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# Infrared Spectroscopic Studies on Metal Carbonyl Compounds. XII.[1a] $^{13}$CO Isotopic Studies with Iron Pentacarbonyl[1b]

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*The $^{13}$CO-content of $Fe(CO)_5$ has been increased by exchange reaction and the C–O stretching frequencies of the two isomeric $Fe(^{12}CO)_4(^{13}CO)$ molecules have been determined and assigned. The infrared inactive $a'_1$ C–O stretching frequencies of $Fe(^{12}CO)_5$ have been calculated and found in very good agreement with previous Raman data. The approximate force constants in the factored C–O stretching force field have been determined as well as the C–O stretching frequencies of the complete series of $Fe(^{12}CO)_{5-n}(^{13}CO)_n$ molecules ($n = 2 \dots 5$) calculated.*

## Introduction

Earlier force constant calculations on $Fe(CO)_5$ were burdened by incorrect wavenumber values and assignments of the C–O stretching fundamentals.[3-7] Since the correction of the assignment of the infrared active vibrations $\nu_3^{CO}(a_2'')$ and $\nu_4^{CO}(e')$[8-10] two brief mentions of the force constants calculated on this new basis have been published[11-12] and also a more detailed study using $^{13}$C–O frequencies.[13] It has been stressed in the paper of Haas and Sheline[13] that « a study of an isotopically enriched sample in n-hexane would be of special interest here ».

We are studying systematically the C–O stretching spectra of $^{13}$CO-enriched metal carbonyls of different types since we learned[2,14] that the infrared inactive C–O stretching frequencies of the parent all- $^{12}$CO molecule can be determined in this way with higher accuracy than from Raman spectra or from the study of the C–O stretching combination and overtone region.

The factored-off C–O stretching model (closely related to the Cotton-Kraihanzel force field[15] without, however, the constraints connecting the interaction constants) although criticized by some authors[16-20] as to its physical correctness, has the very important advantage among other practical values[21] that it furnishes the spectra of isotopically ($^{13}$CO or C$^{18}$O) substituted carbonyl molecules with high accuracy ($\pm 0.5$ cm$^{-1}$).[2,13,22-29]

In this paper the first example of an unsubstituted metal carbonyl having two different sets of CO ligands will be dealt with. It will be shown that the isotopic spectra interpreted on the basis of the factored-off C–O stretching model furnish important additional data as to the extent of coupling of the equatorial and axial ligand vibrations in the two $a_1'$ C–O stretching modes.

## Experimental Section

The enrichment by using carbon monoxide gas having 22.5 per cent $^{13}$CO content has been accomplished as reported previously.[14] It is known, however, from $^{14}$CO-exchange studies[30] that iron pentacarbonyl exchanges slowly. The exchange is accelerated by irradiation with visible light.[30] We have exposed the n-heptane solution[31] of $Fe(CO)_5$ in contact with the $^{13}$CO-rich gas to sunlight for one hour. The exchange was accompanied by photochemical side reactions

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(1) (a) For Part XI see ref. 2. (b) *Paper presented at the First Inorganica Chimica Acta Symposium Venice, September 1968.* (c) Present address: William Ramsay and Ralph Foster Laboratories, University College, London, W.C. 1.
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(formation of $Fe_2(CO)_9$, *etc.*) and it was necessary therefore to purify the solution after irradiation by chromatography on a small silica gel column. The $^{13}CO$-content of the enriched sample (based on the increased intensity of the strongest $^{13}C$–O satellite band) was about 10 per cent, corresponding to about 33 per cent of $Fe(^{12}CO)_4(^{13}CO)$ content.

Spectra were recorded on a Zeiss (Jena) UR-10 spectrometer equipped with lithium fluoride optics. The spectra were calibrated against carbon monoxide and deuterium chloride bands.

*Spectra and assignments.* $Fe(CO)_5$ has two differently mono-$^{13}CO$ substituted derivatives. The equatorially (radially) substituted $[1-^{13}C]-Fe(CO)_5$ belongs to the point group $C_{2v}$ and the axially substituted $[4-^{13}C]-Fe(CO)_5$ to the point group $C_{3v}$. Thus all C–O stretching modes of the two types of $Fe(^{12}CO)_4(^{13}CO)$ molecules are expected to appear in the infrared spectrum.

After $^{13}CO$ enrichment to about 10 per cent the spectrum shown in Figure 1 has been obtained and the C–O stretching frequencies given in Table I have been determined and assigned to the two mono-$^{13}CO$ molecules. Unfortunately the two highest frequency bands (belonging to the two highest $\nu_1(a_1)$ vibrations of the two mono-$^{13}CO$ molecules) could not be resolved clearly. But the separation of the maxima by $2.5 \pm 0.5$ cm$^{-1}$ could nevertheless be measured from spectra run with expanded scale and was of particular importance in the calculations (see Appendix and Figure 3).

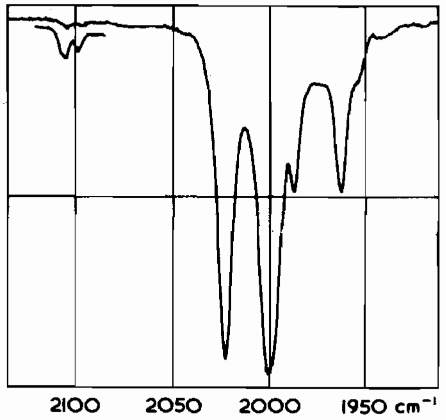

Figure 1. The infrared spectrum of $Fe(CO)_5$ in the C–O stretching region, containing about 10 per cent $^{13}CO$. n-Heptane solution. (The region near to 2100 cm$^{-1}$ is shown also with higher concentration).

**Table I.** C–O stretching frequencies of the two $Fe(^{12}CO)_4$-$(^{13}CO)$ molecules

| equatorial-$^{13}CO$ ($C_{2v}$) | | axial–$^{13}CO$($C_{3v}$) | |
|---|---|---|---|
| $a_1$ | 2108.0 | $a_1$ | 2105.5 |
| | 2027.2 $^a$ | | 2028.6 $^a$ |
| | 1964.0 | | 1987.4 |
| $b_1$: | 2022.9 $^b$ | e: | 2000.3 $^b$ |
| $b_2$: | 2000.3 $^b$ | | |

The underlined frequencies were directly measured. $^a$ Calculated values; masked by the 2022.9 cm$^{-1}$ band of $Fe(^{12}CO)_5$. $^b$ Coinciding with the $a_2''$ and e′ bands of $Fe(^{12}CO)_5$.

Based on these data, the calculations given in detail in the Appendix yield $2113.8 \pm 0.5$ and $2031 \pm 1$ cm$^{-1}$ for the two infrared inactive $a_1'$ frequencies of $Fe(^{12}CO)_5$, in very good agreement with the Raman values 2114 and 2031 cm$^{-1}$ reported by Stammreich and coworkers.[33] The agreement with the calculated values of Haas and Sheline[13] is less good. The infrared active frequencies have been determined earlier[32] and are correctly assigned[8-10] as $a_2''(\nu_3^{CO}) = 2022.9$ and $e'(\nu_4^{CO}) = 2000.3$ cm$^{-1}$ (both $\pm 0.2$ cm$^{-1}$).

## Discussion

The « force constants *vs.* cos β diagram »[11] is shown in Figure 2. As mentioned in the detailed paper[11] on this type of representation of the force and interaction constants of metal carbonyls having two different sets of CO ligands, all connected constants in the cos β region between −1 and +1 reproduce exactly the same $^{12}C$–O frequencies. But this is not true at the same time for the $^{13}C$–O stretching frequencies; on the contrary, only *one* set of constants furnishes isotope frequencies which agree with the observed ones. On this basis the correct value of cos β can be obtained based on the measured isotopic frequencies. The graphical method of this step of the study is shown on Figure 3.

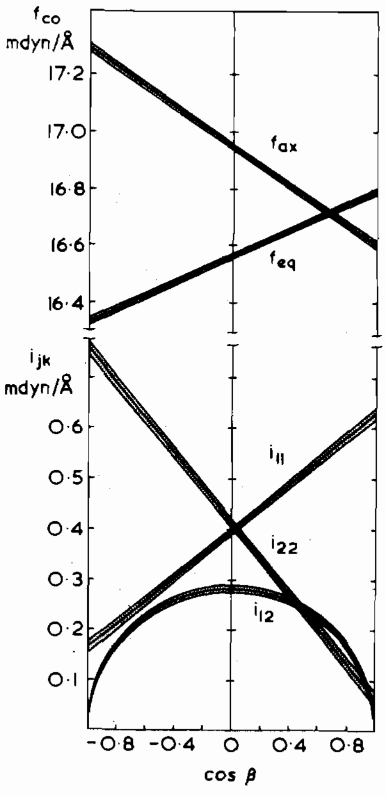

Figure 2. Force constants *vs.* cos β diagram of $Fe(CO)_5$.

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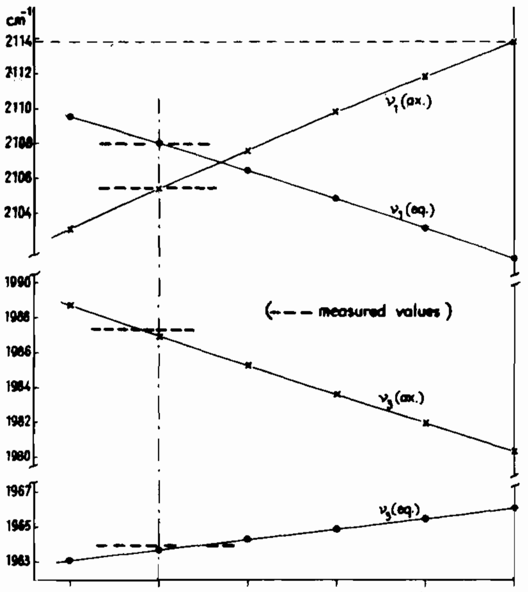

Figure 3. Variation of the calculated mono-$^{13}$CO frequencies $\nu_1$ and $\nu_3$ *vs.* cos β.

The $^{13}$CO-measurements and calculations (for details see the Appendix) unequivocally lead to a value of cos β = 0. This proves that there is maximum coupling between the equatorial and axial ligands in the two $a_1'$ vibrations. Consequently it is not correct to consider the higher $a_1'$ frequency as being mainly an equatorial C—O stretching vibration and the lower one as being the axial one. Clearly the higher one is an in-phase and the lower one an out-of-phase coupling of the equatorial and axial vibrations. From the cosβ = 0 value we can even obtain the relative amplitudes of the C—O vibrations and these two « C—O stretching normal coordinates » are in fact composed from the C—O stretching symmetry coordinates in the following way (cf. equation (38) in ref. 11):

$$Q_1 = (S_1+S_2)/\sqrt{2}$$

$$Q_2 = (S_1-S_2)/\sqrt{2}$$

Since the symmetry coordinates are:

$$S_1 = (d_1+d_2+d_3)/\sqrt{3}$$

$$S_2 = (d_4+d_5)/\sqrt{2}$$

(where $d_1$, $d_2$, and $d_3$ stand for the equatorial and $d_4$ and $d_5$ for the axial C—O stretching inner valence coordinates), we may represent the « normal coordinates » in terms of the inner valence coordinates as:

$$Q_1 = 6^{-1/2}(d_1+d_2+d_3)+\frac{1}{2}(d_4+d_5)$$

$$Q_2 = 6^{-1/2}(d_1+d_2+d_3)-\frac{1}{2}(d_4+d_5)$$

The factored « force constants » (for their definition see Appendix) corresponding to cos β = 0 are the following (in mdynes/Å):

$$f_{eq} = 16.57 \qquad i_{11} = 0.40 \qquad i_{12} = 0.28$$

$$f_{ax} = 16.95 \qquad i_{22} = 0.41$$

These are in good agreement with those briefly reported by Stone and coworkers,[12] *i.e.* 16.54, 16.95, 0.39, 0.43, and 0.28 respectively. It is clear from Figure 2 that $f_{ax}$ is definitely higher than $f_{eq}$ in the major part of the entire mathematically allowed region for real solutions. This is in agreement with the results obtained for trigonal bipyramidal cobalt carbonyl derivatives ($HCo(CO)_4$, $CH_3Co(CO)_4$,[34] $R_3MCo(CO)_4$ [12] and with a series of monosubstituted derivatives of iron carbonyl, $Me_3AFe(CO)_4$,[35] with which $f_{ax}$ was found in all cases to be definitely higher than $f_{eq}$ in contrast to the octahedral complexes $LM(CO)_5$ where $f_{eq} > f_{ax}$.[15,27,36-44]

By using the above « force constants » (however with an accuracy of four decimal places needed for the exact reproduction of the measured frequencies) the C—O stretching frequencies of all differently substituted $Fe(^{12}CO)_{5-n}(^{13}CO)_n$ molecules (n = 1 ... 5) have been calculated and are given in Table II. Hence we can identify the very weak bands present in the spectrum of the enriched sample at 2098.5 and 1955 cm$^{-1}$ as belonging to the 1,4- and 1,2-di-$^{13}$CO substituted molecules, respectively. Noack[45] carrying out catalytic exchange studies of $Fe(CO)_5$ and $Fe_2(CO)_9$ with $^{13}$CO obtained higher substituted isotopic molecules and could confirm the correctness of our calculated values within ± 1 cm$^{-1}$.

The calculations furnish automatically the eigenvectors which are orthonormal and correspond thus directly to the relative amplitudes of the different vibrators. These values have been used in the calculation of the band intensities, similar to those performed with the $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ series[2] but these data are not given here in details for the sake of brevity. Nevertheless the relative intensities of the highest frequency ($\nu_1$) bands of the two mono-$^{13}$CO isomers are worthy of mentioning. We calculated the EQ/AX ratio of 0.024/0.052 (based on $\Sigma I = 5.0$) in contrast to the ratio 0.01/0.04 given by Haas and Sheline.[13] The shape of the unresolved doublet at 2108-2105 cm$^{-1}$ (Figure 1) seems to confirm our intensity ratio.

*Appendix (Details of the calculations).* The relationships between the **F** matrix elements (in the fac-

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(34) See ref. 11. Recent unpublished $^{13}$CO studies indicate a cos β value of about 0.2 to 0.3 (as compared to the tentatively given value of cos β = 0.5[11]) which involves even a higher separation of $f_{ax}$—$f_{eq}$ *i.e.* ~ 0.5 mdyn/Å.

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**Table II.** Calculated C–O stretching frequencies (with assignments) of the $Fe(^{12}CO)_{5-n}(^{13}CO)_n$ molecules

| all-$^{12}$CO | eq | ax | eq, eq | eq, ax | ax, ax |
|---|---|---|---|---|---|
| $a_1'$ 2113.8 | $a_1$ 2108.0 | $a_1$ 2105.4 | $a_1$ 2102.1 | $a'$ 2098.6 | $a_1'$ 2096.0 |
| $a_1'$ 2031.0 | $a_1$ 2027.2 | $a_1$ 2028.6 | $a_1$ 2021.1 | $a'$ 2026.0 | $a_1'$ 2001.5 |
| $a_2''$ 2022.9 | $a_1$ 1963.7 | $a_1$ 1987.0 | $a_1$ 1975.3 | $a'$ 1987.5 | $a_2''$ 1976.8 |
| $e'$ 2000.3 | $b_1$ 2022.9 | $e$ 2000.3 | $b_1$ 2022.9 | $a'$ 1963.1 | $e'$ 2000.3 |
| | $b_2$ 2000.3 | | $b_2$ 1954.7 | $a''$ 2000.3 | |
| **eq, eq, eq** | **eq, eq, ax** | **eq, ax, ax** | **eq, eq, eq, ax** | **eq, eq, ax, ax** | **all-$^{13}$CO** |
| $a_1'$ 2096.0 | $a'$ 2091.3 | $a_1$ 2087.5 | $a_1$ 2083.7 | $a_1$ 2077.6 | $a_1'$ 2065.6 |
| $a_1'$ 2001.5 | $a'$ 2021.5 | $a_1$ 2001.4 | $a_1$ 2008.5 | $a_1$ 2001.1 | $a_1'$ 1984.7 |
| $a_2''$ 2022.9 | $a'$ 1988.9 | $a_1$ 1962.9 | $a_1$ 1981.6 | $a_1$ 1972.4 | $a_2''$ 1976.8 |
| $e'$ 1954.7 | $a'$ 1972.8 | $b_1$ 1976.8 | $e$ 1954.7 | $b_1$ 1976.8 | $e'$ 1954.7 |
| | $a''$ 1954.7 | $b_2$ 2000.3 | | $b_2$ 1954.7 | |

tored C–O stretching block) and the valence force constants are the following for trigonal bipyramidal $M(CO)_5$ molecules having $D_{3h}$ symmetry:

$$a_1' \left\{ \begin{array}{l} F_{11} = f_{eq}+2i_{11} \\ F_{22} = f_{ax}+i_{22} \\ F_{12} = \sqrt{6}\,i_{12} \end{array} \right. \qquad \begin{array}{l} a_2'': F_{33} = f_{ax}-i_{22} \\ \\ e' \ : F_{44} = f_{eq}-i_{11} \end{array} \qquad (1)$$

where $f_{eq}$ and $f_{ax}$ stand for the C–O stretching force constant of the equatorial (radial) and axial carbonyl ligands, respectively, $i_{11}$ for the CO–CO stretch-stretch interaction between two *equatorial* ligands, $i_{22}$ for the same type of interaction between the two *axial* vibrators, finally $i_{12}$ for the equatorial-axial interaction.

By using equation (2) and (3)[11]

$$F_{11}+F_{22} = y_1+y_2 \qquad (2)$$

$$\frac{F_{11}-F_{22}}{y_1-y_2} = \cos\beta \qquad (3)$$

where

$$y_k = \frac{\lambda_k}{\mu} = 0.40407\times10^{-5}\times\nu_k^2 \qquad (4)$$

and keeping in mind that in species $a_2''$ and $e'$ containing only one C–O stretching fundamental: $F_{33} = y_3$ and $F_{44} = y_4$, we obtain the following relationships connecting the valence force constants and the $y_k$ values as functions of the parameter cos$\beta$:

$$f_{eq} = \frac{1}{6}(y_1+y_2)+\frac{2}{3}y_4+\frac{1}{6}(y_1-y_2)\cos\beta$$

$$f_{ax} = \frac{1}{4}(y_1+y_2)+\frac{1}{2}y_3-\frac{1}{4}(y_1-y_2)\cos\beta$$

$$i_{11} = \frac{1}{6}(y_1+y_2)-\frac{1}{3}y_4+\frac{1}{6}(y_1-y_2)\cos\beta \qquad (5)$$

$$i_{22} = \frac{1}{4}(y_1+y_2)-\frac{1}{2}y_3-\frac{1}{4}(y_1-y_2)\cos\beta$$

$$i_{12} = \frac{1}{2\sqrt{6}}(y_1-y_2)\sin\beta$$

The graphical representation of these equations is shown on Figure 2 constructed from the $y_k$ values obtained from the final $\nu_k$ frequencies. The shaded areas represent the uncertainties resulting from the uncertainties of the frequencies.

For the calculation of the isotopic frequencies a computer programme has been written which performes the following steps of operations:

(a) calculates the $y_k$ values from the input frequencies by eq. (4);

(b) calculates the force and interaction constants belonging to several cos $\beta$ values (input) by equations (5);

(c) arranges the force constants to a five-by-five symmetrical square matrix corresponding to the symmetry of $D_{3h}$;

(d) multiplies that row and column of the matrix which corresponds to a $^{13}$CO ligand by the square root of the ratio of the reduced masses of $^{12}$CO and $^{13}$CO; (it proved necessary to input this $a^{1/2}$ value[14] as a variable, *vide infra*);

(e) diagonalises the new matrices obtained in (d), corresponding to the axially and equatorially substituted mono-$^{13}$CO molecules by the Jacobi algorithm;

(f) calculates the frequencies from the eigenvectors obtained in (e) eq. (4); finally

(g) prints the frequencies and the orthonormal eigenvectors of the mono-$^{13}$CO molecules as a function of the varied cos $\beta$.

The infrared active C–O stretching frequencies[32] were held constant and the inactive ones varied in the neighbourhood of the reported Raman values.[35] As the first result the cos $\beta=0$ value could be fixed, since independently of the variation of the frequencies only this parameter value furnished the measured 2.5±0.5 cm$^{-1}$ separation between the two highest isotope bands and at the same time the observed separation of 23.5±0.5 cm$^{-1}$ between the too low frequency satellites (Figure 3). The determination of the higher $a_1'$ band of $Fe(^{12}CO)_5$ at 2113.8±0.5 cm$^{-1}$ was then a straightforward step.

The lower $a_1'$ frequency could not be fixed directly since its « satellites » are masked by the strong band at 2022.9 cm$^{-1}$. It could be determined, however, with an uncertainty of $\pm 1$ cm$^{-1}$ from the effect of the variation of the input $\nu_2$ frequency to the other isotopic frequencies.

It is worthy of mention that the value of $a^{1/2}$ (see step d) had to be changed from the theoretical value of 0.9776 used previously[2,14] to 0.9772 to obtain a good agreement with the measured *low frequency* satellites. As a matter of fact the high and medium frequency isotope bands are only slightly changed by the variation of $a^{1/2}$ (0.01-0.02 cm$^{-1}$ per 0.0001 change in $a^{1/2}$). The « practical » value of $0.9774 \pm 0.0002$ of the square root of the reduced mass ratio $a^{1/2}$ has been found with some mono-carbonyls,[46] which have only one isotope « satellite » and $a^{1/2}$ can be simply obtained from the frequency ratios, *e.g.* 2023.8 ($\pm$0.3)/2070.6$\pm$0.1 for $(\pi\text{-}C_5H_5)Co(CO)I_2$ (in $CS_2$ solution) and 1932.6 ($\pm$0.15)/1977.25 ($\pm$0.15) for $(Et_3P)_2Co(CO)Cl_2$ (in hexane solution). In this latter case the known reaction[47]

$$L_2CoX_2 + CO \rightleftharpoons L_2Co(CO)X_2$$

has been carried out for this measurement by using carbon monoxide with 22.5 per cent $^{13}C$-content.

Presumably the effect of the several neglections or simplifications of the method are reflected in this slight necessary correction of the $a^{1/2}$ value.

This slight uncertainty in the numerical value of $a^{1/2}$ does not influence the finding of the correct $\cos\beta$ value which is performed mainly on the basis of the highest $^{13}CO$-bands. The adjustment of $a^{1/2}$ to fit for the lowest isotope frequencies can be done as a last refinement in step (d) of the calculations.

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