Contribution from the Institute of Physical Chemistry,
University of Perugia, Italy

Some Remarks on the Isotopic ^{13}C-O Stretching Vibrations in Carbonyl-Nitrosyl Complexes[1]

A Poletti, R. Cataliotti, and A. Foffani

Received May 14, 1968

Following recent infrared measurements[2] of solvent effect on carbonyl-nitrosyl complexes of Co and Fe derived from $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$, a brief report on the behaviour of the $^{13}C-O$ stretching vibrations in the natural ^{13}C isotopic species of these compounds seems of interest also in connection with recent work in the field.[3-8]

The assignment of the weak bands of $Co(CO)_3NO$ at 2010 and 2085-2100 cm^{-1} in the vapour[7,9] as stretching vibrations for isotopically substituted species, agrees substantially with the present observations on the cobalt and iron complexes and their phosphinated derivatives (see Ref. 2, Figure 1 and the n-hexane figures given by Ref. 8 for ^{13}CO enriched $Co(CO)_3NO$). Analogous assignments have been reported for $Ni(CO)_4$, $Fe(CO)_5$, and $M(CO)_6$ complexes.[10-12]

Table I. Frequency values (cm^{-1}) in different solvents for the C–O stretching vibrations of $Co(CO)_2(^{13}CO)NO$ and $FeCO(^{13}CO)(NO)_2$

	$Co(CO)_2(^{13}CO)NO$ [b]		$FeCO(^{13}CO)(NO)_2$	
Solvent [a]	ν_1	ν_2	ν_1	ν_2
C_6H_{12}	2092	1999	2066	2000
(1) CCl_4	2089	1998	2074 sh	2003
(2) $(C_2H_5)_2O$	2094 sh	1995 sh	—	2009 sh
(4) $CHCl_3$	2094 sh	2000 sh	2072 sh	2011 sh
(5) Acetone	2092 sh	1997 sh	2083 sh	2013 sh
(6) CS_2	2087	1994	2069 sh	2000
(9) CH_2Cl_2	2087 sh	1997 sh	—	1998 sh
(10) Dioxane	2089 sh	1998 sh	—	2011 sh
(11) CH_2Br_2	—	—	2072 sh	2010 sh
(12) CH_2I_2	2083 sh	1993 sh	2070 sh	2008 sh

[a] For the numbering of the solvents see Ref. 2, Table I. [b] The third CO frequency, arising by isotopic monosubstitution from the degenerate low-frequency CO stretching mode, is covered by the main band of the non-isotopic species (see text).

In Table I are given the frequency values in different solvents for the C–O stretching modes of $Co(CO)_2(^{13}CO)NO$ and $FeCO(^{13}CO)(NO)_2$. These modes are labelled simply ν_1 and ν_2 in view of the partial coupling to be expected for the $^{12}C-O$ and $^{13}C-O$ stretchings.[7,8] The peaks are generally well resolved in C_6H_{12}, CCl_4, and CS_2, appearing as shoulders in the other solvents. Also for a series of monosubstituted derivatives of $Co(CO)_3NO$ a weak band is observed in cyclohexane, shifted by about 30 cm^{-1} to lower frequencies with respect to the C–O stretching A″ mode;[13] this is again attributed to a similar vibrational mode of the isotopic species. The solvent effect shows the general trend reported[2] for the corresponding $^{12}C-O$ vibrations. In particular, for the two unsubstituted complexes, polar solvents tend to increase the frequencies of the vibrational modes concerned.

The lower frequency C–O stretching peaks for the monoisotopic species of $Co(CO)_3NO$ and $Co(CO)_2(NO)P(C_6H_5)_3$ have allowed to perform integrated intensity measurements. These appeared of interest in view of the lack of quantitative intensity data on isotopic stretching bands of tetrahedral metal-carbonyl complexes. The present measurements were obtained as described in Ref. 14, where integrated intensities on fundamental C–O and N–O stretching modes for a series of complexes of this kind are reported. The results obtained by using different standard methods of area evaluation, agree to about 3%. The isotopic species concentrations were assumed to be 3% of the non-isotopic ones (which were kept presently from 7×10^{-2} to 7×10^{-3} molar) for $Co(CO)_2(^{13}CO)NO$ and 2% for $CoCO(^{13}CO)(NO)P(C_6H_5)_3$, following Abel.[15] The significant intensity data for these two complexes are reported in Table II; they should be compared with the following $A\times10^{-4}$ (l mole^{-1} cm^{-2} units, ln basis) figures from Ref. 14 for the corresponding non-isotopic species: 2.91 and 19.25 for the A_1 and E modes of $Co(CO)_3NO$, 6.80 and 11.38 for the A′ and A″ modes of $Co(CO)_2(NO)P(C_6H_5)_3$. The fact that the A″ mode of the phosphine derivative ap-

---

(1) This investigation was supported in part by a research grant from the Italian National Research Council.

(2) A. Foffani, A. Poletti, and R. Cataliotti, *Spectrochim. Acta, 24A* (1968) in press.

(3) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc., 89*, 2844 (1967).

(4) F. A. Cotton, A. Musco, and G Yagupsky, *Inorg. Chem.*, 6, 1357 (1967).

(5) A. P. Hagen, and A. G. MacDiarmid, *Inorg. Chem.*, 6, 686 (1967).

(6) K. Noack, *J. Organometal. Chem., 12*, 181 (1968).

(7) H. Haas, and R. K. Sheline, *J. Chem. Phys., 47*, 2996 (1967).

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

(9) R. S. McDowell, W. D. Horrocks, Jr., and J. T. Yates, *J. Chem. Phys., 34*, 530 (1961).

(10) L. H. Jones, *J. Chem. Phys., 28*, 1215 (1958).

(11) W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta, 19*, 863 (1963).

(12) (a) L. H. Jones, *Spectrochim. Acta, 19*, 329 (1963); (b) K. Noack, *Helvetica Chim. Acta, 45*, 1847 (1962) and references therein.

(13) $Co(CO)_2(NO)P(C_6H_5)_3$, 1952; $Co(CO)_2(NO)As(C_6H_5)_3$, 1953; $Co(CO)_2(NO)Sb(C_6H_5)_3$, 1953; $Co(CO)_2(NO)P(n-C_4H_9)_3$, 1941; $Co(CO)_2(NO)P(OCH_3)_3$, 1966; $Co(CO)_2(NO)P(OC_6H_5)_3$, 1971; $Co(CO)_2(NO)PCl(C_6H_5)_2$, 1970 cm^{-1}. For the frequency values of the corresponding non-isotopic C–O stretching modes see Ref. 14.

(14) A. Poletti and A. Foffani, manuscript in preparation.

(15) E. W. Abel, *Quart. Rev., 17*, 133 (1963).

Table II. Integrated intensity coefficient A, absorption coefficient K and apparent half-band width $\Delta\nu^a_{1/2}$ for the C–O stretching vibrations of $Co(CO)_2(^{13}CO)NO$ and $CoCO(^{13}CO)(NO)P(C_6H_5)_3$

Complex	ν cm^{-1}	$10^{-4}\times A$ [a] (l $mole^{-1}$ cm^{-2})	$10^{-4}\times K$ [b] (l $mole^{-1}$ cm^{-1})	$\Delta\nu^a_{1/2}$ cm^{-1}
$Co(CO)_2(^{13}CO)NO$ [c]	1999	9.83	1.99	4.9
$CoCO(^{13}CO)(NO)P(C_6H_5)_3$ [c]	1952	11.60	1.60	6.6

[a] Logarithms on natural basis. [b] The K values were evaluated from the slope of ln I°/I *vs.* concn. lines. [c] Cyclohexane solution.

parently is almost unaffected by isotopic substitution, indicates that the mass effect on the intensity anyway is small and requires, to be observed, favourable conditions. Apart from the possibility of ^{13}CO enrichment,[16] these should be found presumably, within the present family of tetrahedral complexes, in disubstituted Co- and monosubstituted Fe- derivatives, with only one CO ligand to be isotopically substituted. The $Fe(CO)_2(NO)_2$ and monosubstituted Co- complexes treated in Ref. 14 show the high frequency isotopic band in the natural isotopic composition too weak to allow integrated intensity measurements and consequently the estimation of the specific CO group intensity. For the parent complex $Co(CO)_3NO$, being lost by isotopic monosubstitution the degeneracy of the low-frequency C–O stretching mode, the third C–O frequency is calculated[7] to fall at 2047 cm^{-1}, *i.e.*, covered by the main band of the non-isotopic species.

Some difficulty was encountered in the assignment of the $Fe(CO)_2(NO)_2$ band at 2000 cm^{-1}, which we think for the following reasons to be the isotopic one of the monoisotopic species. This band might have been due to a fundamental mode of $Fe(CO)_5$ (for its spectrum see Ref. 11) present as an impurity in the samples. Mass-spectrometric checks pointed however to a $Fe(CO)_5$ content in the dinitrosyl complex at least four times lower than the natural $FeCO(^{13}CO)(NO)_2$ content of $Fe(CO)_2(NO)_2$, and estimated therefore as being lower than 1%. Moreover, on adding gradually $Fe(CO)_5$ to a cyclohexane solution of the dinitrosyliron complex, the intense band of the iron pentacarbonyl is observed to overlap the ^{13}C–O band, but surely to a lower frequency (1996 cm^{-1}) than the previous one.[17]

Using the approximate force constant given by Van Hecke and Horrocks[18] for the C–O stretching vibrations of $Fe(CO)_2(NO)_2$, the appropriate G matrix and the general secular equation for $ML_2(XO)(ZO)$ molecules[19]

$$\begin{vmatrix} \mu_{xo} f_{xo} - \lambda & \mu_{xo} f'_{xz} \\ \mu_{zo} f'_{xz} & \mu_{zo} f_{zo} - \lambda \end{vmatrix} = 0$$

values of 2065 and 1999 cm^{-1} were calculated for the monoisotopic species $FeCO(^{13}CO)(NO)_2$, the former figure relating to the in-phase C–O stretching frequency, ν_1. These values fit correctly the experimental ones of Table I, supporting the assignments given there.

---

[16] Work in progress in this laboratory.

[17] In our conditions, we observe in C_6H_{12} the two intense ^{12}C–O stretching bands of pure $Fe(CO)_5$ at 2020 and 1996 cm^{-1} almost coincident with the corresponding values of Ref. 12b in C_2Cl_4.

[18] G. R. Van Hecke, and W. D. Horrocks, Jr., *Inorg. Chem.*, 5, 1960 (1966).

[19] Interaction terms between C–O and N–O vibrators were disregarded, being anyway small.[8,18]