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Calculation of Anharmonicity Corrections to the C–O Stretching Frequencies and Force Constants of Metal Carbonyls

G. H. BARNETT and M. K. COOPER
Department of Inorganic Chemistry, University of Sydney, N.S.W. 2006 Australia
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A method is proposed for determining the importance of anharmonicity corrections to the Cotton–Kraihanzel stretching force constants of substituted octahedral metal carbonyls. From an analysis of experimental data, it is shown that if the comparisons are limited to compounds of similar geometry whose frequencies and force constants occur within a narrow range, in keeping with the original intention of the Cotton–Kraihanzel method, the neglect of anharmonicity is entirely valid. Each set of non-equivalent M–C–O groups is regarded as a separate "diatomic" molecule and anharmonicity corrections are calculated from simple diatomic potential functions.

Introduction

Cotton–Kraihanzel (CK) force constants[1] have been widely used to assess the changes occurring in the individual C–O groups of substituted metal carbonyl complexes.[2,3] Variations in the stretching force constants (k) and the interaction constants (k_i) as the substituent ligand was changed were interpreted as being due to changes in the π and/or σ bonding ability of the ligands.[2–8] However, quantitative estimates of the relative importance of the σ and π effects could not be made.[5–10]

Recently the application of these force constant calculations to studies of bonding has been questioned, because of the approximations involved.[11,12] Nevertheless, the method is still in favour for comparing the force constants of a series of closely related molecules.[11] In order to comment on the validity of the method it is necessary to assess the various approximations involved.

Miller[13] has adequately discussed the consequences of high frequency separation (energy factoring) of the various M–C–O vibrations, which is the most important assumption of the CK method. Jones has developed mathematical relationships between the CK force constants and those of a more general force field.[14] These studies led to the conclusion that non-rigorous force constants are valid so long as the coordinate system is properly defined.

Furthermore, Miller has established that the CK stretching force constant (k), which was thought by Cotton and Kraihanzel to apply only to the C–O group, is in fact a composite property of an *uncoupled* M–C–O unit and k_c and k_t are true and rigorous interaction force constants. The stretching force constant k contains only contributions from the M–C and C–O bonds within one M–C–O unit.

Although anharmonicity corrections are also a potential source of inaccuracy, they are ignored in the CK method. In this paper we have developed a method by which we can determine the effects of anharmonicity on the CK stretching force constants and whether or not such corrections are necessary.

Results and Discussion

Although neglect of anharmonicity is a basic assumption of the CK method,[1] anharmonic corrections have been calculated by more rigorous methods for a small number of six coordinate metal carbonyl complexes.[14,15] We have compared our calculations with these values.

Since Miller[13] has shown that a single k value applies to the entire M–C–O unit, uncoupled from other vibrations, we propose that inequivalent M–C–O groups can be regarded as separate "diatomic" molecules (the mass of the metal may be taken as infinite with only a minimal effect on k[13]).

Accepting that we are dealing with a "diatomic" species, the Morse potential and other simple functions[16,17] can be applied. These have been shown to give good agreement (*ca.* 5%) between observed and calculated anharmonic potential corrections for a variety of typical diatomic molecules.[16,17]

For an anharmonic diatomic molecule the potential V(R) (in terms of displacement, R) can be represented as a Taylor series expanded around the equilibrium position (represented by the subscript "e") to give,[18]

$$V(R) = \frac{(R-R_e)^2}{2!}\left(\frac{d^2V}{dR^2}\right)_{R_e} + \frac{(R-R_e)^3}{3!}\left(\frac{d^3V}{dR^3}\right)_{R_e} + \frac{(R-R_e)^4}{4!}\left(\frac{d^4V}{dR^4}\right)_{R_e} + \text{higher terms} \quad (1)$$

whereas for a harmonic diatomic molecule

$$V^1(R) = \frac{(R-R_e)^2}{2!}\left(\frac{d^2V^1}{dR^2}\right)_{R_e} \quad (2)$$

The force constants are defined as

$$k_e = \left(\frac{d^2V}{dR^2}\right)_{R_e} \text{ (quadratic)}, \; l_e = \left(\frac{d^3V}{dR^3}\right)_{R_e} \text{ (cubic)}$$

$$m_e = \left(\frac{d^4V}{dR^4}\right)_{R_e} \text{ (quartic), \textit{etc.} and } (R-R_e) < a,$$

the vibrational amplitude.

For an observed frequency, ν, there is a force constant, k, which includes all the anharmonic terms, such that

$$k = k_e + \frac{2al_e}{3!} + \frac{2a^2m_e}{4!} + \textit{etc.} \quad (3)$$

where

$$\left|\frac{2al_e}{3!}\right| > \left|\frac{2a^2m_e}{4!}\right| > \textit{etc.} \quad (4)$$

The quantities l_e and m_e can be expressed *exactly* in terms of k_e,[17] but in order to make calculation of these quantities more tractable, the expansions are normally truncated after several terms. In this case, series (3) converges too slowly to calculate a reliable value for k.

On the other hand, the frequency, ν, can be represented by a harmonic frequency ν_e and a series of anharmonic contributions $(\nu_e x_e)$, $(\nu_e y_e)$, *etc.* such that[18]

$$\nu = \nu_e - 2(\nu_e x_e) + \frac{13}{4}(\nu_e y_e) - \textit{etc.} \quad (5)$$

Since $\nu_e >> (\nu_e x_e) >> (\nu_e y_e)$ *etc.*, the major anharmonic correction is $(\nu_e x_e)$ where[18, 19]

$$(\nu_e x_e) = \frac{h}{8\pi^2\mu c}\left[\frac{1}{24}\left(\frac{5l_e^2}{k_e^2} - \frac{3m_e}{k_e}\right)\right] \quad (6)$$

(μ = reduced mass).

Truncation of equation (5) at the second term leads to an estimated accuracy of ±4 cm^{-1} (*ca.* 0.2%) in ν_e.

We have used the following approximate equations for l_e and m_e:[17]

$$l_e = \frac{-6k_e}{R_e}\left[1 + \frac{4}{9}\left(\frac{V_A + V_B}{q} - 1\right)\right] \quad (7)$$

$$m_e = \frac{-36k_e}{R_e^2}\left[\frac{5}{6} + \frac{11l_eR_e}{36k_e}\right] \quad (8)$$

(where V_A and V_B are the number of valence electrons in carbon and oxygen respectively and q = 5.22).[17]

Substituting in these equations we obtain

$$l_e = -8.442\frac{k_e}{R_e} \quad (9)$$

$$m_e = 62.86\frac{k_e}{R_e^2} \quad (10)$$

and hence from equation (6)

$$(\nu_e x_e) = \frac{17.19}{R_e^2} \quad (11)$$

Therefore $(\nu_e x_e)$ is dependent only on $(1/R_e^2)$. Since it is well documented that R_e and hence R_e^2 varies over only a small range for C–O bond orders between 2 and 3,[20] it follows that $(\nu_e x_e)$ is almost invariant over this range.

To relate the anharmonic frequency corrections to the stretching force constants it is necessary to introduce some relationship between k and R_e. The assumption that R_e is constant at 1.14 ± 0.02 Å for k between 15.0 and 19.0 m dyne/Å (Table I), will result in a value for $(\nu_e x_e)$ of 13.2 ± 0.4 cm^{-1}.*

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* Calculated from equation (11).

TABLE I. CK Force Constants (m dyne/Å)[a] and Bond Lengths (Å) for Some Six-coordinate Metal Carbonyl Complexes.

Complex	k (m dyne/Å)	R_e(Å)[b]	$k^{1/2}R_e^2$[c]	Ref.
$Mn(CO)_5H$	k_1 16.42	1.143	5.29	21(f)
	k_2 16.93	1.13	5.25	21(f)
$Cr(CO)_6$	16.49	1.137	5.25	21(d)
$Cr(CO)_5P(OPh)_3$	k_1 15.98	1.136	5.16	21(e)
	k_2 16.29	1.131	5.16	21(e)
$Cr(CO)_5PPh_3$	k_1 15.50	1.154	5.19	21(e)
	k_2 15.88	1.14	5.18	21(e)
$Cr(CO)_5$carbene	k_2 15.63	1.155	5.27	21(a)(b)
$Cr(CO)_3(PH_3)_3$	15.07	1.160	5.22	21(c)

[a] m dyne/Å = 100 N/m. [b] From reference 21. [c] Mean value $(k^{1/2}R_e^2)$ = 5.22 m $\text{dyne}^{1/2}$ $\text{Å}^{3/2}$.

TABLE II. Observed and Calculated χ_e Values (m dyne/Å = 100 N/m) of Compounds Containing the C–O Group.

Compound	k	χ_e		
		a	b	c
$Cr(CO)_6$	16.45	0.52[14]	0.43	0.44
$Mo(CO)_6$	16.46	0.49[14]	0.43	0.44
$W(CO)_6$	16.35	0.50[14]	0.43	0.44
$Mn(CO)_5Br$	16.26[e]	0.47[15]	0.43	0 43
$Mn(CO)_5Br$	17.41[d]	0.44[15]	0.45	0.46

[a] Calculated by Jones *et al.*[14,15] from experimental data. [b] Calculated assuming R_e = 1.14 Å. [c] Calculated from equation (15) and (16). [d] k_1. [e] k_2.

TABLE III. Observed and Calculated $(\nu_e x_e)$ Values (cm^{-1}) for CO Gas.

$(\nu_e x_e)$	Method	Discrepancy[a] (cm^{-1})
13.46	Experimental[19]	–
13.22	R_e = constant = 1.14 Å	0.24
13.51	R_e = 1.128 Å [b]	0.05
14.37	Equation (11)	0.91

[a] The difference between the calculated and experimental value of $(\nu_e x_e)$[19]. [b] The experimental value of R_e.

Another approach is to use a well known semi-empirical rule in diatomic spectroscopy which relates ν_e and R_e by,[17]

$$(\nu_e R_e^2) = \text{constant} \tag{12}$$

We have applied this rule to the anharmonic frequencies of a series of metal carbonyl complexes by calculating $(k^{1/2}R_e^2)$ (Table I), since

$$(k^{1/2}R_e^2) = 2\pi c\mu^{1/2}(\nu R_e^2) \tag{13}$$

and therefore $(k^{1/2}R_e^2)$ = constant (14)

For these compounds the relationship (12) appears valid over this narrow range of k, with the constant equal to 5.22 ± 0.04.

By combining equations (11) and (14) we arrive at the relationship

$$(\nu_e x_e) = 3.29\, k^{1/2} \tag{15}$$

and k_e is then calculated from the expression

$$k_e = 4\pi^2c^2\mu\left[\left(\frac{k}{4\pi^2c^2\mu}\right)^{1/2} + 2(\nu_e x_e)\right]^2 \tag{16}$$

In table II our values of the anharmonicity correction to the force constants ($\chi_e = k_e - k$) are compared with the values obtained by Jones *et al.*[14,15] for $M(CO)_6$ (M = Cr, Mo, W) and $Mn(CO)_5Br$.

We have also calculated the $(\nu_e x_e)$ values for CO gas and compared these with the experimental value[19] (Table III).

Conclusion

Our calculated anharmonicity corrections to both k and ν (Tables II and III) are in good agreement with the values obtained by Jones *et al.*[14,15] using more rigorous methods. The most important conclusion to be drawn from these results is that *the anharmonic corrections can be regarded as constant over a narrow range of force constants, or systematic over a more extended range and need not be applied when comparing the force constants of closely related octahedral metal carbonyl complexes.* Although we have not taken into account further approximations, such as the much discussed[1,4,11] $k_j = 2k_t = k_c = k_c'$, we believe that, in the absence of such approximations, it is possible to compare CK stretching force constants to ±0.05 m dyne/Å. This error is only slightly greater than that due to inaccuracies in the measurement of the C–O frequencies.

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