



# Calculating the CO-factored force constants of tricarbonyl complexes with $C_s$ symmetry

Elvan Üstün\*, Cemal Kaya

Department of Chemistry, Cumhuriyet University, 58140 Sivas, Turkey

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## ABSTRACT

The maximum value of the sum of the interaction constants is used as an additional constraint to solve the CO-factored force fields of tricarbonyl complexes with  $C_s$  symmetry. The solution obtained led to the equations by which carbonyl stretching force constants and CO–CO interaction constants can be calculated directly from C–O stretching frequencies of the all- $^{12}C^{16}O$  molecule. The CO-factored force constants and the C–O stretching frequencies of  $^{13}C^{16}O$ -substituted species were calculated for  $Fe(CO)_3^-$  and  $Fe(C_4H_6)(CO)_3$ . The results obtained were found to be very close agreement with those obtained from isotopic enrichment studies.

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## 1. Introduction

Metal carbonyls are very important complexes in organometallic chemistry of transition elements. Since the synthesis of  $Ni(CO)_4$  as the first metal carbonyl complex in 1890 [1], these complexes attracts the scientists' attention. They were synthesized for employing in chemistry such as initial substance of binuclear complexes [2], complex synthesis with photolysis [3], far-infrared studies in gas phase [4], excited state infrared spectrum analysis [5], labeling of the biologically active molecules [6]. Furthermore, DFT (Density Functional Theory) investigations [7–11] and polymerization of metal carbonyl complexes [12,13] take part in scientific literature recently. Because of the increasing popularity, analyzing of these complexes is very important.

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, for providing force constants, usually involves using the CO-factored force field [14–20], 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 [21–29]. In this method, assuming the force constants remain unchanged on isotopic substitution, the set of force constants which gives the best agreement observed and calculated frequencies species enriched isotopically is determined through use of iterative procedures. Unfortunately, for many complexes isotopic data are not available because of experimental difficulty in obtaining the isotopically enriched species. In addition, in many cases band broadening does not allow clear resolution of the important isotope bands. It is, therefore, important to develop methods of calculation which do not require isotopic substitution.

Another way to overcome the problem due to insufficient vibrational data is to impose one or more constraints on the force field. Although these have been some publications [14,18,20,30–35] related to this method, none of them has considered the complexes understudy. One of these is the successful method that suggested by Kaya [34] for  $M(CO)_4$  molecules having  $C_{3v}$  symmetry. The present work describes the application of this method's constraints to tricarbonyls of the types  $M(CO)_3(L-L)$  ( $L-L$ : bidentate ligand) and  $M(CO)_3^-$ , with  $C_s$  symmetry.

## 2. Derivation of the relations

Group theory predicts that  $M(CO)_3^-$  and  $M(CO)_3(L-L)$  complexes with  $C_s$  symmetry have three bands as  $2a' + a''$ . All of these bands are IR and Raman active. The secular equations of complexes which

\* Corresponding author. Tel.: +90 346 2191010; fax: +90 346 2191186.  
E-mail address: [eustun@cumhuriyet.edu.tr](mailto:eustun@cumhuriyet.edu.tr) (E. Üstün).

**Table 1**  
Secular equations of the molecules.

Symmetry species	Secular equations <sup>a</sup>
$a'(1)$	$\begin{vmatrix} \mu(k_1 + k'_c) - \lambda & \sqrt{2}\mu k_c \\ \sqrt{2}\mu k_c & \mu k_2 - \lambda \end{vmatrix} = 0$
$a'(2)$	
$a''$	

<sup>a</sup>  $\mu$  represents the reciprocal or the reduced mass of the CO groups;  $\lambda = 4\pi^2c^2v^2$  where  $v$  is the frequency in  $\text{cm}^{-1}$ .

obtained by applying CO-factored force field method have C–O stretching force constants ( $k_1$  and  $k_2$ ) and CO–CO interaction constants ( $k_c$ ,  $k'_c$ ) and they can be seen in Table 1. The force constants are defined in Fig. 1.

There are only three C–O stretching modes for tricarbonyl while there are four force constants in secular equations. Since this is an unsolvable situation mathematically, solution of the force field necessitates to use an additional constraint. The maximum value of the sum of the interaction constants (MVSIC) was used as an additional constraint to solve the secular equations. In order to solve the force field by 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:

$$k_1 = \frac{1}{4\mu}(\lambda_1 + \lambda_2 + 2\lambda_3 + \beta) \quad (1)$$

$$k_2 = \frac{1}{2\mu}(\lambda_1 + \lambda_2 - \beta) \quad (2)$$

$$k'_c = \frac{1}{4\mu}(\lambda_1 + \lambda_2 - 2\lambda_3 + \beta) \quad (3)$$

where  $\beta = \mu\sqrt{(\lambda_1 - \lambda_2)^2 - 8\mu^2k_c^2}$ ;  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are the  $\lambda$  parameters of  $a'(1)$ ,  $a'(2)$  and  $a''$  modes, respectively.

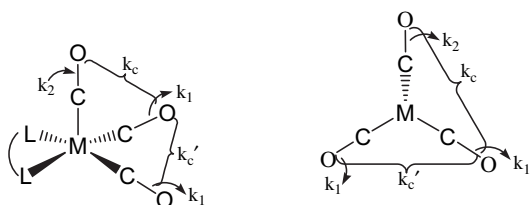
As can be seen in Fig. 1, there are two  $k_c$  and only one  $k'_c$  in the complexes under study. The sum of these interaction constants can be written such as Eq. (4).

$$2k_c + k'_c = 2k_c + \frac{1}{4\mu}\left[\lambda_1 + \lambda_2 - \lambda_3 + \mu\sqrt{(\lambda_1 - \lambda_2)^2 - 8\mu^2k_c^2}\right] \quad (4)$$

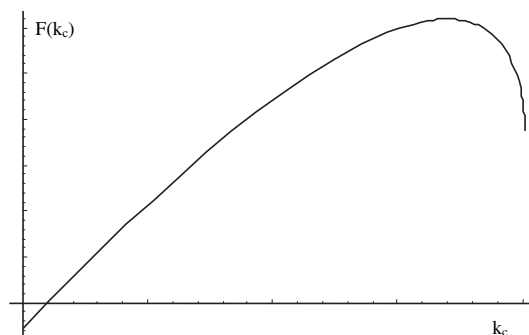
If we rearranged Eq. (4), the following expression can be arrived.

$$f(k_c) = \frac{1}{4\mu}\left[\lambda_1 + \lambda_2 - 2\lambda_3 + \sqrt{(\lambda_1 - \lambda_2)^2 - 8\mu^2k_c^2} + 8\mu k_c\right] \quad (5)$$

When the function  $f(k_c)$  is plotted against  $k_c$ , the curve shown in Fig. 2 is obtained. As can be seen from Fig. 2, the curve has a maximum corresponds to the maximum value of the sum of the interaction constants. Since the curve considered has a maximum point, we may use the partial derivative of the function  $f(k_c)$  with respect to  $k_c$  for obtaining the solution mentioned. When we use  $df(k_c)/dk_c = 0$ , we have



**Fig. 1.**  $M(\text{CO})_3$  and  $M(\text{CO})_3(\text{L-L})$  molecules and their force constants.



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

$$k_c = \frac{\lambda_1 - \lambda_2}{3\mu} \quad (6)$$

If Eq. (6) and  $\beta$  expression insert into Eqns. (1)–(3), the following expressions can be derived for the force constants.

$$k_1 = \frac{1}{6\mu}(2\lambda_1 + \lambda_2 + 3\lambda_3) \quad (7)$$

$$k_2 = \frac{1}{3\mu}(\lambda_1 + 2\lambda_2) \quad (8)$$

$$k'_c = \frac{1}{6\mu}(2\lambda_1 + \lambda_2 - 3\lambda_3) \quad (9)$$

### 3. Results and discussion

Eqns. (1)–(3) obtained with the rearrangement of the secular equations given in Table 1 are an algebraic system which consists of three equations in four unknowns ( $k_1$ ,  $k_2$ ,  $k_c$  and  $k'_c$ ). It is mathematically evident that for such a system an infinite number of solutions will be possible. In fact, the solution corresponding to Eqns. (6)–(9) is the only one of possible solutions of the algebraic system.

In order to test the validity of the solution found here, Eqns. (6)–(9) were employed to calculate CO-factored force constants of  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$  and  $\text{Fe}(\text{CO})_3$  molecules with  $C_s$  symmetry and compared with those obtained from isotopic enrichment studies. Three C–O stretching bands of  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$  were observed by Warren and Clark [36] at 2055.7 ( $a'(1)$ ), 1989.8 ( $a'(2)$ ) and 1979.9 ( $a''$ )  $\text{cm}^{-1}$ . Isotopic enrichment studies indicated that  $\text{Fe}(\text{CO})_3$  has a geometry consistent with a  $C_s$  symmetry [37]. Its two C–O stretching bands were observed by Breeze [38] at 1864.2 ( $a'(2)$ ) and 1854.1 ( $a''$ )  $\text{cm}^{-1}$  in low-temperature matrices. Since the high-frequency  $a'(1)$  mode has not been observed, its calculated value given in Ref. [37] was used in our calculations. Using these frequencies, the force constants calculated by Eqns. (6)–(9) are given in Table 2 together with those obtained from isotopic

**Table 2**  
CO-factored force constants for  $\text{Fe}(\text{CO})_3$  and  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$ .

Complex	Ref.	Force constants ( $\text{Nm}^{-1}$ )			
		$k_1$	$k_2$	$k_c$	$k'_c$
$\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$	(36)	1624.1	1638.9	36.9	41.5
	MVSIC	1627.3	1635.3	35.9	43.8
$\text{Fe}(\text{CO})_3$	(37)	1439.4	1458.6	48.0	49.7
	(39)	1362.4	1343.9	48.9	51.2
	MVSIC	1442.5	1450.1	46.3	53.9

**Table 3**

Secular equations for isotopically substituted species of the tricarbonyls with  $C_s$  symmetry.<sup>a</sup>

$M(^{13}\text{CO})(^{12}\text{CO})_2, (\text{ax}), C_s$	$\begin{vmatrix} \mu'k_2 - \lambda & \sqrt{2}\mu k_c \\ \sqrt{2}\mu'k_c & \mu(k_1 + k'_c) - \lambda \end{vmatrix} = 0$ $\lambda = \mu(k_1 - k'_c)$
$M(^{13}\text{CO})(^{12}\text{CO})_2, (\text{eq}), C_1$	$\begin{vmatrix} \mu k_2 - \lambda & \mu'k_c & \mu k_c \\ \mu k_c & \mu'k_1 - \lambda & \mu k'_c \\ \mu k_c & \mu'k'_c & \mu k_1 - \lambda \end{vmatrix} = 0$
$M(^{13}\text{CO})_2(^{12}\text{CO}), (\text{ax,eq}), C_1$	$\begin{vmatrix} \mu'k_2 - \lambda & \mu'k_c & \mu k_c \\ \mu'k_c & \mu'k_1 - \lambda & \mu k'_c \\ \mu'k_c & \mu'k'_c & \mu k_1 - \lambda \end{vmatrix} = 0$
$M(^{13}\text{CO})_2(^{12}\text{CO}), (\text{eq, eq}), C_s$	$\begin{vmatrix} \mu k_2 - \lambda & \sqrt{2}\mu'k_c \\ \sqrt{2}\mu k_c & \mu'(k_1 + k'_c) - \lambda \end{vmatrix} = 0$ $\lambda = \mu'(k_1 - k'_c)$
$M(^{13}\text{CO})_3, C_s$	$\begin{vmatrix} \mu'k_2 - \lambda & \sqrt{2}\mu'k_c \\ \sqrt{2}\mu'k_c & \mu'(k_1 + k'_c) - \lambda \end{vmatrix} = 0$ $\lambda = \mu'(k_1 - k'_c)$

<sup>a</sup>  $\mu$  and  $\mu'$  denote the reciprocal of the reduced mass of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ , respectively.

enrichment studies and normal coordinate analysis (NCA). Inspection of Table 2 reveals that there exists an excellent fit between the force constants calculated by isotopic spectra and our method (MSVIC). It is also apparent that use of the CO-factored force field leads to somewhat larger values of C–O stretching force constants ( $k_1$  and  $k_2$ ) with respect to NCA method [39]. However, there is a good agreement between CO–CO interaction constants ( $k_c$  and  $k'_c$ ).

As a further check upon the validity of Eqns. (6)–(9), the force constants calculated by them were employed to predict C–O stretching frequencies of  $^{13}\text{C}$ -substituted species of the molecules under study. The secular equations for isotopically enriched species of tricarbonyls with  $C_s$  symmetry were derived by procedures given in Ref. [40] and are presented in Table 3. With use of the equations and the force constants calculated by Eqns. (6)–(9), the C–O stretching frequencies of  $^{13}\text{C}$ -substituted species of  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$  and  $\text{Fe}(\text{CO})_3$  were estimated. The results obtained are given in Tables 4 and 5 together with observed frequencies of the species. As can be seen from the data in the tables, there is a rather good fit between observed and calculated frequencies. The mean error measured as  $(\sigma^2/n)^{1/2}$  was calculated to be  $0.84 \text{ cm}^{-1}$  for  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$  and  $0.93 \text{ cm}^{-1}$  for  $\text{Fe}(\text{CO})_3$ .

**Table 4**

Observed and calculated CO-stretching frequencies for  $^{13}\text{C}$ -substituted species of  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$

Species	Assignment	Frequencies		
		Observed	Calculated <sup>a</sup>	MVSIC
$\text{Fe}(\text{C}_4\text{H}_6)(^{12}\text{CO})_3, C_s$	$a'$	2055.7	2055.1	2055.7
	$a'$	1989.8	1989.2	1989.8
	$a''$	1979.9	1979.3	1979.9
$\text{Fe}(\text{C}_4\text{H}_6)(^{13}\text{CO})(^{12}\text{CO})_2, (\text{ax}), C_s$	$a'$	2044.3	2043.7	2045.7
	$a'$	1956.3	1955.7	1954.9
	$a''$	1979.9	1979.3	1979.9
$\text{Fe}(\text{C}_4\text{H}_6)(^{13}\text{CO})(^{12}\text{CO})_2, (\text{eq}), C_1$	$a'$	2046.0	2045.5	2045.3
	$a'$	1987.5	1986.9	1987.7
	$a''$	1947.1	1946.5	1947.6
$\text{Fe}(\text{C}_4\text{H}_6)(^{13}\text{CO})_2(^{12}\text{CO}), (\text{ax,eq}), C_1$	$a'$	2034.8	2034.3	2032.9
	$a'$	1965.4	1964.8	1967.2
	$a''$	1935.7	1935.2	1935.8
$\text{Fe}(\text{C}_4\text{H}_6)(^{13}\text{CO})_2(^{12}\text{CO}), (\text{eq,eq}), C_s$	$a'$	2031.2	2030.6	2032.1
	$a'$	1962.7	1962.1	1961.5
	$a''$	1941.9	1941.3	1942.1
$\text{Fe}(\text{C}_4\text{H}_6)(^{13}\text{CO})_3, C_s$	$a'$	2009.9	2009.3	2009.9
	$a'$	1945.4	1944.8	1945.4
	$a''$	1935.7	1935.2	1935.8

<sup>a</sup> The frequencies were calculated with the force constants which obtained from the  $^{13}\text{C}$ -substitution study.

**Table 5**

Observed and calculated CO-stretching frequencies for  $^{13}\text{C}$ -substituted species of  $\text{Fe}(\text{CO})_3$ .

Species	Assign.	Frequencies		
		Observed	Calculated <sup>a</sup>	MVSIC
$\text{Fe}(^{12}\text{CO})_3, C_s$	$a'$	1954.2	1954.2	1954.2
	$a'$	1864.2	1864.2	1864.2
	$a''$	1854.1	1854.1	1854.1
$\text{Fe}(^{13}\text{CO})(^{12}\text{CO})_2, (\text{ax}), C_s$	$a'$		1941.6	1943.4
	$a'$	1831.7	1834.0	1832.8
	$a''$	1854.1	1854.8	1854.1
$\text{Fe}(^{13}\text{CO})(^{12}\text{CO})_2, (\text{eq}), C_1$	$a'$		1844.2	1843.2
	$a'$	1862.0	1861.7	1862.2
	$a''$		1824.9	1825.0
$\text{Fe}(^{13}\text{CO})_2(^{12}\text{CO}), (\text{ax,eq}), C_1$	$a'$		1928.7	1929.8
	$a'$	1840.5	1840.7	1839.1
	$a''$	1819.8	1819.1	1819.2
$\text{Fe}(^{13}\text{CO})_2(^{12}\text{CO}), (\text{eq,eq}), C_s$	$a'$		1932.5	1930.2
	$a'$		1842.7	1845.3
	$a''$	1811.6	1813.4	1812.8
$\text{Fe}(^{13}\text{CO})_3, C_s$	$a'$		1910.7	1910.6
	$a'$	1821.0	1822.2	1822.6
	$a''$	1811.6	1813.4	1812.8

<sup>a</sup> The frequencies were calculated with the force constants which obtained from the  $^{13}\text{C}$ -substitution study.

Consequently, the results for both  $\text{Fe}(\text{CO})_3$  and  $\text{Fe}(\text{C}_4\text{H}_6)(\text{CO})_3$ , one concludes that the maximum value of the sum of the interaction constants is an acceptable constraint for solving the CO-factored force fields of tricarbonyls having  $C_s$  symmetry. This constraint makes it easy to calculate CO-factored force constants, allowing direct calculation from the fundamental C–O stretching frequencies of the all- $^{12}\text{CO}$  molecule. In addition, the fact that there is a remarkably good agreement between observed and calculated frequencies of isotopically enriched species indicates that the method presented may be used to analyze isotopic spectra of tricarbonyls under study.

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