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# TRANSITION METAL CHEMISTRY
# IV. CALCULATION OF FORCE CONSTANTS OF SUBSTITUTED GROUP VIIA METAL CARBONYLS IN THE CO STRETCHING REGION

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## SUMMARY

A rigorous algebraic method, based on the Cotton and Kraihanzel force field, is presented for the direct calculation of CO stretching force constants of Group VIIA metal carbonyls of general formula $[LM(CO)_4]_2$ (M = Mn, Tc, Re; L a bridging ligand).

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## SYMMETRY

An X-ray study[1] of the compound $[BrMn(CO)_4]_2$ has established the $D_{2h}$ molecular configuration of the binuclear tetracarbonyl (ligand) manganese compounds of formula $[LMn(CO)_4]_2$. Recent spectroscopic work[2] on binuclear carbonyl complexes indicates that coupling between the CO stretching vibrations of the $M(CO)_4$ groups is negligible and therefore the compounds of the type $[LMn(CO)_4]_2$ could be analysed assuming a local $C_{2v}$ carbonyl environment $[cis\text{-}L_2M(CO)_4]$.

The molecular configuration and the CO stretching force constants are shown in Fig. 1.

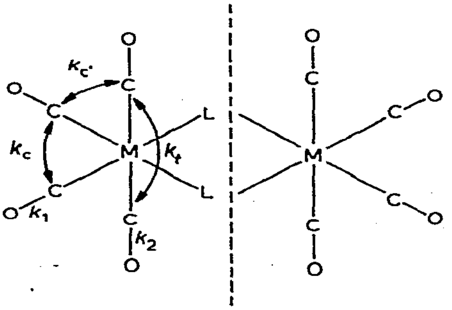

Fig. 1. The $[LMn(CO)_4]_2$ molecule with its CO stretching force constants.

## CALCULATIONS OF FORCE CONSTANTS

For the compounds of the type *cis*-$L_2M(CO)_4$ with local $C_{2v}$ symmetry, there are four CO stretching frequencies ($2\,A_1+B_1+B_2$), which are both IR and Raman active, and five CO stretching force constants ($k_1$, $k_2$, $k_t$, $k_c$, and $k_{c'}$) which must be calculated. The secular equations in the exact formulation of these compounds are presented in Table 1.

TABLE 1

EXACT FORMULATION OF THE SECULAR EQUATIONS FOR *cis*-$L_2M(CO)_4$ COMPOUNDS

| | | |
|---|---|---|
| $2A_1$ | $\begin{vmatrix} k_1+k_c-\lambda/\mu & 2k_{c'} \\ 2k_{c'} & k_2+k_t-\lambda/\mu \end{vmatrix}$ | $=0$ |
| $B_1$ | $\lambda/\mu=k_1-k_c$ | |
| $B_2$ | $\lambda/\mu=k_2-k_t$ | |

Because for the complexes of this type there are only four frequencies against five force constants, all calculations of CO stretching force constants have previously been done using the Cotton and Kraihanzel[3] approximation method based on the assumption that $k_c=k_{c'}=k_t/2=k_i$. However it appears from the results of this work that this assumption is not realistic.

Using orbital overlap theories outlined by Jones[4] we could avoid these approximations by formulating two interaction force constant relationships for compounds of the type *cis*-$L_2M(CO)_4$ [eqns. (1) and (2)].

$$k_t/k_{c'}=2 \tag{1}$$

$$k_c/k_{c'}=\frac{2+y}{1+2y} \tag{2}$$

$y$ is a positive factor related to the change in $\pi$-overlap integral due to the replacement of a CO group by a ligand L in a metal carbonyl.

During this work Abel *et al.*[5] found that the above mentioned relationships could be improved using angular correction terms. Their interaction force constant ratios are presented below [eqns. (3) and (4)]:

$$k_t/k_{c'}=1.4 \tag{3}$$

$$k_c/k_{c'}=\frac{1.3+1.2\,y}{0.7+1.4\,y} \tag{4}$$

As described earlier[6] however, their method used for calculation of the CO stretching force constants could be modified to yield more meaningful results.

The procedure presented in this work consists in the combination of the secular equations of Cotton and Kraihanzel in their exact formulation with the relationships (1) and (2) (method A), allowing the solution of this system by gradually eliminating the various unknowns. In this way one arrives at a resolvent algebraic equation of the second degree in the unknown $y$, providing at once with two sets of values for the force constants in perfect accordance with the spectroscopic data. It is evident that one of these sets must be physically acceptable.

TABLE 2

OBSERVED CARBONYL STRETCHING MODES, ASSIGNMENTS AND FORCE CONSTANTS FOR $[LM(CO)_4]_2$ COMPOUNDS

| Compound | Ref. | Frequencies ($cm^{-1}$) | | | | Force constants (mdynes/Å) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_1(1)$ | $A_1(2)$ | $B_2$ | $B_1$ | $k_1$ radial | $k_2$ axial | $k_{c'}$ | $k_c$ | $k_t$ |
| $[ClMn(CO)_4]_2$[a] | 7 | 2104 | 2012 | 2045 | 1977 | $16.15_6$<br>$16.20_1$ | $17.31_1$<br>$17.26_5$ | $0.2066_3$<br>$0.2626_4$ | $0.3633_3$<br>$0.4089_0$ | $0.4132_6$<br>$0.3677_0$ |
| $[BrMn(CO)_4]_2$[a] | 7 | 2099 | 2011 | 2042 | 1975 | $16.12_7$<br>$16.17_3$ | $17.24_8$<br>$17.20_2$ | $0.2003_1$<br>$0.2530_3$ | $0.3661_2$<br>$0.4125_1$ | $0.4006_2$<br>$0.3542_4$ |
| $[IMn(CO)_4]_2$[a] | 7 | 2087 | 2009 | 2033 | 1976 | $16.11_8$<br>$16.16_3$ | $17.07_4$<br>$17.02_8$ | $0.1869_9$<br>$0.2347_2$ | $0.3411_6$<br>$0.3865_3$ | $0.3739_7$<br>$0.3286_1$ |
| $[ClTc(CO)_4]_2$[a] | 7 | 2119 | 2011 | 2048 | 1972 | $16.12_9$<br>$16.18_2$ | $17.44_2$<br>$17.38_9$ | $0.2476_7$<br>$0.3157_2$ | $0.4161_8$<br>$0.4695_1$ | $0.4953_4$<br>$0.4420_1$ |
| $[BrTc(CO)_4]_2$[a] | 7 | 2116 | 2012 | 2046 | 1973 | $16.14_4$<br>$16.19_9$ | $17.40_1$<br>$17.34_6$ | $0.2434_4$<br>$0.3088_7$ | $0.4156_8$<br>$0.4701_3$ | $0.4868_8$<br>$0.4324_2$ |
| $[ITc(CO)_4]_2$[a] | 7 | 2108 | 2012 | 2042 | 1975 | $16.15_5$<br>$16.20_7$ | $17.30_5$<br>$17.25_2$ | $0.2284_5$<br>$0.2887_8$ | $0.3944_6$<br>$0.4470_8$ | $0.4569_1$<br>$0.4042_9$ |
| $[ClRe(CO)_4]_2$[a] | 7 | 2114 | 2000 | 2032 | 1959 | $15.96_0$<br>$16.02_4$ | $17.24_4$<br>$17.18_0$ | $0.2803_5$<br>$0.3546_3$ | $0.4540_4$<br>$0.5182_7$ | $0.5607_1$<br>$0.4964_8$ |
| $[BrRe(CO)_4]_2$[a] | 7 | 2113 | 2000 | 2031 | 1964 | $16.00_1$<br>$16.06_2$ | $17.22_6$<br>$17.16_5$ | $0.2796_8$<br>$0.3557_8$ | $0.4154_3$<br>$0.4767_0$ | $0.5593_6$<br>$0.4980_9$ |
| $[IRe(CO)_4]_2$[a] | 7 | 2106 | 2001 | 2029 | 1965 | $16.01_0$<br>$16.06_9$ | $17.15_7$<br>$17.09_7$ | $0.2616_0$<br>$0.3310_4$ | $0.4084_9$<br>$0.4682_2$ | $0.5231_9$<br>$0.4634_6$ |
| $[C_6F_5SMn(CO)_4]_2$[b] | 8 | 2100 | 2020 | 2045 | 1995 | $16.36_6$<br>$16.40_5$ | $17.27_6$<br>$17.23_7$ | $0.1891_5$<br>$0.2424_0$ | $0.2850_4$<br>$0.3239_8$ | $0.3783_1$<br>$0.3393_6$ |
| $[PhSMn(CO)_4]_2$[a] | 9 | 2079 | 2006 | 2022 | 1970 | $16.05_2$<br>$16.10_5$ | $16.90_9$<br>$16.85_7$ | $0.1949_3$<br>$0.2409_1$ | $0.3715_6$<br>$0.4241_4$ | $0.3898_5$<br>$0.3372_7$ |
| $[PhSeMn(CO)_4]_2$[b] | 8 | 2065 | 1994 | 2010 | 1962 | $15.89_2$<br>$15.94_1$ | $16.69_4$<br>$16.64_5$ | $0.1851_3$<br>$0.2295_9$ | $0.3382_6$<br>$0.3871_0$ | $0.3702_7$<br>$0.3214_3$ |
| $[PhTeMn(CO)_4]_2$[a] | 9 | 2056 | 1996 | 2006 | 1965 | $15.92_4$<br>$15.97_1$ | $16.59_5$<br>$16.54_8$ | $0.1678_7$<br>$0.2061_1$ | $0.3226_4$<br>$0.3698_2$ | $0.3357_4$<br>$0.2885_5$ |
| $[C_6F_5SRe(CO)_4]_2$[b] | 8 | 2105 | 2000 | 2030 | 1964 | $15.98_8$<br>$16.04_5$ | $17.16_2$<br>$17.10_5$ | $0.2558_5$<br>$0.3247_8$ | $0.4031_3$<br>$0.4601_3$ | $0.5116_9$<br>$0.4546_9$ |
| $[PhSRe(CO)_4]_2$[b] | 8 | 2100 | 1995 | 2022 | 1962 | $15.93_9$<br>$15.99_8$ | $17.04_7$<br>$16.98_8$ | $0.2637_9$<br>$0.3346_7$ | $0.3857_6$<br>$0.4448_0$ | $0.5275_8$<br>$0.4685_4$ |
| $[PhSeRe(CO)_4]_2$[b] | 5 | 2088 | 1988 | 2012 | 1952 | $15.80_2$<br>$15.86_4$ | $16.86_6$<br>$16.80_4$ | $0.2546_9$<br>$0.3200_1$ | $0.4066_8$<br>$0.4680_5$ | $0.5093_8$<br>$0.4480_1$ |
| $[Ph_2PMn(CO)_4]_2$[c] | 10 | 2053 | 1992 | 1992 | 1957 | $15.85_8$ | $16.42_7$ | $0.1970_5$ | $0.3836_1$ | $0.3941_1$ |
| | | | | | | negative $y$ values | | | | |
| $[Me_2PMn(CO)_4]_2$[c] | 10 | 2044 | 1978 | 1978 | 1955 | $15.75_0$<br>$15.81_8$ | $16.22_0$<br>$16.15_2$ | $0.2057_7$<br>$0.2453_6$ | $0.3074_9$<br>$0.3755_3$ | $0.4115_4$<br>$0.3435_0$ |
| $[Ph_2AsMn(CO)_4]_2$[c] | 10 | 2050 | 1987 | 1987 | 1955 | $15.81_2$<br>$15.87_6$ | $16.35_2$<br>$16.28_8$ | $0.1999_4$<br>$0.2398_1$ | $0.3687_7$<br>$0.4329_2$ | $0.3998_8$<br>$0.3357_3$ |

[a] In $CCl_4$. [b] In cyclohexane. [c] In 1,2-dichloroethane.

Using eqns. (3) and (4) instead of the relationships (1) and (2) in an analogous manner, provides another set of force constants (method B).

The calculations were mainly carried out in double precision on the IBM 360 type 30 computer of the Computing Laboratory of the University of Ghent, Director Prof. Dr. C. C. Grosjean.

## RESULTS AND DISCUSSION

The CO stretching force constants for the binuclear complexes of the type $[LMn(CO)_4]_2$ are presented in Table 2. For each compound there are two rows of accepted force constants, the first set has been calculated using method A and the second using method B.

From the results of Table 2 it may be shown that the radial and axial force constants $k_1$ and $k_2$ differ only slightly from those obtained by Abel[5]. Therefore their conclusions about the linear dependence between the Taft polarity constant ($\sigma^*$) of the bridging atoms and the CO stretching force constants can be agreed upon without comments.

It is however also important to note that the interaction force constants obtained by method A follow the sequence $k_{c'} < k_c < k_t$, whereas method B generally results into a pattern of interaction force constants given by the sequence $k_{c'} < k_t < k_c$. It is rather puzzling that, using the method B we found $k_c$ greater than $k_t$. If $k_c$ and $k_t$ are the interaction force constants between respective pairs of *cis*-CO and *trans*-CO groups, we should expect on the basis of the arguments of Cotton and Kraihanzel[3] and Jones[4] that $k_t$ must be greater than $k_c$. Since only method A provides us with reliable interaction force constants we must conclude that the inclusion of angular correction terms in the relationships of interaction force constants does not improve the results.

Finally, it should be mentioned that the values of interaction force constants demonstrate once more that the Cotton and Kraihanzel approximation ($k_t = 2k_c$, $k_c = k_{c'}$) yields less accurate results and can be improved.

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