	8	2074	2031	2048	2012	16.53_9	17.13_6	0.0946_6	0.1823_9	0.1893_1
						16.55_9	17.11_6	0.1209_0	0.2024_4	0.1692_6
$Sn[Fe(CO)_4]_4$[a]	8	2072	2027	2044	2010	16.49_3	17.08_4	0.1014_1	0.1686_6	0.2028_2
						16.51_5	17.06_2	0.1291_5	0.1906_7	0.1808_1
$Pb[Fe(CO)_4]_4$[a]	8	2067	2022	2042	2012	16.46_2	17.03_1	0.0916_7	0.1056_8	0.1833_5
						16.48_0	17.01_3	0.1180_3	0.1237_8	0.1652_4
$(Et_2SnCl)_2Fe(CO)_4$[a]	8	2080	2009	2029	1996	16.26_5	16.99_5	0.1805_8	0.1673_8	0.3611_6
						16.30_9	16.95_1	0.2262_2	0.2118_3	0.3167_1
$(Bu_2SnCl)_2Fe(CO)_4$[a]	8	2077	2005	2026	1991	16.19_1	16.94_6	0.1807_1	0.1743_5	0.3614_1
						16.23_5	16.90_2	0.2267_7	0.2182_9	0.3174_7
$(Me_3Sn)_2Fe(CO)_4$[b]	9	2057	1987	1998	1968	15.88_3	16.53_1	0.2005_9	0.2339_7	0.4011_7
						15.94_0	16.47_3	0.2456_0	0.2913_1	0.3438_3
$[Ph_2SnFe(CO)_4]_2$[a]	8	2051	2010	2010	2001	16.31_8	16.59_3	0.1345_5	0.1402_0	0.2691_0
						16.36_5	16.54_7	0.1590_9	0.1865_7	0.2227_3
$[Me_2SnFe(CO)_4]_2$[a]	8	2046	1998	1998	1988	16.12_8	16.44_3	0.1568_6	0.1589_6	0.3137_2
						16.18_2	16.38_9	0.1854_8	0.2130_1	0.2596_7
$[Et_2SnFe(CO)_4]_2$[a]	8	2042	1994	1994	1982	16.04_7	16.37_8	0.1565_5	0.1746_7	0.3131_0
						16.10_1	16.32_4	0.1851_1	0.2286_1	0.2591_6
$[Bu_2SnFe(CO)_4]_2$[a]	9	2041	1993	1993	1981	16.03_1	16.36_2	0.1564_7	0.1745_8	0.3129_5
						16.08_5	16.30_8	0.1850_2	0.2285_0	0.2590_3
$[Me_2PbFe(CO)_4]_2$[a]	8	2037	1991	1991	1984	16.03_5	16.31_6	0.1497_3	0.1310_8	0.2994_6
						16.08_7	16.26_5	0.1770_5	0.1826_7	0.2478_6
$[Et_2PbFe(CO)_4]_2$[a]	8	2031	1985	1985	1975	15.91_5	16.21_9	0.1492_8	0.1546_4	0.2985_7
						15.96_6	16.16_8	0.1765_2	0.2060_9	0.2471_3
$[Cl_2SiFe(CO)_4]_2$[a]	10	2094	2048	2053	2038	16.92_6	17.31_2	0.1410_1	0.1440_2	0.2820_2
						16.96_9	$17{\cdot}26_9$	0.1709_9	0.1866_6	0.2393_8
		2094	2053	2048	2038	16.99_2	17.24_5	0.1491_6	0.2105_8	0.2983_2
						17.05_3	17.18_5	0.1699_5	0.2709_6	0.2379_3
$[Me_2GeFe(CO)_4]_2$[b]	11	2053	2000	2000	1987	16.14_4	16.50_9	0.1735_9	0.1915_0	0.3471_7
						16.20_4	16.44_9	0.2052_5	0.2513_2	0.2873_6
$[Et_2GeFe(CO)_4]_2$[b]	11	2051	1998	1996	1982	16.09_4	16.45_4	0.1781_8	0.2219_6	0.3563_6
						16.15_9	16.38_9	0.2085_6	0.2863_4	0.2919_9
		2051	1996	1998	1982	16.06_8	16.48_0	0.1749_6	0.1961_3	0.3499_2
						16.12_6	16.42_2	0.2087_4	0.2538_1	0.2922_4

[a] In cyclohexane. [b] In n-hexadecane.

described earlier[1], we were able to calculate all five physically acceptable CO stretching force constants using pure classical mathematics.

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 exact values of the CO stretching force constants for the (organo) Group IV metal iron carbonyl complexes are listed in Table 1. For each compound, the upper row of accepted force constants is found using method A and the lower one using method B. The methods A and B were already described in a previous report[1]. For the compounds of the type *cis*-$L_2M(CO)_4$ with pure C_{2v} symmetry, the physically acceptable force constants calculated according to method A are presented in Table 2,

TABLE 2

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

Compound	Ref.	Frequencies (cm^{-1})				Force constants (mdyne/Å)				
		$A_1(1)$	$A_1(2)$	B_2	B_1	k_1	k_2	$k_{c'}$	k_c	k_t
$(PCl_3)_2Mo(CO)_4$[a]	12	2072	2004	1944	1986	16.22_9	16.55_8	0.2466_3	0.2925_5	0.4932_6
		2072	2004	1986	1944	16.32_7	16.46_0	0.2619_5	0.2619_1	0.5239_0
$(PCl_2OC_2H_5)_2Mo(CO)_4$[a]	12	2063	1988	1977	1968	15.97_0	16.33_3	0.2702_4	0.3212_8	0.5404_7
		2063	1988	1968	1977	16.07_9	16.22_4	0.2873_1	0.2871_3	0.5746_3
$[P(OCH_3)_3]_2Mo(CO)_4$[a]	12	2037	1946	1926	1921	15.32_4	15.65_8	0.3350_6	0.4138_6	0.6701_3
		2037	1946	1921	1926	15.38_5	15.59_8	0.3437_4	0.3965_2	0.6874_8
$[P(C_6H_5)_3]_2Mo(CO)_4$[a]	12	2023	1929	1911	1899	15.01_6	15.43_2	0.3384_6	0.4452_2	0.6769_2
		2023	1929	1899	1911	15.16_0	15.28_8	0.3587_1	0.4047_1	0.7174_2
$\{C_2H_4[P(C_6H_5)_2]_2\}Cr(CO)_4$[b]	13	2009	1914	1899	1877	14.72_0	15.23_8	0.3334_1	0.4850_2	0.6668_2
$\{C_2H_4[P(C_6H_5)_2]_2\}Mo(CO)_4$[b]	13	2020	1919	1907	1881	14.78_8	15.39_0	0.3478_9	0.4924_2	0.6957_8
$\{C_2H_4[P(C_6H_5)_2]_2\}W(CO)_4$[b]	13	2016	1912	1901	1876	14.69_7	15.31_0	0.3543_9	0.4767_5	0.7087_7
$[P(C_2H_5)_3]_2Mo(CO)_4$[a]	12	2016	1915	1900	1890	14.83_6	15.29_3	0.3532_6	0.4033_6	0.7065_2
		2016	1915	1890	1900	14.95_2	15.17_7	0.3717_9	0.3662_9	0.7435_9
$[P(CH_3)_3]_2Mo(CO)_4$[a]	12	2019	1920	1893	1903	15.02_1	15.21_8	0.3693_7	0.3883_6	0.7387_4
		2019	1920	1903	1893	14.90_3	15.33_5	0.3515_0	0.4241_0	0.7030_0
$[(CH_3SCH_2^-)_2]_2Cr(CO)_4$[c]	14	2020	1914	1898	1869	14.68_1	15.29_8	0.3715_0	0.5665_9	0.7429_9
$[(CH_3SCH_2^-)_2]_2Mo(CO)_4$[c]	14	2030	1919	1905	1868	14.71_3	15.43_3	0.3849_0	0.6140_9	0.7698_0
$[(CH_3SCH_2^-)_2]_2W(CO)_4$[c]	14	2023	1910	1896	1867	14.63_8	15.30_4	0.3897_1	0.5541_9	0.7794_2
$(CH_3CN)_2Cr(CO)_4$[d]	15	2019	1882	1908	1843	14.16_2	15.44_5	0.3679_2	0.4382_8	0.7358_3
$(CH_3CN)_2Mo(CO)_4$[d]	15	2023	1881	1912	1833	14.07_6	15.51_3	0.3709_6	0.5006_5	0.7419_2
$(CH_3CN)_2W(CO)_4$[e]	15 16	2023	1880	1900	1840	14.14_9	15.39_2	0.4027_7	0.4699_0	0.8055_4
$(DMF)_2W(CO)_4$	17	1997	1832	1858	1791	13.44_5	14.84_6	0.4489_6	0.4847_2	0.8979_1
$(C_2H_8N_2)Cr(CO)_4$[f]	18	2004	1855	1873	1810	13.75_2	15.01_9	0.4221_0	0.5150_4	0.8442_0
$(C_2H_8N_2)Mo(CO)_4$[f]	18	2015	1864	1890	1818	13.86_2	15.25_4	0.4103_5	0.5076_0	0.8207_0
$(C_2H_8N_2)W(CO)_4$[f]	18	2006	1852	1867	1809	13.73_8	14.97_4	0.4450_4	0.5155_4	0.8900_8
$(C_5H_5N)_2Cr(CO)_4$[e]	18	2020	1878	1899	1837	14.10_8	15.36_4	0.3965_3	0.4726_5	0.7930_6
$(C_5H_5N)_2Mo(CO)_4$[e]	18	2025	1881	1907	1839	14.13_6	15.47_5	0.3908_0	0.4713_9	0.7815_9
$(C_5H_5N)_2W(CO)_4$[c]	18	2012	1869	1888	1828	13.97_9	15.20_9	0.4030_3	0.4771_5	0.8060_6
(2,2'-bipyridyl)$Mo(CO)_4$[c]	18	2017	1878	1909	1829	14.01_9	15.44_6	0.3604_9	0.5025_9	0.7209_7
(2,2'-bipyridyl)$W(CO)_4$[c]	18	2010	1873	1899	1826	13.96_7	15.30_3	0.3662_3	0.4953_5	0.7324_5

[a] In saturated hydrocarbon. [b] In 1,2-dichloroethane. [c] In CH_3Cl. [d] In nujol. [e] In CH_3CN. [f] In CH_3NO_2.

TABLE 3

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS FOR *cis*-$L_2M(CO)_4$ COMPOUNDS. METHOD B[a]

Compound	Frequencies (cm^{-1})				Force constants (mdyne/A)				
	$A_1(1)$	$A_1(2)$	B_2	B_1	k_1	k_2	$k_{c'}$	k_c	k_t
$(PCl_3)_2Mo(CO)_4$	2072	2004	1994	1986	16.33_2	16.45_5	0.2784_6	0.3959_7	0.3898_4
$(PCl_2OC_2H_5)_2Mo(CO)_4$	2063	1988	1977	1968	16.08_3	16.22_0	0.3052_0	0.4344_8	0.4272_8
$[P(C_6H_5)_3]_2Mo(CO)_4$	2023	1929	1911	1899	15.16_8	15.28_1	0.3751_1	0.5969_9	0.5251_5
$\{C_2H_4[P(C_6H_5)_2]_2\}Cr(CO)_4$	2009	1914	1899	1877	14.86_2	15.09_6	0.3750_1	0.6268_2	0.5250_1
$\{C_2H_4[P(C_6H_5)_2]_2\}Mo(CO)_4$	2020	1919	1907	1881	14.92_8	15.25_0	0.3971_5	0.6322_0	0.5560_1
$\{C_2H_4[P(C_6H_5)_2]_2\}W(CO)_4$	2016	1912	1901	1876	14.83_7	15.17_0	0.4063_9	0.6165_7	0.5689_5
$[P(C_2H_5)_3]_2Mo(CO)_4$	2016	1915	1900	1890	14.98_4	15.14_5	0.3988_7	0.5514_7	0.5584_2
$[P(CH_3)_3]_2Mo(CO)_4$	2019	1920	1893	1903	15.21_3	15.02_5	0.3899_0	0.5812_4	0.5458_6
$[(CH_3SCH_2^-)_2]_2Cr(CO)_4$	2020	1914	1898	1869	14.83_7	15.14_2	0.4191_0	0.7228_5	0.5867_3
$[(CH_3SCH_2^-)_2]_2Mo(CO)_4$	2030	1919	1905	1868	14.86_9	15.27_7	0.4383_1	0.7702_5	0.6136_4
$[(CH_3SCH_2^-)_2]_2W(CO)_4$	2023	1910	1896	1867	14.79_6	15.14_7	0.4441_6	0.7117_9	0.6218_2
$(CH_3CN)_2Cr(CO)_4$	2019	1882	1908	1843	14.26_4	15.34_4	0.4530_7	0.5398_1	0.6343_0
$(CH_3CN)_2Mo(CO)_4$	2023	1881	1912	1833	14.17_5	15.41_4	0.4592_1	0.5996_6	0.6429_0
$(CH_3CN)_2W(CO)_4$	2023	1880	1900	1840	14.26_7	15.27_4	0.4912_2	0.5877_2	0.6877_1
$(DMF)_2W(CO)_4$	1997	1832	1858	1791	13.57_4	14.71_8	0.5493_7	0.6135_1	0.7691_1
$(C_2H_8N_2)Cr(CO)_4$	2004	1855	1873	1810	13.87_8	14.89_2	0.5128_1	0.6413_0	0.7179_4
$(C_2H_8N_2)Mo(CO)_4$	2015	1864	1890	1818	13.97_8	15.13_8	0.5036_0	0.6232_7	0.7050_3
$(C_2H_8N_2)W(CO)_4$	2006	1852	1867	1809	13.87_5	14.83_7	0.5380_6	0.6523_4	0.7532_8
$(C_5H_5N)_2Cr(CO)_4$	2020	1878	1899	1837	14.22_2	15.24_9	0.4843_8	0.5875_7	0.6781_4
$(C_5H_5N)_2Mo(CO)_4$	2025	1881	1907	1839	14.24_5	15.36_6	0.4803_9	0.5804_4	0.6725_5
$(C_5H_5N)_2W(CO)_4$	2012	1869	1888	1828	14.09_8	15.09_0	0.4908_5	0.5960_2	0.6871_9
(2,2'-bipyridyl)$Mo(CO)_4$	2017	1878	1909	1829	14.11_5	15.35_0	0.4466_4	0.5982_6	0.6253_0
(2,2'-bipyridyl)$W(CO)_4$	2010	1873	1899	1826	14.06_9	15.20_2	0.4509_9	0.5964_2	0.6313_9

[a] References see Table 2.

whereas those obtained applying method B are given in Table 3.

From the results of Table 1 it may be concluded that the radial and axial force constants k_1 and k_2 do not differ appreciably from the corresponding values found by Dalton *et al.*[5]. Whereas in previous cases[1,6] when the methods A and B were applied to several substituted carbonyls, a choice between the results of methods A and B was rather straightforward, the former being obviously more meaningful, in this case such a decision seems rather purposeless as both series of force constant values are nearly equal. Yet the method A is preferred for the reason that more frequently it results into a pattern of interaction force constants given by the sequence $k_{c'} < k_c < k_t$[7], and in no case were negative y values found for all compounds presented. Nevertheless, it should be remained that in contrast to any iterative scheme, the direct calculation method provides at once with all the solutions in perfect agreement with positive y values.

For the compounds *cis*-$L_2M(CO)_4$ the five CO stretching force constants have not been reported earlier. The values obtained are listed in Tables 2 and 3. Just as for the complexes $[LM(CO)_4]_2$ [1] the method B generally results into the sequence $k_{c'} < k_t < k_c$ which is contrary to theories outlined elsewhere[1,2,3]. That here also and in agreement with earlier results[1,6] the method A shows more reliable patterns of interaction force constants ($k_c < k_t$), certainly strengthens its value.

Finally, the values of interaction force constants provide a demonstration of the fact that the Cotton and Kraihanzel approximation is a less accurate approach to this problem.

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REFERENCES

1 F. T. Delbeke, E. G. Claeys, R. M. de Caluwe and G. P. Van der Kelen, *J. Organometal. Chem.*, 23 (1970) 505.
2 F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
3 L. H. Jones in S. Kirschner (Ed.), *Advances in the Chemistry of the Coordination Compounds*, 1961, p. 398.
4 E. W. Abel, J. Dalton, I. Paul, J. G. Smith and F. G. A. Stone, *J. Chem. Soc. A*, (1968) 1203.
5 J. Dalton, I. Paul and F. G. A. Stone, *J. Chem. Soc. A*, (1968) 1215.
6 F. T. Delbeke, E. G. Claeys, G. P. Van der Kelen and R. M. de Caluwe, *J. Organometal. Chem.*, 23 (1970) 497.
7 H. D. Kaesz, R. Bau, D. Hendrickson and J. M. Smith, *J. Amer. Chem. Soc.*, 89 (1967) 2844.
8 J. D. Cotton, S. A. R. Knox, I. Paul and F. G. A. Stone, *J. Chem. Soc. A*, (1967) 264.
9 O. Kahn and M. Bigorgne, *C. R. Acad. Sci., Ser. C*, 261 (1965) 2483.
10 W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 89 (1967) 2773.
11 O. Kahn and M. Bigorgne, *C. R. Acad. Sci., Ser. C*, 262 (1966) 906.
12 R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.* (1962) 1301.
13 J. Chatt and H. R. Watson, *J. Chem. Soc.*, (1961) 4980.
14 H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, (1962) 4454.
15 B. L. Ross, J. G. Grasselli, W. M. Ritchey and H. D. Kaesz, *Inorg. Chem.*, 2 (1963) 1023.
16 G. R. Dobson, M. F. El Sayed, I. W. Stolz and R. K. Sheline, *Inorg. Chem.*, 1 (1962) 526.
17 F. A. Cotton, *Inorg. Chem.*, 3 (1964) 702.
18 C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 2 (1963) 533.