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# A new method for calculating the CO-factored force constants of pentacarbonyliron

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## Abstract

Using an analytical approach we were able to obtain a valid solution to the CO-factored force field of $Fe(CO)_5$.The solution led to the relations which allow direct calculation of the CO-factored force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule. The force constants calculated from these relations were used to estimate C–O stretching frequencies of $^{13}C^{16}O$-substituted species of $Fe(CO)_5$. The results were found to be in very close agreement with those obtained from isotopic spectra.

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

## 1. Introduction

For trigonal-bipyramidal $Fe(CO)_5$, under the $D_{3h}$ local symmetry of the carbonyls, group theory predicts four C–O stretching modes ($2a_1'+e'+a_2''$). The $e'$ mode is both infrared and Raman-active, whereas the $a_1'$ modes are only Raman-active and the $a_2''$ mode is only infrared active [1,2]. On the basis of the CO-factored force field [3–6] which neglects anharmonicity and all coupling except CO–CO interaction, trigonal-bipyramidal $Fe(CO)_5$ has two carbonyl stretching force constants ($k_1$ and $k_2$) and three physically different CO–CO interaction constants ($k_t$, $k_c'$ and $k_c$), as shown Fig. 1. Since there are five force constants to be calculated and only four observable C–O stretching modes, the CO-factored force field for $Fe(CO)_5$ is underdetermined.

Several methods that enable us to determine the CO-factored force constants for $Fe(CO)_5$ have been reported in the literature. The method developed by Haas and Sheline [1] is based on the assumption that the effects of ligands on force constants are additive. However, this method necessitates the use of C–O stretching frequencies of all $Fe(CO)_{5-n}L_n$ ($n = 0, 1, 2, 3, 4$), species, not only those of $Fe(CO)_5$. Dalton et al. [7], using two relationships between the interaction constants $k_t/k_c = 1.74$ and $k_c'/k_c = 1.58$, derived from orbital overlap theories [8], have calculated CO-factored force constants for $Fe(CO)_5$. In the cos $\beta$ parameter method proposed by Bor [9], the solution of the force field was reduced to the problem of finding the value of the cos $\beta$ parameter. Bor made use of isotopic data to obtain a suitable value for cos $\beta$. Another method that can be used to determine CO-factored force constants for $Fe(CO)_5$ was suggested by Timney [10]. This method is based on several empirical relationships expressed in terms of ligand effect constants and bond angles. In our previous work [11–13] on solving the CO-factored force fields of complexes of the types *cis*-$L_2M(CO)_4$, $M(CO)_4$ and $LM(CO)_5$, we have developed some analytical approaches. These approaches enabled us to calculate force constants from C–O stretching frequencies of the all-$^{12}C^{16}O$ molecule.

In the present report, a new analytical approach was employed in obtaining a valid solution to the CO-factored force field for $Fe(CO)_5$. This approach led to the relations by which carbonyl stretching force constants and interaction constants can be calculated directly from $^{12}C^{16}O$ stretching frequencies.

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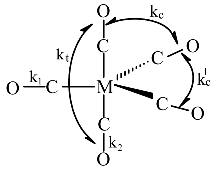

Fig. 1. Definition of CO-factored force constants for trigonal-bipyramidal $Fe(CO)_5$.

## 2. Derivations of relations

The secular equations for $Fe(CO)_5$, which are given elsewhere [1,2,9], are presented in Table 1. Since there are five unknowns (force constants) and only four equations, it is mathematically evident that an infinite number of solutions to the secular equations will be possible. In order to reduce the number of the unknowns we have employed the following substitutions:

$$k_1 + 2k_c^{\prime} = \delta_1 k_c \tag{1}$$

$$k_2 + k_t = \delta_2 k_c \tag{2}$$

With these substitutions, the following relations are obtained from the secular determinant given in Table 1.

$$\lambda_1 = (\mu/2)[(\delta_1 + \delta_2) + \sqrt{(\delta_1 - \delta_2)^2 + 24}]k_c \tag{3}$$

$$\lambda_2 = (\mu/2)[(\delta_1 + \delta_2) - \sqrt{(\delta_1 - \delta_2)^2 + 24}]k_c \tag{4}$$

where $\lambda_1$ and $\lambda_2$ are the $\lambda$ parameters of the $a_1^{\prime}$ modes. $\lambda_1$ denotes the mode at the higher frequency, and $\lambda_2$ the mode at the lower frequency. From Eqs. (3) and (4) two relations for $k_c$ are obtained:

$$k_c = \frac{\lambda_1 + \lambda_2}{\mu(\delta_1 + \delta_2)} \tag{5}$$

$$k_c = \frac{\lambda_1 - \lambda_2}{\mu\sqrt{(\delta_1 - \delta_2)^2 + 24}} \tag{6}$$

These relations indicate that $k_c$ can be calculated from observed frequencies of the $a_1^{\prime}$ modes if $\delta_1$ and $\delta_2$ are known. Combining them gives:

$$\frac{\sqrt{(\delta_1 - \delta_2)^2 + 24}}{\delta_1 + \delta_2} - \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} = 0 \tag{7}$$

Table 1
Secular equations for $Fe(CO)_5$ with $D_{3h}$ symmetry

| Symmetry species | Secular equations [a] |
|---|---|
| $a_1^{\prime}$ | $\begin{vmatrix} \mu(k_1 + 2k_c^{\prime}) - \lambda & \sqrt{6}\mu k_c \\ \sqrt{6}\mu k_c & \mu(k_2 + 2k_t) - \lambda \end{vmatrix} = 0$ |
| $a_1^{\prime}$ | |
| $e^{\prime}$ | $\lambda = \mu(k_1 - k_c^{\prime})$ |
| $a_2^{\prime\prime}$ | $\lambda = \mu(k_2 - k_t)$ |

[a] The various $k$ are defined in Fig. 1; $\mu$ represents the reciprocal of the CO group; $\lambda = 4\pi^2 e^2 v^2$ where $v$ is the frequency in $cm^{-1}$.

This resulting equation enables us to conclude that the determination of $k_c$ is reduced to the problem of finding the values of $\delta_1$ and $\delta_2$ which satisfy it. For a given molecule the left-hand side of Eq. (7) has two variables, $\delta_1$ and $\delta_2$, and may therefore be regarded as a function of $\delta_1$ and $\delta_2$, which is represented by $f(\delta_1,\delta_2)$. When the function $f(\delta_1,\delta_2)$ is plotted against $\delta_2$ for various values of $\delta_1$, such as $\delta_1^{\prime}$, $\delta_1^{\prime\prime}$, $\delta_1^{\prime\prime\prime}$, the curves shown in Fig. 2 are obtained.

As can be seen from Fig. 2, one of the solutions of Eq. (7) corresponds to the point at which the $\delta_2$-axis is tangential to the curve obtained for $\delta_1 = \delta_1^{\prime\prime}$. Since the curve considered has a minimum at the point, we may make use of the partial derivative of the function $f(\delta_1,\delta_2)$ with respect to $\delta_2$ for obtaining the solution mentioned. With the use of $\partial f(\delta_1,\delta_2)/\partial\delta_2 = 0$ and $f(\delta_1,\delta_2) = 0$, we have

$$\delta_1 = \frac{2\sqrt{6}\sqrt{\lambda_1\lambda_2}}{(\lambda_1 - \lambda_2)} \tag{8}$$

$$\delta_2 = \frac{\sqrt{6}(\lambda_1^2 + \lambda_2^2)}{(\lambda_1 - \lambda_2)\sqrt{\lambda_1\lambda_2}} \tag{9}$$

Substituting these relations into Eqs. (5)–(6) gives:

$$k_c = \frac{(\lambda_1 - \lambda_2)\sqrt{\lambda_1\lambda_2}}{\sqrt{6}\mu(\lambda_1 + \lambda_2)} \tag{10}$$

This equation shows that $k_c$ can be calculated from observed frequencies of the $a_1^{\prime}$ modes. Once $k_c$ has been determined, the other four force constants ($k_1$, $k_2$, $k_t$ and $k_c^{\prime}$) can be found from the secular equations. Further-

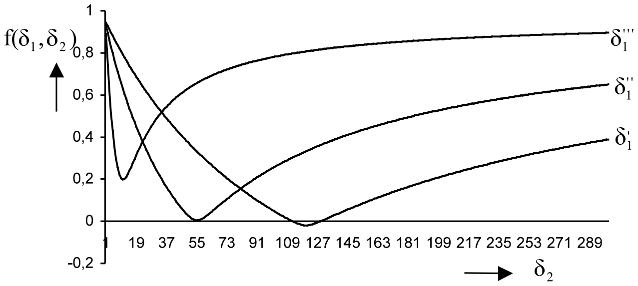

Fig. 2. Model graphs of the function of $(\delta_1,\delta_2)$ vs. $\delta_2$ for various values of $\delta_1$.

Table 2
CO-factored force constants [a] for $Fe(CO)_5$ calculated by various methods

| Methods [b] | $k_1$ | $k_2$ | $k_t$ | $k_c^{\prime}$ | $k_c$ |
|---|---|---|---|---|---|
| A | 16.559 | 16.964 | 0.422 | 0.386 | 0.283 |
| B | 16.54 | 16.95 | 0.43 | 0.39 | 0.28 |
| C | 16.57 | 16.95 | 0.41 | 0.40 | 0.28 |

[a] Force constants are given in mdyn $Å^{-1}$.

[b] A, B and C, respectively, represent our method, the method described by Dalton et al. and the cos $\beta$ parameter method.

Table 3
Secular equations for isotopically substituted species of $M(CO)_5$ molecules with $D_{3h}$ symmetry[a]

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*$M(^{12}CO)_4(^{13}CO)$, ax, $C_{3v}$*

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

$e \quad \lambda = \mu(k_1 - k_c')$

*$M(^{12}CO)_3(^{13}CO)_2$, ax,eq, $C_s$*

$$4a' \quad \begin{vmatrix} \mu^*k_2-\lambda & \mu k_t & \mu^*k_c & \sqrt{2}\mu k_c \\ \mu^*k_t & \mu k_2-\lambda & \mu^*k_c & \sqrt{2}\mu k_c \\ \mu^*k_c & \mu k_c & \mu^*k_1-\lambda & \sqrt{2}\mu k_c' \\ \sqrt{2}\mu^*k_c & \sqrt{2}\mu k_c & \sqrt{2}\mu^*k_c' & \mu(k_1+k_c')-\lambda \end{vmatrix} = 0$$

$a'' \quad \lambda = \mu(k_1 - k_c')$

*$M(^{12}CO)_2(^{13}CO)_3$, ax,eq,eq, $C_s$*

$$4a' \quad \begin{vmatrix} \mu k_2-\lambda & \mu^*k_t & \mu k_c & \sqrt{2}\mu^*k_c \\ \mu k_t & \mu^*k_2-\lambda & \mu k_c & \sqrt{2}\mu^*k_c \\ \mu k_c & \mu^*k_c & \mu k_1-\lambda & \sqrt{2}\mu^*k_c' \\ \sqrt{2}\mu k_c & \sqrt{2}\mu^*k_c & \sqrt{2}\mu k_c' & \mu^*(k_1+k_c')-\lambda \end{vmatrix} = 0$$

$a'' \quad \lambda = \mu^*(k_1 - k_c')$

*$M(^{12}CO)(^{13}CO)_4$, ax,eq,eq,eq, $C_{3v}$*

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

$e \quad \lambda = \mu^*(k_1 - k_c')$

*$M(^{12}CO)_4(^{13}CO)$, eq, $C_{2v}$*

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

$b_1 \quad \lambda = \mu(k_2 - k_t)$
$b_2 \quad \lambda = \mu(k_1 - k_c')$

*$M(^{12}CO)_3(^{13}CO)_2$, eq,eq, $C_{2v}$*

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

$b_1 \quad \lambda = \mu(k_2 - k_t)$
$b_2 \quad \lambda = \mu^*(k_1 - k_c')$

*$M(^{12}CO)_2(^{13}CO)_3$, eq,eq,eq, $D_{3h}$*

$$2a_1' \quad \begin{vmatrix} \mu(k_2+k_t)-\lambda & \sqrt{6}\mu^*k_c \\ \sqrt{6}\mu k_c & \mu^*(k_1+2k_c')-\lambda \end{vmatrix} = 0$$

$a_2'' \quad \lambda = \mu(k_2 - k_t)$
$e' \quad \lambda = \mu^*(k_1 - k_c')$

*$M(^{13}CO)_5$, $D_{3h}$*

$$2a_1' \quad \begin{vmatrix} \mu^*(k_2+k_t)-\lambda & \sqrt{6}\mu^*k_c \\ \sqrt{6}\mu^*k_c & \mu^*(k_1+2k_c')-\lambda \end{vmatrix} = 0$$

$a_2'' \quad \lambda = \mu^*(k_2 - k_t)$
$e' \quad \lambda = \mu^*(k_1 - k_c')$

*$M(^{12}CO)_3(^{13}CO)_2$, ax,ax, $D_{3h}$*

$$2a_1' \quad \begin{vmatrix} \mu^*(k_2+k_t)-\lambda & \sqrt{6}\mu k_c \\ \sqrt{6}\mu^*k_c & \mu(k_1+2k_c')-\lambda \end{vmatrix} = 0$$

$a_2'' \quad \lambda = \mu^*(k_2 - k_t)$
$e' \quad \lambda = \mu(k_1 - k_c')$

*$M(^{12}CO)_2(^{13}CO)_3$, ax,ax,eq, $C_{2v}$*

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

$b_1 \quad \lambda = \mu^*(k_2 - k_t)$
$b_2 \quad \lambda = \mu(k_1 - k_c')$

*$M(^{12}CO)(^{13}CO)_4$, ax,ax,eq,eq, $C_{2v}$*

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

$b_1 \quad \lambda = \mu^*(k_2 - k_t)$
$b_2 \quad \lambda = \mu^*(k_1 - k_c')$

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[a] $\mu^*$ denotes the reciprocal of the reduced mass of $^{13}C^{16}O$.

more, inserting Eq. (10) into the secular equations presented in Table 1 gives the following relations by which $k_1$, $k_2$, $k_t$ and $k_c'$ can be calculated from the observed frequencies of the all-$^{12}C^{16}O$ molecule:

$$k_1 = (\lambda_1 + \lambda_2 + 4\lambda_3 - \beta)/(6\mu) \tag{11}$$

$$k_2 = (\lambda_1 + \lambda_2 + 2\lambda_4 + \beta)/(4\mu) \tag{12}$$

$$k_t = (\lambda_1 + \lambda_2 - 2\lambda_4 + \beta)/(4\mu) \tag{13}$$

$$k_c' = (\lambda_1 + \lambda_2 - 2\lambda_3 - \beta)/6\mu \tag{14}$$

Where $\lambda_3$, $\lambda_4$ are the $\lambda$ parameters of $e'$ and $a_2''$ modes, respectively, and $\beta = (\lambda_1 - \lambda_2)^2/(\lambda_1 + \lambda_2)$.

## 3. Results and discussion

When the secular equations given in Table 1 are rearranged so that four of the five force constants are expressed in terms of the fifth and the observed frequencies, it is obtained an algebraic system which consist of four equations in five unknowns. It is mathematically evident that for such a system that an infinite number of solutions will be possible. In fact, the

Table 4
Observed and calculated C–O stretching frequencies for $^{13}$CO-substituted species of $Fe(CO)_5$

| Species | Frequencies | | | Assignment |
|---|---|---|---|---|
| | Observed | Calculated [a] | Calculated [b] | |
| $Fe(^{12}CO)_4(^{13}CO)$, $C_{3v}$, $^{13}$CO; ax | 2105.5 [c] | 2105.4 | 2105.1 | $a_1$ |
| | | 2028.9 | 2028.9 | $a_1$ |
| | 1988 | 1988.7 | 1987.0 | $a_1$ |
| | 2001 | 2000.9 | 2000.9 | $e$ |
| $Fe(^{12}CO)_4(^{13}CO)$, $C_{2v}$, $^{13}$CO; eq | 2108.0 [c] | 2108.5 | 2108.4 | $a_1$ |
| | | 2027.2 | 2027.1 | $a_1$ |
| | 1964 | 1965.1 | 1963.5 | $a_1$ |
| | 2023 | 2023.6 | 2023.6 | $b_1$ |
| | 2001 | 2000.9 | 2000.9 | $b_2$ |
| $Fe(^{12}CO)_3(^{13}CO)_2$, $D_{3h}$, $^{13}$CO; ax, ax | | 2095.7 | 2095.1 | $a_1'$ |
| | | 2003.1 | 2001.7 | $a_1'$ |
| | 2001 | 2000.9 | 2000.9 | $e'$ |
| | 1976 | 1978.5 | 1976.6 | $a_2''$ |
| $Fe(^{12}CO)_3(^{13}CO)_2$, $C_s$, $^{13}$CO; ax, eq | 2097 | 2098.9 | 2098.5 | $a'$ |
| | | 2026.2 | 2026.2 | $a'$ |
| | 1988 | 1989.1 | 1987.6 | $a'$ |
| | 1964 | 1964.5 | 1962.8 | $a'$ |
| | 2001 | 2000.9 | 2000.9 | $a''$ |
| $Fe(^{12}CO)_3(^{13}CO)_2$, $C_{2v}$, $^{13}$CO; eq, eq | | 2102.9 | 2102.6 | $a_1$ |
| | | 2021.0 | 2020.8 | $a_1$ |
| | 1976 | 1976.3 | 1974.9 | $a_1$ |
| | 2023 | 2023.6 | 2023.6 | $b_1$ |
| | 1955 | 1956.3 | 1954.5 | $b_2$ |
| $Fe(^{12}CO)_2(^{13}CO)_3$, $C_{2v}$, $^{13}$CO; ax, ax, eq | | 2087.5 | 2086.6 | $a_1$ |
| | | 2002.9 | 2001.6 | $a_1$ |
| | 1964 | 1964.2 | 1962.5 | $a_1$ |
| | 1976 | 1978.5 | 1976.6 | $b_1$ |
| | 2001 | 2000.9 | 2000.9 | $b_2$ |
| $Fe(^{12}CO)_2(^{13}CO)_3$, $C_s$, $^{13}$CO; ax, eq, eq | 2090 | 2092.1 | 2091.4 | $a'$ |
| | | 2021.7 | 2021.5 | $a'$ |
| | 1988 | 1990.5 | 1989.1 | $a'$ |
| | 1972 | 1974.0 | 1972.4 | $a'$ |
| | 1955 | 1956.3 | 1954.5 | $a''$ |
| $Fe(^{12}CO)_2(^{13}CO)_3$, $D_{3h}$, $^{13}$CO; eq, eq, eq | | 2097.3 | 2096.8 | $a_1'$ |
| | | 2001.5 | 2000.1 | $a_1'$ |
| | 1955 | 1956.3 | 1954.5 | $e'$ |
| | 2023 | 2023.6 | 2023.6 | $a_2''$ |
| $Fe(^{12}CO)(^{13}CO)_4$, $C_{2v}$, $^{13}$CO; ax, ax, eq, eq | 2076 | 2078.1 | 2076.9 | $a_1$ |
| | 2001 | 2002.4 | 2001.4 | $a_1$ |
| | 1972 | 1973.5 | 1972.0 | $a_1$ |
| | 1976 | 1978.5 | 1976.6 | $b_1$ |
| | 1955 | 956.3 | 1954.5 | $b_2$ |
| $Fe(^{12}CO)(^{13}CO)_4$, $C_{3v}$, $^{13}$CO; ax, eq, eq, eq | 2084 | 2084.9 | 2084.0 | $a_1$ |
| | | 2008.9 | 2007.9 | $a_1$ |
| | | 1982.9 | 1981.1 | $a_1$ |
| | 1955 | 1956.3 | 1954.5 | $e$ |
| Fe $(^{13}CO)_5$, $D_{3h}$ | | 2066.9 | 2064.9 | $a_1'$ |
| | | 1985.7 | 1983.9 | $a_1'$ |
| | 1955 | 1956.3 | 1954.5 | $e'$ |
| | 1976 | 1978.5 | 1976.6 | $a_2''$ |

[a] Calculated without effective reduced mass ratio.
[b] Calculated with an effective reduced mass ratio of 0.9768.
[c] These frequencies were taken from Ref. [9].

solution corresponding to Eqs. (10)–(14) is the only one of possible solutions of the algebraic system.

In order to test the validity of the solution found here Eqs. (10)–(14) were first used to calculate force constants of $Fe(CO)_5$ and then compared with those determined from the cos $\beta$ parameter method [9] and those of Dalton et al. [7]. C–O stretching bands of $Fe(CO)_5$ were reported by many authors [14–17]. In our calculations of force constants, we have employed the frequencies given in Ref. [18], $a_1' = 2114$, $a_1' = 2031$, $e' = 2000.9$ and $a_2'' = 2023.6$ cm$^{-1}$. Our results, together with those of the two methods mentioned above, are presented in Table 2. Inspection of the table reveals that there exists a very good agreement between the force constants calculated by our method and the other two methods. It should also be noted that the method presented utilizes only $^{12}C^{16}O$ stretching frequencies whereas the application of the cos $\beta$ parameter method [9] needs to use frequencies of isotopically enriched species for finding value of cos $\beta$ and the method suggested by Dalton et al. [7] requires some relationships among the interaction constants derived from elementary bonding considerations [7,8]. Therefore, our method is easier to apply than the two methods.

As a further check upon the validity of Eqs. (10)–(14), the force constants calculated were employed to predict C–O stretching frequencies of isotopically enriched species of $Fe(CO)_5$ and the results obtained were compared with observed frequencies of the species. The reliability of such a comparison is based on the assumption that the force constants remain unchanged on isotopic substitution [19]. This also means that C–O stretching frequencies of isotopically substituted species can be determined by using the force constants of the all-$^{12}C^{16}O$ molecule. 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 [6,20]. $^{13}CO$-substituted species of $Fe(CO)_5$ were prepared and their infrared spectra in the carbonyl stretching region were reported by Noack and Ruch [18].

The secular equations for isotopically enriched species of $M(CO)_5$ molecules having $D_{3h}$ symmetry were derived by procedures given in Ref. [19] and are summarized in Table 3. With the use of these equations and the force constants calculated by Eqs. (10)–(14), the C–O stretching frequencies of $^{13}CO$-substituted species of the $Fe(CO)_5$ were estimated. The results obtained are given in Table 4 together with observed frequencies [18] of the species.

It can be seen from Table 4 that a rather good fit between observed and calculated frequencies was obtained for $^{13}CO$-substituted species of $Fe(CO)_5$, with a maximum error of 2.5 cm$^{-1}$. The mean error measured as $(\sigma^2/n)^{1/2}$ was calculated to be 1.41 cm$^{-1}$. A much better fit was obtained by using an 'effective reduced mass ratio' [6,9] of 0.9768. The maximum and mean error were 1.5 and 0.71 cm$^{-1}$, respectively. The effective reduced mass ratio for $Fe(CO)_5$ was determined from observed frequencies of the $e'$ and $a_2''$ modes of $Fe(^{12}C^{16}O)_5$ and $Fe(^{13}C^{16}O)_5$ species. It is noted that our value of the effective reduced mass ratio is very close to that of Bor, 0.9771 [9].

In conclusion, the data in Tables 2 and 4 show that Eqs. (10)–(14) correspond to a valid solution for the CO-factored force field of $Fe(CO)_5$. The relations 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 Table 4, 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. (10)–(14). From this observation, one concludes that the method presented here may be employed to analyze isotopic spectra of $Fe(CO)_5$.

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