THE INFRARED SPECTRA OF ISOTOPICALLY SUBSTITUTED METAL CARBONYLS

I. ^{13}CO-SUBSTITUTED *cis*-Fe(CO)$_4$I$_2$ AND *cis*-Fe(CO)$_4$Br$_2$

I. S. BUTLER AND H. K. SPENDJIAN

Department of Chemistry, McGill University, Montreal, Quebec (Canada)

(Received March 14th, 1969)

SUMMARY

All of the infrared active C–O stretching absorptions including the minor peaks observed in the spectra of *cis*-Fe(CO)$_4$X$_2$ molecules (X = Br or I) have been assigned to modes of the all-^{12}CO derivative (96% natural abundance) and the principal mono-isotopic species Fe(^{12}CO)$_3$(^{13}CO)X$_2$ (2% ^{13}CO-*cis* and 2% ^{13}CO-*trans* to X). The proposed assignments are supported by calculations of the five Cotton–Kraihanzel force constants in the energy factored C–O stretching block of the (*FG*) matrix. The ^{13}CO modes have been experimentally verified through exchange with 50% ^{13}C-enriched CO. The CO groups *cis* and *trans* to I in *cis*-Fe(CO)$_4$I$_2$ are observed to be approximately equally enhanced by ^{13}CO exchange in agreement with previous radio-carbon monoxide studies.

INTRODUCTION

The infrared spectra of the *cis*-Fe(CO)$_4$X$_2$ molecules (X = Cl, Br, or I) in the C–O stretching region have been the subject of numerous investigations over the past few years[1-6]. In most of these, the chief point of interest has been the assignment of the fundamentals of the all-^{12}CO molecules. The weak absorptions in the spectra have either been neglected or attributed without actual proof[2,6] to the absorptions of ^{13}CO substituted molecules present in natural abundance. While the present work was in progress, Johnson *et al.* reported[6] spectroscopic data for the exchange reaction of *cis*-Fe(CO)$_4$I$_2$ with C^{18}O. The C–O stretching frequencies observed during the exchange were assigned to the all-^{12}CO molecule and a number of C^{18}O substituted species. Johnson *et al.*[6] also studied the spectrum of unenriched *cis*-Fe(CO)$_4$Br$_2$ and without any direct proof assigned the minor peaks observed to the absorptions of specific, naturally occurring ^{13}CO substituted molecules. The proposed assignments for both molecules were supported by calculations of the five force constants in the energy factored C–O stretching block of the (*FG*) matrix.

We now wish to report the complete assignment of the C–O stretching modes of the principal species occurring in natural abundance in *cis*-Fe(CO)$_4$X$_2$ (X = Br or I), all-^{12}CO (96%), mono-^{13}CO substitution *cis* to X (2%), and mono-^{13}CO substitution *trans* to X (2%). The ^{13}CO modes have been experimentally verified through exchange with 50% ^{13}C-enriched CO. The CO groups *cis* and *trans* to I in *cis*-

TABLE 1

OBSERVED SPECTRA IN THE C–O STRETCHING REGION OF cis-Fe(CO)$_4$X$_2$ (X = I OR Br) IN CYCLOHEXANE. CALCULATION OF FORCE CONSTANTS TO ASSIGN THE OBSERVED SPECTRA

Molecule and symmetry	Vib.	ν(CO) (cm^{-1})						
		cis-Fe(CO)$_4$I$_2$[a]				cis-Fe(CO)$_4$Br$_2$[b]		
		Obsd.	Band	Input	Calcd.	Obsd.	Input	Calcd.
all-^{12}CO	$A_1^{(2)}$	2128.4	a	2128.4	2128.5	2148.6	2148.6	2148.7
C_{2v}	$A_1^{(1)}$				2080.8	2098.6	2098.6	2098.2
	B_1	2083.5	e	2083.5	2083.6	2108.7	2108.7	2108.5
	B_2	2060.0	f	2060.0	2059.9	2074.4	2074.4	2073.3
mono-^{13}CO	A'	2118.8	b	2118.8	2118.7	2138.7	2138.7	2138.5
axial sub-	A'				2081.3			2100.3
stitution	A'	2046.3	g	2046.3	2046.2	2069.0	2069.0	2069.4
C_s	A''				2059.9			2073.3
mono-^{13}CO	A'				2125.2			2145.9
radial sub-	A'				2073.9	2090.5		2090.1
stitution	A''				2083.6			2108.5
C_s	A'	2023.9	j	2023.9	2024.0	2036.3	2036.3	2037.7
di-^{13}CO	$A_1^{(2)}$	2100.5	d		2104.3			2121.2
1,2-sub-	$A_1^{(1)}$				2057.9			2078.1
stitution	B_1	2034.1	i		2037.3			2061.6
C_{2v}	B_2				2039.9			2073.3
di-^{13}CO	A	2115.7 sh	c		2114.3	2131.4		2135.1
1,3-sub-	A				2075.3			2092.9
stitution	A				2047.1			2069.7
C_1	A				2023.3			2037.3
di-^{13}CO	$A_1^{(2)}$				2122.3			2143.5
3,4-sub-	$A_1^{(1)}$	2038.7 sh	h		2040.5	2055.4		2056.5
stitution	B_1				2083.6			2108.5
C_{2v}	B_2	2013.9	k		2014.2	2026.3		2027.2

[a] Calculated force constants: $k_1 = 17.407$, $k_2 = 17.813$, $k_c = 0.174$, $k_{c'} = 0.273$, and $k_t = 0.283$ (mdyn/Å).
[b] Calculated force constants: $k_1 = 17.652$, $k_2 = 18.212$, $k_c = 0.172$, $k_{c'} = 0.295$, and $k_t = 0.261$ (mdyn/Å).

Fe(CO)$_4$I$_2$ are observed to be approximately equally enhanced during exchange in agreement with previous radio-carbon monoxide studies[7,8].

EXPERIMENTAL

The cis-Fe(CO)$_4$X$_2$ compounds were prepared according to the methods described in the literature[9].

^{13}C-Enriched cis-Fe(CO)$_4$X$_2$

    ^{13}C-enriched cis-Fe(CO)$_4$Br$_2$ and cis-Fe(CO)$_4$I$_2$ were prepared by exchange at room temperature in cyclohexane with 50% ^{13}C-enriched CO (Merck, Sharp and Dohme Ltd., Montreal, Quebec, Canada). The method used was very similar to that
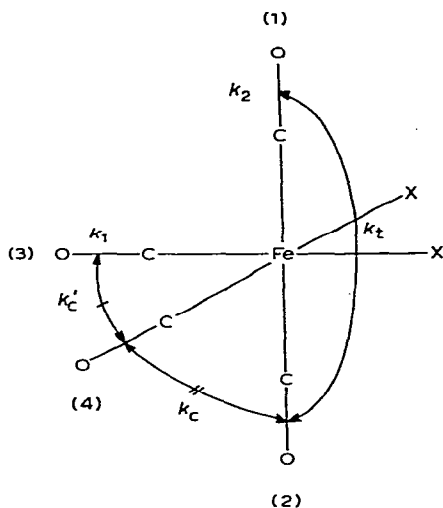
Fig. 1. Idealized geometry and definition of Cotton–Kraihanzel force constants in cis-Fe(CO)$_4$X$_2$.

described by Kaesz et al. in their ^{13}CO exchange studies of M(CO)$_5$X molecules[10,11]. Since solutions of the iron compounds were known to decompose fairly readily in the presence of light, the reaction vessel was painted black and the infrared spectra of the samples taken from the reaction mixtures were recorded immediately after their withdrawal. In spite of these precautions, some decomposition of the dibromide still occurred. Fortunately, the decomposition was slow enough to allow identification of the C–O stretching frequencies of the various ^{13}CO-substituted species present. As expected there was no spectral evidence for the formation of the trans-Fe(CO)$_4$X$_2$ compounds, since the exchange reactions were always carried out in the dark.

Infrared spectra

The infrared spectra in the C–O stretching region were recorded in cyclohexane on a modified Perkin Elmer model 337 grating spectrophotometer equipped with a Texas Instruments Servo/Riter model II expanded scale recorder. A new pair of matched 1.00 mm KBr cells were used for all spectra. The frequencies presented in Table 1 are the mean values obtained from the spectra of about 10 samples taken from the reaction mixtures throughout the exchanges. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene. The measurement of peak differences for several spectra gave a reproducibility of about ± 0.5 cm^{-1}, while the absolute accuracy of the frequencies is 1–2 cm^{-1}.

Calculations

The idealized geometry and definition of force constants in cis-Fe(CO)$_4$X$_2$ molecules are shown in Fig. 1.

The secular equations relating the force constants and the observed C–O stretching frequencies have been given previously[12]. The force constants were calculated using an iterative computer program supplied by Dr. J. M. Smith (California Institute of Technology, Pasadena, California) modified for use on the IBM 360/75 computer of the McGill University Computing Centre.
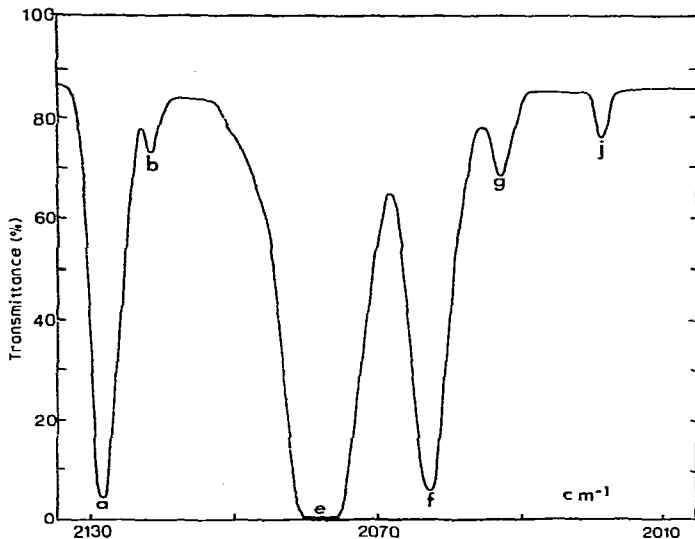
Fig. 2. Spectrum of *cis*-Fe(CO)$_4$I$_2$ with natural abundance of ^{13}C (cyclohexane solution).

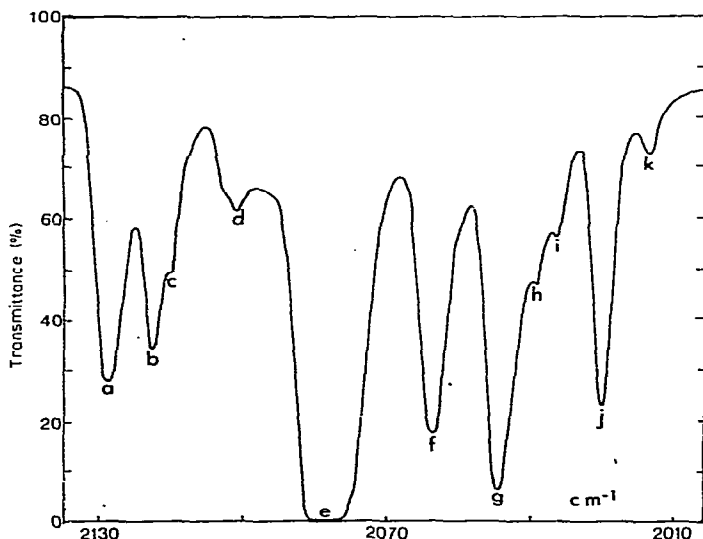Fig. 3. Spectrum of *cis*-Fe(CO)$_4$I$_2$ after 3 h exchange with 50% ^{13}C-enriched CO (cyclohexane solution).

RESULTS AND DISCUSSION

Assignment of the C–O stretching frequencies observed during the ^{13}CO exchange reactions of cis-Fe(CO)$_4$I$_2$ and cis-Fe(CO)$_4$Br$_2$

The *cis*-Fe(CO)$_4$X$_2$ molecules possess C_{2v} symmetry for which four infrared active C–O stretching vibrations are expected ($A_1^{(2)}$, $A_1^{(1)}$, B_1, and B_2). The symmetry coordinates for these vibrations in terms of internal bond stretching coordinates have been given many times before, *e.g.* see ref. 6.

The C–O stretching absorptions of *cis*-Fe(CO)$_4$I$_2$ in cyclohexane before and

after exchange (3 h) with 50% ^{13}C-enriched CO are shown in Figs. 2 and 3, respectively. The actual frequencies and the proposed assignments are given in Table 1. Noack[2] observed a weak band in the spectrum at 2047 cm^{-1} which Johnson et al.[6] recently attributed to monosubstitution by naturally occurring ^{13}CO. This is band g in Figs. 2 and 3. It is evident that Johnson et al. were correct in their assignment of the band as a ^{13}CO mode as it is greatly enhanced during the exchange with ^{13}CO. Similarly, bands b and j in Fig. 2 are also seen to be absorptions of ^{13}CO-substituted molecules present in natural abundance. It will be shown later that bands g, b, and j are in fact all due to mono-^{13}CO substituted molecules.

The assignment shown in Table 1 for the fundamentals of all-^{12}CO cis-Fe(CO)$_4$I$_2$ was originally proposed by Abel and Butler[4] on the basis of force constant calculations using the Cotton–Kraihanzel "approximate" force field[12]. This assignment was supported by the force constant calculations of Johnson et al.[6] in their C^{18}O exchange study. Because of the similarity in the reduced masses of ^{13}CO and C^{18}O, similar isotopic shifts are observed when a ^{12}CO group in a metal carbonyl is substituted by either of these molecules. As a consequence of this, the frequencies observed in the present work and in that by Johnson et al.[6] differ by only about 1 cm^{-1}, and the vibrational assignments for the various ^{13}CO substituted species present during ^{13}CO exchange are identical to those for the C^{18}O substituted species which occurred during C^{18}O exchange. Furthermore, our assignments were derived from essentially the same arguments which Johnson et al.[6] put forward except that, as we did not observe a new isotopic band at about 2075 cm^{-1}, we were unable to conclude that the $A_1^{(1)}$ mode of the all-^{12}CO molecule was degenerate with the B_1 mode at 2083.5 cm^{-1}. We had to confirm this degeneracy through the force constant calculations described below.

In order to test our assignments a set of approximate force constants were adjusted by an iterative computer program to fit the observed frequencies which had been assigned to the all-^{12}CO and mono-^{13}CO axial and radial substituted* cis-Fe(CO)$_4$I$_2$ molecules. The optimum calculated force constants and the associated frequencies are shown in Table 1. In their study, Johnson et al.[6] found that if the assignments of the B_1 and B_2 modes of the all-^{12}CO molecule were reversed, then the agreement between the observed and calculated frequencies was again very close, but the values of k_1 and k_2, and k_c, and k_t were reversed. This was also found to be the case in our work. However, as Johnson et al.[6] pointed out, such a reversal results in $k_1 > k_2$, and since previous studies on Mn(CO)$_5$X[10,11,13] and Re(CO)$_5$X[10,11] have shown that $k_2 > k_1$ (where anharmonicity corrections are ignored), it seems reasonable to assume that a similar situation should exist for cis-Fe(CO)$_4$X$_2$. In any event, for the purposes of the present discussion it will be assumed that $k_2 > k_1$, even though this has not been definitely established.

It can be seen from Table 1 that the $A_1^{(1)}$ frequency for the all-^{12}CO molecule is calculated to be 2080.8 cm^{-1}, indicating, as has previously been suggested[3,4,6], that this mode is accidently degenerate with the B_1 mode at 2083.5 cm^{-1}. The experimental frequencies which were not used as input were predicted to within 4 cm^{-1}, i.e. within the error range expected when using frequencies uncorrected for anhar-

---

* The terms axial and radial refer to the CO groups in Fig. 1 in positions 1 and 2, and in positions 3 and 4 respectively.

monicity[14,15] and the C-O-factored force field. The good agreement between the observed and predicted frequencies serves as an independent check on the validity of the assignments.

The observed C–O stretching frequencies of *cis*-Fe(CO)$_4$Br$_2$ in cyclohexane after [13]CO exchange (2.5 h) and the proposed vibrational assignments are shown in Table 1. In this case it was possible to resolve all four fundamentals of the all-[12]CO molecule. The assignment given for these fundamentals was originally proposed by Abel and Butler[4]. It has recently been supported by the force constant calculations of Johnson *et al.*[6] involving the frequencies of the weak absorptions in the spectrum which these workers attributed, without any direct proof, to naturally occurring [13]CO molecules. We have now experimentally verified through enrichment with [13]CO that these weak absorptions are in fact due to [13]CO substituted molecules present in natural abundance. We were also able to observe two new absorptions in the spectrum of the enriched sample which could be unequivocally assigned to di-[13]CO-substituted molecules. The natural abundance of these molecules is far too low for their absorptions to be detected in the absence of enrichment. The force constants for *cis*-Fe(CO)$_4$Br$_2$ were obtained by the same procedure as that used for the di-iodide. The assignment of the four fundamentals of the all-[12]CO molecule shown in Table 1 was selected because it is similar to that determined for the di-iodide and it leads to a set of force constant data which satisfies our assumption that $k_2 > k_1$ (as before, there is close agreement between the observed and calculated frequencies if the assignments of the B_1 and B_2 modes and the values of k_1 and k_2, and $k_{c'}$ and k_t are reversed). The optimum calculated force constants for our assignment and the associated frequencies for the all-[12]CO and the various mono- and di-[13]CO-substituted molecules are given in Table 1. The observed frequencies of the di-[13]CO species were not used as input and were predicted to within 4 cm^{-1}, indicating the validity of the proposed assignments.

TABLE 2

CALCULATED FORCE CONSTANTS FOR *cis*-Fe(CO)$_4$X$_2$ (X = I OR Br) (MDYN/Å)

	k_1	k_2	k_c	$k_{c'}$	k_t
cis-Fe(CO)$_4$I$_2$					
This work	17.407	17.813	0.174	0.273	0.283
Lewis *et al.*	17.451	17.860	0.160	0.280	0.300
cis-Fe(CO)$_4$Br$_2$					
This work	17.652	18.212	0.172	0.295	0.261
Lewis *et al.*	17.617	18.290	0.098	0.220	0.337

In Table 2 the force constants for the *cis*-Fe(CO)$_4$X$_2$ molecules from the present work are compared with those reported by Johnson *et al.*[6]. At first sight there appear to be some quite significant differences, but it should be remembered that there are a number of factors which can influence the values of the force constants. For example, when we used different sets of input frequencies for either molecule, the remaining frequencies were predicted to within the usual range of error, but the calculated force constants differed from those shown in Table 2 by up to ±0.025 mdyne/Å. The interaction constant, $k_{c'}$, seemed to be particularly affected by the choice of input fre-

quencies. It has become increasingly evident recently from (a) calculations on the effect of small frequency changes on the force constants[16], (b) the effect of including low frequency modes in the force field[14,15], (c) anharmonicity corrections on the observed frequencies[14,15], that the correspondence of observed and calculated frequencies of metal carbonyl derivatives does not mean that the associated force constants have any fundamental significance. Therefore, we feel that it is unwise to discuss either the differences in the force constant data obtained in the two studies, or the apparent trends in the force constants of the compounds themselves.

Stereochemistry of the ^{13}CO exchange reaction of cis-Fe(CO)$_4$I$_2$

Provided that we are correct in assuming $k_2 > k_1$, bands g and j in Figs. 2 and 3 are characteristic of mono-^{13}CO axial and radial substituted cis-Fe(CO)$_4$I$_2$, respec-

TABLE 3

RATIO OF ABSORBANCES OF BANDS g AND j IN THE SPECTRUM OF cis-Fe(CO)$_4$I$_2$ AT DIFFERENT TIMES THROUGHOUT THE EXCHANGE WITH ^{13}CO

Time (min)	A_g/A_j	Time (min)	A_g/A_j
0	2.00	25.0	1.88
1.5	2.09	45.0	1.82
8.0	2.00	60.0	1.90
20.0	1.85	95.0	1.96

tively. The ratio of the absorbances of these bands remained reasonably constant throughout the exchange with ^{13}CO (Table 3). Since it is evident from Fig. 3 that the exchange had not progressed very much beyond the mono-^{13}CO substitution stage in 3 h, it appears that the axial and radial CO groups exchange at qualitatively the same rate. This is in accord with the radio-carbon monoxide studies of Basolo and his coworkers[7,8].

CONCLUSION

The value of isotopic frequencies in assigning the C—O stretching fundamentals of metal carbonyl derivatives is self-evident. It is possible to predict the frequencies for isotopic substitution in specific positions with a great deal of accuracy provided that there are enough frequencies available to calculate all of the force constants in the energy-factored C—O stretching block of the (FG) matrix. The use of such calculations to follow the stereochemical course of ^{13}CO and C^{18}O substitution reactions of metal carbonyl derivatives has recently been demonstrated by Kaesz *et al.*[17] in a study of the ^{13}CO substitution reactions of tetracarbonylnorbornadienemolybdenum(0) and tricarbonylcycloheptatrienemolybdenum(0) to form a variety of isotopically substituted Mo(CO)$_6$ molecules. A number of similar substitution studies are currently in progress in our laboratory.

REFERENCES

1 C. C. BARRACLOUGH, J. LEWIS AND R. S. NYHOLM, *J. Chem. Soc.*, (1961) 2852.
2 K. NOACK, *Helv. Chim. Acta*, 45 (1962) 1847.
3 R. C. TAYLOR AND W. D. HORROCKS, JR., *Inorg. Chem.*, 3 (1964) 584.
4 E. W. ABEL AND I. S. BUTLER, *Trans. Faraday Soc.*, 63 (1967) 45.
5 L. A. W. HALES AND R. J. IRVING, *J. Chem. Soc.*, *A*, (1967) 1389.
6 B. F. G. JOHNSON, J. LEWIS, P. W. ROBINSON AND J. R. MILLER, *J. Chem. Soc.*, *A*, (1968) 1043.
7 A. WOJCICKI AND F. BASOLO, *J. Amer. Chem. Soc.*, 83 (1961) 525.
8 I. A. COHEN AND F. BASOLO, *J. Inorg. Nucl. Chem.*, 28 (1966) 511.
9 W. HIEBER AND G. BADER, *Ber.*, 61 (1928) 1717.
10 H. D. KAESZ, R. BAU, D. HENDRICKSON AND J. M. SMITH, *J. Amer. Chem. Soc.*, 89 (1967) 2844.
11 P. S. BRATERMAN, R. W. HARRILL AND H. D. KAESZ, *J. Amer. Chem. Soc.*, 89 (1967) 2851.
12 F. A. COTTON AND C. S. KRAIHANZEL, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
13 B. F. G. JOHNSON, J. LEWIS, J. R. MILLER, B. H. ROBINSON, P. W. ROBINSON AND A. WOJCICKI, *J. Chem. Soc.*, *A*, (1963) 522.
14 L. H. JONES, *Inorg. Chem.*, 6 (1967) 1269.
15 L. H. JONES, *Inorg. Chem.*, 7 (1968) 1681.
16 P. S. BRATERMAN, R. BAU AND H. D. KAESZ, *Inorg. Chem.*, 6 (1967) 2097.
17 R. W. HARRILL AND H. D. KAESZ, *J. Amer. Chem. Soc.*, 90 (1968) 1449.