ELSEVIER

Journal of Organometallic Chemistry 575 (1999) 209–213

Journal of Organometallic Chemistry

A new approach to solving the CO-factored force field of $M(CO)_4$ molecules having C_{3v} symmetry

Cemal Kaya

Department of Chemistry, Cumhuriyet University, 58140 Sivas, Turkey

Received 21 July 1998

Abstract

The CO-factored force field of $M(CO)_4$ molecules with C_{3v} symmetry was solved using the maximum value of the sum of the interaction constants as an additional constraint. The solution obtained led to the relations which allow direct calculation of force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule. The CO-factored force constants and C–O stretching frequencies of $^{13}C^{16}O$-substituted species were calculated for $Co(CO)_4$ and $Fe(CO)_4^-$. The results were found to be in very close agreement with those obtained from isotopic enrichment studies. © 1999 Elsevier Science S.A. All rights reserved.

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

1. Introduction

The infrared spectra of metal carbonyl complexes in the region of 2150–1750 cm^{-1} contain sharp and commonly intense absorption bands due to carbonyl stretching vibrations. The analysis of these vibrations, to provide force constants, usually involves using the CO-factored force field [1–7] which neglects anharmonicity and all coupling except CO–CO interaction. However, this simplified force field is underdetermined for the complexes in which the number of the force constants exceeds the number of observable C–O stretching modes.

The difficulty mentioned above is most frequently overcome by the method which uses isotopic vibrational data [8–16]. In this method, assuming the force constants remain unchanged on isotopic substitution, the set of force constants which gives the best agreement between observed and calculated frequencies of species enriched isotopically is determined through use of iterative procedures.

Another way to overcome the problem due to insufficient vibrational data is to impose one or more constraints on the force field. Although there have been some publications [1,7,17–23] related to this method, none of them has considered the complexes of the $M(CO)_4$ type having C_{3v} symmetry.

In this paper, the maximum value of the sum of the interaction constants was used as an additional constraint to solve the secular equations for $M(CO)_4$ molecules with C_{3v} symmetry. With the use of this constraint, we were able to derive the relations which allow direct calculation of the CO-factored force constants from CO-stretching frequencies of the all-$^{12}C^{16}O$ molecule.

2. Derivation of relations

For $M(CO)_4$ molecules, under the C_{3v} local symmetry of the carbonyls, group theory predicts three carbonyl stretching modes ($2a_1 + e$). All the modes are both infrared and Raman-active. On the basis of the CO-factored force field, these molecules have two carbonyl stretching force constants (k_1 and k_2) and two CO–CO interaction constants (k_c and k_c'). The secular equations for the molecules are given in Table 1.

PII: S0022-328X(98)00995-4

Since there are four force constants to be calculated and only three observable C–O stretching modes for the all-$^{12}C^{16}O$ molecule, it is mathematically evident that the solution of the force field necessitates the use of an additional constraint. For the molecules under study, we have used the maximum value of the sum of the interaction constants as a constraint. In order to solve the force field using this constraint, the secular equations given in Table 1 were rearranged so that three of the four force constants are expressed in terms of the fourth and the observed frequencies:

$$k_1 = (\lambda_1 + \lambda_2 + 4\lambda_3 + \beta)/(6\mu) \tag{1}$$

$$k_2 = (\lambda_1 + \lambda_2 - \beta)/(2\mu) \tag{2}$$

$$k'_c = (\lambda_1 + \lambda_2 - 2\lambda_3 + \beta)/(6\mu) \tag{3}$$

where $\beta = [(\lambda_1 - \lambda_2)^2 - 12\mu^2 k_c^2]^{1/2}$; λ_1, λ_2 and λ_3 are the λ parameters of $a_1^{(1)}$, $a_2^{(2)}$ and e modes, respectively.

In a molecule of the $M(CO)_4$ type having C_{3v} symmetry there are three k_c and three k'_c. With the use of Eq. (3), the following expression is obtained for the sum of the interaction constants.

$$3k'_c + 3k_c = \{\lambda_1 + \lambda_2 - 2\lambda_3 + [(\lambda_1 - \lambda_2)^2 - 12\mu^2 k_c^2]^{1/2} + 6\mu k_c\}/(2\mu) \tag{4}$$

For a given molecule, the right-hand side of Eq. (4) 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. 1 is obtained. As can be seen from Fig. 1, 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. With the use of $df(k_c)/dk_c = 0$, we have

$$k_c = (\lambda_1 - \lambda_2)/(4\mu) \tag{5}$$

Eq. (5) 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 calculated from them. Once k_c has been calculated, the other force constants can be determined from the secular equations given in Table 1. Furthermore, inserting Eq. (5) into Eqs. (1)–(3) gives the following relations which allow direct calculation of k_1, k_2 and k'_c from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule:

Table 1
Secular equations for $M(CO)_4$ molecules with C_{3v} symmetry

Symmetry species	Secular equations[a]		
$a_1^{(1)}$	$\mu(k_1+2k'_c)-\lambda$	$\sqrt{3}\mu k_c$	$=0$
$a_1^{(2)}$	$\sqrt{3}\mu k_c$	$\mu k_2-\lambda$	
e	$\lambda=\mu(k_1-k'_c)$		

[a] k_1 and k_2 are the stretching force constants of the equatorial and axial CO groups, respectively; k_c and k'_c refer to the interaction constants for CO_{ax}–CO_{eq} and CO_{eq}–CO_{eq}; μ represents the reciprocal of the reduced mass of the CO group; $\lambda = 4\pi^2c^2\nu^2$ where ν is the frequency in cm^{-1}.

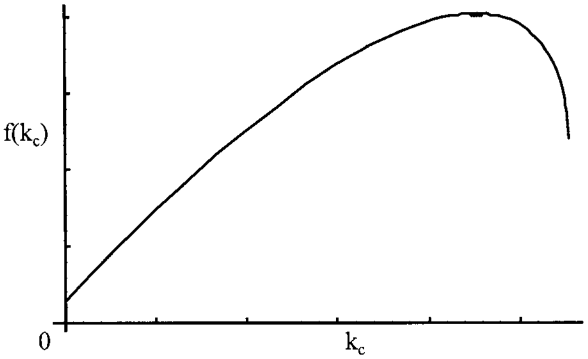

Fig. 1. Graph of the function $f(k_c)$ versus k_c.

$$k_1 = \alpha(3\lambda_1 + \lambda_2 + 8\lambda_3) \tag{6}$$

$$k_2 = 3\alpha(\lambda_1 + 3\lambda_2) \tag{7}$$

$$k'_c = \alpha(3\lambda_1 + \lambda_2 - 4\lambda_3) \tag{8}$$

where $\alpha = 1/(12\mu)$

3. Results and discussion

As can be seen from Eqs. (1)–(3), the determination of force constants from C–O stretching frequencies leads to an algebraic system which consists of three equations in four 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. (5)–(8) is the only one of possible solutions of the algebraic system.

To ascertain whether the solution found here was the valid one or not, Eqs. (5)–(8) were used to calculate force constants and C–O stretching frequencies of ^{13}CO-substituted species of $Co(CO)_4$. Both ESR [24,25] and isotopic enrichment studies [26,27] indicated that $Co(CO)_4$ has a geometry consistent with a C_{3v} symmetry. Its C–O stretching bands were observed by Hanlan et al. [27] at 2107.0(a_1), 2028.8(a_1) and 2010.7(e) cm^{-1}. Using these frequencies, the force constants for $Co(CO)_4$ were calculated from Eqs. (5)–(8). As can be seen from Table 2, the force constants calculated in this way are in excellent agreement with those of Hanlan et al., obtained from isotopic enrichment studies.

The secular equations required for isotopically enriched species of $M(CO)_4$ molecules having C_{3v} symmetry were derived by procedures given in Ref. [28] and are summarised in Table 3. With the use of these equations and the force constants calculated, the C–O

Table 2
CO-factored force constants[a] for $Co(CO)_4$ and $[Fe(CO)_4]^-$

Complex	Ref.	Force constants (Nm^{-1})			
		k_1	k_2	k'_c	k_c
$Co(CO)_4$	[27]	1675.5	1695.2	42.5	32.8
		1675.67	1695.36	42.51	32.66
$[Fe(CO)_4]^-$	[30]	1425	1431	38	30
		1425.13	1435.24	36.45	31.40

[a] Presented in the order of the experimental method in the Refs. [27,30] and our method, for each complex.

stretching frequencies of ^{13}CO-substituted species of the $Co(CO)_4$ were estimated. The results obtained are given in Table 4 together with observed frequencies [27] of the species. Inspection of Table 4 reveals that there exists an excellent fit between observed and calculated frequencies. The mean error measured as $(\sigma^2/n)^{1/2}$ was 0.32 cm^{-1}. Such a excellent fit indicates that it is not necessary to use the effective reduced mass correction, introduced by Bor [13], as an additional parameter included in the force field of $Co(CO)_4$

As another evidence for the validity of the relations derived here, similar calculations were made for $[Fe(CO)_4]^-$. From both ESR [29] and isotopic enrichment studies [30] it has been suggested that this anion has also a C_{3v} structure. Its two C–O stretching bands were observed by Breeze et al. [30] at 1864.2(a_1) and 1854.1(e) cm^{-1} in low-temperature matrices. Since the

Table 4
Observed [27] and calculated CO stretching frequencies for ^{13}CO-substituted species of $Co(CO)_4$

Species	Frequencies (cm^{-1})		Assignments
	Observed	Calculated	
$Co(^{12}CO)_3(^{13}CO)$, C_{3v}		2099.1	a_1
(^{13}CO); ax	1991.3	1991.1	a_1
	2010.7	2010.7	e
$Co(^{12}CO)_3(^{13}CO)$, C_s		2098.6	a′
(^{13}CO); eq	2026.4	2027.4	a′
	1974.6	1975.2	a′
	2010.7	2010.7	a″
$Co(^{12}CO)_2(^{13}CO)_2$, C_s		2089.1	a′
^{13}CO; ax, eq	1992.7	1993.0	a′
	1973.3	1973.3	a′
	2010.7	2010.7	a″
$Co(^{12}CO)_2(^{13}CO)_2$, C_s		2089.2	a′
^{13}CO; eq, eq	2024.6	2024.6	a′
	1986.8	1986.8	a′
	1965.7	1965.9	a″
$Co(^{12}CO)(^{13}CO)_3$, C_{3v}		2078.3	a_1
^{13}CO; eq, eq, eq	2010.7	2010.9	a_1
	1965.7	1965.9	e
$Co(^{12}CO)(^{13}CO)_3$, C_s		2077.0	a′
^{13}CO; ax, eq, eq	1997.9	1998.0	a′
	1979.6	1979.8	a′
	1965.7	1965.9	a″
$Co(^{13}CO)_4$, C_{3v}		2060.0	a_1
	1983.6[a]	1983.6	a_1
	1965.7	1965.9	e

[a] This frequency was observed by Crichton et al. [26], equal to our calculated value.

Table 3
Secular equations for isotopically substituted species of $M(CO)_4$ molecules with C_{3v} symmetry[a]

$M(^{12}CO)_3(^{13}CO)$, (ax), C_{3v}

$$2a_1\begin{vmatrix} \mu(k_1+2k'_c)-\lambda & \sqrt{3}\mu^*k_c \\ \sqrt{3}\mu k_c & \mu^*k_2-\lambda \end{vmatrix}=0$$

e $\lambda=\mu(k_1-k'_c)a''$

$M(^{12}CO)_3(^{13}CO)$, (eq), C_s

$$3a'\begin{vmatrix} \mu^*k_1-\lambda & \sqrt{2}\mu k'_c & \mu k_c \\ \sqrt{2}\mu^*k'c & \mu(k_1+k'_c)-\lambda & \sqrt{2}\mu k_c \\ \mu^*k_c & \sqrt{2}\mu k_c & \mu k_2-\lambda \end{vmatrix}=0$$

$\lambda=\mu(k_1-k'_c)$

$M(^{12}CO)_2(^{13}CO)_2$, (ax, eq), C_s

$$3a'\begin{vmatrix} \mu^*k_1-\lambda & \sqrt{2}\mu k'_c & \mu^*k_c \\ \sqrt{2}\mu^*k'_c & \mu(k_1+k'_c)-\lambda & \sqrt{2}\mu^*k_c \\ \mu^*k_c & \sqrt{2}\mu k_c & \mu^*k_2-\lambda \end{vmatrix}=0$$

a″ $\lambda=\mu(k_1-k'_c)$

$M(^{12}CO)_2(^{13}CO)_2$, (eq, eq), C_s

$$3a'\begin{vmatrix} \mu k_1-\lambda & \sqrt{2}\mu^*k'_c & \mu k_c \\ \sqrt{2}\mu k'_c & \mu^*(k_1+k'_c)-\lambda & \sqrt{2}\mu k_c \\ \mu k_c & \sqrt{2}\mu^*k_c & \mu k_2-\lambda \end{vmatrix}=0$$

a″ $\lambda=\mu^*(k_1-k'_c)$

$M(^{12}CO)(^{13}CO)_3$, (ax, eq, eq), C_s

$$3a'\begin{vmatrix} \mu k_1-\lambda & \sqrt{2}\mu^*k'_c & \mu^*k_c \\ \sqrt{2}\mu k'_c & \mu^*(k_1+k'_c)-\lambda & \sqrt{2}\mu^*k_c \\ \mu k_c & \sqrt{2}\mu^*k_c & \mu^*k_2-\lambda \end{vmatrix}=0$$

a″ $\lambda=\mu^*(k_1-k'_c)$

$M(^{12}CO)(^{13}CO)_3$, (eq, eq, eq), C_{3v}

$$2a_1\begin{vmatrix} \mu^*(k_1+2k'_c)-\lambda & \sqrt{3}\mu k_c \\ \sqrt{3}\mu^*k_c & \mu k_2-\lambda \end{vmatrix}=0$$

e $\lambda=\mu^*(k_1-k'_c)$

[a] μ and μ^* denote the reciprocal of the reduced mass of $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively; the secular equations for $M(^{13}CO)_4$ species can be obtained easily from the secular equations of the parent molecule given in Table 1, replacing μ with μ^*.

Table 5
Observed [30] and calculated CO stretching frequencies for ^{13}CO-substituted species of $[Fe(CO)_4]^-$

Species	Frequencies (cm^{-1})			Assignments
	Observed	Calculated[a]	Calculated[b]	
$Fe(^{12}CO)_3(^{13}CO)$, C_{3v}		1938.2	1938.0	a_1
^{13}CO; ax	1828.8	1829.8	1828.8	a_1
	1854.1	1854.1	1854.1	e
$Fe(^{12}CO)_3(^{13}CO)$, C_s		1937.9	1937.8	a′
^{13}CO; eq	1863.3	1863.3	1863.3	a′
	1819.8	1821.0	1820.0	a′
	1854.1	1854.1	1854.1	a″
$Fe(^{12}CO)_2(^{13}CO)_2$, C_s		1929.0	1928.7	a′
^{13}CO; ax, eq	1831.7	1833.4	1832.5	a′
	1816.3	1817.9	1816.7	a′
	1854.1	1854.1	1854.1	a″
$Fe(^{12}CO)_2(^{13}CO)_2$, C_s		1929.0	1928.7	a′
^{13}CO; eq, eq	1862	1861.5	1861.5	a′
	1831.7	1831.2	1830.3	a′
	1811.6	1812.8	1811.6	a″
$Fe(^{12}CO)(^{13}CO)_3$, C_{3v}		1918.5	1917.9	a_1
^{13}CO; eq, eq, eq	1850	1848.6	1848.0	a_1
	1811.6	1812.8	1811.6	e
$Fe(^{12}CO)(^{13}CO)_3$, C_s		1917.9	1917.3	a′
^{13}CO; ax, eq, eq	1840.5	1840.8	1840.2	a′
	1821	1821.1	1819.9	a′
	1811.6	1812.8	1811.6	a″
$Fe(^{13}CO)_4$, C_{3v}		1902.4	1901.2	a_1
		1822.6	1821.5	a_1
	1811.6	1812.8	1811.6	e

[a] Calculated without practical reduced mass ratio.

[b] Calculated with a practical reduced mass ratio of 0.9771.

high-frequency a_1 mode has not been observed, its calculated value given in Ref. [30] was used in our calculations. The force constants calculated by using Eqs. (5)–(8) are presented in Table 2. It can be seen from Table 2 that the calculated force constants are in close agreement with those obtained from isotopic enrichment studies. Using these force constants and the equations given in Table 3, a good fit between observed and calculated frequencies was obtained for ^{13}CO-substituted species of $[Fe(CO)_4]^-$ (Table 5). The mean error was calculated to be 0.98 cm^{-1}. A somewhat better fit was obtained by using the practical reduced mass ratio, with a mean error of 0.70 cm^{-1}. It is worth noting that this value is very close to that of Breeze et al., 0.62 cm^{-1}. The practical reduced mass ratio for $[Fe(CO)_4]^-$ was calculated from observed frequencies of the e modes of $[Fe(^{12}CO)_4]^-$ and $[Fe(^{13}CO)_4]^-$ species.

In conclusion, the results obtained for both $Co(CO)_4$ and $[Fe(CO)_4]^-$ show that the constraint based on 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 belonging to the C_{3v} point-group. The relations derived by this constraint make it easy to calculate force constants, allowing direct calculation of them from fundamental C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule. As can be seen from Tables 4 and 5, a remarkably good agreement between observed and calculated frequencies of ^{13}CO-substituted species was obtained using the set of force constants calculated from Eqs. (5)–(8). This indicates that the method presented may be used to analyse isotopic spectra of the tetracarbonyls under study.

References

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

[2] F.A. Cotton, Inorg. Chem. 3 (1964) 702.

[3] H. Haas, R.K. Sheline, J. Chem. Phys. 47 (1967) 2996.

[4] L.M. Haines, M.H.B. Stiddard, Adv. Inorg. Chem. Radiochem. 12 (1963) 53.

[5] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.

[6] J.K. Burdett, M. Poliakoff, J.A. Timney, J.J. Turner, Inorg. Chem. 17 (1978) 948.

[7] J.A. Timney, Inorg.Chem. 18 (1979) 2502.

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

[9] P.S. Braterman, R.W. Harril, H.D. Kaesz, J. Am. Chem. Soc. 89 (1967) 2851.

[10] F.A. Cotton, A. Musco, G.Y. Yagupsky, Inorg. Chem. 6 (1967) 1357.

[11] B.F.G. Johnson, J. Lewis, J.R. Miller, B.H. Robinson, P.W. Robison, A. Wojcicki, J. Chem. Soc. A (1968) 522.

[12] I.S. Butler, H.K. Spendjian, J. Organometal. Chem. 18 (1969) 145.

[13] G. Bor, Inorg. Chim. Acta. 3 (1969) 191.

[14] R.N. Perutz, J.J. Turner, Inorg. Chem. 14 (1975) 262.

[15] R.N. Perutz, J.J. Turner, J. Am. Chem. Soc. 97 (1975) 4800.

[16] M.F. Gregory, M. Poliakoff, J.J. Turner, J. Mol. Struct. 127 (1985) 247.

[17] F.T. Debleke, E.G. Claeys, G.P. vander Kelen, R.M. de Caluwe, J. Organomet. Chem. 23 (1970) 497.

[18] F.T. Debleke, E.G. Claeys, R.M. de Caluwe, G.P. van der Kelen, J. Organomet. Chem. 23 (1970) 505.

[19] J. Dalton, I. Paul, J.G. Smith, F.G.A. Stone, J. Chem, Soc. A 1968 (1199).

[20] R.T. Jernigan, R.A. Brown, G.R. Dobson, J. Coord. Chem. 2 (1972) 47.

[21] B.J. Brisdon, G.F. Griffin, J. Mol. Struct. 41 (1977) 99.

[22] C. Kaya, Spectrochim. Acta Part A 50 (1994) 1101.

[23] C. Kaya, Spectrochim. Acta Part A 52 (1996) 615.

[24] H.J. Keller, H. Wawersik, Z. Naturforsch. 206 (1965) 938.

[25] S.A. Fieldhouse, B.W. Fullam, G.W. Neilson, M.C.R. Symson, J. Chem. Soc. Dalton Trans. 1974 (567).

[26] O. Crichton, M. Poliakoff, A.J. Rest, J.J. Turner, J. Chem. Soc. Dalton Trans. (1973)1321.

[27] L. Hanlan, H. Huber, E.P. Künding, B.R. McGarvey, G.A. Ozin, J. Am. Chem. Soc. 97 (1975) 7054.

[28] E.B. Wilson Jr., J.F. Decius, P.C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.

[29] P.J. Krusic, J. San Filippo, B. Hutchinson, R.L. Hance, L.M. Daniels, J. Am. Chem. Soc. 103 (1981) 2129.

[30] P.A. Breeze, J.K. Burdett, J.J. Turner, Inorg. Chem. 20 (1981) 3369.