[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Infrared Spectra and Structures of the Iron Carbonyls[1]

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The metal carbonyls are a class of compounds which are by no means fully understood. The geometrical structures of the iron carbonyls $Fe(CO)_5$ and $Fe_2(CO)_9$ have been established with reasonable certainty by electron and X-ray diffraction, respectively.[3,4]

Iron carbonyl, $Fe(CO)_5$, is reported to be a trigonal bipyramid.[3] Iron enneacarbonyl, $Fe_2(CO)_9$, has been found to have the most interesting bridged structure[4] shown in Fig. 1.

The nature of the bonding as well as other detailed properties are less well established. The molecular vibration spectra obtained in this investigation should contribute some information in this respect. In particular it is not well established whether the metal-to-carbon bonds are single or double and correspondingly whether the carbon–oxygen bonds are like that in carbon monoxide or that of an organic ketone or aldehyde.[5,6]

Preparation of Sample.—The iron carbonyl used in these experiments was obtained from the General Motors Corporation as a 50% solution in kerosene. It was triply distilled with a final boiling point range of 102.9–103.1°. Iron carbonyl undergoes photodecomposition into the iron enneacarbonyl when dissolved in suitable solvents and exposed to visible and ultraviolet light.[7] Extreme care had to be observed at all times to keep visible light from reaching the sample and initiating the photochemical decomposition to the iron enneacarbonyl.

The iron enneacarbonyl was prepared by dissolving 10 cc. of purified $Fe(CO)_5$ in 40 cc. of reagent grade ether dried with sodium. This solution was then sealed off in an evacuated bulb and exposed to the sunlight or a photoflood light. The golden hexagonal platelets which precipitated out were filtered and washed several times with dry ether. This procedure may be modified by dissolving the $Fe(CO)_5$ in petroleum ether or glacial acetic acid rather than in dry ether. The iron enneacarbonyl so obtained was apparently stable for several days when kept in small amounts in ordinary air. However, large amounts, especially when placed in a desiccator, spontaneously ignite in the period of a day. This seems to indicate that there is an exothermic decomposition of the iron enneacarbonyl which, when the material is concentrated, raises the temperature to the kindling point. This investigation along with previous ones has shown that, when the iron enneacarbonyl is exposed to ordinary moist air, it very slowly decomposes to iron oxide on the surface of the crystal. Therefore, it seems reasonable that this decomposition might protect it from the more rapid decomposition which is observed when the crystals are placed in a desiccator.

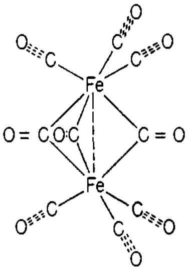

Fig. 1.—Structure of iron enneacarbonyl.

Infrared Spectrum.—Measurements were made on the $Fe(CO)_5$ gas in a 9.4-cm. glass cell with potassium bromide windows using the Perkin–Elmer 12B automatic prism spectrometer in the region 2–22 μ. All spectral data were obtained at room temperature. Pressures of 29, 20, 7 and 4 mm. were used. In order to obtain a greater thickness of iron carbonyl and thus obtain the weaker absorption bands, the liquid was run in the Perkin–Elmer liquid cell using amalgamated lead spacers of thickness 0.025 and 0.127 mm. The absorption curves are given in Figs. 2 and 3 and the frequencies are summarized in Table I.

TABLE I

THE INFRARED SPECTRUM OF $Fe(CO)_5$ (GAS AND LIQUID)

s. = strong; m. = medium; w. = weak; v. = very

Gas (ν cm.$^{-1}$)	Liquid (ν cm.$^{-1}$)	Gas (ν cm.$^{-1}$)	Liquid (ν cm.$^{-1}$)
472 v.s.	472 v.s.	1935 w.	
552 v.w.	553 m.	1994 v.s.	
614 v.s.	622 v.s.	2028 v.v.s.	2020 v.s.
	(unresolved)		(unresolved)
639 v.s.		2084 s.	
796 v.w.	745 w.	2220 v.w.	2222 s.
	801 m.	2425 w.	2430 m.
853 w.	853 s.		(shoulder)
	920 w.	2470 w.	2477 s.
994 w.	993 m.	2598 v.w.	2600 m.
1024 m.	1022 s.	2662 v.w.	2650 m.
1105 v.w.	1103 m.	2726 v.w.	2730 m.
1196 w.	1192 s.	2980 v.w.	2900 m.
1258 v.w.	1261 m.		2980 s.
	1369 w.	4005 w.	4025 s.
1470 v.w.	1468 m.	4115 w.	4130 s.

Iron enneacarbonyl is insoluble in acetone, benzene, butyl alcohol, carbon tetrachloride, glacial acetic acid, heptane, hexane, isopropyl alcohol, iron carbonyl, methyl alcohol, toluene and certain mixtures. Therefore, it was necessary to obtain the spectrum of $Fe_2(CO)_9$ in the solid state. The crystals were ground into a fine powder of particle size 0.5–10 μ (average ~ 1 μ). It was spread over the potassium bromide plate in a uniform film. The absorption curve is given in Fig. 4. There are two very strange features about this absorption curve. First, it has extremely broad and unresolved absorption from 5000 to 2300 cm.$^{-1}$. Second, the peak at 2110 cm.$^{-1}$ shows a decidedly higher transmission than any other part of the absorption curve. In order to adequately interpret these details, it was necessary to study in some detail the effects of the solid state on infrared spectra.

Accordingly, in the region from 5000 to 1400 cm.$^{-1}$ the infrared spectrum of $Fe_2(CO)_9$ was run in three different solid states. First, the powder, particle size 0.5 μ to 10 μ (average ~ 1 μ), was spread over a potassium bromide salt plate. Second, hexagonal platelets of $Fe_2(CO)_9$, approximately 2000 μ in diameter and 1 μ thick were spread over a potassium bromide salt plate in a semi-continuous crystal

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[1] Based on a thesis submitted by R. K. S. in partial fulfillment of the requirements for the Ph.D. degree at the University of California. This research was aided by the Office of Naval Research, under N7ONR-295 Task Order X, Project Number NR-058-097.

[2] On leave of absence from the University of California as Director of Research, Atomic Energy Commission, Washington, D. C.

[3] R. V. G. Ewens and M. L. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[4] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

[5] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd ed., 1940, pp. 251–254.

[6] L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, **43**, 342 (1947).

[7] E. Speyer and H. Wulf, *Ber.*, **60B**, 1424 (1927).

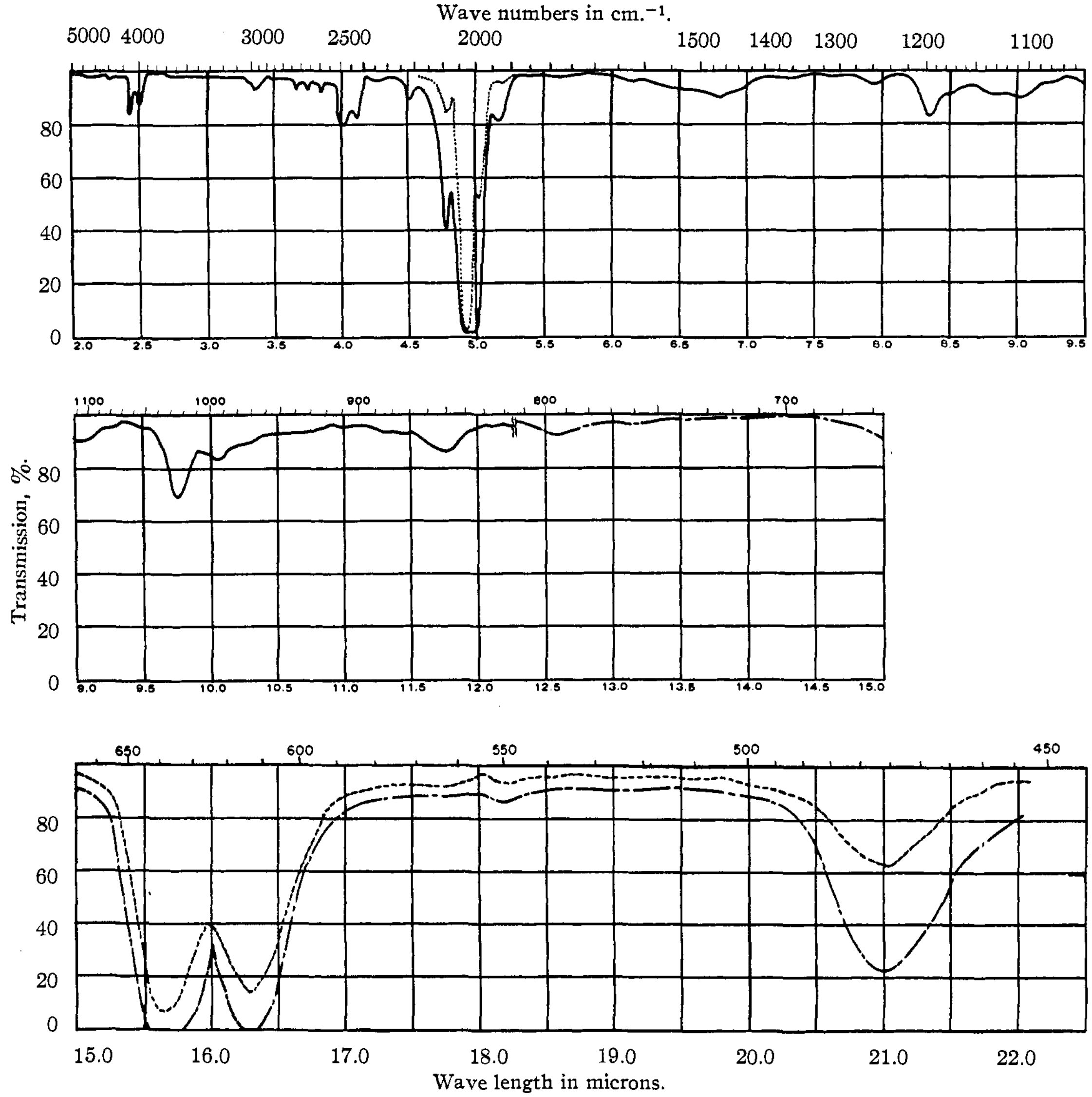

Fig. 2.—The infrared spectrum of gaseous $Fe(CO)_5$, General Motors product, b. p. 102.9–103.1°; Perkin–Elmer spectrometer, 9.4 cm. cell, gas at 25°: —, at 29 mm.; ......, 4 mm.; — — —, 20 mm.; - - - - -, 7 mm.

layer. Third, the powder was spread over the plate as in case one, but in addition it was immersed in carbon tetrachloride. The infrared absorption curves for these three different solid states are shown in Fig. 5.

The semi-continuous layer of large crystals does not exhibit the extremely broad and unresolved band from 5000 to 2300 cm.$^{-1}$ which both the powder samples show. It is therefore to be concluded that this band is caused by the scattering of the infrared light by the particles of the powder. This scattering is at a maximum at a wave length of 1 μ at which wave length it is equal to the average powder particle size and decreases as higher wave lengths are approached where the powder is no longer as effective a scatterer. The powder immersed in carbon tetrachloride does not exhibit the transmission peak at 2110 cm.$^{-1}$ whereas the ordinary powder exhibits a high peak, and the semi-continuous crystal shows only the appendage of such a peak. It is to be concluded that this transmission peak is the result of the Christiansen filter effect.[8,9]

With this understanding of solid state effects it was possible to determine the vibrational frequencies which are summarized in Table II. It seemed strange that there were so few definite bands in this 20-atom molecule. Since $Fe_2(CO)_9$ crystallizes in such very thin platelets, there is a possibility that even after grinding, the powder crystals may line up in a plane parallel to the salt plate. To investigate this possibility, the semi-continuous crystal layer was run perpendicular to the infrared beam and at an angle of 10° from perpendicular to the beam. No new lines appeared. Hence the lack of a more abundant spectrum for this complicated molecule was ascribed to difficulties in taking the infrared spectra of solids. It should be pointed out, however (see Fig. 5) that considerably

TABLE II

THE INFRARED SPECTRUM OF SOLID IRON ENNEACARBONYL

w. = weak; s. = strong; v. = very

Frequency in cm.$^{-1}$	557	597	662	1828	2034	2080
	w.?	s.	s.	v.s.	v.s.	s.

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(8) R. B. Barnes and L. G. Bonner, *J. Opt. Soc. Am.*, **37**, 713 (1947).

(9) W. C. Price and K. S. Tetlow, *J. Chem. Phys.*, **16**, 1157 (1948).

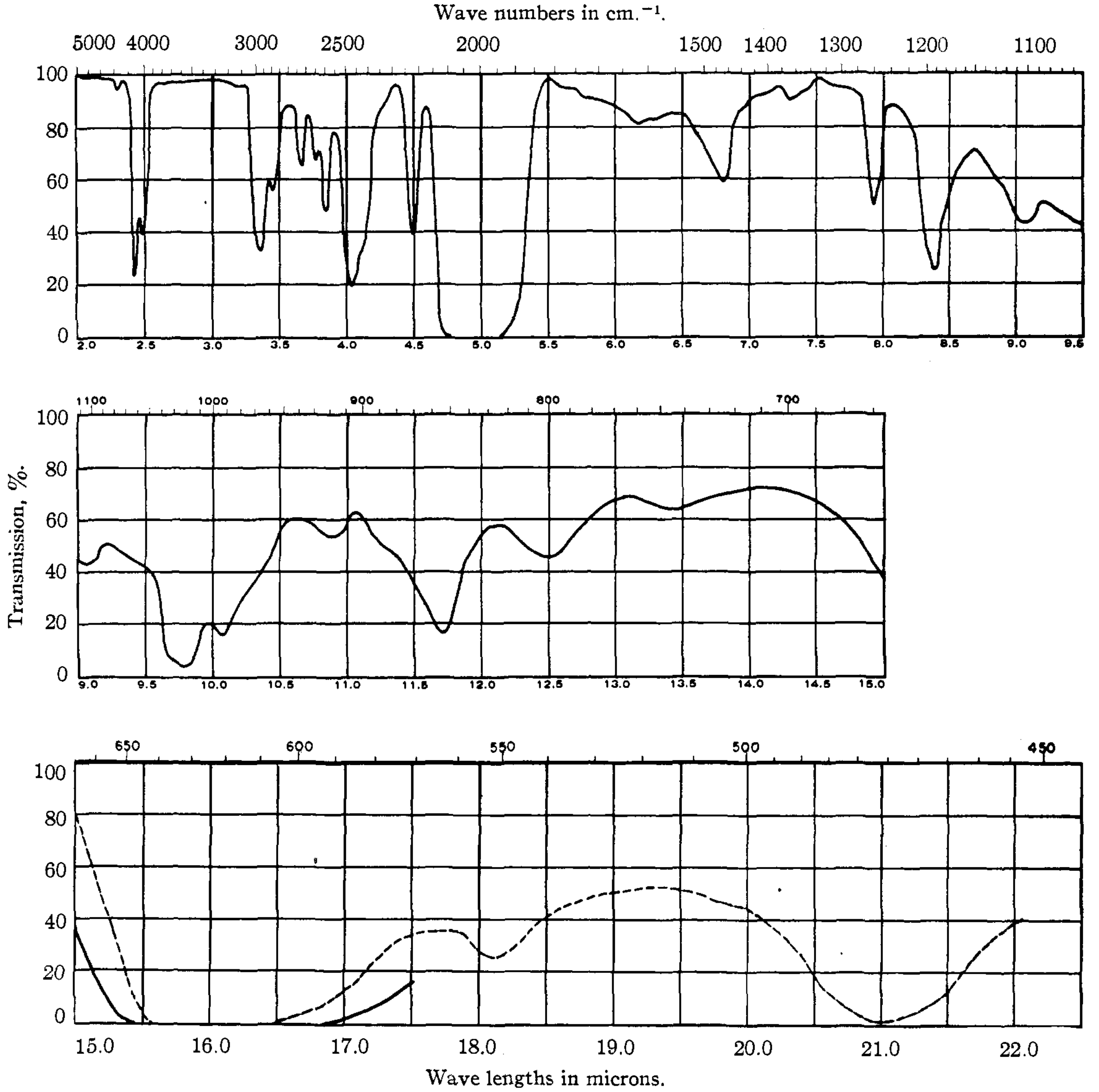

Fig. 3.—The infrared spectrum of liquid $Fe(CO)_5$, General Motors product, b. p. 102.9–103.1°; Perkin-Elmer spectrometer, liquid at 25°: —, cell length 0.127 mm.; – – –, cell length 0.025 mm.

greater detail in the infrared spectrum is obtained when the solid powder is immersed in a solvent than in any of the other solid states used.

Frequency Assignments.—Duncan and Murray[10] were unable to obtain the Raman spectrum of $Fe(CO)_5$ because the intense mercury arc initiated the photochemical decomposition to the iron enneacarbonyl. In view of the lack of data, particularly at the lower frequencies, a complete assignment is impossible. However, a partial assignment by analogy with $Ni(CO)_4$ will be attempted. Bond hybridization in which the five carbonyl groups are coördinately bonded to the iron leads to a dsp^3 hybrid which indicates a trigonal bipyramid structure. Since electron diffraction also indicates this structure, attempts at assignment will be made on this basis. The trigonal bipyramid has D_{3h} symmetry. The expected classes, numbers and activities of vibrations for an eleven atom molecule of D_{3h} symmetry are listed in Table III.[11] Table III indicates that 10 infrared active frequencies are to be expected, 4 non-degenerate and 6 degenerate frequencies. These are made up of 3 Fe–C bending, 3 C–O bending, 2 Fe–C stretching and 2 C–O stretching motions. Of these 10 frequencies, the two C–O stretchings and the two Fe–C stretchings are definitely to be expected in the region 2–23μ which has been examined. The C–O bendings are to be expected in the region

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(10) A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.*, **2**, 636 (1934).

(11) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

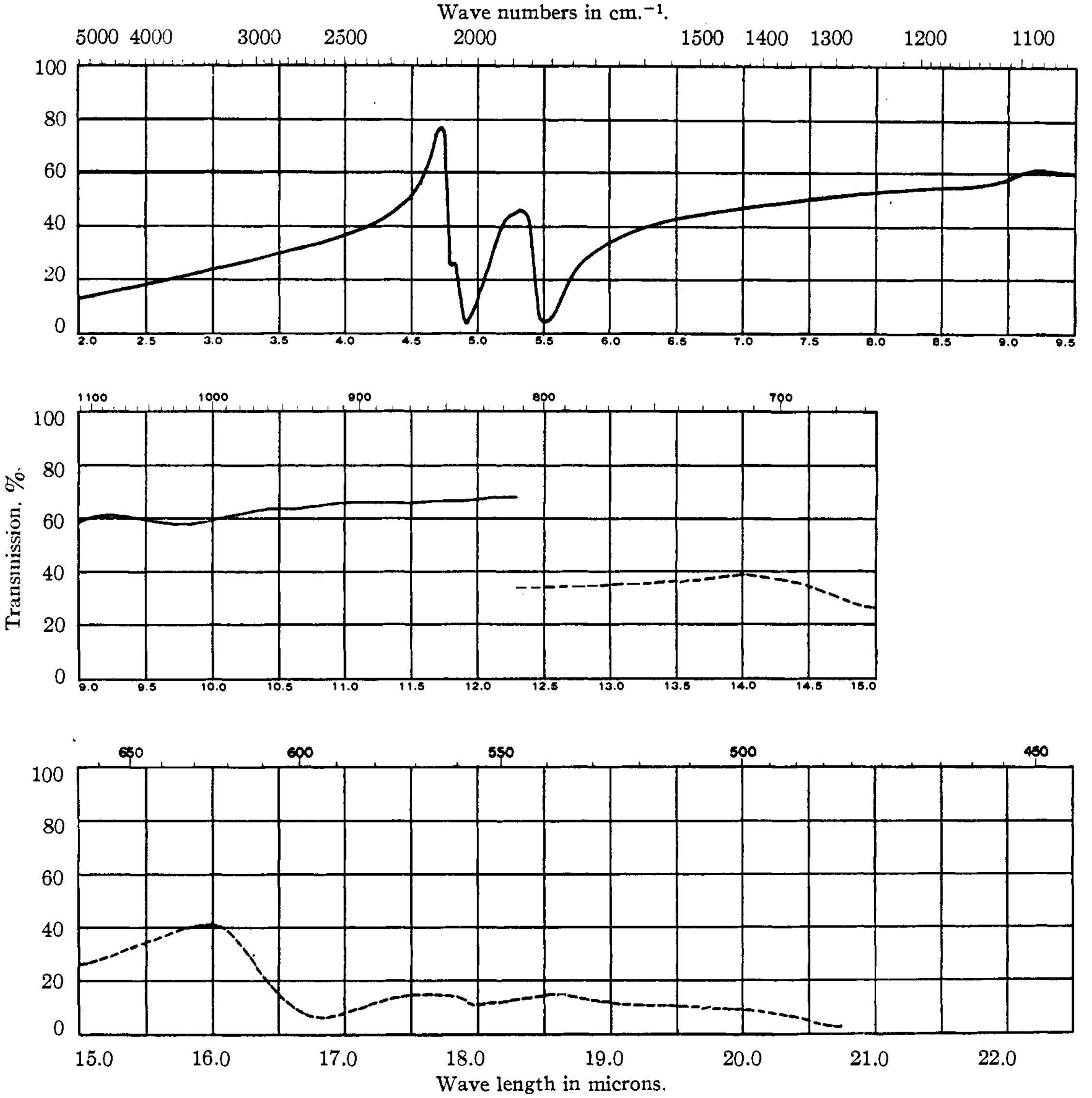

Fig. 4.—The infrared spectrum of solid $Fe_2(CO)_9$, prepared from $Fe(CO)_5$, carefully washed, Perkin-Elmer spectrometer, fine powder at 25°, unknown cell length: —, NaCl prism; - - -, KBr prism.

TABLE III

CLASSES, ACTIVITIES AND NUMBERS OF VIBRATIONS OF IRON CARBONYL

Activity	Class of vibration	Skeletal vibrations	Designation	Total vibrations	Designation
Raman (polarized)	A_1'	2	ν_3, ν_4	4	ν_1–ν_4
Infrared	A_1''	..	...	..	...
Inactive	A_2'	..	...	1	ν_5
Infrared	A_2''	2	ν_8, ν_9	4	ν_6–ν_9
Infrared and Raman (dp)	E′	3	ν_{13}, ν_{15}	6	ν_{10}–ν_{15}
Raman (depolarized)	E″	1	ν_{18}	3	ν_{16}–ν_{18}

350–500 cm.$^{-1}$ of which only the upper 50 cm.$^{-1}$ is included in the potassium bromide infrared region. Since two of the strongest bands in the spectrum occur right in the carbon–oxygen stretching frequency range, their designation as ν_6 and ν_{10} is strongly implied. The two other very strong bands which occur in the region expected for Fe–C stretchings are at 639 and 614 cm.$^{-1}$ and are assigned as ν_8 (axial) and ν_{13} (equi.), respectively. This assignment is in accord with the calculations of Duffey[12] which suggest that the axial bond strength should be somewhat greater than the equitorial bond strength in the trigonal bipyramid dsp^3. The strong frequency at 472 cm.$^{-1}$ is assigned as ν_{12} the C–O(E′) bending frequency, by analogy with the frequency at 461 cm.$^{-1}$ which is the C–O(E) bending frequency in Ni-

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[12] G. H. Duffey, *J. Chem. Phys.*, **17**, 196 (1949).

$(CO)_4$. The assignment along with the analogous assignment of the CO frequencies in $Ni(CO)_4$[13] is presented in Table IV. It is to be emphasized that these assignments should be considered tentative. The need of a successful Raman spectrum of $Fe(CO)_5$ to check the expected coincidences and make possible a complete assignment is apparent. Nevertheless, the experimental observation that the 4 strongest bands lie precisely in the expected ranges adds considerable weight to the D_{3h} trigonal bipyramid structure.

The small finite dipole moment observed by Graffunder and Heymann[14] and Bergmann and Engel[15] appears to contradict the trigonal bipyramid structures. However, in both cases the total polarization was determined at one temperature only and in a benzene solution. Solution effects or inability to estimate the atomic polarization correctly could easily account for this small dipole.

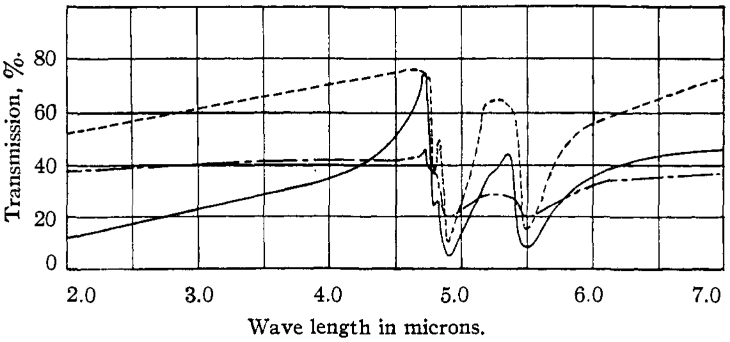

Fig. 5.—Solid state effect on infrared spectrum of iron enneacarbonyl, $Fe_2(CO)_9$: —, uniform layer of finely ground $Fe_2(CO)_9$, particle size range 0.5–10 μ; — — —, hexagonal platelets of $Fe_2(CO)_9$, (~2000 μ diameter, 1 μ thick) in a semi-continuous layer; - - -, uniform layer of finely ground $Fe_2(CO)_9$, particle size range 0.5–10 μ, average 1 μ, immersed in liquid chloroform.

TABLE IV

ASSIGNMENT OF SOME IRON CARBONYL FREQUENCIES

Infrared frequency of $Fe(CO)_5$ (cm.$^{-1}$)	Assignment	Infrared frequency of $Ni(CO)_4$ (cm.$^{-1}$)	Assignment[13]
472	ν_{12}	461	ν_4
614	ν_{13}		
639	ν_8		
1994	ν_6	2039	ν_2
2028	ν_{10}	2050	ν_8

The expected modes of vibration of iron enneacarbonyl and their characteristics are listed[11] in Table V on the basis of the Powell and Ewens structure[4] which has D_{3h} symmetry. Table V indicates that 16 infrared active bands are expected. An analysis of particular vibrations indicates that 7 of these vibrations should occur in the region of the infrared spectrum covered. They are 3 C–O stretchings and 4 Fe–C stretchings. The sample proved so opaque below 500 cm.$^{-1}$ that no measurements were obtained in the region of C–O bending frequencies. Accordingly, the infrared spectrum is assigned in Table VI.

TABLE V

CLASSES, ACTIVITIES AND NUMBERS OF VIBRATIONS IN $Fe_2(CO)_9$

Activity	Class of vibration	No. of skeletal vibrations	Designation	No. of total vibrations	Designation
Raman (polarized)	A_1'	4	ν_4–ν_7	7	ν_1–ν_7
Not active	A_1''	1	ν_9	2	ν_8–ν_9
Not active	A_2'	1	ν_{12}	3	ν_{10}–ν_{12}
Infrared	A_2''	3	ν_{16}–ν_{18}	6	ν_{13}–ν_{18}
Infrared and Raman (depol.)	E'	5	ν_{24}–ν_{28}	10	ν_{19}–ν_{28}
Raman (depolarized)	E''	4	ν_{33}–ν_{36}	8	ν_{29}–ν_{36}

TABLE VI

ASSIGNMENT OF SOME $Fe_2(CO)_9$ FREQUENCIES

Infrared band (cm.$^{-1}$)	557 ?	597	662	1828	2034	2080
Assignment	ν_{25} ?	ν_{24}	ν_{16}	ν_{20}	ν_{13}	ν_{19}

It is to be emphasized that these assignments are very tentative and, in the light of the rather meager spectral data, do not in themselves provide strong evidence for the D_{3h} bridge model. However, there is one piece of evidence which provides very strong evidence for the D_{3h} bridge model of Powell and Ewens. Their model uses 3 carbonyls as bridges between the 2 iron atoms. These carbonyls in the process of bridging become like ketones. The ketone stretching frequencies are much lower than typical carbonyl stretching frequencies. Ketone frequencies are usually in the region from 1800–1700 cm.$^{-1}$. Therefore, the fact that $Fe_2(CO)_9$ has one very strong band at 1828 cm.$^{-1}$ whereas there is no similar band in $Fe(CO)_5$ is very strong evidence of a ketone carbonyl. Since the bridge structure of Powell and Ewens is the only one proposed for $Fe_2(CO)_9$ which contains a ketone carbonyl, this evidence is fortunately effective in confirming the correct structure.

Bond Character in Carbon Monoxide and Metal Carbonyls.—There continues to be considerable discussion and disagreement as to the bond character in these compounds.[5,6] Most recent authors agree that there is considerable triple bond character in carbon monoxide which

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(13) B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938); see also B. L. Crawford, Jr., and W. Horwitz, *ibid.*, **16**, 147 (1948).

(14) W. Graffunder and E. Heymann, *Z. physik. Chem.*, **B15**, 377 (1932).

(15) E. Bergmann and L. Engel, *ibid.*, **B13**, 232 (1931).

may be indicated by $:C\overset{\leftarrow}{=}O:$ or as resonance among

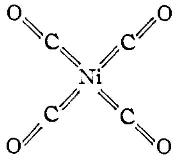
$$:\overset{-}{C}\equiv\overset{+}{O}: \qquad :C=\overset{\cdot}{\underset{\cdot}{O}}: \qquad :\overset{+}{C}-\overset{-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}:$$

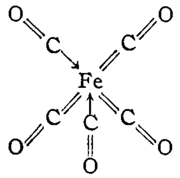
However, Long and Walsh[6] have challenged this and advocated the use of only a double bond structure.

Since bond character is not a direct experimental quantity, conclusions with respect to it naturally vary according to the relative importance an author gives to the various pertinent experimental quantities. Some have given most weight to the bond distances. We would urge that more attention be given to bond stretching force constants as they become available. With caution with respect to dynamic interactions, vibration frequencies may be taken as approximate measures of force constants (together with masses, of course). Thus the frequencies of single, double and triple carbon–carbon bonds lie near 1000, 1650 and 2050 cm.$^{-1}$, respectively. For carbon–oxygen bonds the values are usually a little higher, organic carbonyl frequencies being 1700–1800 cm.$^{-1}$. The carbon monoxide frequency at 2168 cm.$^{-1}$ is thus in the triple bond range. The corresponding frequencies for $Ni(CO)_4$ and $Fe(CO)_5$ are near 2030 cm.$^{-1}$ which indicates that the carbon–oxygen bond, although intermediate, is nearer that in carbon monoxide than that of a ketone or aldehyde.

It has also been suggested that the metal-to-carbon bonds are something approaching double bonds in these carbonyls. The observed frequencies correspond, however, to M–C force constants[16] of about 2.5×10^5 dynes/cm. which are about the same as for metal alkyls in this region of the periodic table.[17] This tends to indicate that the M–C bonds are not far from single bonds in agreement with the near triple bond C–O frequency.

One particular conclusion of Long and Walsh can be tested. Their structures for $Ni(CO)_4$





and for $Fe(CO)_5$ show the former to have strictly double Ni=C bonds whereas the Fe–C bonds are resonating with $1^3/_5$ average order. Thus the Ni–C force constant should be distinctly higher. If any difference is noted, it is in the opposite direction, the skeletal stretching frequencies in iron carbonyl being considerably higher than those of nickel carbonyl.

Summary

Infrared spectra in the region 2–23μ are reported for the iron carbonyls, $Fe(CO)_5$ and $Fe_2(CO)_9$. Some frequency assignments are made. The data on iron carbonyl are fully consistent with the reported trigonal bipyramid structure. The spectrum of iron enneacarbonyl was obtained only for the solid and is relatively meager. However, the bridged structure involving ketone-like carbonyl groups is strongly supported by the observation of a strong band at 1828 cm.$^{-1}$ in addition to the usual metal carbonyl C–O frequencies near 2000 cm.$^{-1}$. The implications of the results in terms of bond types are discussed briefly.

[16] Ref. 13 for $Ni(CO)_4$ and calculations based on the present data for $Fe(CO)_5$.

[17] For example, 2.39×10^5 in zincdimethyl; H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949); additional values to be summarized by R. K. Sheline.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND OF BIOLOGY, UNIVERSITY OF OREGON]

Partition Chromatography of Red Eye Pigment of *Drosophila melanogaster*[1]

BY HANS HEYMANN, FRANK L. CHAN AND CLARENCE W. CLANCY

The red pigment in the eyes of *Drosophila melanogaster* has been shown[2,3] to consist of several colored constituents by means of chromatography of eye extracts on talc columns with the aid of alkaline developing agents. Whereas the brown pigment component of wild-type eye color appears to be related to tryptophan *via* kynurenine,[4] and is apparently melanic in nature,[5] no specific precursor for the red pigment has as yet been demonstrated, and the chemical nature of the red bodies remains obscure. Lederer,[6] on the basis of an elementary analysis of a preparation of not specified purity from wild-type flies, regarded the substances as related to the pterines, a conclusion with which Maas[3] disagreed because he found a much lower amount of nitrogen (6%) in the mercuric chloride precipitate of a purified fraction.

The present work was undertaken in an endeavor to find (a) a reproducible method of chromatographic fractionation of the red pigment complex preliminary to its systematic application to a pigmentary analysis of the various eye color mu-

[1] This work was carried out under a contract between the Office of Naval Research and the University of Oregon.

[2] Wald and Allen, *J. Gen. Physiol.*, **30**, 41 (1946).

[3] Maas, *Genetics*, **33**, 177, (1948).

[4] Beadle and Tatum, *Am. Naturalist*, **75**, 107 (1941).

[5] Tatum and Beadle, *Growth*, **6**, 27 (1942).

[6] Lederer, *Biol. Rev. Cambridge Phil. Soc.*, **15**, 273 (1940).