Correspondence

CO Force Constants and CO–CO Interaction Constants of Metal Carbonyls[1]

Sir:

Recently Cotton, *et al.*,[2] published another in a series of papers which present calculation of CO stretching force constants and CO–CO interaction constants with neglect of all other force constants and all frequencies but those from CO stretching vibrations. They claim that these calculations[2] on $BrMn(CO)_5$, $HMn(CO)_5$, $CH_3Mn(CO)_5$, and especially $CF_3Mn(CO)_5$ show that the "...highly simplified (Cotton–Kraihanzel) force field is not only practical but satisfactory in comparison to more elaborate schemes and that it comes fairly close to being literally correct in its assumptions, at least for $XMn(CO)_5$ molecules." As evidence for the validity of this force field, they showed that correct frequencies were calculated for the mono-^{13}C-substituted species and that the ratio k_t/k_c was found to be close to 2, as hypothesized in the Cotton–Kraihanzel force field.[3]

The use of this simplified force field is an enticing procedure. However, it is important to know how much these approximate results may deviate from the true quadratic force constants. The author has shown[4] that for $Mo(CO)_6$ inclusion of MC stretching vibrations, MC–CO interactions, and anharmonicity corrections leads to quite different results than obtained by the approximate method of Cotton and Kraihanzel.[3] Inasmuch as Cotton, *et al.*,[2] present their results on $CF_3Mn(CO)_5$, $BrMn(CO)_5$, etc., as strong evidence that $k_t/k_c \approx 2$ as assumed in their approximate treatment, it seems that comparison with a more rigorous approach for these compounds is especially in order. Therefore a series of calculations has been made to show what values the CO force constants, and especially the CO–CO interaction constants, may have in a more general force field for $Mn(CO)_5Br$.

A complete general quadratic force field was used. The MCO and CMC bending frequencies were assumed to be about the same as for $M(CO)_6$[5] (575 ± 100 and 80 ± 20 cm^{-1}, respectively). The MnBr stretching frequency was chosen[6,7] as 218 cm^{-1}. The CMnBr bending frequencies were chosen[7] as 50 cm^{-1}. From a large number of calculations it was found that changes of greater than 50% in the frequencies mentioned in this paragraph have negligible effect on the calculated CO force constants. Furthermore, it was found that inclusion of the stretch–bend, bend–bend, MnX–CO, and MnX–MnC interaction constants in the generous range +0.3 to −0.3 mdyn/Å has negligible effect on the calculated CO force constants.

In order to make the calculations tractable, the following reasonable assumptions were adopted: (1) the *cis*-interaction constants for CO–CO interaction are the same for radial CO with radial CO as they are for radial CO with axial CO (Cotton's[2] $k_c = k_c'$); (2) the *cis* MC–C′O′ interaction is the same for radial–radial and radial–axial groups; (3) the MC–CO interaction involving the same carbon is the same for radial as for axial MCO groups. The results of these calculations can be summarized by

$$k_1 \approx (k_1)_0 - 0.34F_{MC} + 1.2F_{MC-CO} + \chi_1 \quad (1)$$

$$k_2 \approx (k_2)_0 - 0.34F_{MC} + 1.2F_{MC-CO} + \chi_2 \quad (2)$$

$$k_c = k_c' = (k_c)_0 - 0.34F^c_{MC-MC'} + 1.2F^c_{MC-C'O'} + \chi_c \quad (3)$$

$$k_t \approx (k_t)_0 - 0.34F^t_{MC-MC'} + 1.2F^t_{MC-C'O'} + \chi_t \quad (4)$$

The force constants are defined as follows: k_1, the harmonic axial CO stretching force constant; k_2, the harmonic radial CO stretching force constant; k_c, the harmonic constant for interaction of axial CO with a radial CO; k_c', the harmonic constant for interaction of two *cis* radial CO groups (assumed equal to k_c); k_t, the harmonic constant for interaction of two *trans* radial CO groups. The same symbols with a subscript zero are the zero approximation values calculated in the CO-factored force field (neglecting all force constants but CO stretch and CO–CO interactions and all vibrational frequencies except those arising from CO stretching). The superscripts c and t are for *cis* and *trans* interaction, respectively. The χ_i are correction terms to allow for anharmonicity. As pointed out above, the general quadratic force constants not appearing in eq 1–4, if held within a reasonable range of values, have negligible effect on k_1, k_2, k_c, and k_t.

In order to evaluate the various anharmonicity correction terms (χ_i) in eq 1–4, the author has measured CO fundamentals and binary and ternary combinations of CO vibrations for $Mn(CO)_5Br$ in CCl_4 solution. These are listed in Table I along with the CO stretching fundamentals. These frequencies have been observed before[2,8] but different solvents were used for fundamentals and combinations.

The frequencies of Table I were treated in the same manner as those of $M(CO)_6$[9] to arrive at the anharmonicity constants and harmonic fundamental frequencies given in Table II.

Using the data of Table II the following values are calculated for the χ_i in eq 1–4: $\chi_1 = 0.44$ mdyn/Å; $\chi_2 = 0.43$ mdyn/Å; $\chi_c = 0.06$ mdyn/Å; and $\chi_t = -0.18$ mdyn/Å. These correspond to $\chi_{CO} = 0.54$, $\chi_c = 0.02$, and $\chi_t = -0.19$ mdyn/Å for $Mo(CO)_6$;[4]

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, **6**, 1357 (1967).

[3] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[4] L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967).

[5] L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

[6] M. A. Bennett and R. J. H. Clark, *Chem. Ind.* (London), 861 (1963).

[7] J. A. Cengel, Ph.D. Thesis, Purdue University, 1965.

[8] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

[9] J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

TABLE I

OBSERVED CO FUNDAMENTALS AND COMBINATIONS (IN CM^{-1}) FOR $Mn(CO)_5Br$ (C_{4v} SYMMETRY) IN CCl_4 SOLUTION

ν_1 (A_1)	2135.2	$\nu_2 + \nu_{15}$	4053.2
ν_2 (A_1)	2001.5	$\nu_9 + \nu_{15}$	4120.4
ν_9 (B_1)	2083[a]		
ν_{15} (E)	2052.1	$2\nu_1 + \nu_2$	6255
$2\nu_1$	4265.0	$2\nu_1 + \nu_{15}$	6300
$2\nu_2$	3982.2	$\nu_1 + 2\nu_9$	
$2\nu_{15}$	4089.7	$\nu_1 + \nu_2 + \nu_{15}$	6176
$\nu_1 + \nu_2$	4132.1	$\nu_2 + 2\nu_9$	
$\nu_1 + \nu_{15}$	4179.1	$3\nu_{15}$	6108

[a] This frequency of B_1 symmetry was observed in the Raman spectrum. All others were observed in absorption.

TABLE II

ANHARMONICITY CONSTANTS AND HARMONIC FUNDAMENTAL CO STRETCHING FREQUENCIES (IN CM^{-1}) FOR $Mn(CO)_5Br$ IN CCl_4 SOLUTION

X_{11}	-2.7	X_{29}	[0][b]
X_{22}	-10.4	$X_{2,15}$	-0.4
X_{99}	[+7][a]	$X_{9,15}$	-14.7
$X_{15,15}$	-7.3	ω_1	2156.1
X_{12}	-4.6	ω_2	2025.0
X_{19}	[−10][a]	ω_9	2088.7
$X_{1,15}$	-8.2	ω_{15}	2085.7

[a] Not determinable from observed data. The vibration ν_9 involves motion similar to that of the E_g CO stretching vibration of $M(CO)_6$; therefore, X_{99} is chosen as $+7$ cm^{-1} and X_{19} as -10 cm^{-1} by analogy with $M(CO)_6$.[9] [b] This value was chosen as zero because it involves vibrations which are perpendicular to each other, as for $X_{2,15}$.

thus, the anharmonic corrections appear to be somewhat transferable from $M(CO)_6$ to $M(CO)_5X$.

Now it is possible to estimate the various correction terms in eq 1–4. For $M(CO)_6$, calculations based on the frequency assignments of ref 9 show that $F_{MC} \approx 2$ mdyn/Å, $F^c_{MC-MC'} \approx 0$, and $F^t_{MC-MC'} \approx 0.5$ mdyn/Å, regardless of values chosen for the other interaction constants. Furthermore, for $Ni(CO)_4$ it was found[10] that $F_{MC-CO} \approx 0.5$ mdyn/Å.

If we transfer these force constants to $Mn(CO)_5Br$, we find

$$k_1 \approx (k_1)_0 + 0.36 \quad (5)$$

$$k_2 \approx (k_2)_0 + 0.35 \quad (6)$$

$$k_c \approx (k_c)_0 + 1.2F^c_{MC-C'O'} + 0.06 \quad (7)$$

$$k_t \approx (k_t)_0 + 1.2F^t_{MC-C'O'} - 0.36 \quad (8)$$

The corrections to the CO force constants arise primarily from anharmonicity terms as the terms involving F_{MC} and F_{MC-CO} nearly cancel each other. It appears that it may be appropriate to evaluate relative CO bond strengths by comparing CO force constants, $(k_{CO})_0$, calculated with the approximate method for different carbonyls assuming an uncertainty of ±0.1 mdyn/Å in the relative values.

In order to compare k_c and k_t and especially the ratio k_t/k_c to the Cotton–Kraihanzel values, we must have an estimate of $F^c_{MC-C'O'}$ and $F^t_{MC-C'O'}$. Certainly they should each be less than F_{MC-CO}, which involves only one carbon atom, as we expect adjacent interactions to be the most important. For $Ni(CO)_4$ it was found[10] that $F_{MC-C'O'} \approx -0.1$ mdyn/Å. Unfortunately we cannot expect that this value would necessarily apply to k_c and k_t of hexacarbonyls and pentacarbonyl halides, as the interactions are at 90 and 180° rather than the 109.5° for $Ni(CO)_4$. Nevertheless, it is apparent from eq 7 and 8 that it would be completely fortuitous if k_c, k_t, and k_t/k_c were approximately equal to $(k_c)_0$, $(k_t)_0$, and $(k_t)_0/(k_c)_0$, respectively. The correction terms to $(k_c)_0$ and $(k_t)_0$ are of the same order of magnitude as $(k_c)_0$ and $(k_t)_0$ themselves. If $k_c \approx (k_c)_0$ and $k_t \approx (k_t)_0$ it would mean that $F^c_{MC-C'O'} \approx -0.05$ while $F^t_{MC-C'O'} \approx +0.3$ mdyn/Å. The latter value is too large and of the wrong sign to be reasonable.[10,11]

Inspection of eq 7 and 8 shows also that the less stringent restriction that $k_t/k_c \approx (k_t)_0/(k_c)_0 \approx 2$ would require quite unreasonable[10,11] values for one or both of $F^t_{MC-C'O'}$ and $F^c_{MC-C'O'}$. [The resulting relation is $F^t_{MC-C'O'} = 2F^c_{MC-C'O'} + 0.4$].

The two points mentioned by Cotton, *et al.*,[2] in support of their simplified approach may now be taken up.

First, the frequencies of the monosubstituted ^{13}C species are just not very sensitive to the force constants. The solutions arrived at by the approximations used in the calculations discussed in this paper (including $F^t_{MC-C'O'} = F^c_{MC-C'O'} \approx -0.1$ mdyn/Å) yield CO stretching frequencies for the equatorial and axial mono-^{13}C species of $Mn(CO)_5Br$ within 1 cm^{-1} of the observed values. Furthermore, any number of solutions can be chosen to fit all of the observed isotope shifts exactly by inclusion of various interaction constants. It is not profitable to do so unless all of the isotope shifts are known to better than 0.3 cm^{-1}. From these observations one can conclude that the agreement of calculated and observed isotopic frequency shifts shown in ref 1 is *not* a proof of the validity of the Cotton–Kraihanzel force field.

Second, the results presented above indicate that for reasonable approximations concerning the MC–CO interactions $k_t/k_c \not\approx 2$. The hypothesis that $k_t/k_c \approx 2$ was made by the author[12] and by Cotton and Kraihanzel[3] on the basis of π-bonding arguments. However, such arguments are not very compelling and the available evidence gives them no support. The fact that $(k_t)_0/(k_c)_0$ is close to 2.0 is remarkably fortuitous, but it by no means indicates that $k_t/k_c \approx 2$. Thus it should be realized that *the CO–CO interactions calculated with a CO-factored force field have no fundamental significance, either in their relative or absolute values.*[13]

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(10) L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, in press.

(11) L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962).

(12) L. H. Jones, "Advances in the Chemistry of Coordination Compounds," S. Kirchner, Ed., The Macmillan Co., New York, N. Y., 1961, p 398.

(13) NOTE ADDED IN PROOF.—Braterman, Bau, and Kaesz [*Inorg. Chem.*, **6**, 2097 (1967)] have recently stated that inclusion of reasonable values for MC stretching and MC–CO and MC–MC interaction force constants leads to calculated CO stretching and CO–CO interaction force constants very close to those calculated from the "energy factoring model." However, this is contrary to the calculations presented in this paper and Dr. Kaesz has recently informed me that their calculations are in error.

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