

## EXERCÍCIO 16

Segue anexo o artigo do Prof. Hans Stammreich sobre os espectros Raman de  $\text{Co(CO)}_4^-$  e  $\text{Fe(CO)}_4^{2-}$  e do derivado  $\text{HFe(CO)}_4^-$  (H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, S. Bril, *J. Chem. Phys.* **32**, 1482 (1960)).

No caso das moléculas tetraédricas  $\text{Co(CO)}_4^-$  e  $\text{Fe(CO)}_4^{2-}$  é dito no artigo:

The nine fundamental modes of vibration of such molecules belong to the species  $A_1$  (2),  $E$  (2),  $F_2$  (4) and  $F_1$  (1). All of them, except the  $F_1$  species, are

No caso da estrutura do derivado  $\text{HFe(CO)}_4^-$  pertencer ao grupo  $C_{3v}$ , então, as espécies de simetria correspondentes são:  $A_1$  (7),  $A_2$  (1),  $E$  (8) (ver a Table I do artigo).

Mostre que esses números de vibrações de cada espécie de simetria para  $\text{Co(CO)}_4^-$ ,  $\text{Fe(CO)}_4^{2-}$  e  $\text{HFe(CO)}_4^-$  mostrados na tabela do artigo estão corretos.

## Raman Spectra of Metal Carbonyl Compounds. II. Raman Spectra, Structure, and Force Constants of Cobalt and Iron Tetracarbonylate Anions

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The Raman spectra of the ions  $\text{Co}(\text{CO})_4^-$ ,  $\text{Fe}(\text{CO})_4^{2-}$ , and  $\text{HFe}(\text{CO})_4^-$  have been studied in aqueous solutions of the corresponding sodium salts. The spectra of  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$ , excited by the helium radiations 5875.6 and 6678.1 Å are in full agreement with the expected  $T_d$  symmetry of these ions; all observed frequencies were assigned to fundamental vibrational modes. A normal coordinate treatment was carried out under the assumption of a simplified valence force field model making use of only two interaction constants. The values of the fundamental frequencies of the tetrahedral ions, calculated by means of the potential constants of this model, were found to be in satisfactory agreement with the observed Raman shifts.

The Raman spectrum of  $\text{HFe}(\text{CO})_4^-$ , put in correlation with that of  $\text{Fe}(\text{CO})_4^{2-}$ , points strongly to a  $C_{3v}$  symmetry of the former ion.

### INTRODUCTION

THE present paper deals with the Raman spectra of the tetracarbonylate anions  $\text{Co}(\text{CO})_4^-$ ,  $\text{Fe}(\text{CO})_4^{2-}$ , and  $\text{HFe}(\text{CO})_4^-$ . It seems that no vibrational spectral data on the iron carbonylate ions have been reported previously; an investigation of the ir absorption spectrum of the cobalt carbonylate ion has been carried out by Friedel *et al.*<sup>1</sup> using a solution of dicobalt octacarbonyl in pyridine where the  $(\text{Co}(\text{Pyr})_6)^{2+}$  cation and  $\text{Co}(\text{CO})_4^-$  anion are formed. Only two absorption bands were found, namely, 555 and 1883  $\text{cm}^{-1}$ , the latter being assigned to a carbonyl stretching mode. A systematic investigation of the position of the infrared-active C-O stretching vibrations of various cobalt carbonyl derivatives has been reported by Vohler<sup>2</sup> who observed in all compounds containing the  $\text{Co}(\text{CO})_4^-$  anion an absorption band at approximately 1900  $\text{cm}^{-1}$ , whereas the corresponding frequencies of the nonionic species were found between 2000 and 2100  $\text{cm}^{-1}$ .

An additional interest of the present study is provided by the fact that  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$  are isoelectronic with nickel tetracarbonyl, whereas  $\text{HFe}(\text{CO})_4^-$  is isoelectronic with cobalt hydrocarbonyl. The vibrational spectra of these neutral molecules have been the object of numerous investigations, especially in the ir, but until now the interpretation of the experimental results proved to be difficult and not thoroughly satisfactory. Because of the selection rules governing the activities of the vibrational modes of tetrahedral molecules belonging to the  $T_d$  point group, it is expected to obtain more direct information from Raman than

from ir spectra. Hence, the results here reported may possibly contribute toward a fuller understanding of the vibrational spectra of nickel carbonyl and cobalt hydrocarbonyl and, eventually, to the elucidation of some questions concerning the chemical bonding in these molecules.

### EXPERIMENTAL

#### Preparation of Samples

Aqueous solutions of the sodium salts of metal carbonyl hydrides were prepared by making use of a technique previously described by one of us and Stettiner.<sup>3</sup> All operations had to be performed under nitrogen absolutely free from oxygen and, owing to the photosensitivity of the compounds, especially of  $\text{NaHFe}(\text{CO})_4$ , in dim red light. The Raman tubes were sealed beforehand to the apparatus and the solutions were filtered from the reaction vessel into the tubes through dense sintered glass filters at very low speed.

Sodium cobalt carbonylate  $\text{NaCo}(\text{CO})_4$  was prepared according to Hieber and co-workers<sup>4,5</sup> from  $\text{Hg}(\text{Co}(\text{CO})_4)_2$  and  $\text{Na}_2\text{S}$ . The mercury salt was purified and brought into a finely divided and reactive form by dissolving it in a tenfold quantity of methanol, and subsequent filtering and precipitating by addition of an equal amount of water. The purified mercury cobalt carbonylate was shaken during 12 hr with 10% less than the theoretical quantity of a 0.15M solution of sodium sulfide. The pale yellow solution of  $\text{NaCo}(\text{CO})_4$  was separated from the excess of the original material and from the formed mercury sulfide

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<sup>1</sup> R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Am. Chem. Soc.* **77**, 3951 (1955).

<sup>2</sup> A. Vohler, *Chem. Ber.* **91**, 1161, 1235 (1958).

<sup>3</sup> P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.* **71**, 3035 (1949).

<sup>4</sup> W. Hieber, E. O. Fischer, and E. Boeckly, *Z. anorg. u. allgem. Chem.* **269**, 308 (1952).

<sup>5</sup> W. Hieber and R. Breu, *Chem. Ber.* **90**, 1259, 1270 (1957).

by careful filtering. The samples used in the spectroscopic work were 0.28*M*.

Solutions of the monobasic salt  $\text{NaHFe}(\text{CO})_4$  were prepared<sup>8</sup> by shaking iron pentacarbonyl for 4 hr with equimolecular amounts of barium hydroxide and sodium hydroxide of a total normality 0.9. The solutions, filtered from the formed barium carbonate, were 0.28*M* in  $\text{NaHFe}(\text{CO})_4$  and 0.01–0.015*M* in  $\text{Na}_2\text{Fe}(\text{CO})_4$ , as determined by the reaction with  $\text{HgCl}_2$ .<sup>3</sup> The pale yellow or slightly pinkish solutions are very sensitive to radiations below 5500 or 5000 Å; exposed to daylight they rapidly turn dark red. When kept at room temperature in the dark and, naturally, under complete absence of oxygen, the samples showed no appreciable change of color for several days or even weeks, and the Raman spectra of freshly prepared and of older solutions were found to be identical. The dimerization to binuclear carbonyl derivatives, recently reported by Sternberg *et al.*,<sup>6</sup> seems thus to be a photochemical reaction.

The spectroscopic study of  $\text{Na}_2\text{Fe}(\text{CO})_4$  in solutions of stoichiometric composition appeared inadvisable since iron tetracarbonyl hydride is a very weak bibasic acid ( $K_2 \approx 4 \cdot 10^{-14}$ ) and its bibasic salts are strongly hydrolyzed. In order to limit the hydrolysis to about 10% or less, we prepared samples containing an excess of about 1 mole NaOH per liter. To that purpose 0.03 mole of  $\text{Fe}(\text{CO})_5$  were shaken for 4 hr with 50 ml 0.6*M* barium hydroxide and 25 ml 6.0*M* NaOH. The solution of barium hydroxide was prepared at 50°C and cooled to room temperature before the addition of the iron pentacarbonyl. The filtered solutions were pale yellow and contained 0.38 mole per liter of  $\text{Na}_2\text{Fe}(\text{CO})_4$ ; they were found to be much less photosensitive than the solutions of the monobasic salt.

### Spectroscopic Technique

The photosensitivity of the three investigated species of sodium salts of metal carbonyl hydrides in aqueous solution prevented the excitation of the Raman spectra in the conventional way through mercury radiations of 4358 Å, or even 5461 Å. We found, however, that spectra of good quality could be obtained in the red region of the spectrum by excitation with He 5875.6 and 6678.1 Å. In order to avoid the incidence of radiations of shorter wavelengths on the samples, filters possessing a sharp spectral cutoff had to be used.

The technique of excitation of Raman spectra in the red and near infrared region has been described previously by one of us<sup>7</sup> and details can be omitted here.

The Raman spectrograph was provided with a Bausch & Lomb 600 grooves/mm plane grating blazed in the first order for 7500 Å. The spectra were photographically recorded with cameras having apertures 1:1.9 and 1:2.8 corresponding to reciprocal dispersions of about

110 and 70 Å/mm, respectively. Dispersions of this order proved to be quite sufficient for the present work. It must be considered that the dispersion in frequency units in the 7500-Å region increases by a factor of nearly 3 as compared with the spectral range in which Raman spectra are usually obtained.

The Raman spectra excited by He 5875.6 Å were photographed on Kodak spectroscopic plates of the types 103 aC, 103 aE, and 103 aF, those excited by He 6678.1 Å on plates 103 aF, 103 U, and IN, the last type being hypersensitized before use. Making use of the highest aperture camera we recorded the spectra excited by He 5875.6 Å with exposures ranging from 5 to about 80 min. Longer exposures were necessary for the spectra excited by He 6678.1 Å and particularly for those photographed on IN plates.

Our excitation unit consists of a helium discharge tube helicoidally wound around the Raman tube. The direction of incidence of the exciting radiation is, therefore, not sufficiently defined to carry out correct quantitative measurements of the state of polarization of the Raman shifts and to distinguish weakly polarized from depolarized lines. The arrangement enables us, however, to identify with certainty depolarization factors <0.5 or 0.4; such strongly polarized shifts are indicated in the following by *P*. Consequently, the Raman lines without indication may be depolarized or weakly polarized.

### THE RAMAN SPECTRA

About one hundred spectra of the three molecular species studied in this work were recorded; the frequencies, estimated intensities, and further characteristics of the observed shifts are the following:

$\text{NaCo}(\text{CO})_4$ : 90 (30) *b*; 439 (15) *P*; 532 (8); 619 (2.5); 715 (4); 1883 (2); 1918 (10).

The strong Raman line 1918  $\text{cm}^{-1}$  is probably weakly polarized; a definite result could not be obtained due to the experimental difficulties mentioned in the foregoing.

$\text{Na}_2\text{Fe}(\text{CO})_4$ : 85–100 (50) *vb*; 464 (20) *P*; 550 (6); 644 (4); 785 (1) *b, d*; 1788 (10) *vb*.

The weak Raman line 785  $\text{cm}^{-1}$ , marked *d*, was observed only in overexposed spectra and must be regarded as questionable. In such prolonged exposures appears the emission spectrum of the  $\text{He}_2$  molecule with band systems interfering with the observation of weak Raman shifts in this spectral range. Comparative measurements of intensities indicated, however, that the 785- $\text{cm}^{-1}$  shift is probably genuine.

The strong Raman line found at 1788  $\text{cm}^{-1}$  is very broad; with increasing exposure it enlarges asymmetrically, and its center is shifted by about 7  $\text{cm}^{-1}$  toward lower wave numbers, thus indicating the presence of two components, a stronger one at about 1790  $\text{cm}^{-1}$  and a weaker one at perhaps 1783  $\text{cm}^{-1}$ . Our attempts at resolving this shift clearly into two components were not successful.

<sup>6</sup> H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.* **79**, 6116 (1957).

<sup>7</sup> H. Stammreich, *Spectrochim. Acta* **8**, 41 (1956).

$\text{NaHFe}(\text{CO})_4$ : 80–95 (50) *vb*; 451 (20) *P*; 518 (3); 539 (6); 598 (2) *sh*; 610 (5); 708 (0) *d*; 780 (0) *b, d*; 1768 (3); 1835 (10) *P*; 1895 (10).

The Raman line  $598\text{ cm}^{-1}$  appears as a shoulder in- completely resolved from the main shift  $610\text{ cm}^{-1}$ . The genuineness of the faint lines 708 and  $780\text{ cm}^{-1}$  is questionable due to the same circumstances that diffi- culted the observation of the Raman band  $785\text{ cm}^{-1}$  of  $\text{Na}_2\text{Fe}(\text{CO})_4$ .

#### ASSIGNMENT OF FREQUENCIES OF THE TETRAHEDRAL IONS

It will be seen that the Raman spectra of  $\text{NaCo}(\text{CO})_4$  and  $\text{Na}_2\text{Fe}(\text{CO})_4$  are fully consistent with those which would be expected regular tetrahedral  $\text{A}(\text{BC})_4$  mole- cules. Hence, the observed frequencies have to be attributed to the isolated ions  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$ , respectively, and will be assigned under the point group  $T_d$ .

The nine fundamental modes of vibration of such molecules belong to the species  $A_1$  (2),  $E$  (2),  $F_2$  (4) and  $F_1$  (1). All of them, except the  $F_1$  species, are Raman active whereas only the  $F_2$  modes are allowed in absorption. The approximate forms of the normal vibrations are shown by Crawford and Cross.<sup>8</sup> How- ever, their numbering of the fundamentals differs slightly from ours in the present work, which is the same as that used by Jones<sup>9</sup> and by Murata and one of us.<sup>10</sup> These papers refer to the vibrational spectrum of nickel carbonyl.

The fundamental modes may be described as C—O stretching vibrations (1  $A_1$ ; 1  $F_2$ ) expected to be found around  $2000\text{ cm}^{-1}$ , as M—(CO) stretching modes (1  $A_1$ ; 1  $F_2$ ) and M—C—O bending modes (1  $E$ ; 1  $F_2$ ; 1  $F_1$ ) to be observed in the middle-frequency region extending from about  $400\text{ cm}^{-1}$  to perhaps as high as  $785\text{ cm}^{-1}$ , and as (CO)—M—(CO) bending motions (1  $E$ ; 1  $F_2$ ) with frequencies around  $100\text{ cm}^{-1}$  or lower. needless to say, such descriptions (in which the group (CO) is considered as a rigid unit) must be regarded as being only roughly approximate. Especially in the middle-frequency region different vibrational motions are expected to couple.

Before discussing in detail the assignment of the observed frequencies to the fundamental modes of vibration of the two investigated species of tetra- hedral metal carbonylate ions, we must point out that the Raman spectra of  $\text{Co}(\text{CO})_4^-$  were of exceptionally good quality, all shifts being of high or at least reason- able intensity. Even strongly overexposed spectra were obtained without any interfering background, and no additional Raman lines were found in such pro- longed exposures. Since the number of the observed shifts is fully consistent with the theoretical expectancy,

we feel justified in assigning all observed frequencies to fundamental modes.

#### C—O Stretching Vibrations

Friedel *et al.*<sup>1</sup> found in the ir spectrum of the  $\text{Co}(\text{CO})_4^-$  ion a strong absorption band at  $1883\text{ cm}^{-1}$  in exact agreement with our Raman shift. Thus this frequency is readily assigned to the  $F_2$  mode  $\nu_6$ , whereas  $1918\text{ cm}^{-1}$  must be attributed to the symmetric C—O stretching vibration  $\nu_1$ . As mentioned in the foregoing, we did not succeed in resolving the broad band  $1788\text{ cm}^{-1}$  in the spectrum of the  $\text{Fe}(\text{CO})_4^{2-}$  ion into two components, but we obtained indications of a separa- tion of the symmetric and antisymmetric C—O stretch- ing modes by about  $7\text{ cm}^{-1}$ .

#### (CO)—M—(CO) Bending Vibrations

In the low-frequency region two modes,  $\nu_4$  and  $\nu_8$ , belonging to species  $E$  and  $F_2$ , respectively, are ex- pected. In the spectra of both ions only one large band was observed whose frequency had to be assigned to the two species. An identical situation was found in the Raman spectrum of nickel carbonyl by Duncan and Murray<sup>11</sup> and Crawford and Horwitz.<sup>12</sup>

#### M—(CO) Stretching and M—C—O Bending Vibrations

The very intense and strongly polarized Raman shifts  $439$  and  $464\text{ cm}^{-1}$  of  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$ , respectively, are immediately assigned to the sym- metric metal-carbon stretching mode  $\nu_2(A_1)$ .

The ir absorption band  $555\text{ cm}^{-1}$  observed by Friedel *et al.*<sup>1</sup> in the spectrum of  $(\text{Co Pyr}_6)^{2+}(\text{Co}(\text{CO})_4^-)_2$ , attributed to the  $\text{Co}(\text{CO})_4^-$  anion, differs appreciably from our Raman shift  $532\text{ cm}^{-1}$ . Nevertheless, in the absence of another coincidence we must assign this Raman line to an  $F_2$  mode. Since further ir data on the two ions are not available we depend on other evi- dence for the assignment of the remaining funda- mentals in the middle-frequency region.

The results of a normal coordinate treatment of the vibrational spectrum of  $\text{Ni}(\text{CO})_4$ , recently carried out by Murata and Kawai<sup>10</sup> under the assumption of a Urey-Bradley force field, show that one should expect to find  $\nu_3(E) > \nu_6(F_2) > \nu_7(F_2)$ . We arrived at the same conclusion through a normal coordinate analysis, to be discussed in the following, which is based on a valence force model. It will be shown, also, that a reasonable correlation between the spectra of the ions  $\text{Fe}(\text{CO})_4^{2-}$  and  $\text{HFe}(\text{CO})_4^-$  can be established when the foregoing order is assumed. Furthermore, a comparative study of all available Raman data on metal carbonyl com- pounds leads to the purely qualitative conclusion that

<sup>8</sup> B. L. Crawford and P. C. Cross, J. Chem. Phys. **6**, 525 (1938).

<sup>9</sup> L. H. Jones, J. Chem. Phys. **28**, 1215 (1958).

<sup>10</sup> H. Murata and K. Kawai, J. Chem. Phys. **26**, 1355 (1957).

<sup>11</sup> A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).

<sup>12</sup> B. L. Crawford and W. Horwitz, J. Chem. Phys. **16**, 147 (1948).

TABLE I. Raman spectra of metal carbonylate ions, assignments of frequencies, and tentative scheme of correlation.

Approximate description of modes	$\nu_i$	Point group $T_d$			Point group $C_{3v}$		
		Species	$\text{Co}(\text{CO})_4^-$	$\text{Fe}(\text{CO})_4^{2-}$	$\text{HFe}(\text{CO})_4^-$	Species	$\nu_i$
$\nu_{\text{C-O}}$	1	$A_1$	1918	1788	1895	$A_1$	1
$\nu_{\text{M-(CO)}}$	2	$A_1$	439	464	451	$A_1$	2
$\delta_{\text{M-C-O}}$	3	$E$	715	785	780 or 708	$E$	3
$\delta_{(\text{CO})-\text{M-(CO)}}$	4	$E$	90	85-100	80-95	$E$	4
$\nu_{\text{C-O}}$	5	$F_2$	1883	1788	1835 1768	$A_1$ $E$	$5_a$ $5_c$
$\delta_{\text{M-C-O}}$	6	$F_2$	619	644	610 598	$A_1$ $E$	$6_a$ $6_c$
$\nu_{\text{M-(CO)}}$	7	$F_2$	532	550	539 518	$A_1$ $E$	$7_a$ $7_c$
$\delta_{(\text{CO})-\text{M-(CO)}}$	8	$F_2$	90	85-100	80-95 80-95	$A_1$ $E$	$8_a$ $8_c$
$\delta_{\text{M-C-O}}$	9	$F_1$	<i>i.a.</i>	<i>i.a.</i>	<i>i.a.</i> 708 or 780?	$A_2$ $E$	$9_a$ $9_c$
H    to $C_3$ axis	...	...	...	...	See discussion	$A_1$	10
H $\perp$ to $C_3$ axis	...	...	...	...	See discussion	$E$	11

the shifts corresponding to M-(CO) stretching motions appear with higher intensities and at lower frequencies than those of the M-C-O bending modes.

With these indications pointing to identical conclusions we assign the frequencies 715 and 785  $\text{cm}^{-1}$  of  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$ , respectively, to the bending mode  $\nu_3(E)$ , 619 and 644  $\text{cm}^{-1}$  to the bending mode  $\nu_6(F_2)$  and 532 and 550  $\text{cm}^{-1}$  to the stretching mode  $\nu_7(F_2)$ .

The resulting vibrational assignments for  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$  are shown in the first columns of Table I.

#### STRUCTURE AND FREQUENCY ASSIGNMENT OF $\text{HFe}(\text{CO})_4^-$

The  $\text{HFe}(\text{CO})_4^-$  ion is isoelectronic with cobalt hydrocarbonyl. Sternberg *et al.*,<sup>13</sup> Friedel *et al.*,<sup>1</sup> and Edgell *et al.*<sup>14</sup> have reported ir absorption measurements on the latter compound and have found the spectrum to be consistent with a  $C_{3v}$  structure of the molecule. Edgell *et al.*<sup>14</sup> and Edgell and Gallup<sup>15</sup> proposed a particular "bridge model" of  $C_{3v}$  symmetry for cobalt hydrocarbonyl in which the hydrogen atom is located symmetrically between three CO groups at a distance of about 2.0 Å from the cobalt atom. Bonding is primarily to the CO groups and to a lesser extent only to the cobalt atom. Cotton,<sup>16</sup> however, considers the contribution of the Co-H overlap to the bonding of the hydrogen atom as being quite important and arrives at a probable Co-H distance of about 1.2 Å. It thus appears to be justified to consider the proton,

as proposed by Cotton and Wilkinson,<sup>17</sup> as being buried in the electron density of the metal atom. This picture is rather close to the conception of a "pseudo-nickel" atom,  $\text{CoH}$ , previously advanced by Hieber.<sup>18</sup>

An uncommon type of bonding of the hydrogen to the metal carbonyl skeleton is suggested, also, by the results of NMR measurements on  $\text{HCo}(\text{CO})_4$ ,<sup>19</sup>  $\text{H}_2\text{Fe}(\text{CO})_4$ ,<sup>17</sup> and  $\text{HMn}(\text{CO})_5$ ,<sup>20</sup> showing much larger negative proton resonance shifts as found when hydrogen is bound in the ordinary way to oxygen or carbon atoms.

However, the ir absorption spectra of  $\text{HCo}(\text{CO})_4$  mentioned in the foregoing offer no conclusive evidence for the  $C_{3v}$  structure of the molecule. The transition from  $T_d$  to  $C_{3v}$  symmetry, brought up by the hydrogen atom, is expected to cause a splitting of the triply degenerate vibrations of the regular tetrahedron into two modes belonging to species  $A_1$  (or  $A_2$ ) and  $E$ , respectively. All fundamentals of the  $C_{3v}$  model are active in Raman and in the ir, except one  $A_2$  mode which is forbidden in both. The ir spectrum of cobalt carbonyl hydride indicates that the selection rules of the  $C_{3v}$  point group are indeed operative, however, the expected splitting was observed only for the antisymmetric C-O stretching vibration, but not for the two  $F_2$  modes of the middle-frequency region. Edgell and co-workers<sup>14</sup> believe that the slight perturbation of the tetrahedral skeleton, produced by the hydrogen atom, is just sufficient to make the selection rules of the  $C_{3v}$  point group operative, but not large enough to cause an observable splitting of the  $F$  modes of lower fre-

<sup>13</sup> H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, J. Am. Chem. Soc. **75**, 2717 (1953).

<sup>14</sup> W. F. Edgell, Ch. Magee, and G. Gallup, J. Am. Chem. Soc. **78**, 4185 (1956).

<sup>15</sup> W. F. Edgell and G. Gallup, J. Am. Chem. Soc. **78**, 4188 (1956).

<sup>16</sup> F. A. Cotton, J. Am. Chem. Soc. **80**, 4425 (1958).

<sup>17</sup> F. A. Cotton and G. Wilkinson, Chem. & Ind. (London) **1956**, 1305.

<sup>18</sup> W. Hieber, Chemie Die **55**, 24 (1942).

<sup>19</sup> H. S. Gutowsky, quoted in references 1 and 14.

<sup>20</sup> F. A. Cotton, J. L. Down, and G. Wilkinson, J. Chem. Soc. **1959**, 833.

quency into  $A$  and  $E$  species. That would mean that the intrinsically degenerated modes of the  $T_d$  model become in part accidentally degenerated ones in the  $C_{3v}$  model. Hence, the spectroscopic evidence for the  $C_{3v}$  structure of  $\text{HCo}(\text{CO})_4$  rests essentially on the assignment of the C–O stretching modes. The spectrum observed in the  $2000\text{-cm}^{-1}$  region is certainly not inconsistent with the given assignment but cannot be said to require it, owing to the presence of numerous further bands in this range.

Therefore, it is particularly interesting that the splitting pattern, expected for the transition from  $T_d$  to  $C_{3v}$  symmetry, becomes clearly evident in the Raman spectrum of  $\text{HFe}(\text{CO})_4^-$ , not only in the high- but also in the middle-frequency region. The observed splittings have to be interpreted as the result of a considerable disturbance of the tetrahedral symmetry of the  $\text{Fe}(\text{CO})_4$  skeleton. The correlation between the spectra of the ions belonging to the  $T_d$  point group and of  $\text{HFe}(\text{CO})_4^-$ , assigned under  $C_{3v}$  symmetry, is shown in Table I. The components belonging to species  $A$  and  $E$  originating from the triply degenerate species of the undisturbed tetrahedron are indicated by subscripts  $a$  and  $e$ , respectively. The observed frequencies have been assigned to these components under the criterion that the  $A_1$  modes appear usually with higher intensities in Raman spectra than the  $E$  modes. Also in relation to some other details the correlation scheme of Table I must be regarded as tentative.

In the high-frequency region we found three Raman shifts, one of them ( $1835\text{ cm}^{-1}$ ), being strongly polarized. This frequency has been assigned to the  $A_1$  mode  $\nu_{3a}$ ; the assignment to  $\nu_1$  would be possible too. The shift of lowest intensity has been attributed to the  $E$  mode  $\nu_{5e}$  according to the foregoing criterion.

In the middle-frequency region we have two pairs of Raman lines, namely  $610/598$  and  $539/519\text{ cm}^{-1}$ , which are readily assigned to the  $A_1$  and  $E$  modes produced by the splitting of the  $F_2$  species  $\nu_6$  and  $\nu_7$ , respectively. The strongly polarized and very intense Raman shift  $451\text{ cm}^{-1}$  corresponds without doubt to the symmetric M–(CO) stretching mode that was observed in the spectra of the undisturbed tetrahedral species  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$  at  $439$  and  $464\text{ cm}^{-1}$ , respectively. There remain the weak Raman lines  $780$  and  $708\text{ cm}^{-1}$  whose genuineness is not absolutely certain. They have been assigned in a purely tentative way to the  $E$  modes  $\nu_3$  and  $\nu_{9e}$ . The latter is expected to arise from the splitting of the inactive species  $F_1$  into an  $A_2$  and an  $E$  mode, the  $A_2$  species being inactive both in Raman and in the ir.

In addition to the vibrational modes of the disturbed tetrahedral carbonyl skeleton we have to expect in the spectra of  $\text{HCo}(\text{CO})_4$  and  $\text{HFe}(\text{CO})_4^-$ , assuming a  $C_{3v}$  symmetry, two more fundamentals which may be described, in zero approximation, as motions of the hydrogen atom parallel and perpendicular to the principal axis. They belong to species  $A_1$  ( $\nu_{10}$ ) and

$E$  ( $\nu_{11}$ ), respectively. Since the bonding of the H atom to the skeleton is certainly of an unusual kind, the frequencies of such vibrations cannot be foreseen. In the foregoing assignment we attributed all observed Raman shifts of  $\text{HFe}(\text{CO})_4^-$  to the fundamental modes of the  $\text{Fe}(\text{CO})_4$  skeleton, the number of them being exactly that which must be expected for a disturbed tetrahedron with  $C_{3v}$  symmetry. Now, we shall discuss briefly an alternative assignment of one or two of the observed frequencies to motions involving the hydrogen atom.

The most reliable evidence of a hydrogen stretching vibration in metal hydrocarbonyls has been recently obtained from the ir spectra of  $\text{HMn}(\text{CO})_5$  and  $\text{DMn}(\text{CO})_5$  as reported by Wilson,<sup>21</sup> Cotton *et al.*,<sup>20</sup> and by Edgell and co-workers,<sup>22</sup> whose measurements are in excellent agreement. The value of the hydrogen stretching frequency in  $\text{HMn}(\text{CO})_5$  was found to be  $1782\text{ cm}^{-1}$ .

Earlier, Edgell *et al.*<sup>14</sup> had assigned a strong absorption band of  $\text{HCo}(\text{CO})_4$ , observed at  $703\text{ cm}^{-1}$ , to a hydrogen stretching mode, arguing that no skeletal vibration of so high a frequency (except the C–O stretching modes) can be expected. In our opinion, the weight of this argument is impaired by the fact that we found in the spectra of  $\text{Co}(\text{CO})_4^-$ ,  $\text{Fe}(\text{CO})_4^{2-}$ , and  $\text{Fe}(\text{CO})_5$ <sup>23</sup> Raman lines at  $715$ ,  $785$ , and  $753\text{ cm}^{-1}$ , respectively, which must be attributed to fundamental skeletal vibrations.

Taking into account the foregoing observations on related metal hydrocarbonyl compounds, we cannot exclude the possibility that one of the high-frequency shifts, observed in the  $\text{HFe}(\text{CO})_4^-$  spectrum, or one of the weak lines in the  $700\text{--}800\text{-cm}^{-1}$  region belongs to the  $\nu_{10}$  or  $\nu_{11}$  mode. The latter hypothesis is consistent with the results of a normal coordinate analysis, referring to the tetrahedral ions, which will be discussed later. We calculated the frequencies of the inactive  $F_1$  species of  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$  to be  $489$  and  $459\text{ cm}^{-1}$ , respectively. Since the  $\nu_{9e}$  mode of  $\text{HFe}(\text{CO})_4^-$  has its origin in the  $F_1$  species of the undisturbed skeleton one should expect for this fundamental a frequency considerably lower than  $708$  or  $780\text{ cm}^{-1}$ . The Raman spectrum of the isotopic species  $\text{NaDFe}(\text{CO})_4$  in a heavy water solution should be helpful in order to reach an unambiguous decision of the question.

#### POTENTIAL FUNCTION AND FORCE CONSTANTS OF $\text{Co}(\text{CO})_4^-$ AND $\text{Fe}(\text{CO})_4^{2-}$

A normal coordinate analysis of the tetrahedral ions  $\text{Co}(\text{CO})_4^-$  and  $\text{Fe}(\text{CO})_4^{2-}$  was carried out making use of Wilson's **FG** matrix method. It was less our aim to reproduce the observed frequencies with the highest

<sup>21</sup> W. Wilson, Z. Naturforsch. **13b**, 349 (1958).

<sup>22</sup> W. F. Edgell, G. Asato, W. Wilson, and C. Angell, J. Am. Chem. Soc. **81**, 2022 (1959).

<sup>23</sup> H. Stammreich, O. Sala, and Y. Tavares, J. Chem. Phys. **30**, 856 (1959).

possible accuracy than to introduce a simple but adequate force field in order to obtain the values of the more significant potential constants which could be compared with the corresponding force constants of related molecules. Furthermore, the results of the analysis have to be regarded as a test of the reasonableness of our frequency assignment.

Similar treatments for nickel carbonyl have been recently reported by Murata and Kawai<sup>10</sup> and by Jones.<sup>9</sup> The former authors have made use of a Urey-Bradley force field model whereas Jones assumed as a starting point a most general quadratic valence force potential function, resorting subsequently to the assumption of certain values for many of the involved constants. Jones has pointed out that for the treatment of metal carbonyl compounds the valence force model seems to be more promising than the Urey-Bradley field, since the latter model neglects resonance interactions which are probably quite important in these molecules; particularly, it is to be expected that a significant C-O stretching interaction will arise from the change of the structure of this bond during distortion.

In agreement with Jones's point of view, we used in the present analysis the following simplified quadratic valence force potential function:

$$\begin{aligned}
 2V = & \sum_{i=1}^4 [f_{(C-O)}(\Delta R_i)^2 + f_{(M-C)}(\Delta r_i)^2] \\
 & + \sum_{i < j=1}^4 f_{(C-M-C)}(r\Delta\alpha_{ij})^2 \\
 & + \sum_{i=1}^4 \sum_{k=a}^b f_{(M-C-O)}[(rR)^{\frac{1}{2}}\Delta\pi_{ik}]^2 \\
 & + 2 \sum_{i < j=1}^4 f_{(C-O)(C-O)}(\Delta R_i)(\Delta R_j) \\
 & + 2 \sum_{i < j=1}^4 \sum_{l,k=a}^b f_{(M-C-O)(M-C-O)}[(rR)^{\frac{1}{2}}\Delta\pi_{il}][(rR)^{\frac{1}{2}}\Delta\pi_{jk}].
 \end{aligned}$$

Here  $R$  and  $r$  are, respectively, the equilibrium values of the C-O and M-C bond lengths; the other symbols in the foregoing expressions correspond to those used by Murata and Kawai<sup>10</sup> in the setting up of the internal coordinates. It is seen that only two cross terms,

TABLE II. Valence force constants of tetrahedral metal carbonylate ions.

Force constant	Co(CO) <sub>4</sub> <sup>-</sup> md/Å	Fe(CO) <sub>4</sub> <sup>2-</sup> md/Å
$f_{(C-O)}$	13.22	11.40
$f_{(M-C)}$	3.55	4.06
$f_{(M-C-O)}$	0.45	0.48
$f_{(C-M-C)}$	0.09	0.09
$f_{(C-O)(C-O)}$	0.14	0.05
$f_{(M-C-O)(M-C-O)}$	0.06	0.09

TABLE III. Observed and calculated frequencies of tetrahedral ions.

Species	$i$	Co(CO) <sub>4</sub> <sup>-</sup>		Fe(CO) <sub>4</sub> <sup>2-</sup>	
		obs	calc	obs	calc
$A_1$	1	1918	1918	1788	1792
$A_1$	2	439	444	464	468
$E$	3	715	712	785	772
$E$	4	90	88	85-100	88
$F_2$	5	1883	1885	1788	1785
$F_2$	6	619	626	644	648
$F_2$	7	532	523	550	537
$F_2$	8	90	93	85-100	93
$F_1$	9	<i>i.a.</i>	489	<i>i.a.</i>	459

referring to C-O stretching and M-C-O bending interactions, have been considered, the different interactions of the latter kind were assumed to be equal.

For the calculation of valence force constants we used the  $G$  matrix elements given by the forenamed authors; the M-C and C-O equilibrium distances which are 1.83 and 1.15 Å, respectively, in Ni(CO)<sub>4</sub> were assumed to be 1.82 and 1.18 Å in the Co(CO)<sub>4</sub><sup>-</sup> ion and 1.82 and 1.19 Å in the Fe(CO)<sub>4</sub><sup>2-</sup> ion. These values of the bond lengths were estimated from the alternation of the frequencies of the corresponding totally symmetric stretching modes in going from Ni(CO)<sub>4</sub> by Co(CO)<sub>4</sub><sup>-</sup> to Fe(CO)<sub>4</sub><sup>2-</sup>. It must be pointed out, however, that the numerical values of the valence force constants, as given in Table II, are but little affected by small changes of the assumed bond distances.

By using the potential constants given in Table II we calculated the frequencies of the normal modes of the two ions, including the inactive  $F_1$  species. The results as compared with the observed values are shown in Table III.

From the satisfactory agreement between observed and calculated values one may conclude that the simplified force field, as assumed in our treatment, describes in a good approximation the vibrational properties of the two tetrahedral metal carbonylate ions. The results of the present work suggested also the convenience of a reexamination of the Raman spectrum of nickel tetracarbonyl and of the vibrational analytical data on this molecule as reported in previous publications. This work will be described in a subsequent paper, together with a comparative study of spectral data, force constants, and bond properties of the three isoelectronic species.

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