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Infrared Spectroscopic Studies on Metal Carbonyl Compounds. XI.* Study of the Spectrum of ^{13}CO-enriched Molybdenum Hexacarbonyl

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By the enrichment of the ^{13}CO content of $Mo(CO)_6$ to 6—8 percent the C—O stretching frequencies of $Mo(^{12}CO)_5(^{13}CO)$ have been measured. Using these data the infrared inactive C—O stretching frequencies and the nonrigorous (factored off) C—O stretching force constants of $Mo(^{12}CO)_6$ have been determined (Table 1). The ratio of the dipole moment gradients of ^{12}CO and ^{13}CO ligands has been obtained and the C—O stretching frequencies and relative band intensities all $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ ($n=1$ ..... 6) molecules calculated.

Introduction

Previous studies on the ^{13}CO-isotope spectra of metal carbonyls were performed with the following aims: (a) determination of the IR-inactive C—O stretching frequencies of all-^{12}CO compound;[2] (b) comparison of the observed and calculated $M_x(^{12}CO)_{n-r}(^{13}CO)_r$ spectra for checking the correctness of assignments and force constant calculations;[2,3,4,5] (c) utilization of ^{13}CO isotopic data in the course of computations of force constants;[6,7] (d) the determination of reaction mechanisms involving CO uptake or insertion.[7,8,9,10,14]

These studies were based in part on spectra of isotopically enriched compounds.[2,6,7,8,9,10]

The force constant calculations quoted in points (b) and (c) were performed, with the exception of the paper of Bouquet and Bigorgne,[3] on the basis of simplified force fields based solely on the C—O stretching fundamentals.[11,12,13]

The non-rigorous C—O stretching force constants and stretch-stretch interaction constants obtained on the basis of the factored-off C—O streching block of the **F** and **G** matrix reproduce exactly not only the C—O stretching frequencies (which is not the case *e.g.* with the Urey-Bradley force field), but even the C—O frequencies of the isotopically substituted molecules are obtained in this way with high accuracy.[2] This fact ensures not only the unequivocal identification of the ^{13}CO « satellite » bands but furnishes a new method for the exact determination of the IR-inactive C—O stretching frequencies of the parent all-^{12}CO compounds from the infrared bands of the mono-^{13}CO substituted molecules.

In this paper a further example, that of molybdenum hexacarbonyl is dealt with. A somewhat similar study has been performed recently also by Harrill and Kaesz.[14] These authors investigated, however, mainly the stereochemistry of the products obtained in the reactions of $(C_7H_8)Mo(CO)_4$ and $(C_8H_{10})Mo(CO)_3$ with ^{13}CO, whereas the emphasis of our paper is put on the calculation of the all-^{12}CO frequencies, and on the method of computation. Besides the C—O stretching frequencies, the eigenvectors of the corresponding vibrations will be also dealt with which are of importance from the point of view of band intensity considerations aswell as for the determination of the ratio of the dipole gradients, $\frac{\partial\mu'_{^{13}CO}}{\partial r} / \frac{\partial\mu'_{^{12}CO}}{\partial r}$.

Experimental Section

Molybdenum hexacarbonyl was of commercial origin and has been purified by sublimation in vacuo. Composition of the ^{13}CO enriched carbon monoxide, the accomplishment of the experiments and scanning and calibration conditions of the spectra were the same as given in previous papers.[2,15]

The exchange rates[16] of molybdenum carbonyl is

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(1) G. Bor, *J. Organometal. Chem. 11,* 195 (1968).

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

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

much lower than of those studied in our previous paper.[2] Therefore a considerably lower ^{13}C-concentration was reached after two or three exchange cycles (about 6 - 8 percent ^{13}CO content). Consequently only the «isotope» bands belonging to the mono-^{13}CO-derivative could be identified straightforwardly. However, after the calculation of the C—O stretching frequencies of the higher substituted molecular species some of the bands belonging to the di-^{13}CO substituted derivatives could also be detected.

Method of Calculation

We did not perform corrections for anharmonicity for the reasons given by Cotton and Kraihanzel.[11] Of course force constants being physically more meaningful can be obtained based on frequencies corrected for anharmonicity.[21] However, we wish to apply the present method for different other metal carbonyl types for which no experimental data are available for performing anharmonicity corrections.

In the first step the non-rigorous force and interaction constants of the simplified (*i.e.* only C—O stretching) force field are obtained from the $y_k=\lambda_k/\mu$ values which are connected with the C—O stretching frequencies, ν_k by Eq. (1):[13]

$$y_k = \lambda_k/\mu = 0.40407\times10^{-5}\times\nu_k^2 \quad \text{mdyn/Å} \tag{1}$$

where λ_k stands for $4\pi^2c^2\nu_k^2/N$ and $1/\mu$ for the reduced mass of ^{12}CO.

For molybdenum hexacarbonyl having only one C—O stretching fundamental in each species the force constants are easily expressed from the relationships (2), (3), and (4):

$$\text{(species } a_{1g}) \ldots y_1 = \lambda_1/\mu = f_{CO} + i_t + 4\,i_c \tag{2}$$

$$\text{(species } e_g) \ldots y_2 = \lambda_2/\mu = f_{CO} + i_t - 2\,i_c \tag{3}$$

$$\text{(species } f_{1u}) \ldots y_3 = \lambda_3/\mu = f_{CO} - i_t \tag{4}$$

to yield equations (5), (6), and (7):

$$f_{CO} = (y_1 + 2y_2 + 3y_3)/6 \tag{5}$$

$$i_c = (y_1 - y_2)/6 \tag{6}$$

$$i_t = (y_1 + 2y_2 - 3\,y_3)/6 \tag{7}$$

where f_{CO} stands for the C—O stretching force constant, i_c for the CO—CO interaction constant between ligands in *cis* position, and i_t for the same type of interaction between *trans* ligands.

$Mo(^{12}CO)_6$ having O_h symmetry only one C—O stretching fundamental, belonging to species f_{1u} is infrared active. The other two C—O stretching frequencies (a_{1g} and e_g) are known from Raman studies[17] or from extrapolation from the frequencies of substituted derivatives.[18] These data, however, are not of such high accuracy which is attainable in the direct infrared measurement using medium or high resolution, *i.e.* at least ± 0.5 cm^{-1}. Therefore the literature data on the infrared-inactive frequencies could be used only as rough starting values and they had to be refined to give the best agreement with the observed frequencies of the mono-^{13}CO molecules.

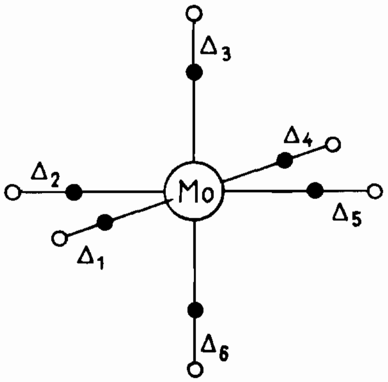

Figure 1. Numbering scheme of the C-O stretching inner coordinates.

The force constants are arranged to a six-by-six **F** matrix in terms of inner valence coordinates,[19] thus the same matrix can be used for the calculation of differently ^{13}CO-substituted molecules differing generally in symmetry. According to the numbering scheme of the ligands shown in Figure 1 we have

$$\begin{aligned} &F_{ii} = f_{CO} \\ &F_{12} = F_{13} = F_{15} = F_{16},\ \text{etc.} && = i_c \\ &F_{14} = F_{25} = F_{36} && = i_t \\ &\text{and } F_{ij} = F_{ji} \end{aligned} \tag{8}$$

To preserve the advantage of the substitution

$$\mathbf{G}^{-1} = \frac{1}{\mu}\mathbf{E}$$

(where $\mathbf{G}^{-1}$ stands for the kinetic energy matrix, **E** for the unit matrix, and $1/\mu$ for the reduced mass of carbon-12 monoxide) introduced by Cotton and Kraihanzel.[11] and thus the convenient form (9) of the secular equation by substituting $y=\lambda/\mu$:[13]

$$|\mathbf{F} - y\,\mathbf{E}| = 0 \tag{9}$$

the **F** matrix is in the next step transformed according (10):[2]

$$\mathbf{A}^{1/2}\,\mathbf{F}\,\mathbf{A}^{1/2} = \Phi \tag{10}$$

The diagonal matrix $\mathbf{A}^{1/2}$ differs from the unit matrix **E** only in the element(s) corresponding to the position(s) of a ^{13}CO ligand, these element(s) being

$$a^{1/2} = \left(\frac{1}{\mu(^{12}CO)} \Big/ \frac{1}{\mu(^{13}CO)}\right)^{1/2} = 0.9776 \tag{11}$$

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(17) A. Danti and F. A. Cotton, *J. Chem. Phys. 28*, 4736 (1958).
(18) R. Poiblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).
(19) A. G. Meister and F. F. Cleveland, *Am. J. Phys. 14*, 10 (1946).

The determination of the spectrum of the ^{13}CO-substituted carbonyl is then equivalent with the solution of the simple secular equation (12):

$$|\Phi - y^{(i)}\mathbf{E}| = 0 \tag{12}$$

The computation of the eigenvalues of matrix Φ by its diagonalization (13)

$$\mathbf{V}'\Phi\mathbf{V} = \mathbf{Y}^{(i)} \tag{13}$$

leads straightforwardly to the $y_k^{(i)} = \lambda_k^{(i)}/\mu(^{12}\mathrm{CO})$ values of the ^{13}CO-substituted molecules, which are converted according (1) to the $\nu^{(i)}$ isotopic frequencies sought for.

The computer program itself uses the numerical elements of the matrix of the type (8) as input data. It then multiplies by $a^{1/2} = 0.9776$ those rows and columns which correspond to the positions of the ^{13}CO ligands according to the numbering scheme. The elements of matrix Φ (10) obtained on this way are now used as input values to the next procedure which furnishes the eigenvalues of Eq. (12) by diagonalizing Φ.

The diagonalization is carried out by the well known Jacobi eigenvalue algorithm.[20] It proved useful, however, to perform a minor change in this procedure for our special cases. In the Jacobi algorithm namely the square roots of expressions are frequently calculated in which the differences of the diagonal matrix elements occure. Since in the C—O stretching force constant matrices of metal carbonyls many if not all the diagonal elements are equal, the program stopped if negative difference values were obtained as an effect of rounding off errors. This incovenience has been avoided by inserting a conditional statement in which, prior to the square root computations the equality of the elements in question was checked.

In a final procedure the frequencies $\nu_k^{(i)}$ are obtained from the $y_k^{(i)}$ values according to Eq. (1). Besides the frequencies the elements of the orthonormal matrix **V** of the eigenvectors are also printed out.

Spectra and Results

The frequency data published on the single IR-active C—O stretching fundamental (species f_{1u}) all but one[18] refer to vapour phase spectra.

Several data exist in the literature also concerning the IR-inactive C—O stretching frequencies of $Mo(CO)_6$ obtained from Raman spectra[17] or by extrapolation from the corresponding frequencies of substituted derivatives.[18] The data given by Poilblanc and Bigorgne[18] obtained in unpolar solvents seemed to serve as the best starting values: $\nu_1^{CO}(a_{1g}) = 2118$, $\nu_2^{CO}(e_g) = 2020$, and $\nu_3^{CO}(f_{1u}) = 1986$ cm^{-1}. Using these data the following C—O stretching frequencies have been computed for species a_1 vibrations of $Mo(^{12}CO)_5(^{13}CO)$, point group C_{4v}: 2112.10, 2011.60, and 1955.07 cm^{-1}. The IR-inactive b_1 frequency of the mono-^{13}CO molecule must coincide with the e_g frequency of the all-^{12}CO compound, and similarly the e frequency of the isotopically monosubstituted species must have the same value as the very strong IR-active f_{1u} frequency of $Mo(^{12}CO)_6$.

This f_{1u} vibration was found in hexane solution to have the frequency of 1989.3 cm^{-1}. The lowest ^{13}CO-satellite is easily recognized even from the spectra of the complex with natural abundance of ^{13}CO and it has the frequency of 1958.0 cm^{-1}. With highly concentrated solutions two additional very weak bands can also be observed at 2110.6 and 2010.9 cm^{-1}. Undoubtedly these are the other two a_1 bands of the mono-^{13}CO compound. (The broad band at about 2080 cm^{-1} is attributed to a combination.)

All the mentioned three weak bands grew intenser after ^{13}CO enrichment (Figure 2) confirming thus their assignment.

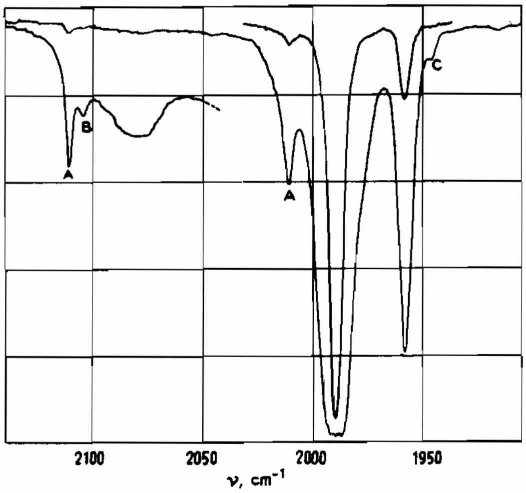

Figure 2. Spectrum of ^{13}CO-enriched $Mo(CO)_6$ in the C-O stretching region; *n*-hexane solution, three concentrations.
A: bands of $Mo(^{12}CO)_5(^{13}CO)$;
B: band of *cis*-$Mo(^{12}CO)_4(^{13}CO)_2$;
C: band of *trans-Mo*$(^{12}CO)_4(^{13}CO)_2$.

Table I. Fundamental C-O stretching frequencies (±0.2 cm^{-1}) of $Mo(^{12}CO)_6$ obtained from ^{13}CO isotopic data, and approximate force constants derived thereof (hexane solution, without anharmonic correction).

$\nu_1^{CO}(a_{1g}) = 2116.5$ cm^{-1}	$f_{CO} = 16.5018 \pm 0.0032$ mdyn/Å
$\nu_2^{CO}(e_g) = 2018.9$ cm^{-1}	$i_c = 0.2718 \pm 0.0011$ mdyn/Å
$\nu_3^{CO}(f_{1u}) = 1989.3$ cm^{-1}	$i_t = 0.5115 \pm 0.0032$ mdyn/Å

The force constans are given to a degree of precision which was used in the calculation of the isotopic frequencies.

After the exact measurement of the wave numbers of these isotope bands (± 0.2 cm^{-1}) the starting all-^{12}CO frequencies had to be refined to furnish exactly the observed mono-^{13}CO values. This is easily done in one step, since the changes in the frequency of a certain all-^{12}CO band influences specifically the frequency of its particular « satellite », the other bands of the same species being altered only insignificantly.

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(20) T. G. Evans, Algorithm 85, Jacobi, in « Collected Algorithms 1960-1963 from the Communications of the Association for Computing Machinary » by R. E. Grench et al., Argonne National Laboratory, Argonne, Illinois, July 1965, p. 59; J. S. Hillmore, ibid, p. 60 « Certification of Algorithm 85 Jacobi ».

Table II. Assignments, calculated frequencies and relative intensities (in square brackets) of the C-O stretching vibrations of $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ molecules.

$n=0$	$n=1$	$n=2$		$n=3$		$n=4$		$n=5$	$n=6$
		trans	cis	trans	cis	trans	cis		
O_h	C_{4v}	D_{4h}	C_{2v}	C_{2v}	C_{3v}	D_{4h}	C_{2v}	C_{4v}	O_h
$\nu_1(a_{1g})$ 2116.5 [0.000]	$\nu_1(a_1)$ 2110.6[a] [0.017]	$\nu_1(a_{1g})$ 2104.8 [0.000]	$\nu_1(a_1)$ 2104.2[b] [0.040]	$\nu_1(a_1)$ 2097.7 [0.024]	$\nu_1(a_1)$ 2096.9 [0.076]	$\nu_1(a_{1g})$ 2090.4 [0.000]	$\nu_1(a_1)$ 2089.3 [0.065]	$\nu_1(a_1)$ 2080.5 [0.046]	$\nu_1(a_{1g})$ 2069.1 [0.000]
$\nu_2(e_g)$ 2018.9 [0.000]	$\nu_4(b_1)$ 2018.9 [0.000]	$\nu_4(b_{1g})$ 2018.9 [0.000]							
	$\nu_2(a_1)$ 2011.1[c] [0.328]		$\nu_2(a_1)$ 2014.5 [0.171]	$\nu_2(a_1)$ 2013.0 [0.230]					
			$\nu_4(b_1)$ 2008.4 [0.473]		$\nu_3(e)$ 2008.4 [0.947]		$\nu_4(b_1)$ 2008.4 [0.473]		
						$\nu_2(a_{1g})$ 1998.3 [0.000]		$\nu_2(a_1)$ 1996.0 [0.429]	
$\nu_3(f_{1u})$ 1989.3 [6.00]	$\nu_5(e)$ 1989.3 [4.00]	$\nu_5(e_u)$ 1989.3 [4.00]	$\nu_6(b_2)$ 1989.3 [2.00]	$\nu_5(b_1)$ 1989.3 [2.00]		$\nu_3(a_{2u})$ 1989.3 [2.00]			
		$\nu_2(a_{1g})$ 1984.6 [0.000]		$\nu_3(a_1)$ 1985.1 [0.197]			$\nu_2(a_1)$ 1985.4 [0.380]		
						$\nu_4(b_{1g})$ 1973.7 [0.000]		$\nu_4(b_1)$ 1973.7 [0.000]	$\nu_2(e_g)$ 1973.7 [0.000]
	$\nu_3(a_1)$ 1957.7[d] [1.56]		$\nu_3(a_1)$ 1960.4 [1.69]	$\nu_4(a_1)$ 1956.7 [1.45]	$\nu_2(a_1)$ 1962.9 [1.83]		$\nu_3(a_1)$ 1958.4 [1.46]	$\nu_3(a_1)$ 1956.2 [1.43]	
			$\nu_5(b_1)$ 1954.9 [1.43]		$\nu_4(e)$ 1954.9 [2.86]		$\nu_5(b_1)$ 1954.9 [1.43]		
		$\nu_3(a_{2u})$ 1944.7[e] [1.81]		$\nu_6(b_2)$ 1944.7 [1.81]		$\nu_5(e_u)$ 1944.7 [3.61]	$\nu_6(b_2)$ 1944.7 [1.81]	$\nu_5(e)$ 1944.7 [3.61]	$\nu_3(f_{1u})$ 1944.7 [5.42]

[a] Found: 2110.6; [b] Found: 2104.2; [c] Found: 2010.9; [d] Found: 1958.0; [e] Found: 1946.0 cm^{-1}.

Thus the frequencies given in Table I have been found to represent best the C—O stretching fundamentals of $Mo(^{12}CO)_6$ in hexane solution (without anharmonic corrections).

The non-rigorous force and interaction constants obtained by equations (5), (6), and (7) are also given in Table I. These may be compared with the values 16.46, 0.27, and 0.55 mdyn/Å respectively obtained by Jones[21] under identical assumptions, however from frequencies obtained in CCl_4 solutions.

Arranging these values into the force constant matrix (8) and performing the calculations given previously the C—O stretching frequencies of all differently ^{13}CO subsituted $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ molecules were obtained. The numerical values are given in Table 2 together with the assignments to the corresponding symmetry species and intensities dealt with later.

An important regularity in the frequency values given in Table II is worth of emphasizing. The degenerate and antisymmetric vibrations respectively (symmetry species f_{1u}, e, e_g, b_1, b_{1g}, b_2, or a_{2u}) involving only one type of bond (*i.e.* only ^{12}C-O *or* ^{13}C-O) distinguish themselves in having identical frequencies in more (in three and in six, respectively) of the differently isotopically substituted molecules. On the other hand, the frequencies belonging to totally symmetric species, although falling in distinct regions, show irregular variations as due to the coupling of ^{12}C—O and ^{13}C—O vibrations in this species.

It is clear from the data of Table II that the two very weak bands to be observed on the spectrum of the enriched compound at 2104.1 and 1946 ± 1 cm^{-1} belong to the *cis*- and *trans*-di-^{13}CO substituted molecules, respectively.

In Table III the eigenvectors of the « C—O stretching type » normal coordinates of the differently ^{13}CO-substituted molecules are compiled. Only those species are given in which two or more symmetry coordinates are mixing to give the corresponding normal coordinates, since in the singly occupied species the eigenvectors have trivial values.

As a consequence of the construction of the matrix **F** in terms of inner valence coordinates the eigenvectors correspond directly to the orthonormal (relative) amplitudes of the individual ligand vibrations.

By using the eigenvector values of the mono-^{13}CO compound the ratio, d, of the dipole moment gradients of the ^{13}C—O and ^{12}C—O stretchings, respectively, could be obtained

$$d = \frac{\partial\mu'_{^{13}CO}}{\partial r} \Big/ \frac{\partial\mu'_{^{12}CO}}{\partial r} \qquad (14)$$

Since in the molecule of C_{4v} symmetry only ligands 6 (^{13}CO) and 3 (trans to ^{13}CO) contribute to the intensity in species a_1 we have the following equations for

Table III. Eigenvectors of the C—O stretching normal coordinates of $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ (n = 1—5) molecules.

$Mo(^{12}CO)_5(^{13}CO)$

species a_1

	Q_1	Q_2	Q_3
Δ_1	0.4307	−0.2448	−0.0679
Δ_2	0.4307	−0.2448	−0.0679
Δ_3	0.4117	0.8292	−0.3780
Δ_4	0.4307	−0.2448	−0.0679
Δ_5	0.4307	−0.2448	−0.0679
$^{(13)}\Delta_6$	0.2976	0.2697	0.9158

trans-$Mo(^{12}CO)_4(^{13}CO)_2$

species a_{1g}

	Q_1	Q_2
Δ_1	0.4546	−0.2082
Δ_2	0.4546	−0.2082
$^{(13)}\Delta_3$	0.2944	0.6429
Δ_4	0.4546	−0.2082
Δ_5	0.4546	−0.2082
$^{(13)}\Delta_6$	0.2944	0.6429

cis-$Mo(^{12}CO)_4(^{13}CO)_2$

species a_1 / species b_1

	Q_1	Q_2	Q_3	Q_4	Q_5
Δ_1	0.4599	0.5282	−0.0971	0	0
Δ_2	0.4375	−0.4426	−0.3357	0.6778	0.2014
Δ_3	0.4375	−0.4426	−0.3357	−0.6778	−0.2014
Δ_4	0.4599	0.5282	−0.0971	0	0
$^{(13)}\Delta_5$	0.3115	−0.1582	0.6147	0.2014	−0.6778
$^{(13)}\Delta_6$	0.3115	−0.1582	0.6147	−0.2014	0.6778

trans-$Mo(^{12}CO)_3(^{13}CO)_3$

species a_l

	Q_1	Q_2	Q_3	Q_4
Δ_1	0.4926	0.4606	−0.2082	−0.0434
Δ_2	0.4657	−0.7171	−0.4022	−0.3385
$^{(13)}\Delta_3$	0.3093	−0.0688	0.6123	−0.1571
Δ_4	0.4926	0.4606	−0.2082	−0.0434
$^{(13)}\Delta_5$	0.3262	−0.2441	0.0419	0.9123
$^{(13)}\Delta_6$	0.3093	−0.0688	0.6123	−0.1571

cis-$Mo(^{12}CO)_3(^{13}CO)_3$

species a_1

	Q_1	Q_2
Δ_1	0.4732	−0.3307
Δ_2	0.4732	−0.3307
Δ_3	0.4732	−0.3307
$^{(13)}\Delta_4$	0.3307	0.4732
$^{(13)}\Delta_5$	0.3307	0.4732
$^{(13)}\Delta_6$	0.3307	0.4732

species e

Q_{3a}	Q_{3b}	Q_{4a}	Q_{4b}
0.7827	0	0.2326	0
−0.3913	0.6778	−0.1163	0.2014
−0.3913	−0.6778	−0.1163	−0.2014
0.2326	0	−0.7827	0
−0.1163	0.2014	0.3913	−0.6778
−0.1163	−0.2014	0.3913	0.6778

trans-$Mo(^{12}CO)_2(^{13}CO)_4$

species a_{1g}

	Q_1	Q_2
Δ_1	0.5371	−0.4599
$^{(13)}\Delta_2$	0.3252	0.3798
$^{(13)}\Delta_3$	0.3252	0.3798
Δ_4	0.5371	−0.4599
$^{(13)}\Delta_5$	0.3252	0.3798
$^{(13)}\Delta_6$	0.3252	0.3798

Table III. (continued)

cis-$Mo(^{12}CO)_2(^{13}CO)_4$

species a_1

	Q_1	Q_2	Q_3
Δ_1	0.5156	−0.3999	−0.2725
Δ_2	0.5156	−0.3999	−0.2725
$^{(13)}\Delta_3$	0.3315	0.5820	−0.2268
$^{(13)}\Delta_4$	0.3526	0.0376	0.6118
$^{(13)}\Delta_5$	0.3526	0.0376	0.6118
$^{(13)}\Delta_6$	0.3315	0.5820	−0.2268

species b_1

Q_4	Q_5
0.6778	−0.2014
−0.6778	0.2014
0	0
0.2014	0.6778
−0.2014	−0.6778
0	0

$Mo(^{12}CO)(^{13}CO)_5$

species a_1

Δ_1	0.5810	0.7470	−0.3232
$^{(13)}\Delta_2$	0.3584	−0.3288	−0.1159
$^{(13)}\Delta_3$	0.3584	−0.3288	−0.1159
$^{(13)}\Delta_4$	0.3857	0.0971	0.9175
$^{(13)}\Delta_5$	0.3584	−0.3288	−0.1159
$^{(13)}\Delta_6$	0.3584	−0.3288	−0.1159

the determination of d:

$$\sqrt{I_1} = 0.4117 - 0.2976\, d$$

$$\sqrt{I_2} = 0.8292 - 0.2697\, d$$

$$\sqrt{I_3} = 0.3780 + 0.9158\, d$$

From the square roots of the absorptivity ratios of the bands at 2110.6, 2011, and 1958 cm^{-1} we obtained: $d = 0.95 \pm 0.05$, in accord with the same value obtained from the spectrum of $Ni(^{12}CO)_3(^{13}CO)$.*

Thus although the ratio of the dipole moment gradients does not differ significantly from unity ($\partial\mu'_{^{13}CO} = \partial\mu'_{^{12}CO}$ has been assumed by Kaesz *et al.*),[22] the obtained difference influences considerably the intensity ratio of the C—O stretching bands. Whereas $\partial\mu'_{^{13}CO} = \partial\mu'_{^{12}CO}$ demands $I_1 : I_2 : I_3 = 1 : 24 : 129$, with $d = 0.9$ the intensity ratios $I_1 : I_2 : I_3 = 1 : 17 : 70$ are obtained.

By using $d = 0.95$ the relative intensities of the C—O stretching bands of differently ^{13}CO-substituted $Mo(^{12}CO)_{6-n}(^{13}CO)_n$ molecules have been calculated and are given in Table II related to the value 6.00 of the f_{1u} band of $Mo(^{12}CO)_6$.

(*) In the paper dealing with the ^{13}CO-isotope spectra of $Ni(CO)_4$[2] we did not report the eigenvectors. These are *e.g.* for species a_1 of $Ni(^{12}CO)_3(^{13}CO)$:

Q_1	Q_2
0.5452	−0.1899
0.5452	−0.1899
0.5452	−0.1899
0.3289	0.9444

(21) L. H. Jones, *Inorg. Chem.* 6, 1269 (1967).

(22) P. S. Braterman, R. Bau és H. D. Kaesz, *Inorg. Chem.* 6, 2097 (1967).