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Direct calculation of CO-factored force constants from $^{12}C^{16}O$ stretching frequencies in $LM(CO)_4$ molecules with C_{3v} symmetry

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Abstract

The CO-factored force constants for $LM(CO)_4$ molecules having C_{3v} symmetry were calculated using the relations $k_1 = \alpha(3\lambda_1 + \lambda_2 + 8\lambda_3)$, $k_2 = 3\alpha(\lambda_1 + 3\lambda_2)$, $k_c = 3\alpha(\lambda_1 - \lambda_2)$ and $k_c^i = \alpha(3\lambda_1 + \lambda_2 - 4\lambda_3)$ where $\alpha = 1/(12\mu)$. The force constants obtained in this way were compared with those determined by the cos β parameter method and isotopic substitution. This comparison led us to conclude that the mentioned relations which allow direct calculation of force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule work very well for the complexes under study. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

For $LM(CO)_4$ molecules, under the C_{3v} local symmetry of the carbonyls, group theory predicts three C–O stretching modes ($2a_1 + e$), all of which are both infrared- and Raman-active. On the basis of the CO-factored force field [1–4], these molecules have two C–O stretching force constants and two CO–CO interaction constants. Since the number of force constants is more than the number of observable C–O stretching modes, the force field is underdetermined. Such a problem can in principle be solved by isotopic substitution [4–13]. However, in systems where isotopic data are not available because of experimental difficulty in obtaining the isotopically enriched species or if band broadening does not allow clear resolution of the important isotope bands, in order to solve the secular equations, it is necessary to impose one or more constraints on the force field.

In the case of insufficient vibrational data, several methods that enable us to evaluate force constants for complexes treated in this study have been reported in the literature. The method developed by Haas and Sheline [14] is based on the assumption that the effects of ligands on force constants are additive. However, with this method, the determination of force constants of $LM(CO)_4$ molecules necessitates the use of C–O stretching frequencies of all $M(CO)_{5-n}L_n$ ($n = 0,1,2,3,4$) species, not only those of $LM(CO)_4$. In the cos β parameter method proposed by Bor [15], the solution of the force field was reduced to the problem of finding the value of the cos β parameter. Since cos β depends on both the declination angle of equatorial ligands and the intensity ratio of two absorption bands belonging to the same symmetry species a_1, the method, therefore, has a difficulty in finding a suitable range for cos β.

Dalton and co-workers [16], using a relationship between the interaction constants, derived from orbital overlap considerations [17], have calculated force constants for a series of complexes of the type $LM(CO)_4$ with C_{3v} symmetry. In their calculations, it was shown that the force constants calculated in this way are nearly equal to those obtained from the assumption that maximum coupling occurs between the two a_1 modes. This assumption corresponds to the maximum value of the Co_{ax}–CO_{eq} interaction constant. Combination of this result with the cos β parameter method [15] leads to cos $\beta = 0$.

Another method which can be used to determine force constants for complexes under study has been developed by Timney [18]. However, this method is

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restricted to complexes whose ligand effect constants and bond angles are known because the relationships suggested for force constants are expressed in terms of the mentioned parameters.

In a recent work [19] on calculating the CO-factored force constants for $M(CO)_4$ molecules having C_{3v} symmetry, we have developed a method that utilizes only $^{12}C^{16}O$ stretching frequencies. In this paper we applied this method to $LM(CO)_4$ molecules belonging to the C_{3v} point-group. The force constants calculated by the method were compared with those obtained by the $\cos\beta$ parameter method and by isotopic substitution.

2. Results and discussion

In our previous paper [19], the following relations were derived for $M(CO)_4$ molecules with C_{3v} symmetry, using the constraint based on the maximum value of sum of the interaction constants. A relation between the sum of the interaction force constants and k_c was derived. Determination of the maximum in this function led to Eq. (4). Substitution into the equations for k_1, k_2 and k_c^i gave Eqs. (1)–(3):

$$k_1 = \alpha(3\lambda_1 + \lambda_2 + 8\lambda_3) \tag{1}$$

$$k_2 = 3\alpha(\lambda_1 + 3\lambda_2) \tag{2}$$

$$k_c^i = \alpha(3\lambda_1 + \lambda_2 - 4\lambda_3) \tag{3}$$

$$k_c = 3\alpha(\lambda_1 - \lambda_2) \tag{4}$$

where $\alpha = 1/(12\mu)$; k_1 and k_2 are the stretching force constants for equatorial and axial CO groups; k_c^i and k_c are the constants for Co_{eq}–CO_{eq} and Co_{ax}–CO_{eq} interactions; λ_1, λ_2 and λ_3 are the λ parameters of $a_1^{(1)}$, $a_1^{(2)}$ and e modes, respectively.

Since the secular equations for $M(CO)_4$ and $LM(CO)_4$ molecules belonging to the same point-group, C_{3v}, are the same on the basis of the CO-factored force field, it seems quite reasonable to assume that the above relations and the constraint employed to obtain them are valid for the latter molecules. In order to test the validity of this assumption, Eqs. (1)–(4) were first applied to some complexes whose force constants have previously been determined by the $\cos\beta$ parameter method [15]. Inspection of Table 1 reveals that there exists a very good agreement between the force constants calculated by the two methods for $HCo(CO)_4$ $CH_3Co(CO)_4$ and $Ph_3PFe(CO)_4$ complexes. It should also be noted that the method presented here utilizes only $^{12}C^{16}O$ stretching frequencies, whereas the application of the $\cos\beta$ parameter method needs to find a suitable value for $\cos\beta$, in addition to the use of the mentioned frequencies. Therefore, our method is easier to apply than the $\cos\beta$ parameter method.

As a further check upon the validity of Eqs. (1)–(4), they were employed to predict C–O stretching frequencies of isotopically enriched species and the results obtained were compared with observed frequencies of the species. For such a comparison we have made use of ^{13}CO-substituted species, since the CO-factored force field works best for $^{13}C^{16}O$-substitution [20,21]. Isotopically enriched species with ^{13}CO occupying an equatorial position of $Cl_3SiCo(CO)_4$, $Ph_3SiCo(CO)_4$ and $Ph_3PFe(CO)_4$ complexes were prepared and their infrared spectra in the carbonyl stretching region were reported by Darensbourg [22]. Using the C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule, which have been reported by Darensbourg, the force constants for the complexes mentioned above were calculated from Eqs. (1)–(4). As can be seen from Table 2, the force constants calculated in this way are in close agreement with those obtained by using ^{13}CO frequency data with an iterative computer program [22].

The secular equations for isotopically enriched species with ^{13}CO in an equatorial position of $LM(CO)_4$ molecules belonging to C_{3v} symmetry were derived by procedures given in Ref. [23] and are presented in Table 3. With the use of these equations and the force constants calculated by Eqs. (1)–(4), the C–O stretching

Table 1
Comparison of our results with those obtained by the $\cos\beta$ parameter method

	Frequencies (cm^{-1}) [a]			Force constants (mdyn/Å) [b]				
Complex	$a_1^{(1)}$	$a_1^{(2)}$	e	k_1	k_2	k_c^i	k_c	$\cos\beta$ [b]
$HCo(CO)_4$	2116.1	2052.3	2029.8	17.037	17.298	0.389	0.272	0.48
				17.036	17.283	0.392	0.269	0.50
$CH_3Co(CO)_4$	2104.6	2035.5	2018.5	16.845	17.031	0.382	0.289	0.50
(Solution)				16.840	17.026	0.382	0.289	0.50
$CH_3Co(CO)_4$	2111.0	2045.9	2031.2	17.025	17.186	0.354	0.274	0.50
(Vapour)				17.020	17.182	0.354	0.273	0.50
$Ph_3PFe(CO)_4$	2051.7	1979.1	1946.4	15.755	16.188	0.447	0.314	0.39
				15.775	16.118	0.468	0.296	0.50

[a] Taken from Ref. [15].

[b] Force constants and $\cos\beta$ are presented in the order the $\cos\beta$ parameter method and our method, for each complex.

Table 2
CO-factored force constants for some complexes of the type $LM(CO)_4$ with C_{3v} symmetry

	Frequencies (cm^{-1}) [a]			Force constants (mdyn/Å) [b]			
Complex	$a_1^{(1)}$	$a_1^{(2)}$	e	k_1	k_2	k_c^i	k_c
$Cl_3SiCo(CO)_4$	2120.6	2064.8	2039.4	17.14	17.56	0.347	0.260
				17.177	17.458	0.376	0.236
$Ph_3SiCo(CO)_4$	2100.3	2033.5	2005.8	16.63	17.14	0.379	0.315
				16.682	16.983	0.429	0.279
$Ph_3PFe(CO)_4$	2052.2	1979.7	1946.6	15.74	16.22	0.441	0.320
				15.777	16.127	0.470	0.295

[a] Taken from Ref. [22].

[b] Force constants presented in the order isotopic substitution and our method, for each complex.

frequencies of isotopically enriched species with ^{13}CO in an equatorial position of $Cl_3SiCo(CO)_4$ $Ph_3SiCo(CO)_4$ and $Ph_3PFe(CO)_4$ were estimated. It can be seen from Table 4 that a rather good fit between observed and calculated frequencies was obtained, with a maximum error of 2.4 cm^{-1}. The mean error measured as $(\sigma^2/n)^{1/2}$ was calculated to be 1.5 cm^{-1}. In Table 2, the frequencies calculated by Darensbourg through use of iterative procedures are also given. The mean and maximum errors in his calculations are 1.6 and 4.1 cm^{-1}, respectively. It is clearly seen that our mean error is very close to that of Darensbourg. It is also worth noting that the maximum error in our calculation is much smaller. This is a further evidence for the validity of Eqs. (1)–(4) for complexes under study.

Table 5 shows the CO-factored force constants calculated from Eqs. (1)–(4) for a number of complexes of the type $R_3MCo(CO)_4$ with C_{3v} symmetry. It seems possible to sort out these complexes into series: those in which only R differs from one complex to another, such as $Et_3GeCo(CO)_4$, $Ph_3GeCo(CO)_4$, $I_3GeCo(CO)_4$, $Br_3GeCo(CO)_4$, $Cl_3GeCo(CO)_4$, and those in which only M differs from one to another, such as $Et_3SiCo(CO)_4$, $Et_3GeCo(CO)_4$, $Et_3SnCo(CO)_4$, $Et_3PbCo(CO)_4$. As can be seen from Table 5, in the series of the first class the carbonyl stretching force constants (k_1 and k_2) increase as the electron-withdrawing ability of R increases; in the series being assigned to the second class the mentioned force constants are decreased with increasing the size of M. These trends can be explained in terms of simple π bonding model [24–27]. According to this model, in a molecule of the type $R_3M(CO)_4$ there is a competition between R_3M and CO ligands for electron density in the filled cobalt d orbitals capable of π bonding. This competition leads us to conclude that an increase in the M–Co π bonding will cause the carbonyl stretching force constants to increase. The model mentioned also predicts that the extent of π bonding in the M–Co linkage depends on both the inductive effect of R and the size of M. As the electron-pulling ability of R increases, the electron affinity of the empty dπ orbitals of M is increased and as a result an increase in the M–Co π bonding will occur. The π interaction in the M–Co is decreased with increasing size of M because the energy difference

Table 3
Secular equations for isotopically enriched species with ^{13}CO in an equatorial position of $LM(CO)_4$ molecules

Secular equations [a]	Symmetry species
$\begin{vmatrix} \mu^* k_1-\lambda & \sqrt{2}\mu k_c^1 & \mu k_c \\ \sqrt{2}\mu^* k_c^1 & \mu(k_1+k_c^1)-\lambda & \sqrt{2}\mu k_c \\ \mu^* k_c & \sqrt{2}\mu k_c & \mu k_2-\lambda \end{vmatrix} = 0$	a^1 a^1 a^1
$\lambda=\mu(k_1-k_c^1)$	a^{11}

[a] μ and μ^* denote the reciprocal of the reduced mass of $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively; $\lambda = 4\pi^2c^2\nu^2$ where ν is the frequency in cm^{-1}.

Table 4
Observed and calculated frequencies for some isotopically enriched species of complexes of the type $LM(CO)_4$

	Frequencies (cm^{-1})			
Species	Observed [a]	Calculated [a]	Calculated [b]	Assignment
$Cl_3SiCo(^{12}CO)_3$	2113.0	2113.9	2112.7	a^1
(^{13}CO)				
$(^{13}CO,eq)$	–	2062.2	2063.0	a^1
	2001.1	2002.4	2003.2	a^1
	2039.4	2038.8	2039.4	a^{11}
$Ph_3SiCo(^{12}CO)_3$	2089.6	2093.7	2092.0	a^1
(^{13}CO)				
$(^{13}CO,eq)$	–	2030.6	2031.6	a^1
	1969.1	1969.9	1970.7	a^1
	2005.8	2005.4	2005.8	a^{11}
$Ph_3PFe(^{12}CO)_3$	2046.2	2044.7	2043.8	a^1
(^{13}CO)				
$(^{13}CO,eq)$	–	1977.0	1977.6	a^1
	1911.6	1912.5	1913.1	a^1
	1946.6	1946.2	1946.6	a^{11}

[a] From Ref. [22].

[b] Calculated by our force constants.

Table 5
CO-factored force constants for complexes of the type $R_3M(CO)_4$ with C_{3v} symmetry [a]

Complex	Frequencies (cm^{-1})			Force constants (mdyn/Å)			
	$a_1^{(1)}$	$a_1^{(2)}$	e	k_1	k_2	k_c^i	k_c
$Et_3SiCo(CO)_4$	2088.7	2025.0	1994.5	16.499	16.829	0.430	0.265
$Et_3GeCo(CO)_4$	2084.2	2020.7	1991.0	16.437	16.758	0.424	0.263
$Et_3SnCo(CO)_4$	2079.5	2015.6	1985.1	16.347	16.676	0.429	0.264
$Et_3PbCo(CO)_4$	2070.3	2006.5	1978.5	16.227	16.526	0.412	0.263
$Ph_3GeCo(CO)_4$	2091	2030	2006	16.640	16.901	0.384	0.254
$Ph_3SnCo(CO)_4$	2087	2027	1999	16.543	16.847	0.401	0.249
$Ph_3PbCo(CO)_4$	2081	2022	1997	16.490	16.760	0.380	0.245
$Cl_3GeCo(CO)_4$	2122	2069	2050	17.306	17.517	.0330	0.224
$Cl_3SnCo(CO)_4$	2120	2068	2048	17.274	17.496	0.331	0.220
$Br_3GeCo(CO)_4$	2118	2066	2048	17.263	17.462	0.319	0.220
$Br_3SnCo(CO)_4$	2116	2063	2043	17.195	17.416	0.334	0.224
$I_3GeCo(CO)_4$	2113	2062	2042	17.170	17.391	0.326	0.215
$I_3SnCo(CO)_4$	2109	2058	2037	17.092	17.323	0.330	0.215

[a] Spectra of the first four complexes were measured in *n*-hexadecane; see Ref. [28]. Spectra of the remaining complexes were measured in cyclohexane; see Refs. [25,29].

between the filled d–π orbitals of Co and the empty d–π orbitals of M becomes greater. It is clearly seen that these theoretical considerations are consistent with our observations related to the series mentioned above.

In conclusion, comparison of our results with those obtained by the cos β parameter method and isotopic substitution shows that Eqs. (1)–(4) are applicable to molecules of the type $LM(CO)_4$ having C_{3v} symmetry. This also means that the mentioned equations correspond to a valid solution for the secular equations of $LM(CO)_4$ molecules. From the data in Table 4, one concludes that the method presented here may be employed to analyze isotopic spectra of the complexes under study, using C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule. The fact that our conclusions about the complexes given in Table 5 are consistent with theoretical predictions could be taken as an indirect evidence for the validity of Eqs. (1)–(4).

The results of the present and our previous studies [19] encourage us to apply the constraint by which Eqs. (1)–(4) are obtained to other complexes with different symmetries. Examples of such kind of application will be published in subsequent papers.

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