Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

INFRARED SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

IX*. INFRARED SPECTRA OF ^{13}CO-ENRICHED COBALT NITROSYL CARBONYL AND NICKEL TETRACARBONYL

G. BOR
Hungarian Oil and Gas Research Institute "MÁFKI", Veszprém (Hungary)

(Received March 30th, 1967)

INTRODUCTION

In the C–O stretching region of the infrared spectra of metal carbonyl compounds usually a weak absorption band is present shifted by about 30–45 cm^{-1} to lower frequencies from the strongest fundamental absorption band. This type of "satellite" bands has been first recognized by Jones[2] in the case of $Ni(CO)_4$ as an isotope band arising from the ^{13}CO containing molecules.

Obviously, a molecule of the general composition $M_m(^{12}CO)_{n-1}(^{13}CO)$(I) has not only one "isotope" band, but an individual spectrum, the other bands of which being very weak or overlapping with those of the pure all-^{12}CO compound. Since it follows from the natural abundance of ^{13}C (1.1 %) that the percentage of species (I) is roughly equal to the number of CO ligands per molecule (n), in higher coordinated carbonyls this concentration will surely give rise to weak bands in more parts of the C–O stretching region of the spectrum thus causing difficulties in assignment or symmetry considerations. This kind of problem has been met in the studies concerning the structures of the two isomers of $Co_2(CO)_8$ recognized by us[3], and independently by Noack[4].

The only paper dealing with spectroscopic studies of isotopically enriched metal carbonyls seems to be that of McDowell, Horrocks and Yates[5] who used ^{15}NO and ^{13}CO enriched samples for the normal coordinate treatment of $Co(CO)_3NO$. However, no data are known on the spectra of molecules containing more than one ^{13}CO ligand.

We have performed studies on the spectra of some ^{13}CO enriched simple carbonyls with the aim of assigning the C–O stretching frequencies of a complete series of compounds formed during the consecutive replacement of ^{12}CO ligands by ^{13}CO ones. The two examples presented in this paper have the advantage, that due to the equivalent position of all CO ligands no isomeric structures of the same isotopic composition can be present.

We have studied the spectra in n-hexane solutions since the sharpness of absorption bands in this medium[6,7,8] is very advantageous as compared with the P–Q–R band structure of the vapour spectra.

---

* For Part VIII see ref. 1.

EXPERIMENTAL

Cobalt nitrosyl carbonyl has been prepared by our previously published method[9].

Nickel tetracarbonyl was of commercial origin.

The enriched carbon monoxide contained 22.6±0.4% of ^{13}CO, as determined mass spectrometrically. It contained also 2.5% of ^{18}O.

Enrichment of the metal carbonyls was accomplished by repeated exchange reactions in hexane solution. Nickel carbonyl is known from ^{14}CO experiments to exchange CO ligands very fast[10]. In the case of $Co(CO)_3NO$ irradiation with UV light was used to accelerate exchange.

The exchange reactions have been performed in "Schlenk" tubes[11] of 20–25 ml volume. Some 0.1 ml of the carbonyl dissolved in 8–10 ml of n-hexane were filled into the vessel, followed by cooling to −70° in an acetone/dry ice bath. After evacuation the tube was filled with ^{13}CO-rich gas (about 10–12 ml). After warming up the gas was in contact with the solution at room temperature. This procedure was repeated several times. A small sample was taken from the solution with a syringe after each exchange cycle and its spectrum was scanned.

^{13}CO-contents of the enriched samples have not been determined, but exchanges were carried on till the spectra ceased to change considerably.

IR spectra were recorded with a VEB Carl Zeiss UR-10 spectrometer equipped with LiF prism. Spectra were calibrated for gaseous DCl bands[12,13]. Scanning conditions are given in previous papers[13]. All spectra were recorded in n-hexane solution.

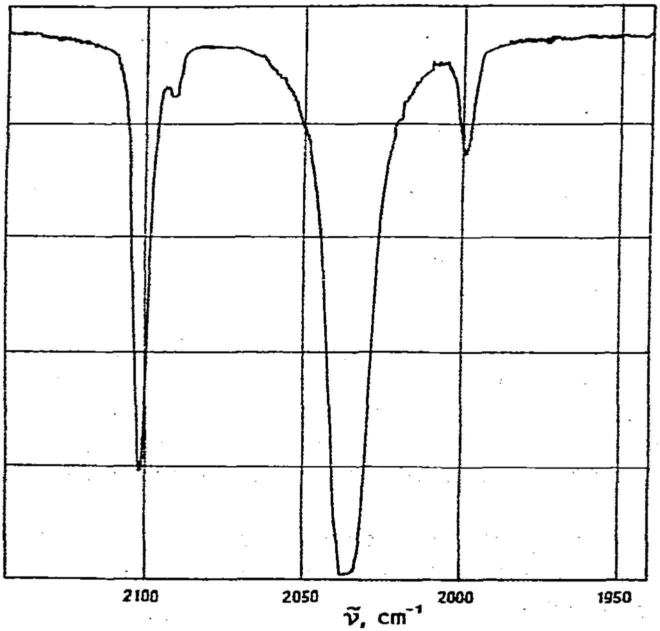

Fig. 1. Spectrum of $Co(CO)_3NO$ with natural abundance of ^{13}C (n-hexane solution).

SPECTRA

Cobalt nitrosyl carbonyl

Fig. 1 shows the spectrum of $Co(CO)_3NO$ with natural ^{13}CO content, Fig. 2 is the spectrum of a partly enriched sample, Fig. 3 shows the spectrum after maximal exchange. (The frequency of the N–O stretching band at 1808 cm^{-1} did not show any change during ^{13}CO enrichment, therefore this part of the spectrum is not reproduced in the Figures.)

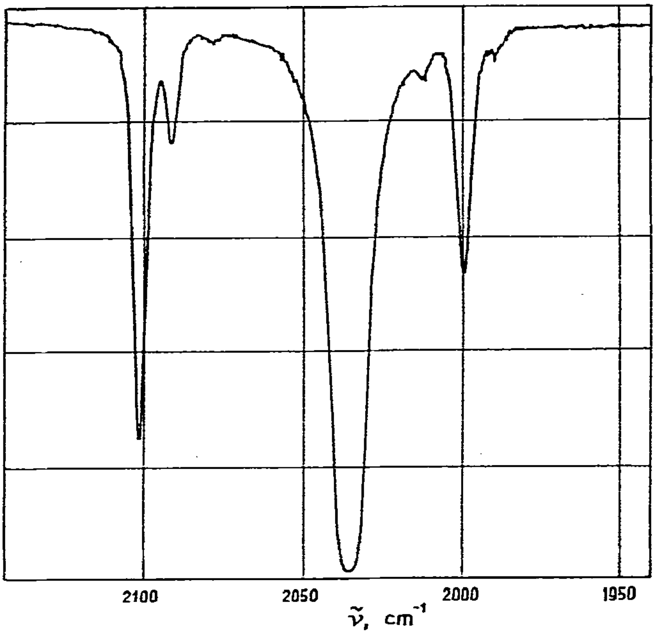

Fig. 2. Spectrum of $Co(CO)_3NO$ with slightly enriched ^{13}CO-content.

The band at 1999.3 cm^{-1}, reported already earlier[7a], shows a considerable gain in intensity even after very limited enrichment. Another band at 2091.2 cm^{-1}, identifiable only as a very weak shoulder in the spectrum with natural abundance, is also characteristic for this step of enrichment.

New bands at 2078.1, 2012.0, and 1989.5 cm^{-1} appear as the concentration of ^{13}CO in the complex is increased. In addition to these a very weak shoulder appears at 2054 cm^{-1} and another weak band at 1955 cm^{-1}.

Nickel tetracarbonyl

The spectrum of $Ni(CO)_4$ with natural abundance of ^{13}C shows the very strong triply degenerate fundamental of $Ni(^{12}CO)_4$ at 2045.7 cm^{-1} and a weak band at 2007.2 cm^{-1} (ref. 7a). With more concentrated solutions, however, another very weak band appears at 2117.8 cm^{-1} (Fig. 4).

These two bands become considerably more intense after the first steps of exchange. On continuation of the ^{13}CO enrichment, new bands appear in the spectrum

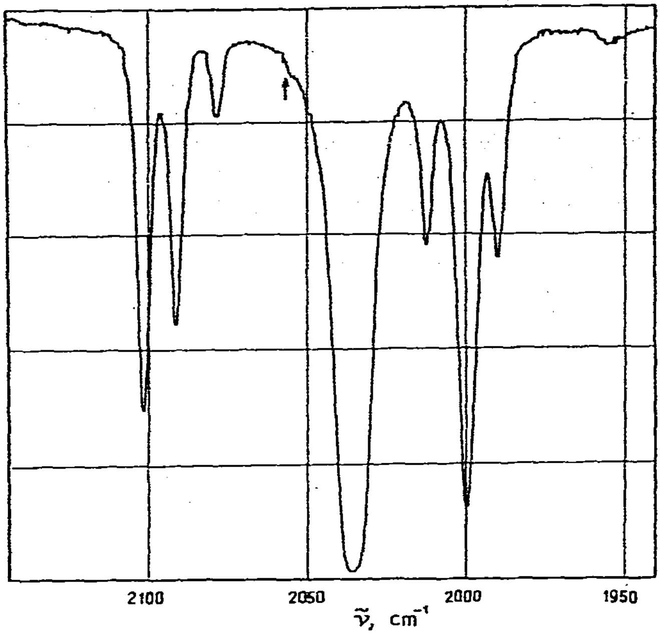

Fig. 3. Spectrum of Co(CO)$_3$NO with 22% ^{13}CO-content.

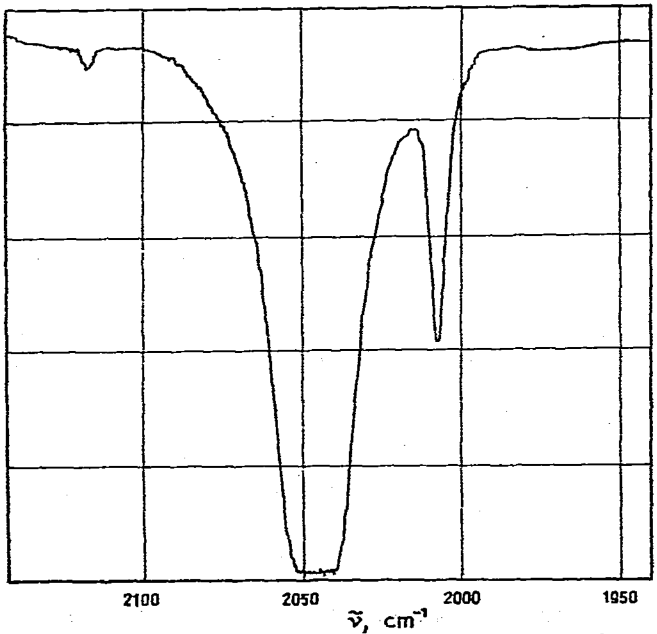

Fig. 4. Spectrum of Ni(CO)$_4$ with natural abundance of ^{13}C (n-hexane solution).

at 2108.0 and 2016.4 cm^{-1}, then with further increase of ^{13}CO a shoulder at 1999.9 cm^{-1} (Fig. 5). As this shoulder becomes a well separated band, with increasing ^{13}CO-concentration, again new bands are to be observed at 2095.9, 2027.5 (shoulder), and

1964 cm^{-1}. By continuing the enrichment to the stage where a repeated exchange does not effect further perceptible changes in the spectrum, no more new bands are observed but those already mentioned gain in intensity. The final state obtained is shown in Fig. 6.

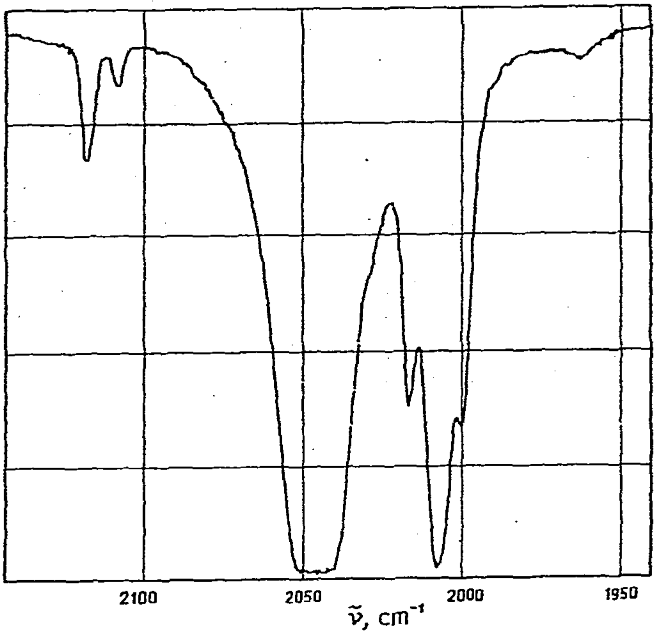

Fig. 5. Spectrum of $Ni(CO)_4$ with partly enriched ^{13}CO-content.

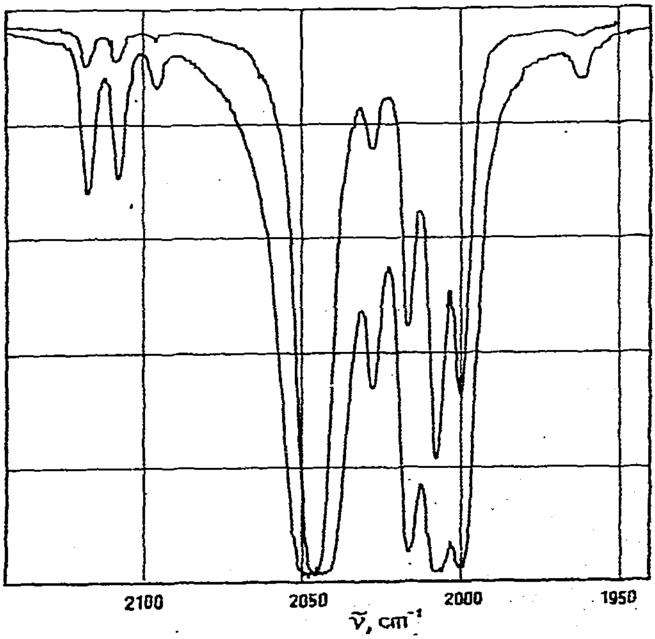

Fig. 6. Spectrum of $Ni(CO)_4$ with 22% ^{13}CO content; two different concentrations of hexane solution.

THEORY

The concentration of the different molecular species $M(^{12}CO)_{n-r}(^{13}CO)_r$ is given by the binomial distribution formula

$$W_r = \binom{n}{r} \cdot p^r \cdot (1-p)^{n-r} \qquad (1)$$

where W_r is the concentration of a species containing r ^{13}CO ligands, n is the number of all coordinated CO ligands in the molecule, and p is the ^{13}CO-concentration of the gas mixture being in equilibrium with the complex. (Concentrations are given in mole fractions.)

The application of the formula for tri- and tetracarbonyls ($n = 3, 4$) is shown in Fig. 7 and 8.

The interpretation of the spectra of the different $M(^{12}CO)_{n-r}(^{13}CO)_r$ molecular types will be dealt with on the basis of the Cotton–Kraihanzel force field[14,15] the calculation methods of which have been extended in details and elaborated for carbonyl types having two sets of CO ligands in our previous paper[1].

The G^{-1} matrix in the Cotton–Kraihanzel force field of the all-^{12}CO metal carbonyls has a very simple form:

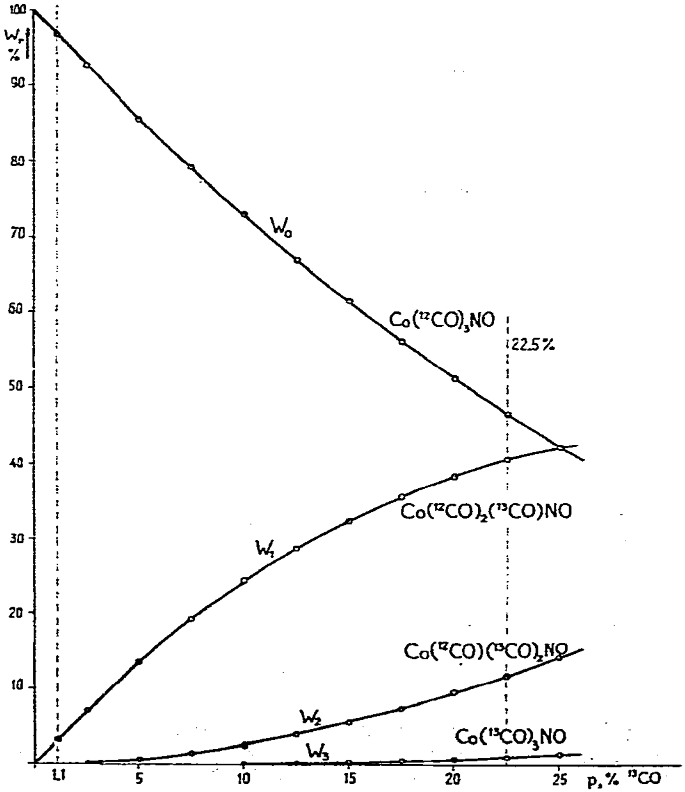

Fig. 7. Distribution of the molecular species $Co(^{12}CO)_{3-r}(^{13}CO)_rNO$ vs. ^{13}CO concentration.

$$G^{-1} = \frac{1}{\mu} E \tag{2}$$

where $1/\mu$ stands for the reduced mass of carbon-12 monoxide, $m(^{12}\text{C})\cdot m(^{16}\text{O})/[m(^{12}\text{C})+m(^{16}\text{O})] = 6.8404$, and E for the unit matrix.

The ^{13}CO-substitution has the consequence for both compounds studied in this paper that a species containing two C–O stretching fundamentals arises. In order to obtain the secular equation of second order we have to apply now a G^{-1} matrix in which one diagonal element corresponding to the ^{13}CO-containing symmetry coordinate will be $1/\mu(^{13}\text{CO})$, *i.e.* 7.1784.

In our previous paper the convenience of the substitution $y = \lambda/\mu$ was shown[1] which results in the following form of the secular equation:

$$|F - y\cdot E| = 0 \tag{3}$$

To preserve this advantage we introduce the notation a for the ratio of the reduced masses of ^{12}CO and ^{13}CO:

$$a = \frac{1}{\mu(^{12}\text{CO})}\bigg/\frac{1}{\mu(^{13}\text{CO})} = 0.9557 \tag{4}$$

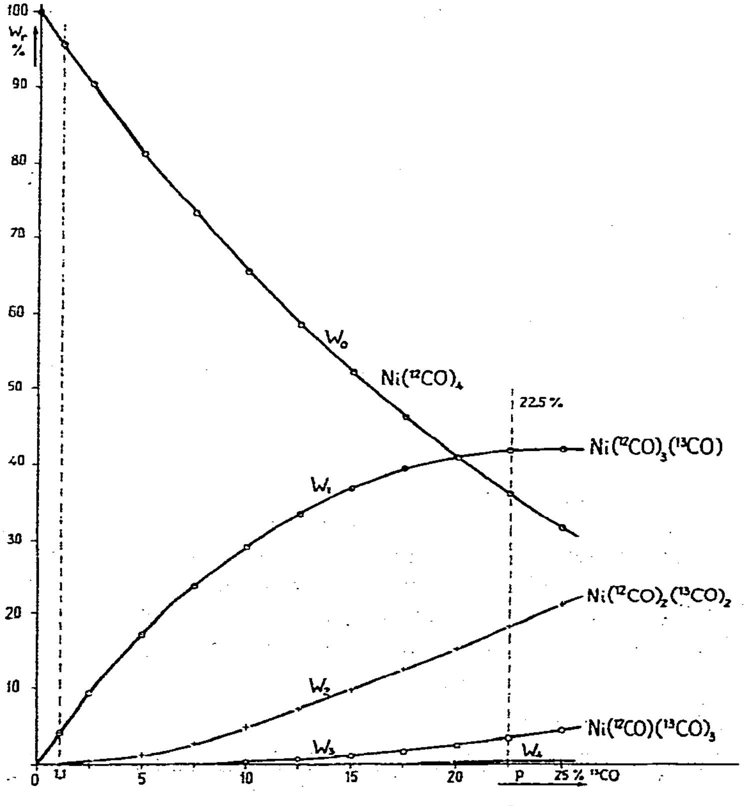

Fig. 8. Distribution of the molecular species $\text{Ni}(^{12}\text{CO})_{4-r}(^{13}\text{CO})_r$ *vs.* ^{13}CO concentration.

and substitute it in the secular equation thus resulting in the following form (in the second order case):

$$\begin{vmatrix} F_{11}-\dfrac{\lambda}{\mu(^{12}\text{CO})} & F_{12} \\ F_{21} & F_{22}-\dfrac{\lambda}{a\cdot\mu(^{12}\text{CO})} \end{vmatrix} = \begin{vmatrix} F_{11}-y & F_{12} \\ F_{21} & F_{22}-\dfrac{y}{a} \end{vmatrix} = 0 \qquad (5)$$

In matrix notation the following general form is obtained:

$$\left|F-\lambda\cdot\frac{1}{\mu}\cdot A^{-1}\right| = \left|F-y\cdot A^{-1}\right| = 0 \qquad (6)$$

and hence

$$|A\cdot F-y\cdot E|=0 \qquad (7)$$

where A stands for a diagonal matrix which has the value of a, *i.e.* 0.9557 in the position(s) corresponding to the symmetry coordinate(s) composed of ^{13}C–O vibration(s) the other diagonal elements being unity. This step is equivalent to multiplying the whole determinant by a (or by a^m if there are m symmetry coordinates in one species composed of ^{13}C–O vibrations), but this has no effect on the roots $y_1=\lambda_1/\mu$ and $y_2=\lambda_2/\mu$ [$\mu=\mu(^{12}\text{CO})$]. By expanding for instance the equation of second order

$$\begin{vmatrix} F_{11}-y & F_{12} \\ a\cdot F_{21} & a\cdot F_{22}-y \end{vmatrix} = 0 \qquad (8)$$

we get the following form (since $F_{12}=F_{21}$):

$$y^2-(F_{11}+a\cdot F_{22})y+a(F_{11}\cdot F_{22}-F_{12}^2)=0 \qquad (8a)$$

The two roots are then obtained easily from (9):

$$\begin{aligned} y_1+y_2 &= F_{11}+a\cdot F_{22} \\ y_1-y_2 &= [(F_{11}-a\cdot F_{22})^2+4\,a\cdot F_{12}^2]^{\frac{1}{2}} \end{aligned} \qquad (9)$$

Keeping in mind the connection between y values and ν vibrational frequencies [*cf.* eqn. (3) in ref. 1]:

$$y=0.40407\,[\nu(\text{CO})]^2\times 10^{-5}\ \text{mdyn/Å} \qquad (10)$$

the frequencies of ^{13}CO-substituted molecules are obtained.

The same procedure can be used also for cases where secular determinants of higher degree are arising as a consequence of decreased symmetry caused by ^{13}CO-substitution. In these cases, however, machine computation may be necessary and it is convenient if the modified F matrix maintains its original symmetric character. In order to effect this, eqn. (7) can be written in the following form:

$$|A^{\frac{1}{2}}\cdot F\cdot A^{\frac{1}{2}}-y\cdot E|=0 \qquad (7a)$$

The elements of the modified matrix $\bar{F}=A^{\frac{1}{2}}\cdot F\cdot A^{\frac{1}{2}}$ are easily obtained by eqn. (11):

$$\bar{F}_{ij}=(A_{ii}\cdot A_{jj})^{\frac{1}{2}}\cdot F_{ij} \qquad (11)$$

consequently the multiplier for diagonal F_{ii} elements will be 1 or a, for off-diagonal F_{ij} elements 1 or $a^{\frac{1}{2}}$.

ASSIGNMENTS

Cobalt nitrosyl carbonyl

The assignment of the C–O stretching frequencies of $(NO)Co(^{12}CO)_3$ is known[5,7c] to be the following, a_1: 2101.2 cm^{-1} and e: 2035.4 cm^{-1}.

As to the assignment of the ^{13}CO-substituted molecules it must be emphasized, that it is fundamentally incorrect to assign frequencies (*i.e.* normal modes) as "pure" $^{12}C–O$ or $^{13}C–O$ stretchings, respectively. In symmetry species to which more C–O stretching fundamentals belong, there exists a considerable coupling between $^{12}CO–^{12}CO$ pairs aswell as between $^{12}CO–^{13}CO$ and, if present, $^{13}CO–^{13}CO$ pairs. The symmetry coordinates, however, should be composed of pure $^{12}C–O$ and $^{13}C–O$ stretchings, respectively.

The molecule $(NO)Co(^{12}CO)_2(^{13}CO)$ possesses C_s symmetry, the selection rules of which demand two a' and one a'' C–O stretching modes. The symmetry coordinates have the following forms:

$$a' \text{ species:} \begin{cases} S_1 = \dfrac{1}{\sqrt{2}}({}^{(12)}\Delta_1 + {}^{(12)}\Delta_2) \\ S_2\, {}^{(13)}\Delta_3 \end{cases} \tag{12}$$

$$a'' \text{ species:} \quad S_3 = \frac{1}{\sqrt{2}}({}^{(12)}\Delta_1 - {}^{(12)}\Delta_2)$$

where ${}^{(12)}\Delta_1$ and ${}^{(12)}\Delta_2$ stands for the change in the bond length of the two $^{12}C–O$ bonds, and ${}^{(13)}\Delta_3$ for that of the $^{13}C–O$ bond.

The F matrix elements are the following:

$$\text{species } a'\text{:} \begin{cases} F_{11} = f(CO) + f_i \\ F_{22} = f(CO) \\ F_{12} = \sqrt{2}f_i \end{cases} \tag{13}$$

$$\text{species } a''\text{:} \quad F_{33} = f(CO) - f_i \tag{14}$$

(Since the results confirmed conclusively the theoretical predictions that $^{12}C–O$ and $^{13}C–O$ stretching force and interaction constants are exactly equal in all compounds of similar chemical composition, no special labeling is needed in the F_{ij} elements *vs.* valence force constants equations.)

The a'' mode involves only the antisymmetric vibration of the ^{12}CO groups, thus its frequency must coincide with the e vibration of the all-^{12}CO compound, *i.e.* $a'' = 2035.4$ cm^{-1}.

To the species a' belong two vibrations corresponding to the in-phase and the anti-phase coupling of the symmetry coordinates S_1 and S_2. Following the general rule, that in metal carbonyl vibrations the totally symmetric, in-phase vibration has always the highest of all C–O stretching vibrations[3], the 2091.2 cm^{-1} band (ν_1) is assigned to normal mode Q_1 resulting from the in-phase coupling of S_1 and S_2, whereas the band at 1999.3 cm^{-1} (ν_2) to the normal mode Q_2 comprising the counter-phase coupling of S_1 and S_2.

The molecule (NO)Co(^{12}CO)(^{13}CO)$_2$ has analogous symmetry and selection rules to the previously discussed one, but in the symmetry coordinates the role of the ^{12}CO and ^{13}CO vibrators are interchanged:

$$a' \text{ species:} \begin{cases} S_1 = {}^{(12)}\Delta_1 \\ S_2 = \dfrac{1}{\sqrt{2}}\left({}^{(13)}\Delta_2 + {}^{(13)}\Delta_3\right) \end{cases} \qquad (15)$$

$$a'' \text{ species:} \quad S_3 = \frac{1}{\sqrt{2}}\left({}^{(13)}\Delta_2 - {}^{(13)}\Delta_3\right)$$

The F_{ij} elements have consequently the following forms:

$$\text{species } a': \begin{cases} F_{11} = f(\text{CO}) \\ F_{22} = f(\text{CO}) + f_i \\ F_{12} = \sqrt{2} f_i \end{cases} \qquad (16)$$

$$\text{species } a'': \quad F_{33} = f(\text{CO}) - f_i \qquad (17)$$

The assignment is analogous to the former one. The band at 2078.1 cm^{-1} is assigned to the in-phase, that at 2012.0 cm^{-1} to the counter-phase coupling of S_1 and S_2. $S_3(\nu_3)$ in species a'' involves only ^{13}C–O vibrators, consequently the lowest frequency at 1989.5 cm^{-1} is obviously assigned to this mode.

After these assignments the very weak shoulder at 2054 cm^{-1} and the weak band at 1955 cm^{-1} remained unexplained. The former is assigned to vibration $\nu_1(a_1)$ of (NO)Co(^{13}CO)$_3$ present in very small concentration. This molecule of C_{3v} symmetry has analogous spectrum to that of the tri-^{12}CO compound, and its frequencies can be exactly predicted by multiplying the all-^{12}CO frequencies by $\mu(^{13}\text{CO})/\mu(^{12}\text{CO}) = 0.9776$. In this way a_1: 2054.1 cm^{-1} and e: 1989.8 cm^{-1} are obtained. The e frequency thus coincides exactly with the a'' frequency of the di-^{13}CO compound, similarly to the e–a'' coincidence with the tri-^{12}CO and di-^{12}CO compounds. The

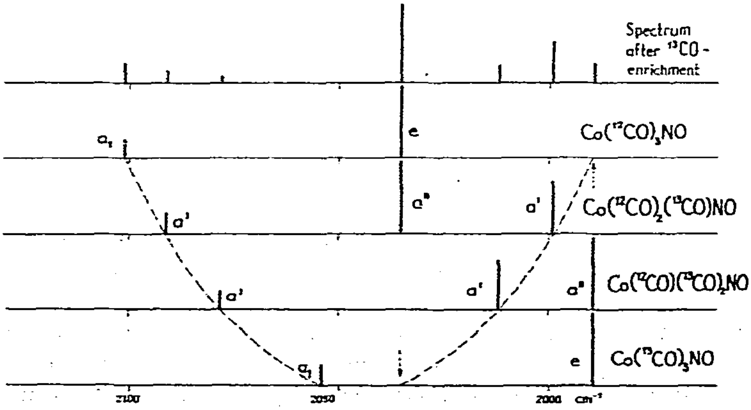

Fig. 9. Schematic spectra of the different molecular species Co(^{12}CO)$_{3-r}$(^{13}CO)$_r$NO in the C–O stretching region.

weak band at 1955 cm^{-1} can be explained by assigning it to the lowest-frequency vibration of the molecule $(NO)Co(^{12}C^{16}O)_2(^{13}C^{18}O)$.

The assignments are graphically shown in Fig. 9.

Nickel tetracarbonyl

The band at 2045.7 cm^{-1} belongs obviously to the f_2 vibration of $Ni(^{12}CO)_4$. The infrared inactive a_1 vibrational frequency 2127.5 cm^{-1} has been determined from the Raman spectrum in n-pentane solution at −55° by Bigorgne[16]. We shall later determine the "infrared" value of this frequency by extrapolation from the frequencies of the ^{13}CO-substituted molecules.

The molecule $Ni(^{12}CO)_3(^{13}CO)$ has C_{3v} symmetry for which the selection rules demand two a_1 and one e vibrations of C–O stretching type. The form of the symmetry coordinates will be:

$$\begin{aligned} &a_1 \text{ species:} \begin{cases} S_1 = \dfrac{1}{\sqrt{3}}\left({}^{(12)}\Delta_1 + {}^{(12)}\Delta_2 + {}^{(12)}\Delta_3\right) \\ S_2 = {}^{(13)}\Delta_4 \end{cases} \\ &e \text{ species:} \begin{cases} S_{3a} = \dfrac{1}{\sqrt{6}}\left(2\,{}^{(12)}\Delta_1 - {}^{(12)}\Delta_2 - {}^{(12)}\Delta_3\right) \\ S_{3b} = \dfrac{1}{\sqrt{2}}\left({}^{(12)}\Delta_2 - {}^{(12)}\Delta_3\right) \end{cases} \end{aligned} \tag{18}$$

The following F_{ij} elements are derived from them:

$$\text{species } a_1: \begin{cases} F_{11} = f(CO) + 2f_i \\ F_{22} = f(CO) \\ F_{12} = \sqrt{3}f_i \end{cases} \tag{19}$$

$$\text{species } e: \quad F_{33} = f(CO) - f_i \tag{20}$$

Following the reasoning given for the nitrosylcobalt tricarbonyl, the ν_1 frequency at 2117.8 cm^{-1} is assigned to the in-phase coupling of S_1 and S_2, and ν_2 at 2007.2 cm^{-1} to their counter-phase coupling. Frequency $\nu_3(e)$ involving only the ^{12}CO ligands, coincides with the f_2 value of $Ni(^{12}CO)_4$, *i.e.* 2045.7 cm^{-1}.

The molecular species $Ni(^{12}CO)_2(^{13}CO)_2$ belongs to point group C_{2v}. The symmetry coordinates and the F_{ij} elements are defined in the following way:

$$\begin{aligned} &a_1 \text{ species:} \begin{cases} S_1 = \dfrac{1}{\sqrt{2}}\left({}^{(12)}\Delta_1 + {}^{(12)}\Delta_2\right) \\ S_2 = \dfrac{1}{\sqrt{2}}\left({}^{(13)}\Delta_3 + {}^{(13)}\Delta_4\right) \end{cases} \\ &b_1 \text{ species:} \quad S_3 = \dfrac{1}{\sqrt{2}}\left({}^{(12)}\Delta_1 - {}^{(12)}\Delta_2\right) \\ &b_2 \text{ species:} \quad S_4 = \dfrac{1}{\sqrt{2}}\left({}^{(13)}\Delta_3 - {}^{(13)}\Delta_4\right) \end{aligned} \tag{21}$$

$$\text{species } a_1: \begin{cases} F_{11} = f(\text{CO}) + f_i \\ F_{22} = f(\text{CO}) + f_i \\ F_{12} = 2f_i \end{cases} \tag{22}$$

$$\text{species } b_1: \; F_{33} = f(\text{CO}) - f_i \tag{23}$$

$$\text{species } b_2: \; F_{44} = f(\text{CO}) - f_i \tag{24}$$

The b_1 and b_2 vibrations include again only pure ^{12}C–O and ^{13}C–O stretchings respectively, consequently they must coincide with the corresponding frequencies of the other molecular species. Thus the b_1 mode is assigned to 2046.7 cm^{-1}, the b_2 mode to 1999.9 cm^{-1}. The two a_1 vibrations are to be considered as $S_1 + S_2$ and $S_1 - S_2$, respectively, and the frequencies 2108.0 and 2016.4 cm^{-1} are assigned to these modes.

The molecule Ni(^{12}CO)(^{13}CO)$_3$ has C_{3v} symmetry, and the symmetry coordinates and F_{ij} elements are analogous to those of the mono-^{13}CO derivative:

$$\begin{aligned} a_1 \text{ species}: & \begin{cases} S_1 = {}^{(12)}\Delta_1 \\ S_2 = \dfrac{1}{\sqrt{3}}({}^{(13)}\Delta_2 + {}^{(13)}\Delta_3 + {}^{(13)}\Delta_4) \end{cases} \\ e \text{ species}: & \begin{cases} S_{3a} = \dfrac{1}{\sqrt{6}}(2\,{}^{(13)}\Delta_2 - {}^{(13)}\Delta_3 - {}^{(13)}\Delta_4) \\ S_{3b} = \dfrac{1}{\sqrt{2}}({}^{(13)}\Delta_3 - {}^{(13)}\Delta_4) \end{cases} \end{aligned} \tag{25}$$

$$\text{species } a_1: \begin{cases} F_{11} = f(\text{CO}) \\ F_{22} = f(\text{CO}) + 2f_i \\ F_{12} = \sqrt{3}f_i \end{cases} \tag{26}$$

$$\text{species } e: \quad F_{33} = f(\text{CO}) - f_i \tag{27}$$

The doubly degenerate vibration takes place only with ^{13}CO ligands, thus it is assigned to the same band at 1999.9 cm^{-1} as the b_2 mode of Ni(^{12}CO)$_2$(^{13}CO)$_2$. The frequency ν_1 being the in-phase coupling of S_1 and S_2 was assigned at 2095.9 cm^{-1}, ν_2, the counter-phase coupling at 2027.5 cm^{-1}.

The all-^{13}CO species is theoretically present at most in the concentration of 0.26%, if equilibrium was reached. Even if a higher proportion were present no new bands would be expected. The f_2 frequency was calculated from 2046.7 × 0.9776 to 1999.9 cm^{-1} which is in excellent agreement with the observed one.

The weak band at 1964 cm^{-1} is assigned to a mono-^{13}C^{18}O substituted molecular species.

The assignments are shown graphically in Fig. 10.

RESULTS AND DISCUSSION

Cobalt nitrosyl carbonyl

The calculation of the spectra of the ^{13}CO-containing molecules needs the knowledge of the C–O stretching force constant and CO–CO stretch–stretch inter-

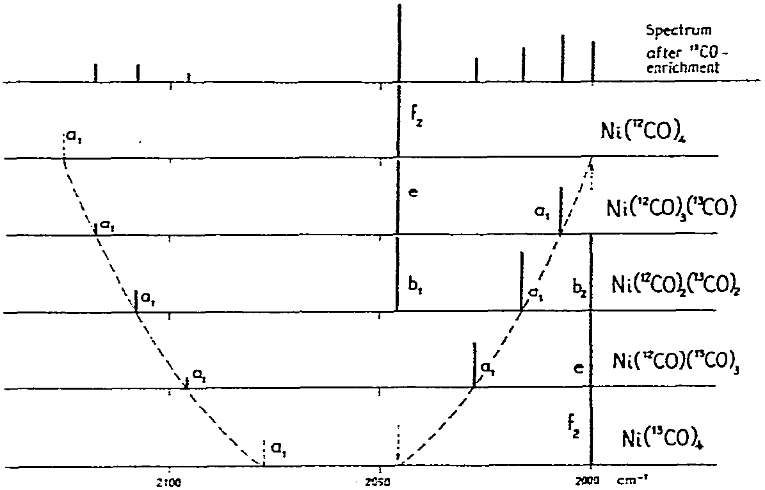

Fig. 10. Schematic spectra of the different molecular species Ni(^{12}CO)$_{4-r}$(^{13}CO)$_r$ in the C–O stretching region.

action constant of Co(^{12}CO)$_3$NO. The symmetry force constants obtained by McDowell and coworkers[5] from the vapour frequencies (and by neglecting all off-diagonal elements of the F matrix) are not suitable for our purpose. The values reported by Beck[17] are quoted as approximative.

We applied the "cos β parameter method"[1] to calculate these constants and to obtain information on the effect of the CO–NO stretch–stretch interaction on the C–O force constant.

The following $y = \lambda/\mu$ values are obtained from the frequencies:

y_1 $(a_1) = 17.840$ mdyn/Å
y_2 $(a_1) = 14.382$ mdyn/Å
(from the N–O stretching frequency: 1808.1 cm^{-1}, calculated with the reduced mass of NO)
y_3 $(e) = 16.740$ mdyn/Å

The force constants *vs.* cos β formulae, calculated from eqns. (19)–(22) of ref. 1 will have the following numerical forms:

$$f(\mathrm{CO}) = 16.530 + 0.576 \cos\beta$$
$$f(\mathrm{NO}) = 16.111 - 1.729 \cos\beta$$
$$f(\mathrm{CO,CO}) = -0.210 + 0.576 \cos\beta$$
$$f(\mathrm{CO,NO}) = 0.983 \sin\beta$$

The corresponding diagram is shown in Fig. 11.

The choice of the most satisfactory set of constants is based on the assumption that the CO–NO stretch–stretch interaction must be smaller than the CO–CO one. This relation fixes the very narrow interval (shaded in the Figure) between cos $\beta = +0.96 \sim 1.00$, which results in the following force and interaction constants:

$f(\mathrm{CO}) = 17.094 \pm 0.012$ mdyn/Å
$f(\mathrm{NO}) = 14.417 \pm 0.035$ mdyn/Å

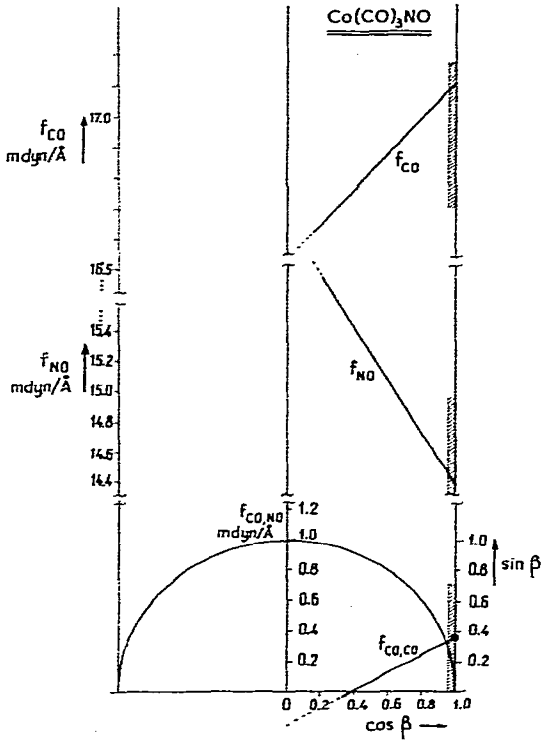

Fig. 11. Force constants *vs.* cos β diagram of Co(CO)$_3$NO.

$$f(\mathrm{CO, CO}) = 0.354 \pm 0.012 \text{ mdyn/Å}$$
$$f(\mathrm{CO, NO}) = 0 \sim 0.276 \text{ mdyn/Å}$$

The best fitting frequencies for the ^{13}CO-containing derivatives have been obtained with the following values, hence chosen as the true C–O stretching and interaction constants for Co(CO)$_3$NO (in hexane solution) in the Cotton–Kraihanzel force field: $f(\mathrm{CO}) = 17.106$ mdyn/Å and $f(\mathrm{CO, CO}) = f_i = 0.366$ mdyn/Å. These values belong to cos $\beta = +1$, thus proving that the CO–NO interaction is negligible.

We used this $f(\mathrm{CO})$ and f_i value for the calculation of the a' frequencies of the two mixed ^{12}CO–^{13}CO containing molecular species of Co(CO)$_3$NO by applying eqns. (9), (10), (13), and (16). The results are shown in Table 1.

The coincidence of measured and calculated frequencies is surprisingly perfect lying within the limits of experimental error, *i.e.* ± 0.2 cm^{-1}.

TABLE 1

EXPERIMENTAL AND CALCULATED VALUES OF C–O STRETCHING FREQUENCIES IN SPECIES a' OF MIXED ^{12}CO AND ^{13}CO CONTAINING Co(CO)$_3$NO MOLECULES

Compound	ν_1 *(cm^{-1})*			ν_2 *(cm^{-1})*		
	Calcd.	*Found*	$\Delta\nu$	*Calcd.*	*Found*	$\Delta\nu$
(NO)Co(^{12}CO)$_2$(^{13}CO)	2091.0	2091.2	−0.2	1999.4	1999.3	+0.1
(NO)Co(^{12}CO)(^{13}CO)$_2$	2078.0	2078.1	−0.1	2012.0	2012.0	0

For the a'' vibrations the calculation gives obviously the same frequencies as the e ones of the tri-^{12}CO and tri-^{13}CO compounds respectively, therefore these are not discussed.

Nickel tetracarbonyl

The frequencies obtained for molecular types containing ^{13}CO served for the determination of the IR-inactive a_1 frequencies of $Ni(^{12}CO)_4$ and $Ni(^{13}CO)_4$. Fig. 10 shows very strikingly that the curves connecting the high and low frequency a_1 bands respectively have almost symmetric slopes. Extrapolation yields 2125.2±0.3 cm^{-1} for $Ni(^{12}CO)_4$. This value has been refined by calculations of the ^{13}CO-containing derivatives to yield 2125.5 cm^{-1} as the true $\nu_1(a_1)$ frequency of $Ni(^{12}CO)_4$ in n-hexane solution. This frequency is lower by 2.0 cm^{-1} than that determined by Bigorgne[16] from the Raman spectrum in n-pentane solution at −55°.

We used the value obtained in the above way for the calculation of the f(CO) force constant and CO–CO stretching interaction constant in $Ni(^{12}CO)_4$. The $\nu_2(f_2)$ has already been determined earlier[7]:

$$\nu_1(a_1) = 2125.5 \text{ cm}^{-1} \qquad y_1 = 18.255 \text{ mdyn/Å}$$
$$\nu_2(f_2) = 2045.7 \text{ cm}^{-1} \qquad y_2 = 16.910 \text{ mdyn/Å}$$

Since for the point group T_d

$$F_{11} = y_1 = f(\text{CO}) + 3f_i$$

and

$$F_{22} = y_2 = f(\text{CO}) - f_i$$

the constants are readily obtained as

$$f(\text{CO}) = 17.246 \text{ mdyn/Å}$$
$$f_i = +0.336 \text{ mdyn/Å}$$

These values have been used for the calculation of the C–O stretching frequencies of mixed ^{13}CO-containing nickel tetracarbonyl molecules by applying eqns. (9), (10), (19), (22), and (26). The results are compiled in Table 2, demonstrating again an excellent agreement of calculated and experimental frequencies.

TABLE 2

EXPERIMENTAL AND CALCULATED C–O STRETCHING FREQUENCIES IN SPECIES a_1 OF MIXED ^{12}CO AND ^{13}CO CONTAINING $Ni(CO)_4$ MOLECULES

Compound	$\nu_1(cm^{-1})$			$\nu_2(cm^{-1})$		
	Calcd.	*Found*	$\Delta\nu$	*Calcd.*	*Found*	$\Delta\nu$
$Ni(^{12}CO)_3(^{13}CO)$	2117.4	2117.8	−0.4	2007.5	2007.2	+0.3
$Ni(^{12}CO)_2(^{13}CO)_2$	2108.0	2108.0	0	2016.4	2016.4	0
$Ni(^{12}CO)(^{13}CO)_3$	2096.3	2095.9	+0.4	2027.6	2027.5	+0.1

The frequency of the Raman-active C–O stretching vibration of $Ni(^{13}CO)_4$, $\nu_1(a_1) = 2077.9$ cm^{-1} has been calculated from the corresponding frequency of the all-^{12}CO compound.

General remarks

The results obtained with these two metal carbonyls seem to have general validity, since analogous calculations with other symmetry types (based although on the isotope bands of "natural" spectra without ^{13}CO enrichment) have lead to similarly correct results.

The accuracy of ±0.4 cm^{-1} with which the spectra of these isotopically substituted compounds could be calculated by this relatively simple method is of great importance from the point of view of the validity of the Cotton–Kraihanzel force field and of the physical significance of the force and interaction constants obtained on its basis. Since the frequencies of other types of vibrations, *e.g.* M–C stretchings, skeletal deformations are also shifted by isotopic substitution, general vibrational theory demands to extend calculation over all vibrations of a given species[18]. The results of this paper prove that exact results can be obtained for ^{13}CO substituted metal carbonyls based solely on the C–O stretching frequencies and on the C–O stretching and interaction constants obtained therefrom and this finding can serve as a strong evidence for the efficiency of the Cotton–Kraihanzel force field for metal carbonyls.

The extension of this method for symmetry types involving two different sets of CO ligands as published in our previous paper[1] by the so called "parameter cos β method" opens the possibility for further applications, especially for cases where ^{13}CO substitution gives rise to two derivatives of different symmetry type. Moreover, the study of the spectra of isotopically enriched complexes may contribute not only to the clarification of uncertain assignments but also to the more exact determination of C–O stretching and interaction constants by the above mentioned method, since force constants belonging to different cos β parameter values of the all-^{12}CO compounds result in different frequencies of ^{13}CO-containing molecules. Examples of such kind of application will be published in subsequent papers.

ACKNOWLEDGEMENT

The author is indebted to Mr. S. IGLEWSKI for mass spectroscopic analysis and to Mr. Z. TRÓCSÁNYI and Mr. P. SZARVAS Jr. for their assistance in the exchange experiments with nickel carbonyl. The support of this work by Professor M. FREUND, head of the Institute and Dr. E. KERÉNYI head of the Department is gratefully acknowledged.

SUMMARY

$Co(CO)_3NO$ and $Ni(CO)_4$ were successively enriched with ^{13}CO to the extent of 22%, their infrared spectra in the C–O stretching region recorded, and all absorption bands assigned to the different ^{12}CO and ^{13}CO containing molecular species. A method for the calculation of the C–O stretching frequencies of isotopically substituted metal carbonyls is given which enables these frequencies to be calculated with an accuracy of ±0.4 cm^{-1}. The results furnish novel evidence for the validity of the Cotton-Kraihanzel force field, as well as of the "parameter cos β method" derived therefrom by the author.

The frequency of the infrared inactive a_1 stretching fundamental of $Ni(CO)_4$

has been determined from the isotopic data: $\nu_1\,(a_1)$ 2125.5 cm^{-1} (in n-hexane solution). The C–O stretching force constants and CO stretch–stretch interaction constants of the two compounds (in n-hexane solution) have been calculated:

$$\mathrm{Co(CO)_3NO}: f(\mathrm{CO}) = 17.106 \text{ mdyn/Å}, \quad f_i = 0.366 \text{ mdyn/Å}$$
$$\mathrm{Ni(CO)_4}: \quad f(\mathrm{CO}) = 17.246 \text{ mdyn/Å}, \quad f_i = 0.336 \text{ mdyn/Å}$$

REFERENCES

1 G. BOR, *Inorg. Chim. Acta*, 1 (1967) in press.
2 L. H. JONES, *J. Chem. Phys.*, 23 (1955) 2448.
3 G. BOR, *Proc. 7th ICCC*, Stockholm, 1962, p. 8; *Spectrochim. Acta*, 19 (1963) 1209, 2065.
4 K. NOACK, *Spectrochim. Acta*, 19 (1963) 1925; *Helv. Chim. Acta*, 47 (1964) 1064, 1555.
5 S. MCDOWELL, W. D. HORROCKS AND J. T. YATES, *J. Chem. Phys.*, 34 (1961) 530.
6 C. C. BARRACLOUGH, J. LEWIS AND R. S. NYHOLM, *J. Chem. Soc.*, (1961) 2582.
7 (a) G. BOR AND L. MARKÓ, *Spectrochim. Acta*, 16 (1960) 1105;
(b) G. BOR, *Spectrochim. Acta*, 18 (1962) 817;
(c) G. BOR, *Acta Chim. Acad. Sci. Hung.*, 34 (1962) 395.
8 L. E. ORGEL, *Inorg. Chem.*, 1 (1962) 25.
9 G. BOR AND B. MOHAI, *Acta Chim. Acad. Sci. Hung.* 8 (1956) 335.
10 D. F. KEELEY AND R. E. JOHNSON, *J. Inorg. Nucl. Chem.*, 11 (1959) 33.
11 S. HERZOG AND J. DEHNERT, *Z. Chem.*, 4 (1964) 1.
12 *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*. IUPAC Commission on Molecular Structure and Spectroscopy, Butterworths, London, 1961 [*cf.*: *Pure Appl. Chem.*, 1 (1961) 580].
13 G. BOR, *Acta Chim. Acad. Sci. Hung.*, 34 (1962) 315.
14 F. A. COTTON AND C. S. KRAIHANZEL, *J. Am. Chem. Soc.*, 84 (1962) 4432.
15 C. S. KRAIHANZEL AND F. A. COTTON, *Inorg. Chem.*, 2 (1963) 533.
16 M. BIGORGNE, *Compt. Rend.*, 251 (1960) 355.
17 W. BECK, *Chem. Ber.*, 94 (1961) 1214.
18 E. B. WILSON, J. C. DECIUS AND P. C. CROSS, *Molecular Vibrations*, McGraw-Hill, London, 1955, p.182.