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Force constant calculations for octahedral complexes of the type $M(CO)_5L$, based on the CO-factored force field

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Abstract

Using the maximum value of the sum of the interaction constants, the CO-factored force field of octahedral $M(CO)_5L$ molecules was solved to give the relations which allow direct calculation of force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule. The force constants calculated by these relations were used to predict C–O stretching frequencies of isotopically enriched species of some complexes of the type $M(CO)_5L$. The results obtained showed that there exists a very good agreement between observed and calculated frequencies. This led us to conclude that the solution presented for the force field of $M(CO)_5L$ molecules is a valid solution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pentacarbonyls; Infrared spectra; CO-factored force field; Force constants

1. Introduction

It is well known that the CO-factored force field is widely used to evaluate CO-stretching force constants and CO–CO interaction constants in metal carbonyl complexes [1–6]. This force field, which is generally known as the Cotton–Kraihanzel force field, neglects anharmonicity and all coupling except CO–CO interaction. However, the application of this simplified force field to complexes in which more than one fundamental vibration belong to the same nondegenerate irreducible representation leads to an undetermined algebraic system.

For octahedral complexes of the type $M(CO)_5L$ in which two fundamental vibrations belong to the a_1 symmetry species, several attempts have been made to overcome the mentioned problem. Some authors [1,7–9] have employed various relationships among the interaction constants derived from elementary bonding considerations [1,10]. However, force constant data obtained from isotopic enrichment studies [11–13] indicated that these relationships are not applicable. Haas and Sheline [14] have developed a method based on the assumption that the effect of ligands on force constants are additive. With this method, the determination of force constants for $M(CO)_5L$ molecules necessitates the use of C–O stretching frequencies of all $M(CO)_{6-n}L_n$, ($n = 0$–6), species, not only those of $M(CO)_5L$. Another method, which is nearly similar to that of Haas–Sheline, has been developed by Timney [15]. However, this method is restricted to complexes whose ligand effect constants and bond angles are known because the relationships derived empirically are expressed in terms of the mentioned parameters. In a recent work [16], on calculating the CO-factored force constants for pentacarbonyl complexes with C_{4v} symmetry, an equation for the CO_{ax}–CO_{eq} interaction constant, related to observable C–O stretching modes, has been suggested.

A few years ago [17], we showed that the constraint based on the maximum value of the sum of the interaction constants leads to a valid solution of the CO-factored force field of $M(CO)_4$ and $M(CO)_4L$ molecules having C_{3v} symmetry. This paper presents the application of this constraint to octahedral complexes of the type $M(CO)_5L$.

2. Application of the constraint

Octahedral complexes of the type $M(CO)_5L$, under the local symmetry of the carbonyls, belong to the C_{4v}

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point group, for which group theory predicts four C–O stretching modes ($2a_1 + b_1 + e$). The a_1 and e modes are both infrared and Raman-active, whereas the b_1 mode is only Raman-active [18]. On the basis of the CO-factored force field [1], in the $M(CO)_5L$ molecules having C_{4v} symmetry there are two C–O stretching force constants (k_1 and k_2) and three CO–CO interaction constants (k_t, $k_{c'}$ and k_c). The force constants are defined in Fig. 1. The secular equations for the molecules, which are given elsewhere [1,9], are presented in Table 1.

Since there are five CO-factored force constants to be determined and only four observable C–O stretching modes for the all-$^{12}C^{16}O$ molecule, four equations in five unknowns are obtained from the secular equations. This means that the solution of the force field necessitates the use of an additional constraint. In order to obtain a constraint which can give a valid solution, we have made use of the constraint employed in our previous work [17], in which it was shown that the maximum value of the sum of the interaction constants leads to a valid solution for the CO-factored force field of $M(CO)_4$ molecules with C_{3v} symmetry. In order to apply this constraint to the molecules under study, the secular equations given in Table 1 were rearranged so that four of the five constants are expressed in terms of the fifth and the observed frequencies:

$$k_1 = (\lambda_1 + \lambda_2 - \beta)/(2\mu) \quad (1)$$

$$k_2 = (\lambda_1 + \lambda_2 + 2\lambda_3 + 4\lambda_4 + \beta)/(8\mu) \quad (2)$$

$$k_t = (\lambda_1 + \lambda_2 + 2\lambda_3 - 4\lambda_4 + \beta)/(8\mu) \quad (3)$$

$$k_{c'} = (\lambda_1 + \lambda_2 - 2\lambda_3 + \beta)/(8\mu) \quad (4)$$

where $\beta = [(\lambda_1 - \lambda_2)^2 - 16\mu^2 k_c^2]^{1/2}$, λ_1, λ_2, λ_3 and λ_4 are the λ parameters of $a_1^{(1)}$, $a_1^{(2)}$, b_1 and e modes, respectively.

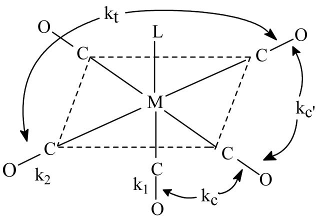

Fig. 1. Definition of the CO-factored force constants in $M(CO)_5L$ molecules.

Table 1
Secular equations for $M(CO)_5L$ molecules with C_{4v} symmetry

Secular equations [a]	Symmetry species
$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_2 + k_t + 2k_{c'}) - \lambda \end{vmatrix} = 0$	$a_1^{(1)}$ $a_1^{(2)}$
$\lambda = \mu(k_2 + k_t - 2k_{c'})$	b_1
$\lambda = \mu(k_2 - k_t)$	e

[a] The various k values are defined in Fig. 1; μ represents the reciprocal of the reduced mass of the CO group; $\lambda = 4\pi^2 c^2 \nu^2$ where ν is the frequency in cm^{-1}.

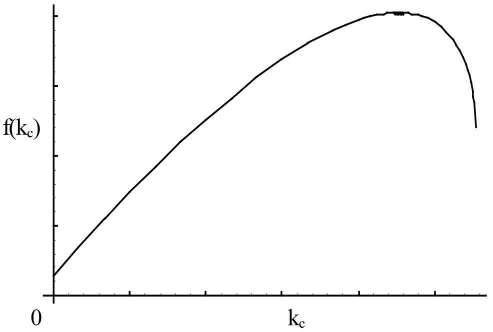

Fig. 2. Graph of the function $f(k_c)$ versus k_c.

As can be seen from Fig. 1, in $M(CO)_5L$ molecules there are four k_c, four $k_{c'}$ and two k_t. With the use of Eqs. (3) and (4), the following expression is obtained for the sum of the interaction constants:

$$k_{sum} = \{3\lambda_1 + 3\lambda_2 - 2\lambda_3 - 4\lambda_4 + 3[(\lambda_1 - \lambda_2)^2 - 16\mu^2 k_c^2]^{1/2} + 16\mu k_c\}/(4\mu) \quad (5)$$

where $k_{sum} = 2k_t + 4k_{c'} + 4k_c$. For a given molecule, the right-hand side of Eq. (5) has only one variable, k_c, and may therefore be regarded as a function of k_c, which is represented by $f(k_c)$. When the function $f(k_c)$ is plotted against k_c, the curve shown in Fig. 2 is obtained. It is clearly seen from the figure that the point at which the curve has a maximum corresponds to the maximum value of the sum of the interaction constants. In order to find the value of k_c that corresponds to the point, we have made use of the derivative of $f(k_c)$ with respect to k_c. Using the condition $df(k_c)/dk_c = 0$ gives the following expression for k_c:

$$k_c = (\lambda_1 - \lambda_2)/(5\mu) \quad (6)$$

This equation indicates that k_c is dependent only on the frequencies of the C–O stretching modes which belong to the same symmetry species (a_1) and that can be determined from their frequencies. Once k_c has been calculated, the other force constants can be determined from the secular equations given in Table 1. Furthermore, inserting Eq. (6) into Eqs. (1)–(4) gives the following relations:

$$k_1 = (\lambda_1 + 4\lambda_2)/(5\mu) \quad (7)$$

$$k_2 = (4\lambda_1 + \lambda_2 + 5\lambda_3 + 10\lambda_4)/(20\mu) \quad (8)$$

$$k_t = (4\lambda_1 + \lambda_2 + 5\lambda_3 - 10\lambda_4)/(20\mu) \quad (9)$$

$$k_{c'} = (4\lambda_1 + \lambda_2 - 5\lambda_3)/(20\mu) \quad (10)$$

It is worth noting that Eqs. (6)–(10) allow direct calculation of the CO-factored force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule.

3. Results and discussion

Eqs. (1)–(4) show that the determination of force constants for complexes of the type $M(CO)_5L$ with C_{4v} symmetry from frequencies of fundamental modes leads to an algebraic system which consists of four equations in five unknowns. It is mathematically evident for such a system that an infinite number of solutions will be possible. In fact, the solution corresponding to Eqs. (6)–(10), which is obtained using the maximum value of the sum of the interaction constants, is the only one possible solutions of the algebraic system. The validity of this solution can be tested by means of the assumption [19] that the force constants remain unchanged on isotopic substitution. This assumption also means that C–O stretching frequencies of isotopically enriched species can be determined by using the force constants of the all-$^{12}C^{16}O$ molecule.

For a large number of complexes of the type $M(CO)_5L$ with C_{4v} symmetry, the fully ^{12}CO-substituted and the radially substituted mono-^{13}CO derivatives have been prepared and their C–O stretching frequencies have been reported in the literature [11,12,20–24]. The force constants for some of the complexes mentioned were calculated by Eqs. (6)–(10) and are presented in Table 2. Since the determination of force constants from Eqs. (6)–(10) necessitates the use of all the fundamental C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule, not only the infrared-active ones, the λ_3 parameters of the $Cr(CO)_5(NHC_5H_{10})$, $Mo(CO)_5(PPh_3)$ and $M(CO)_5(H_2)$, (M = Cr, Mo, W) complexes whose b_1 frequencies have not been reported were calculated from their 'best fit' force constants given in the literature, by using the equation $\lambda_3 = \mu(k_2 + k_t - 2k_{c'})$.

The secular equations for the radially substituted mono-^{13}CO species of $M(CO)_5L$ molecules were derived by procedures given in Ref. [19] and are summarised in Table 3. With the use of these equations and the force constants presented in Table 2, the C–O stretching frequencies of isotopically enriched species with ^{13}CO in a radial position of $M(CO)_5L$ complexes were predicted. The results obtained are given in Table 4 together with the observed frequencies of the species.

Inspection of Table 4 reveals that there exists a very good agreement between observed and calculated frequencies, with a maximum error of 1.7 cm^{-1}. The mean error measured as $(\sigma^2/n)^{1/2}$ was calculated to be 0.8 cm^{-1}. Such an excellent fit indicates that Eqs. (6)–(10) can be used to calculate CO-factored force constants for the complexes under study, on the basis of the assumption that force constants remain unchanged on isotopic substitution.

In conclusion, the remarkably good agreement between observed and calculated frequencies of ^{13}CO substituted species shows that the solution corresponding to Eqs. (6)–(10) is a valid solution for the CO-factored force field of $M(CO)_5L$ molecules with C_{4v} symmetry. This also means that the constraint based on the maximum value of the sum of the interaction constants is applicable to the mentioned molecules. It should also be noted that the method presented allow direct calculation of CO-factored force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule and eliminates the necessity of isotopic vibrational data. For many complexes, isotopic data are not available because of experimental difficulty in obtaining the isotopically enriched derivatives and in many cases band broadening does not allow clear resolution of the important isotope bands. Therefore, it is important to develop methods of calculation that do not require isotopic substitution. As can be seen from the data in Table 4, one concludes that our method may be employed to analyse isotopic spectra of the complexes

Table 2
CO-factored force constants for some complexes of the type $M(CO)_5L$ with C_{4v} symmetry [a]

Complex	Force constants (N m^{-1})				
	k_1	k_2	k_t	$k_{c'}$	k_c
$Mn(CO)_5H$	1663.31	1684.08	44.74	22.21	36.65
$Mn(CO)_5D$	1661.73	1685.07	45.40	21.38	37.17
$Mn(CO)_5(CH_3)$	1639.42	1676.78	42.48	19.65	39.71
$Re(CO)_5D$	1658.96	1692.15	52.81	22.67	43.78
$Cr(CO)_5(NHC_5H_{10})$	1531.84	1570.04	59.88	23.61	48.43
$Mo(CO)_5(PPh_3)$	1577.45	1592.54	54.29	24.12	39.20
$Mo(CO)_5(N_2)$	1600.90	1631.09	50.29	22.90	42.09
$Cr(CO)_5(H_2)$	1610.85	1627.72	53.15	25.15	40.11
$Mo(CO)_5(H_2)$	1611.59	1633.18	51.59	25.64	41.49
$W(CO)_5(H_2)$	1611.63	1625.20	53.98	28.76	41.69

[a] C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule were taken from Refs. [11,12,20–24].

Table 3
Secular equations for the radially substituted mono-^{13}CO species of $M(CO)_5L$ molecules with C_{4v} symmetry

Secular equations [a]	Symmetry species
$\begin{vmatrix} \mu(k_2+k_t)-\lambda & \sqrt{2}\mu k_{c'} & \sqrt{2}\mu' k_{c'} & \sqrt{2}\mu k_c \\ \sqrt{2}\mu k_{c'} & \mu k_2-\lambda & \mu' k_t & \mu k_c \\ \sqrt{2}\mu k_{c'} & \mu k_t & \mu' k_2-\lambda & \mu k_c \\ \sqrt{2}\mu k_c & \mu k_c & \mu' k_c & \mu k_1-\lambda \end{vmatrix} = 0$	a′ a′ a′ a′
$\lambda = \mu(k_2-k_t)$	a″

[a] μ and μ' denote the reciprocal of the reduced mass of $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively.

Table 4
Observed and calculated frequencies for the species with one equatorial ^{13}CO

Species	Reference	Frequencies (cm^{-1}) [a]				
		a′	a′	a′	a′	a″
$Mn(CO)_4(^{13}CO)H$	[11]	2109.8	2035.4	–	1981.8	2014.5
		2110.1	2036.3	2007.5	1980.5	2014.5
$Mn(CO)_4(^{13}CO)D$	[11]	2109.8	2036.5	–	1981.5	2014.7
		2110.4	2038.0	2006.5	1980.7	2014.7
$Mn(CO)_4(^{13}CO)(CH_3)$	[12]	2103.3	2033.4	–	1976.1	2011.4
		2103.4	2033.5	1993.7	1974.6	2011.4
$Re(CO)_4(^{13}CO)D$	[11]	2122.9	2043.0	–	1982.1	2014.5
		2123.9	2044.4	2001.7	1980.4	2014.5
$Cr(CO)_5(^{13}CO)(NHC_5H_{10})$	[20]	2058.9	–	1917.8	1902.7	1933.5
		2059.8	1972.1	1919.2	1901.0	1933.5
$Mo(CO)_4(^{13}CO)(PPh_3)$	[21]	2064.8	1982.6	–	1921.2	1951.4
		2065.2	1982.6	1951.4	1920.6	1951.4
$Mo(CO)_4(^{13}CO)(N_2)$	[22]	2085.0	–	1965.7	–	1978.2
		2086.0	2005.8	1966.3	1944.8	1978.2
$Cr(CO)_4(^{13}CO)(H_2)$	[23]	2086.1	2002.6	–	1943.4	1974.3
		2087.1	2002.7	1972.1	1942.6	1974.3
$Mo(CO)_4(^{13}CO)(H_2)$	[24]	2090.1	2004.6	–	1947.2	1978.7
		2090.8	2004.7	1972.3	1946.2	1978.7
$W(CO)_4(^{13}CO)(H_2)$	[24]	2090.3	1997.5	–	1940.8	1972.2
		2091.2	1997.6	1971.5	1940.5	1972.2

[a] Frequencies are presented in the order of observed and calculated, for each species.

under study, using C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule.

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