Contribution from the Hungarian Oil and Gas Research Institute, Veszprém, Hungary

Infrared Spectroscopic Studies on Metal Carbonyl Compounds. XIII.[1a] Study of the Infrared Spectrum of ^{13}CO-enriched Mercury Dicobalt Octacarbonyl[1b]

G. Bor[1c]

Received March 25, 1969

Via ^{13}CO-enriched $Co_2(CO)_8$, ^{13}CO-enriched $Hg[Co(CO)_4]_2$ has been obtained and its infrared spectrum studied in the C–O stretching region. The infrared, inactive C–O stretching frequencies of $HgCo_2(^{12}CO)_8$ have been determined from the frequencies of the $HgCo_2(^{12}CO)_7(^{13}CO)$ molecules. The first combination region of the spectrum has been studied and assigned on the basis of the new « g » species frequencies. The approximate force and interaction constants (in a factored C–O stretching force field) have been calculated. Also the C–O stretching frequencies of the $HgCo_2(^{12}CO)_{8-n}(^{13}CO)_n$ ($n = 0 \dots 3$) molecular species are presented.

Introduction

In the previous papers dealing with the infrared spectra of ^{13}CO-enriched metal carbonyls[2-4] we were able to prove that the infrared inactive C–O stretching frequencies of the compounds dealt with could be obtained and assigned with high accuracy from the frequencies of the mono-^{13}CO substituted species. In all cases a very good agreement has been found with the infrared inactive frequencies obtained previously by other methods (Raman spectra, extrapolation by the method of filiation curves[5]).

Now we present the first complete study of a binuclear carbonyl, $Hg[Co(CO)_4]_2$.

The cobalt atoms of this compound are in trigonal bipyramidal coordination; thus mercury cobalt carbonyl is closely related to iron pentacarbonyl dealt with in the preceding paper.[4]

The infrared active[5,6] and the Raman active[7] C–O stretching frequencies of $Hg[Co(CO)_4]_2$ have been reported earlier and the molecular symmetry of D_{3d} has been proposed[5] and later confirmed.[7] The same geometry has been found in the crystalline state.[8] It must be stressed that a not too high accuracy of the Raman frequencies has been claimed[7] as due to some coincidences with shifts excited by different emission bands of the He source.

An analysis of the first combination C–O stretching region based on the reported Raman frequencies of the « g » modes has recently been published.[9] No force constant calculations seem to be reported so far for $Hg[Co(CO)_4]_2$.

Experimental Section

Since $Hg[Co(CO)_4]_2$ itself, being very stable, exchanges CO very slowly, and indirect route has been used to the preparation of ^{13}CO-enriched samples. The exchange reaction has been performed, in a way similar to that reported earlier,[2] with $Co_2(CO)_8$, which is known to exchange its CO ligands very fast.[10] Using a gas phase having 22.5 per cent ^{13}CO content a complete equilibration could be achieved in four cycles. (The study of the spectrum of ^{13}CO-enriched $Co_2(CO)_8$ will be published at a later date.) The hexane solution of the ^{13}CO-enriched $Co_2(CO)_8$ has been reacted with metallic mercury to yield, through the known[11] insertion reaction, the enriched $Hg[Co(CO_4]_2$. Its ^{13}CO content was found by mass spectrometric analysis of the thermal decomposition gases to be 22.5 per cent thus proving the complete exchange.

In some phases of the spectral studies, however, it proved necessary to use the spectra of less highly enriched samples. These have been prepared by the same route from $Co_2(CO)_8$ equilibrated in only one or two cycles of exchange reactions.

The spectra were recorded on a Zeiss (Jena) UR-10 spectrometer equipped with lithium fluoride optics. The spectra were calibrated to carbon monoxide and deuterium chloride gas bands. All measurements were performed in n-hexane solution.

Results and Discussion

The enrichment of the ^{13}CO content from the natural abundance to 22.5 per cent leads to the spectrum

---

(1) (a) For Part XII of this series see ref. 4. (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, Gower Street, W.C. 1.

(2) G. Bor, *J. Organometal. Chem.*, *10*, 343 (1967).

(3) G. Bor and G. Jung, *Inorg. Chim. Acta*, *3*, 69 (1969).

(4) G. Bor, *Inorg. Chim. Acta*, *3*, 191 (1969).

(5) G. Bor and L. Markó, *Spectrochim. Acta*, *16*, 1105 (1960).

(6) K. Noack, *Helv. Chim. Acta*, *47*, 1555 (1964).

(7) H. Stammreich, K. Kawai, O. Sala and P. Krumholz, *J. Chem. Phys.*, *35*, 2175 (1961).

(8) G. M. Sheldrick and R. N. F. Simpson, *Chem. Commun.*, 1015 (1967).

(9) L. M. Bower and M. H. B. Stiddard, *J. Organometal. Chem.*, *13*, 235 (1968).

(10) D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, *11*, 33 (1959).

(11) S. V. Dighe and M. Orchin, *Inorg. Chem.*, *1*, 965 (1962).

shown in Figure 1. However, the study of the statistical distribution (Figure 2) shows that with this concentration of isotopic ligand we have, beside the two isomeric mono-^{13}CO molecules about in equal concentration, the disubstituted species (six isomers) and even the concentration of the tri-^{13}CO molecules (eight isomers) is as high as 18 per cent. The spectrum shown in Figure 1 hence results from the overlap of many individual spectra of the components and is less useful for the intended study as compared with the spectra obtained with less enriched samples, where the frequencies of the two $HgCo_2(^{12}CO)_7(^{13}CO)$ isomers could be determined more easily.

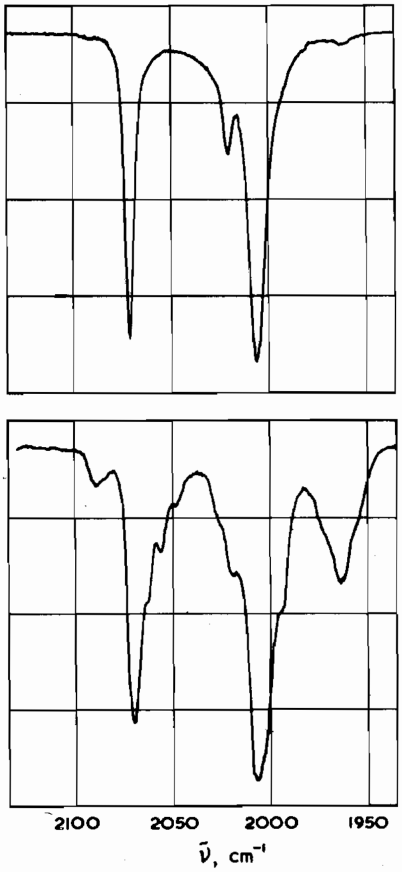

Figure 1. Infrared spectrum of $Hg[Co(CO)_4]_2$ in the C—O stretching region (n-hexane solution)
upper trace: with natural abundance of ^{13}CO
lower trace: with ^{13}CO content enriched to 22.5 per cent

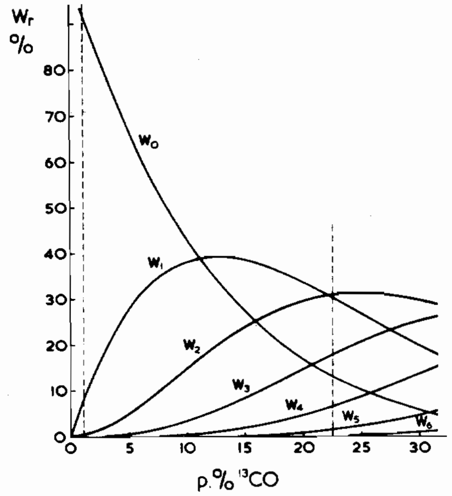

Figure 2. Statistical distribution of the molecular species $HgCo_2(^{12}CO)_{8-n}(^{13}CO)_n$; species concentration W_n vs. overall ^{13}CO concentration.

$HgCo_2(^{12}CO)_8$ molecules have D_{3d} symmetry[5-9] and thus two C—O stretching vibrations belong to species a_{1g} (Raman-active), two to a_{1u} (infrared active), one to e_g (Raman), and one to e_u (infrared). The earlier reported frequencies[5,7] have been correctly assigned by Bower and Stiddard.[9] For this compound two C—O stretching force constants, two direct, and four indirect C—O stretch-strech interaction constants can be defined in the factored C—O stretching model (Figure 3). Thus we have *two* frequencies less than constants to be determined. All eight constants can be, however, expressed as a function of only *one* parameter called cos β, defined in an earlier paper[12] for expressing the whole mathematically allowed region of C—O force and interaction constants of metal carbonyls having two different sets of C—O ligands. The equations are given in the Appendix.

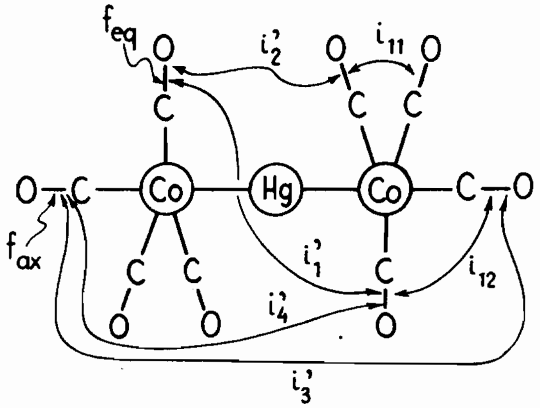

Figure 3. Definition of the C—O stretching force and interaction constants.

Owing to the presence of two different sets of CO groups two isomers of mono-^{13}CO-substituted molecules are to be expected. The equatorially (radially) substituted derivative belongs to point group C_s and thus six C—O stretching frequencies are to be expected in species a' and two frequencies in the antisymmetric species a'' all being infrared actives. These latter ones, however, must coincide with the e_g and e_u modes of the parent all-^{12}CO molecule.

The axial isomer on the other hand belongs to point group C_{4v} demanding four C—O stretching frequencies in species a_1 and two in e, the latter ones coinciding again with the parent e_g and e_u bands.

The six a' frequencies of the EQ-isomer are connected with the roots of a secular equation of sixth order thus all are shifted from the parent all-^{12}CO frequencies. However, preliminary calculations proved that a great shift (30 to 35 cm^{-1}) arises only for the « satellite » of the *lower* frequency degenerate band,

---

(12) G. Bor, *Inorg. Chim. Acta*, *1*, 81 (1967).

and for the other five bands shifts of only 0 to 5 cm^{-1} are to be expected, the sum of the shifts being 46 cm^{-1}.

For the four a_1 frequencies of the AX-isomer (connected with the roots of a secular equation of fourth order) shifts between 0 and 9.6 cm^{-1} are to be expected for the satellites of the three higher frequencies and the satellite of the *lowest* a_{1g} or a_{2u} band of the original spectrum is shifted by 29 to 43 cm^{-1}.

The magnitude of these shifts, *i.e.* the separation between the parent all-^{12}CO bands and their ^{13}CO-satellites varies in several cases very sensitively with the extent of coupling between the equatorial and axial symmetry coordinates in species a_{1g} and a_{2u}, *i.e.* with the value of cos β (or sin β respectively) in equations (4) [see Appendix] and can thus be used for its determination.

Since the isotopic frequencies all belong to the same symmetry species a change in only one of the starting all-^{12}CO frequencies influences all isotopic frequencies. However, the influence of the highest ^{12}C–O frequencies on the lowest isotopic ones is very small and *vice versa*. Nevertheless it must be stressed that there exists only one single set of the all-^{12}CO frequencies assigned only in a single way which results in an exact agreement between found and calculated values of the isotopic frequencies. This fact is the great advantage of the isotope method as compared with others since it allows no ambiguities in the assignment of the all-^{12}CO frequencies.

The individual steps in the calculation of the isotopic frequencies were given in details in the Appendix ref. 3. The most important point for the further steps is the determination of the cos β value. This could not be determined, however, in this case on the basis of the separation of the two highest isotopic frequencies (as in the case of Fe(CO)$_5$ [3] since the highest band of the axial mono-^{13}CO derivative had too low intensity and was merged into the corresponding band of the radial mano-^{13}CO substituted molecule. The important parameter cos β could nevertheless be determined from the separation of 9.5 cm^{-1} of the^{13}CO-satellite of the all-^{12}CO band at 2072.3 cm^{-1} and was found to be cos β = 0.0±0.05 (Figure 4). This finding proved, similarly to Fe(CO)$_5$,[3] the maximal coupling between the axial and radial type symmetry coordinates.[12]

By applying this cos β value and using the highest frequency of the equatorial (radial) mono-^{13}CO molecule at 2092.2 cm^{-1} we obtained 2094.6 cm^{-1} for the higher a_{1g} frequency, ν_1^{CO}, of the all-^{12}CO compound. This differs considerably from the reported Raman value at 2107 cm^{-1}.[7]

The lower a_{1g} frequency (ν_2^{CO}) could be obtained from the weak shoulder at 2026 cm^{-1} in the spectra of the enriched sample. This satellite is very slightly shifted from the inactive a_{1g} frequency which has been fixed in this way at 2027.5 cm^{-1} (as compared with the Raman value at 2030 cm^{-1}).

The determination of the e_g (ν_5^{CO}) frequency could be achieved after a systematic series of computations. The lowest isotope band at 1963.7 cm^{-1} is not a direct satellite of the strong infrared band at 2007.3 cm^{-1} (ν_6, e_u) but rather that of the Raman-active ν_5^{CO} (e_g) vibration as reflected by the form of the normal vector obtained for this vibration, aswell as by the observation that the variation of the input value of ν_5^{CO} influences the calculated value of this satellite much stronger than the change of the value of ν_6^{CO} (e_u). Since, however, this later one is known with high accuracy (at least ±0.2 cm^{-1}) we were forced to assign the frequency 1996.0±0.5 cm^{-1} to ν_5^{CO} to obtain the observed isotopic frequency at 1963.7 cm^{-1}.

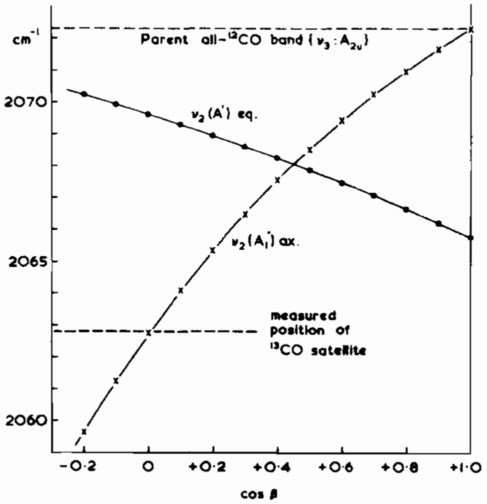

Figure 4. Variation of the calculated ν_2 mono-^{13}CO frequencies *vs.* change of cos β.

The C–O stretching frequencies of HgCo$_2$(^{12}CO)$_8$ obtained in this way are summarized in Table I. The « force constants *vs.* cos β diagram »[12] based on these frequencies is shown in Figure 5, and the C–O stretching and interaction constants of the factored C–O stretching model (« force field ») belonging to cos β = 0 are given in Table II.

Table I. C–O stretching frequencies of Hg[Co(CO)$_4$]$_2$, cm^{-1} (hexane solution)

assignment		IR inactives Raman data[7]	present work	IR actives
a_{1g}	ν_1^{CO}	2107	2094.6	
	ν_2^{CO}	2030	2027.5	
a_{2u}	ν_3^{CO}			2072.3
	ν_4^{CO}			2021.7
e_g :	ν_5^{CO}	1990	1996.0	
e_u :	ν_6^{CO}			2007.3

Table II. Force and interaction constants of Hg[Co(CO)$_4$]$_2$ in the factored C–O stretching force field, belonging to maximum equatorial-axial coupling, *i.e.* cos β = 0 (mdyn/Å)

f_{eq} = 16.477
f_{ax} = 17.052
i_{11} = 0.287
i_{12} = 0.282
i_1' = −0.022
i_2' = 0.070
i_3' = 0.118
i_4' = 0.041

The C–O stretching frequencies of the molecular species HgCo$_2$(^{12}CO)$_{8-n}$(^{13}CO)$_n$ have been calculated from these constants and these are shown up to a value of $n = 3$ in Figure 6. The observed spectrum with the ^{13}CO content of 22 per cent (Figure 1) results as the superposition of these individual spectra.

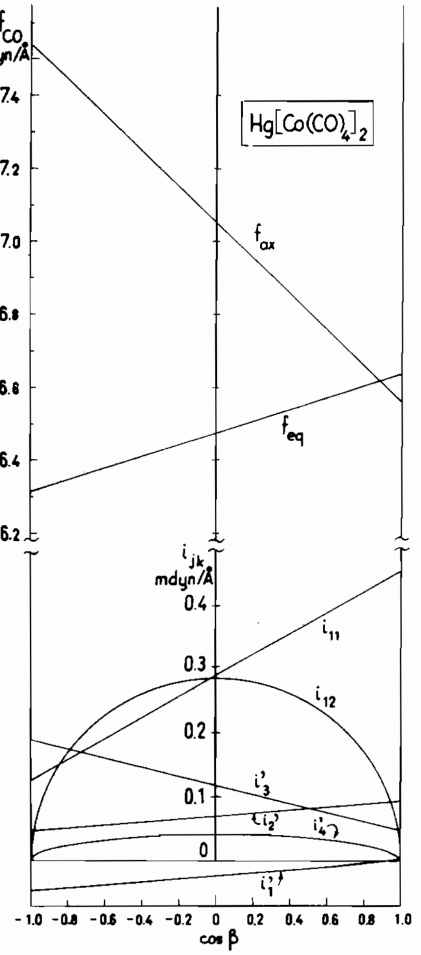

Figure 5. Force constants *vs.* cos β diagram of Hg[Co(CO)$_4$]$_2$.

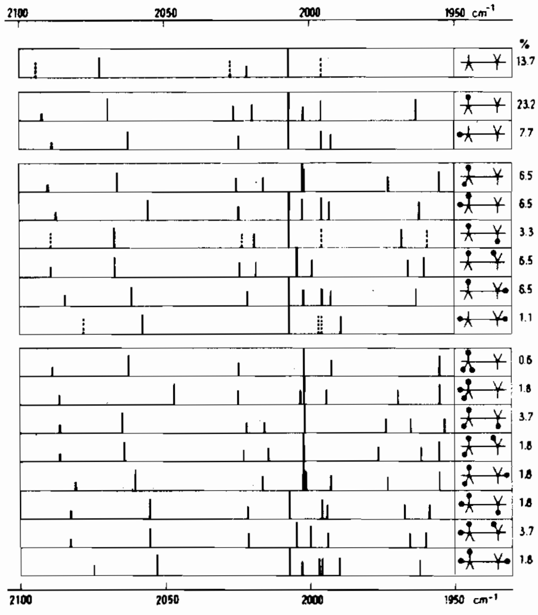

Figure 6. The C—O stretching frequencies of $HgCo_2(^{12}CO)_{8-n}(^{13}CO)_n$ molecules for $n = 0 \ldots 3$.

The first C—O stretching combination region has been also investigated (Figure 7). All nine allowed combinations are to be assigned with considerable certainty as given in Table III. Especially the Δν value of 8 cm^{-1} for the highest frequency combination (as compared with Δν = 22 cm^{-1} based[9] on the Raman value of ν_1^{CO}) confirms the essential correctness of the new « *g* » frequencies reported herein.

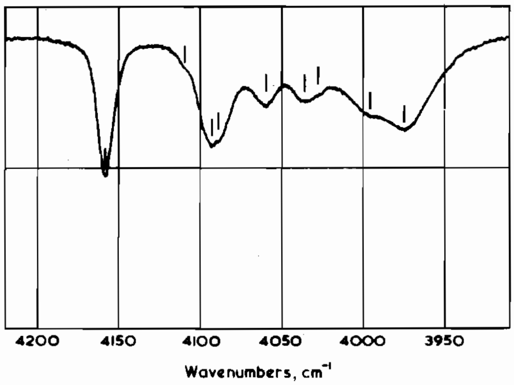

Figure 7. Infrared spectrum of Hg[Co(CO)$_4$]$_2$ in the binary C—O stretching combination region (CCl_4 solution).

With Hg[Co(CO)$_4$]$_2$ we have thus a new demonstration, as with trigonal bipyramidal metal carbonyls, that the axial C—O stretching force constant is higher than the equatorial (radial) one similarly to HCo(CO)$_4$, $CH_3Co(CO)_4$, $Ph_3PFe(CO)_4$ [12] and Fe(CO)$_5$.[3]

Table III. Assignment of the spectrum of Hg[Co(CO)$_4$]$_2$ in the first C—O stretching combination region

Frequencies, cm^{-1} Observed [a]	Calculated	Δν	Assignments
4159	4166.9	7.9	$\nu_1(a_{1g})+\nu_3(a_{2u}) = A_{2u}$
4110 (sh)	4116.3	6.3	$\nu_1(a_{1g})+\nu_4(a_{2u}) = A_{2u}$
4093	4101.9	8.9	$\nu_1(a_{1g})+\nu_6(e_u) = E_u$ [b]
4089 (sh)	4099.8	10.8	$\nu_2(a_{1g})+\nu_3(a_{2u}) = A_{2u}$ [b]
4060	4068.3	8.3	$\nu_3(a_{2u})+\nu_5(e_g) = E_u$
4036	4049.2	13.2	$\nu_2(a_{1g})+\nu_4(a_{2u}) = A_{2u}$
4028 (sh)	4034.8	6.8	$\nu_2(a_{1g})+\nu_6(e_u) = E_u$
3997	4017.7	20.7	$\nu_4(a_{2u})+\nu_5(e_g) = E_u$
3976	4003.3	27.3	$\nu_5(e_g)+\nu_6(e_u) = A_{2u}+E_u$

[a] In CCl_4 solution, ±2 cm^{-1}. [b] The assignment of these two bands may be interchanged.

The results shown in Table 2 prove that within the framework of the C—O stretching force field (which is identical with the « Cotton - Kraihanzel Force Field »[13] but without the constraints between the interaction constants) none of the « indirect » C—O stretch-stretch interactions between CO ligands bonded to different metal atoms have vanishing values, although only one of them (i_3') exceeds 0.1 mdyn/Å, acting through a

---

(13) F .A. Cotton and C. K. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432 (1962).

linear sequence of bonds between the two trans CO groups.

It is worth mentioning that the indirect interaction i_2' acting between CO groups in cisoid position is as low as 0.07 mdyn/Å, whereas in $Co_2(CO)_6(PBu_3)_2$ where these ligands are much closer due to the absence of the mercury atom the same type of interaction constant has the value of 0.23 mdyn/Å.[14]

Appendix

For $HgCo_2(CO)_8$ we have the following relationships between the factored **F** matrix elements and the force and interaction constants defined in Figure 3:

$$a_{1g}: \left\{ \begin{array}{l} F_{11} = f_{eq} + 2i_{11} + i_1' + 2i_2' \\ F_{22} = f_{ax} + i_3' \\ F_{12} = \sqrt{3}\,(i_{12} + i_4') \end{array} \right.$$

$$a_{2u}: \left\{ \begin{array}{l} F_{33} = f_{eq} + 2i_{11} - i_1' - 2i_2' \\ F_{44} = f_{ax} - i_3' \\ F_{45} = \sqrt{3}\,(i_{12} - i_4') \end{array} \right. \tag{1}$$

$$e_g: \quad F_{55} = f_{eq} - i_{11} + i_1' - i_2'$$

$$e_u: \quad F_{66} = f_{eq} - i_{11} - i_1' + i_2'$$

For the species e_g and e_u containing only one C–O stretching coordinate we have:

$$F_{55} = y_5 \qquad \text{and} \qquad F_{66} = y_6$$

For the two second order species, however, we have to introduce the parameter cos β[12] and then we have:

$$\frac{F_{11} - F_{22}}{y_1 - y_2} = \frac{F_{33} - F_{44}}{y_3 - y_4} = \cos\beta \tag{2}$$

where

$$y_k = \frac{\lambda_k}{\mu_{CO}} = 0.40407 \times 10^{-5} \times \nu_k^2 \quad \text{mdyn/Å} \tag{3}$$

We can apply the same parameter cos β for both species a_{1g} and a_{2u} since the type of coupling between the radial and axial ligand vibrations is the same for one $Co(CO)_4$ group in both of these species.

By combining the above relationships we obtain the following equations connecting the force and interaction constants with the y_k values as a function of cos β:

$$\begin{aligned} f_{eq} &= \frac{1}{12}(y_1+y_2+y_3+y_4) + \frac{1}{3}(y_5+y_6) + \\ &\quad + \frac{1}{12}[(y_1-y_2)+(y_3-y_4)]\cos\beta \\ f_{ax} &= \frac{1}{4}(y_1+y_2+y_3+y_4) - \frac{1}{4}[(y_1-y_2)+(y_3-y_4)]\cos\beta \\ i_{11} &= \frac{1}{12}(y_1+y_2+y_3+y_4) - \frac{1}{6}(y_5+y_6) + \\ &\quad + \frac{1}{12}[(y_1-y_2)+(y_3-y_4)]\cos\beta \\ i_{12} &= \frac{1}{4\sqrt{3}}[(y_1-y_2)+(y_3-y_4)]\sin\beta \\ i_1' &= \frac{1}{12}(y_1+y_2-y_3-y_4) + \frac{1}{3}(y_5-y_6) + \\ &\quad + \frac{1}{12}[(y_1-y_2)-(y_3-y_4)]\cos\beta \\ i_2' &= \frac{1}{4}(y_1+y_2-y_3-y_4) - \frac{1}{4}[(y_1-y_2)-(y_3-y_4)]\cos\beta \\ i_3' &= \frac{1}{12}(y_1+y_2-y_3-y_4) - \frac{1}{6}(y_5-y_6) + \\ &\quad + \frac{1}{12}[(y_1-y_2)-(y_3-y_4)]\cos\beta \\ i_4' &= \frac{1}{4\sqrt{3}}[(y_1-y_2)-(y_3-y_4)]\sin\beta \end{aligned} \tag{4}$$

The constants calculated by the above equations were arranged in an eight-by-eight matrix the numerical values of which varied with the variation of cos β. By changing cos β between –0.2 and +1.0 in steps of 0.1 units 13 different force constant matrices were obtained. The C–O stretching frequencies of the equatorially and axially mono-^{13}CO substituted molecules were calculated for all these variations according to the steps given in the Appendix of our previous paper. All these operations were performed by a single computer programme which yielded the isotopic frequencies as functions of cos β starting from the all-^{12}CO frequencies.

---

[14] G. Bor, unpublished results.