Structure and Reactions of Matrix-isolated Tetracarbonyliron(0)

By **Martyn Poliakoff** and **James J. Turner**, Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne NE1 7RU

U.v. photolysis of ^{13}CO enriched pentacarbonyliron in SF_6 and Ar matrices at 20 K indicates that tetracarbonyliron has a C_{2v} structure, with bond angles *ca.* 145 and 120°, as estimated from i.r. intensities. Photolysis of [$Fe(CO)_5$] in an N_2 matrix produces [$Fe(CO)_4$] which can be reacted reversibly with the matrix to form [$Fe(CO)_4(N_2)$]. Equivalent experiments in CH_4 or Xe matrices produce two [$Fe(CO)_4$] species; one is [$Fe(CO)_4$] with the same structure as in other matrices, and there is strong circumstantial evidence for the other being [$Fe(CO)_4(CH_4)$] or [$Fe(CO)_4Xe$]. The behaviour of [$Os(CO)_5$] is similar. The results are compared with those obtained in frozen hydrocarbon glasses at 77 K. In matrices with high concentrations of [$Fe(CO)_5$] (>1 : 1 000 carbonyl compound : matrix), polynuclear iron carbonyls, [$Fe_2(CO)_8$], [$Fe_2(CO)_9$], and [$Fe_3(CO)_{12}$], are formed.

I.r. Spectrum and Structure of Tetracarbonyliron.—U.v. photolysis of [$Fe(CO)_5$] in low-temperature matrices produces progressive loss of CO, giving [$Fe(CO)_4$],[1] [$Fe(CO)_3$],[2] [$Fe(CO)_{2\text{ or }1}$],[2] and, eventually, Fe atoms in small yields.[3] When reporting evidence for the formation of [$Fe(CO)_4$], we suggested that this species had a 'slightly distorted C_{3v} structure'. At that time attempts to obtain good spectra of ^{13}CO-substituted [$Fe(CO)_4$] were unsuccessful. We subsequently obtained well resolved spectra, by photolysis of isotopically 'scrambled' [$Fe(CO)_5$], which confirm the assignment of bands to an [$Fe(CO)_4$] species. However, the frequencies and intensities of the bands strongly suggest that the fragment has C_{2v} symmetry.

Figure 1(*a*) shows the spectrum obtained by u.v. photolysis of [$Fe(CO)_5$], enriched with 40% ^{13}CO, in an SF_6 matrix † at 20 K; Figure 1(*b*) shows the spectrum predicted for a C_{2v} [$M(CO)_4$] fragment. The spectrum was calculated by means of a C–O factored force field, using methods similar to those of Haas and Sheline[4] and Darling and Ogden.[5] It can be seen that the agreement between observed and calculated spectra is remarkably close. Figure 1(*c*) shows a spectrum calculated on the basis of a C_{3v} structure which has one fewer force constant and an F matrix of different symmetry. As can be seen, it was impossible to reproduce either the frequencies or intensities of the observed bands using this structure (see Appendix). Similar lack of agreement was obtained with a D_{2d} structure.

The labelling of the force constants in C_{2v} [$Fe(CO)_4$] and the symmetries of the nine possible ^{13}CO-substituted molecules are shown in Figure 2, and the wavenumbers of the bands and their assignment are summarized in Table 1. Details of how the bands were assigned are given in the Appendix. Assuming that the most likely structure is the one which produces good agreement between observed and calculated spectra with the fewest force constants, we conclude that [$Fe(CO)_4$] has a C_{2v} structure in an SF_6 matrix.

Similar spectra of ^{13}CO-enriched [$Fe(CO)_4$] were obtained for argon matrices, although several bands were obscured by those of [$Fe(CO)_5$] and [$Fe(CO)_3$]. A further complication was that the bands of the unsubstituted molecule [$Fe(^{12}CO)_4$] were split. The way in which these split bands were treated in the least-squares refinement is discussed in the Appendix, but in practice it made very little difference to the calculated force constants if these split bands were left out of the refinement altogether. Full data are given in Table 2. The spectrum of [$Fe(CO)_4$] in a methane matrix was also obtained (Table 3). Spectra in both these matrices could be satisfactorily assigned on the basis of a C_{2v} structure. Thus in all three matrices [$Fe(CO)_4$] had C_{2v} symmetry.

---

† SF_6 Was chosen as the matrix for the initial experiments since less 'matrix splitting' was observed than in other matrices, the yield of [$Fe(CO)_4$] was high, and no [$Fe(CO)_3$] was formed.

[1] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1973, 1351.

[2] M. Poliakoff, *J.C.S. Dalton*, 1974, 210.

[3] M. Poliakoff and J. J. Turner, *J.C.S. Faraday II*, 1974, **70**, 93.

[4] H. Haas and R. K. Sheline, *J. Chem. Phys.*, 1967, **47**, 2996.

[5] J. H. Darling and J. S. Ogden, *J.C.S. Dalton*, 1972, 2496.

We estimated the bond angles of [Fe(CO)$_4$] in the three matrices, using relative intensities of the i.r. bands of [Fe(^{12}CO)$_4$]. The intensities of the bands and calculated bond angles are summarized in Table 4 (see Appendix for details of the calculation). There is some uncertainty in the exact values of the angles, first because the intensity of the high-frequency A_1 band could not be measured, and secondly because there are two solutions corresponding to positive or negative square roots. However, it is clear from Table 4 that the distortion from tetrahedral is substantial and that [Fe(CO)$_4$] appears to have very similar bond angles in all three matrices.

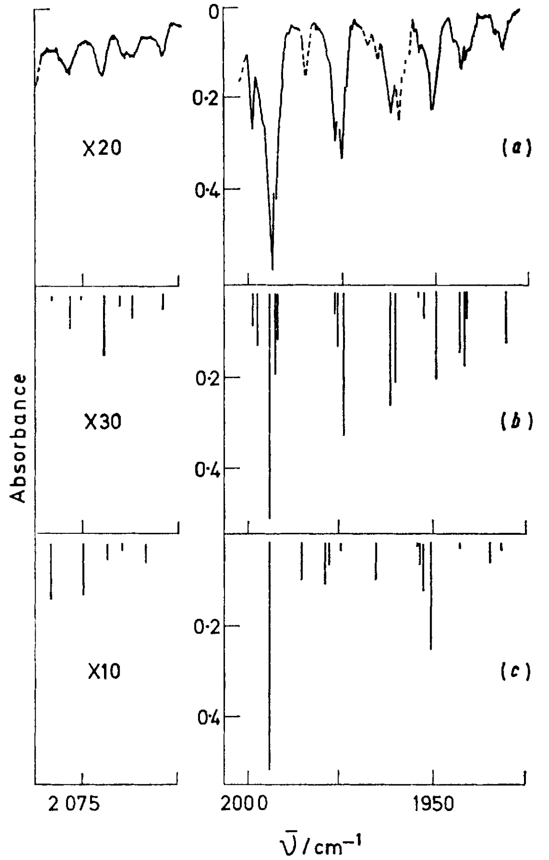


FIGURE 1 (*a*) I.r. spectrum of [Fe(CO)$_4$] with ^{13}CO enrichment (40%) in an SF$_6$ matrix at 35 K. (— — —), Bands due to [Fe(CO)$_5$]. The bands in the region (2 090—2 050 cm^{-1}) were recorded with larger amounts of [Fe(CO)$_4$] on the window, using × 5 ordinate expansion; their intensities are × 20 relative to the lower-frequency bands; (*b*) calculated spectrum using bond angles of 140 and 115° and dipole-derivative ratio 0·875 : 1 as estimated from optical densities of the bands of unenriched [Fe(CO)$_4$] (see Appendix). The spectrum is plotted with a ' resolution ' of 0·5 cm^{-1}; and (*c*) calculated spectrum using a C_{3v} structure with bond angle 105°, between axial and radial groups, and dipole-derivative ratio (axial : radial) 0·8 : 1 (see Appendix)

Although a tetrahedral [Fe(CO)$_4$] fragment, with a $^3T_1$ ground state, would be expected to undergo Jahn–Teller distortion, such a large C_{2v} distortion is somewhat surprising. However, recent molecular orbital (m.o.) calculations by Burdett [6] predict that [Fe(CO)$_4$] should have a C_{2v} geometry with bond angles of 130 and 115°, remarkably close to those estimated in Table 4. Thus the C_{2v} structure ' may ' well be that of ' free ' [Fe(CO)$_4$] rather than a distortion imposed by the matrix. Interestingly, the m.o. calculations suggest that [Fe(CO)$_4$] should have a triplet ground state, since the singlet state would be unstable with respect to a square-planar structure (*cf.* Ni^{2+} salts).

Reaction of [Fe(CO)$_4$] *with Dinitrogen.*—It has been reported that u.v. photolysis of a large number of transition-metal carbonyl compounds in dinitrogen matrices at 20 K results in replacement of CO by dinitrogen ligands which have N–N stretching bands in the region 2 300—2 150 cm^{-1}.[7] Ogilvie showed that [Fe(CO)$_5$]

$$[M(CO)_x] + N_2 \longrightarrow [M(CO)_{x-1}(N_2)] + CO \quad (1)$$

undergoes similar reactions.[8] In this section we show that, for [Fe(CO)$_5$], substitution of CO by N$_2$ is a two-step process and that both steps can be reversed by irradiation with light of appropriate wavelength.

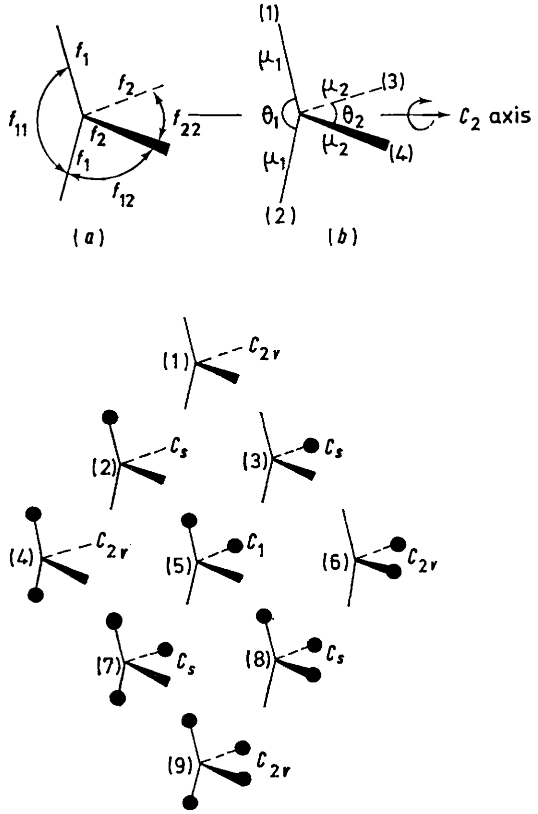


FIGURE 2 (*a*) Labelling of force constants of C_{2v} [Fe(CO)$_4$]; (*b*) labelling of bond angles and MC–O group dipole moments; and (*c*) nine possible molecules of [Fe(^{12}CO)$_{4-x}$(^{13}CO)$_x$] and their symmetries

---

[6] J. K. Burdett, *J.C.S. Faraday II*, 1974, **70**, 1599.

[7] A. J. Rest, *J. Organometallic Chem.*, 1972, **40**, C76; O. Crichton, Ph.D. Thesis, Cambridge University, 1974.

[8] J. F. Ogilvie, personal communication, 1970.

(a) [Fe(CO)$_5$] *in pure nitrogen.* Figure 3 illustrates the behaviour of [Fe(CO)$_5$] in pure nitrogen under various photolytic conditions. Concentrating on the region below 2 080 cm^{-1}, certain conclusions can be immediately drawn. (*i*) Apart from [Fe(CO)$_5$] itself,* there are at least two other species, (X) and (Y), produced [equation (2)]. The reversal (Y) ⟶ (X) is

$$[\mathrm{Fe(CO)_5}] \xrightarrow{\text{Hg arc}} (\mathrm{X}) + \text{little } (\mathrm{Y}) \underset{\lambda>357\text{ nm}}{\overset{\text{Nernst}}{\rightleftharpoons}} \mathrm{Y} \qquad (2)$$

clearly seen by comparison of Figures 3(*b*)—(*d*). The process (X) ⟶ (Y) ⟶ (X) can be repeated almost indefinitely. The wavenumbers of the bands are given in Table 5(*a*) and their assignment to (X) and (Y) is based on detailed study of the growth and decay of the bands. (*ii*) in the N–N stretching region, the behaviour indicates that (Y) contains an N$_2$ ligand, and that (X) does not.

TABLE 1

Observed and calculated wavenumbers for [Fe(CO)$_4$] with ^{13}CO enrichment in an SF$_6$ matrix at 35 K. Force constants: $f_1 = 16{\cdot}5546$, $f_2 = 16{\cdot}2146$, $f_{11} = 0{\cdot}4989$, $f_{12} = 0{\cdot}3543$, and $f_{22} = 0{\cdot}4703$ mdyn Å^{-1} (for numbering of force constants and molecules see Figure 2)

			Wavenumber/cm^{-1}	
Molecule	Symmetry		Obs.	Calc.
[Fe(CO)$_4$] (1)	C_{2v}	A_1	*a*	2 087·88
		A_1	1 999·1	1 999·14
		B_1	1 994·1 [b]	1 994·1
		B_2	1 974·3 [b]	1 974·67
[Fe(^{12}CO)$_3$(^{13}CO)] (2)	C_s	A'	2 078	2 077·28
		A'	*a*	1 997·89
		A'	1 960·7	1 960·81
		A''	1 974·3 [b]	1 974·67
(3)	C_s	A'	*a*	2 081·55
		A'	*a*	1 992·61
		A'	*a*	1 942·86
		A''	1 994·1 [b]	1 994·1
[Fe(^{12}CO)$_2$(^{13}CO)$_2$] (4)	C_{2v}	A_1	2 064	2 064·66
		A_1	*a*	1 976·55
		B_1	1 949·7 [b]	1 949·65
		B_2	1 974·3 [b]	1 974·67
(5)	C_1		2 070	2 069·56
			a	1 991·93
			a	1 962·05
			1 942·0	1 941·45
(6)	C_{2v}	A_1	*a*	2 075·14
		A_1	*a*	1 966·57
		B_1	1 994·1 [b]	1 994·1
		B_2	1 930·6 [b]	1 930·65
[Fe(^{12}CO)(^{13}CO)$_3$] (7)	C_s	A'	2 061	2 061·48
		A'	1 976·1 [c]	1 976·18
		A'	1 953·1	1 953·03
		A''	1 930·6 [b]	1 930·65
(8)	C_s	A'	2 054	2 054·11
		A'	1 976·1 [c]	1 976·06
		A'	*a*	1 941·04
		A''	1 949·7 [b]	1 949·65
[Fe(^{13}CO)$_4$] (9)	C_{2v}	A_1	*a*	2 041·34
		A_1	*a*	1 954·58
		B_1	1 949·7 [b]	1 949·65
		B_2	1 930·6 [b]	1 930·65

Standard deviation 0·36 cm^{-1}

[a] Bands not observed because either they were too weak or overlapped with other bands of [Fe(CO)$_4$] or [Fe(CO)$_5$]. [b] Although these bands are assigned to several molecules, the wavenumber of each band was only entered in the refinement once, since the vibrations are necessarily degenerate. [c] Wavenumber not entered since two bands are accidentally degenerate.

TABLE 2

Observed and calculated wavenumbers of [Fe(CO)$_4$] with ^{13}CO enrichment in an argon matrix at 20 K. Assignments are to molecules as numbered in Figure 2. Force constants $f_1 = 16{\cdot}5539$, $f_2 = 16{\cdot}1493$, $f_{11} = 0{\cdot}4794$, $f_{12} = 0{\cdot}4049$, $f_{22} = 0{\cdot}4250$ mdyn Å^{-1}

Wavenumber/cm^{-1}		
Obs.	Calc.	Assignment
2 080	2 079·53	(2)
2 072·5	2 072·02	(5)
2 065·5	2 065·94	(4)
2 063·5	2 064·02	(7)
2 056	2 055·99	(8)
1 996·3 1 994·2 } 1 995·3 [a]	1 995·27	(1), (3), (6)
1 988·5	1 988·28	(1)
1 984	1 983·68	(3)
1 974·7	1 974·27	(7)
1 973·5 1 973·0 } 1 973·3 [a]	1 973·4	(1), (2), (4)
1 961·2	1 961·28	(5)
1 951	1 950·79	(4), (8), (9)
1 945	1 945·47	(7)
1 939·4	1 939·74	(3)
1 930 1 929·3 } 1 929·7 [a]	1 929·42	(6), (7), (9)

Standard deviation 0·33 cm^{-1}

[a] Average wavenumbers of split bands were entered (see text). Force constants obtained when split bands were omitted were $f_1 = 16{\cdot}5546$, $f_2 = 16{\cdot}1468$, $f_{11} = 0{\cdot}4790$, $f_{12} = 0{\cdot}4049$, and $f_{22} = 0{\cdot}4275$ mdyn Å^{-1}.

TABLE 3

Observed and calculated wavenumbers of [Fe(CO)$_4$] with ^{13}CO enrichment in a methane matrix at 20 K. (See Figure 2 for numbering of molecules.) Force constants $f_1 = 16{\cdot}516$, $f_2 = 16{\cdot}080$, $f_{11} = 0{\cdot}481$, $f_{12} = 0{\cdot}414$, and $f_{22} = 0{\cdot}466$ mdyn Å^{-1}

Wavenumber/cm^{-1}		
Calc.	Obs.	Assignment
1 993·0 1 991·6 } 1·992·3 [a]	1 992·81	(1), (3), (6)
1 985	1 985·24	(1)
1 971·5	1 971·3	(7)
1 966·5	1 966·48	(1), (2), (4)
1 958·5	1 957·81	(5)
1 949·8 1 948·2 } 1 949·0 [a]	1 948·39	(4), (8), (9)
1 941	1 940·99	(9)
1 932·8	1 932·16	(5)
1 921·9	1 922·64	(6), (7), (9)

Standard deviation 0·51 cm^{-1}

No high-frequency bands could be measured because the bands of [Fe(CO)$_4$Q] which were more intense obscured the region 2 090—2 040 cm^{-1}.

[a] Average wavenumbers of split bands were entered in the refinement.

---

* In Figure 3(*a*) there are more bands than the two ($A_2'' + E'$) expected for D_{3h} symmetry. These ' extra ' bands are due to different sites in the matrix and have been extensively discussed previously.[1]

The C–O stretching bands of (X) are very close in frequency to those of [Fe(CO)$_4$] in a CO matrix and the u.v.–visible spectrum of (X) had an absorption at almost exactly the same wavelength ($\lambda_{\text{max.}}$ 325 nm) as [Fe(CO)$_4$] in an SF$_6$ matrix.[1] The C–O stretching bands of (Y) are similar in position and intensity to [Fe(CO)$_4$PH$_3$] (axial PH$_3$) isolated in an argon matrix.[9]

These observations suggest that (X) = [Fe(CO)$_4$] and (Y) = [Fe(CO)$_4$(N$_2$)] (axial N$_2$). Spectra obtained on photolysis of [Fe(^{12}CO)$_{5-x}$(^{13}CO)$_x$] in nitrogen were consistent with this interpretation, but matrix splittings of the bands of the ^{12}CO compounds are so large (Figure 3) as to make detailed analysis pointless. However, the identities of (X) and (Y) were confirmed by photolysis of [Fe(CO)$_5$] in argon doped with 5% nitrogen.

TABLE 4

Relative intensities ($\leqslant\pm10\%$) of bands of [Fe(CO)$_4$] in different matrices and relevant bond angles (see text and Appendix)

Molecule	[Fe(CO)$_4$]			[Fe(CO)$_4$Q]
Matrix	SF$_6$ [a]	Ar	CH$_4$	CH$_4$
A_1	0·01	0·01	0·01	0·2
A_1	1	1	1	1 [b]
B_1	2·7	3·3 [b]	3·8 [b]	3·5 [b]
B_2	1·7	2·2 [b]	2·1 [b]	4·5 [b]

	Bond angles (°) [c] Angle [(1), (2)]	Bond angles (°) [c] Angle [(3), (4)]	Dipole-derivative ratio $\mu_1 : \mu_2$
[Fe(CO)$_4$]			
SF$_6$	135 ± 4	121 ± 5	0·84 ∓ 0·04
d	144 ± 4	114 ± 4	0·89 ∓ 0·04
Ar	139 ± 3	127 ± 3	0·85 ∓ 0·08
d	147 ± 2	120 ± 3	0·90 ∓ 0·1
CH$_4$	141 ± 3	127 ± 3	0·80 ∓ 0·1
d	150 ± 3	120 ± 3	0·84 ∓ 0·1
[Fe(CO)$_4$Q]			
CH$_4$	129 ± 1·5	146 ± 2	1·07 ∓ 0·07
d	173·5 ± 1	125 ± 2·5	1·28 ∓ 0·08

[a] Optical densities. [b] Total intensity of split bands. [c] See Figure 2. [d] A_1 Bands out of phase.

TABLE 5

Wavenumbers of species produced on photolysis of [Fe(CO)$_5$] in nitrogen-containing matrices at 20 K

(*a*) Pure nitrogen matrix (Figure 3)

(X)	(Y)	
	2 251·9	vvw ν(N=N)
	2 249·9	
1 997 [a]	2 244·8	
1 987·4	2 090vw	
1 984	2 082.1w	
1 973·4	2 016·7m	
1 969·0	2 011·5m	
	1 990·8s [b]	
	1 984·5s [b]	
	1 975·3s [b]	

(*b*) Argon-containing 5% nitrogen (Figure 4)

(4)	(N)	
	2 249	ν(N=N)
	2 246	
1 990	2 083·2	
	2 014	
1 972	1 993	
	1 989	

[a] Overlapped with a band of [Fe(CO)$_5$]. [b] These bands showed additional fine structure.

(b) [Fe(CO)$_5$] *in argon with* 5% *nitrogen.* Figure 4 shows spectra obtained in this experiment which was, photochemically, identical to pure nitrogen. The crucial point is that this experiment confirms the initial formation of [Fe(CO)$_4$]. The bands labelled (4) in Figure 4 are at the same frequency [Table 5(*b*)] as those of [Fe(CO)$_4$] in argon, although the broadness of the bands in the doped matrix obscured the splittings observed in pure argon. The bands labelled (N) are very close in frequency to those of (Y) in the previous experiment. In a pure-argon matrix, the bands (N), which include bands in the N–N stretching region, are not formed. Thus the most plausible assignment is that (X) = (4) = [Fe(CO)$_4$] and (Y) = (N) = [Fe(CO)$_4$(N$_2$)]. A surprising

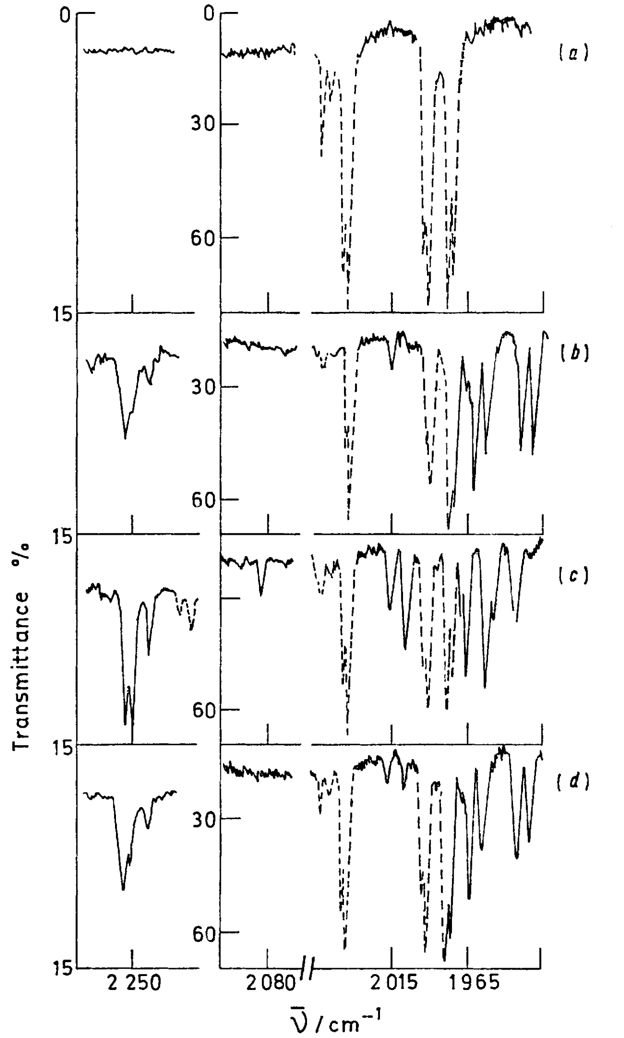


FIGURE 3 I.r. spectra of [Fe(CO)$_5$] in a nitrogen matrix (1 : 8 000) at 20 K: (*a*) after deposition; (*b*) 2 min photolysis with Hg arc; (*c*) 2 min exposure to unfiltered light from Nernst glower; (*d*) 5 min photolysis, $\lambda > 375$ nm; (— — — —), bands due to [Fe(CO)$_5$] and [Fe(CO)$_3$(N$_2$)$_x$] species. The ordinate scale is expanded in the region of 2 250 cm^{-1}; bands in this region were obtained in essentially identical experiments but with more sample deposited

---

[9] M. Poliakoff, Ph.D. Thesis, Cambridge University, 1972.

feature of these experiments is destruction of $[Fe(CO)_4(N_2)]$ by light ($\lambda > 375$ nm). Since photolysis of $[Fe(CO)_5]$ at these wavelengths produces no detectable $[Fe(CO)_4]$, the latter must be produced directly from $[Fe(CO)_4(N_2)]$. Thus it can be seen that formation of $[Fe(CO)_4(N_2)]$ from $[Fe(CO)_5]$ is a two-step process, both steps being reversible photochemically [equations (3) and (4)].

$$[Fe(CO)_5] \underset{\text{Nernst}}{\overset{\text{Hg arc}}{\rightleftharpoons}} [Fe(CO)_4] + CO \qquad (3)$$

$$[Fe(CO)_4] + N_2 \underset{\lambda\,>\,375\text{ nm}}{\overset{\text{Nernst}}{\rightleftharpoons}} [Fe(CO)_4(N_2)] \qquad (4)$$

The photochemical behaviour can be rationalized on the basis of the u.v.-visible absorptions of the compounds; $[Fe(CO)_5]$ has a maximum at *ca.* 285 nm, $[Fe(CO)_4]$ at *ca.* 325 nm, and although $[Fe(CO)_4(N_2)]$ shows no definite maximum below 300 nm, it appears yellow when in high concentration in the nitrogen matrix. Thus both $[Fe(CO)_4]$ and $[Fe(CO)_4(N_2)]$ absorb light from the Nernst glower ($\lambda > 330$ nm), but only $[Fe(CO)_4(N_2)]$ absorbs $\lambda > 375$ nm. The compounds $[Fe(CO)_4]$ and $[Fe(CO)_4(N_2)]$ are thus in photochemical equilibrium. When both compounds absorb light the major component is $[Fe(CO)_4(N_2)]$, but when only $[Fe(CO)_4(N_2)]$ absorbs, $[Fe(CO)_4]$ is the major product. The compound $[Fe(CO)_4(N_2)]$ also appears to be destroyed by u.v. light $\lambda > 300$ nm. This behaviour is reminiscent of the $[Cr(CO)_6]$–$[Cr(CO)_5]$ photochemical equilibrium.[10] There has been argument as to whether such addition reactions in the matrix $\{[Cr(CO)_5] + CO \longrightarrow [Cr(CO)_6]$ or $[Fe(CO)_4] + N_2 \longrightarrow [Fe(CO)_4(N_2)]\}$ are genuine photochemical reactions or merely thermal processes initiated by local melting of the matrix, caused by non-radiative decay of the excited states of the carbonyl molecule. However most authors agree that the thermal process is the more likely explanation.[10,11]

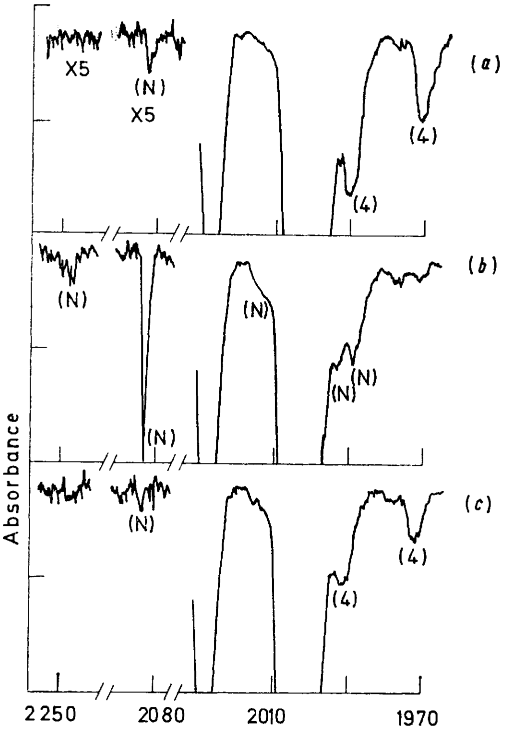


FIGURE 4 I.r. spectra of $[Fe(CO)_5]$ in an argon matrix containing 5% nitrogen at 20 K: (*a*) after 3 min photolysis with Hg arc; (*b*) 3 min photolysis with the unfiltered Nernst glower; (*c*) 5 min photolysis, $\lambda > 375$ nm; (4), bands due to $[Fe(CO)_4]$; and (N), bands due to $[Fe(CO)_4(N_2)]$. The scale is expanded by $\times 5$ in the high-frequency regions

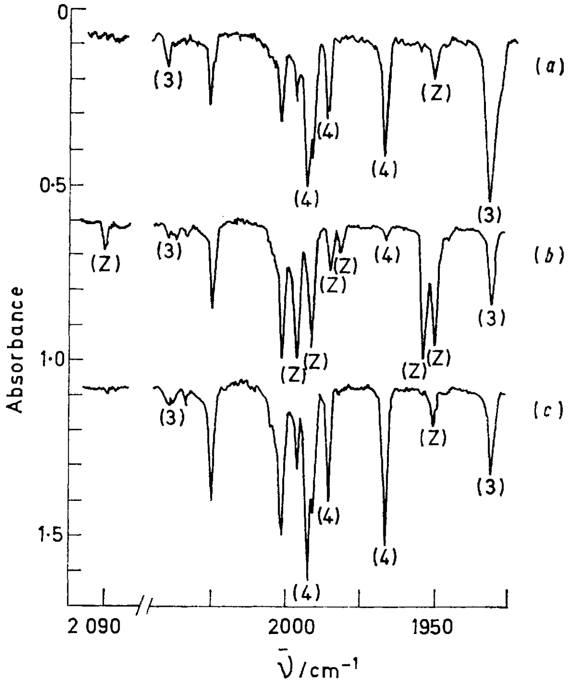


FIGURE 5 I.r. spectra of $[Fe(CO)_5]$ in a methane matrix (1 : 8 000) at 20 K: (*a*) after 4 min photolysis with Hg arc; (*b*) 2 min photolysis with the Nernst glower; (*c*) 2 min photolysis, $\lambda > 375$ nm; unlabelled bands due to $[Fe(CO)_5]$; (3), bands due to $[Fe(CO)_3]$; (4), bands due to $[Fe(CO)_4]$; and (Z), bands due to $[Fe(CO)_4Q]$ (see text). The ordinate is expanded ($\times 3$) in the region of 2 090 cm^{-1}

Reaction of $[Fe(CO)_4]$ *in Methane Matrices.*—Figure 5 shows spectra, recorded on photolysis of $[Fe(CO)_5]$ in a methane matrix. Bands labelled (4) and (3) are due to $[Fe(CO)_4]$ and $[Fe(CO)_3]$,[2] as confirmed by ^{13}CO enrichment. Studies of relative intensities of the bands show that all bands marked (Z) belong to the same compound, which appears to occupy two different matrix sites (see Appendix). The results in Figure 5 can be summarized by equation (5). The photochemical balance is such that

$$\begin{tikzcd}
{[Fe(CO)_5]} \arrow[r, shift left, "\text{Hg arc}"] & {[Fe(CO)_4]} \arrow[l, shift left, "\text{Nernst}"] \arrow[r, shift left, "\text{Hg arc}"] \arrow[d, shift left, "\text{Nernst}"] & {[Fe(CO)_3]} \arrow[l, shift left, "\text{Nernst}"] \qquad (5) \\
 & (Z) \arrow[u, shift left, "\lambda > 375\text{ nm}"] &
\end{tikzcd}$$

---

[10] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

[11] M. J. Boylan, P. S. Braterman, and A. Fullarton, *J. Organometallic Chem.*, 1971, **31**, C29.

the Nernst glower increases the intensity of the [Fe(CO)$_5$] bands, approximately halves the amount of [Fe(CO)$_3$], destroys the [Fe(CO)$_4$], and produces (Z). Photolysis with light ($\lambda > 375$ nm) destroys (Z), regenerating [Fe(CO)$_4$] with intensity greater than that produced by the original photolysis of [Fe(CO)$_5$] with the Hg arc [Figures 5(*a*) and 5(*c*)]. Thus the sequence Hg arc, Nernst glower, $\lambda > 375$ nm produces a considerable amount of [Fe(CO)$_4$] and a modest concentration of [Fe(CO)$_3$]. This behaviour is remarkably similar to that of [Fe(CO)$_4$] in a nitrogen matrix and suggests that (Z) may be [Fe(CO)$_4$Q] where Q is a new ligand. Table 7 gives ^{13}CO data for (Z) and shows that the wavenumbers can be fitted on the basis of a C_{2v} [Fe(CO)$_4$] group with force constants significantly different from [Fe(CO)$_4$].

TABLE 6

Wavenumbers observed on photolysis of [Fe(CO)$_5$] in CH$_4$ and Xe matrices (20 K) and hydrocarbon glass (77 K)

Assignment	CH$_4$	Xe	Glass
[Fe(CO)$_4$]	1 993·0 1 991·6 } vs	1 989vs	
	1 985m	1 983vs	
	1 966·5s	1 967s	
[Fe(CO)$_4$Q] [a]	(Z)	(W)	
	2 088vw	2 085vw	2 086vw
	1 995·6 [b] 1 991·0 } s	1 990s	1 990s [c]
	1 984·2 1 981·3 [b] } w	1 984 1 981 } w	1 980w [c]
	1 953 [b] 1 949·8 } vs	1 952 1 948 } vs	1 947vs [c]
[Fe(CO)$_3$] [d]	2 040·1w	2 036w	2 037w
	1 930·4s	1 927s	1 925s

[a] For identity of Q see text. [b] Bands which disappeared on annealing the matrix. [c] Sheline and his co-workers reported bands at 1 990s, 1 980w, and 1 946s cm^{-1}.[21] [d] For details of assignment see Ref. 2.

Bond angles calculated for (Z), using intensities of the ^{12}CO bands, are given in Table 4. The 'in-phase' solution (see Appendix) gives angles for (Z) almost identical to those of [Fe(CO)$_4$], but between the other pair of equivalent CO groups. Photochemical reaction would therefore represent an isomerization of [Fe(CO)$_4$], analogous to the 'umbrella' mode of NH$_3$. Such a reaction seems unlikely since, in the absence of a ligand, the only difference between the two types of CO group in [Fe(CO)$_4$] is the angles between them, and exchanging angles should merely exchange the labelling of the groups and the force constants. The 'out-of-phase' solution gives angles (173·5 and 125°) very close to those expected for a C_{2v} [Fe(CO)$_4$Q] molecule where the Q group replaces an equatorial CO group in [Fe(CO)$_5$].*

These results are similar to those of Black and Braterman who observed isomerization of [Mo(CO)$_4$PR$_3$], produced by photolysis of [Mo(CO)$_5$PR$_3$] in hydrocarbon glasses at 77 K.[12] Straightforward isomerization is unlikely to be the explanation of the behaviour of [Fe(CO)$_4$] in methane matrices for the following reason. In an argon matrix containing 5% methane essentially the same photochemistry was observed as in pure methane. [The (Z) bands were at 2 090, 1 998, 1 984, and 1 954 cm^{-1}.] Since these bands do not appear when [Fe(CO)$_5$] is photolysed in pure argon, methane must be actively required to produce [Fe(CO)$_4$Q]. The most plausible explanation is that the ligand Q is simply CH$_4$. Although the interaction between [Fe(CO)$_4$] and CH$_4$ would presumably be small, it might be sufficiently large to make a different structure of [Fe(CO)$_4$] energetically favourable. Unfortunately, we did not observe any i.r. bands, which could be assigned specifically to bound CH$_4$, partly because the matrix itself blotted out large regions of the spectrum, and partly because the bands would be expected to be very weak in comparison with CO stretching bands. It is unlikely that Q is H or CH$_3$

TABLE 7

Observed and calculated wavenumbers of [Fe(CO)$_4$Q] with ^{13}CO substitution in a methane matrix (for numbering of molecules see Figure 2)

Wavenumbers/cm^{-1}			
Obs.		Calc.[a]	Assignment
2 088		2 087·77	(1)
2 083		2 083·44	(3)
2 075		2 074·63	(2)
2 069·5		2 069·36	(5)
2 064		2 064·15	(7)
2 056·5		2 057·25	(4)
2 050		2 049·51	(8)
1 995·6 [b] 1 991·0 [c]	1 993·3 [a]	1 993·24	(1), (3), (6)
1 984·2 [c] 1 981·3 [b]	1 982·7	1 982·83	(1)
1 979·2		1 979·21	(5)
1 957·8		1 957·64	(5)
1 953·5 [c] 1 949·8 [b]	1 951·6 [a]	1 951·44	(1), (2), (4)
1 951·2 1 946·0	1 948·6 [a]	1 948·51	(4), (8), (9)
1 920·4		1 920·34	(3)
1 919		1 919·72	(5)
1 909·2 1 905·5	1 907·3 [a]	1 907·94	(6), (7), (9)

Force constants (mdyn Å^{-1}) (see Appendix)

	a	*d*	*e*	*f*	[Fe(CO)$_4$]
f_1	16·607	16·610	16·619	16·583	16·516
f_2	15·839	15·842	15·819	15·867	16·080
f_{11}	0·565	0·560	0·539	0·579	0·481
f_{12}	0·372	0·375	0·378	0·373	0·414
f_{22}	0·463	0·449	0·470	0·469	0·466
Standard deviation of bands (cm^{-1})	0·38	0·34	0·43	0·38	0·51

[a] Average wavenumbers were entered for split bands. [d] Omitting split bands. [e] Entering bands marked *b* for split bands. [f] Entering bands marked *c* for split bands.

---

* *Added at Proof:* Perutz and Turner have obtained i.r. spectra of C_{2v} [Mo(CO)$_4$] in a methane matrix.[15] For this molecule, the high frequency A_1 C–O stretching band is relatively much more intense than for [Fe(CO)$_4$] or [Fe(CO)$_4$(CH$_4$)]. Using the intensity pattern of the bands of the ^{13}CO enriched compound in this region, they have shown that, for [Mo(CO)$_4$], the out-of-phase solution is the correct one. It is highly probable therefore that it is also the correct solution for [Fe(CO)$_4$] and [Fe(CO)$_4$(CH$_4$)].

[12] J. D. Black and P. S. Braterman, *J. Organometallic Chem.*, 1973, **63**, C19.

since such ligands would be expected to produce a larger shift in frequency from $[Fe(CO)_4]$.[13]

It might be argued that Q is an impurity in the matrix. However, experiments with $[Fe(CO)_5]$ in argon matrices doped with N_2, CO, or O_2 suggest that to observe appreciable reaction with the doping molecule it must be present in at least 1% concentration in the argon. The stated purity of the methane was 99·95%, so it seems unlikely that such a high impurity concentration could have been present. Moreover doped matrices invariably produce broad bands in the carbonyl spectra, whereas in pure methane the $[Fe(CO)_4]$ and $[Fe(CO)_4Q]$ bands were very sharp (Figure 5). Thus all the experiments indicate that $[Fe(CO)_4]$ reacts with methane to form $[Fe(CO)_4(CH_4)]$.

Qualitatively similar behaviour was observed for $[Os(CO)_5]$ isolated in a methane matrix. Two new bands (1 955 and 1 972 cm^{-1}) were produced by photolysis of $[Os(CO)_5]$ (2 034, 1 989, and 1 987 cm^{-1}). Although the yield was rather poor, these bands were presumably due to $[Os(CO)_4]$. The bands slowly disappeared as the matrix was irradiated with the Nernst glower, and were replaced by 'new' bands (2 005m, 2 003s, 1 992, 1 962vs, and 1 959 cm^{-1}). The rate of photolysis was much slower than that of $[Fe(CO)_4]$ and the course of the reaction could be followed by running spectra during the photolysis. These bands indicate that $[Os(CO)_4]$ undergoes similar reactions to $[Fe(CO)_4]$ and were probably due to $[Os(CO)_4(CH_4)]$. No ^{13}CO enrichment was attempted with $[Os(CO)_5]$.

We previously reported that the colour of $[Cr(CO)_5]$ varies from one matrix to another, being purple in argon and red in methane.[14] Perutz and Turner have since shown that this colour change is due to a specific carbonyl-methane ground-state interaction,[15] which, presumably, is similar to the Mo–H–C bond recently reported by Cotton.[16] The experiments described here also indicate a ground-state interaction between methane and $[Fe(CO)_4]$. It is striking that $[Fe(CO)_4]$ can exist in both complexed and uncomplexed forms in the methane matrix, while it is impossible to obtain 'naked' $[Cr(CO)_5]$ under these conditions. This may be a consequence of differences in the u.v. absorption spectra of products or to a genuine difference in reactivity, which could be rationalized on the basis of a triplet ground state of $[Fe(CO)_4]$ and singlet $[Cr(CO)_5]$.

The absence of any i.r. bands assignable to bound CH_4 makes it difficult to propose a detailed bonding scheme for $[Fe(CO)_4(CH_4)]$. However, it is surprising that CH_4 should occupy an equatorial position rather than an axial one, which is normal for poor π-acceptor ligands (*e.g.* NH_3, MeCN, *etc.*). A tentative explanation of this is that interaction with CH_4 stabilizes the singlet state of $[Fe(CO)_4]$, and that the reactions described represent triplet to singlet conversion. This hypothesis could be verified by magnetic measurements.

Although flash-photolysis experiments suggest that, in solution, $[Fe(CO)_4]$ is far more reactive than $[Cr(CO)_5]$,[17] the reactions in the methane matrix indicate the opposite conclusion. However, the reaction rates in solution could be explained if $[Cr(CO)_5]$ were *more reactive* than $[Fe(CO)_4]$ towards the hydrocarbon solvent. Solutions would then contain totally complexed $[Cr(CO)_5]$ and only partially complexed $[Fe(CO)_4]$, making $[Fe(CO)_4]$ apparently more reactive towards other species in the solution. There is some experimental evidence to support this explanation. Perutz and Turner have shown that in a matrix $[Cr(CO)_5]$ interacts less strongly with fluorocarbons than hydrocarbons,[15] and preliminary flash-photolysis results of Kelly and Koerner von Gustorf indicate that $[Cr(CO)_5]$ is far more reactive in fluorinated solvents than in cyclohexane solution.[18] There are also some kinetic data which suggest that $[Fe(CO)_4]$ may be present in solution in two different forms.[19]

Reactions of $[Fe(CO)_4]$ *in Xenon and Krypton Matrices.*—The photochemical behaviour of $[Fe(CO)_4]$ in xenon (1 : 4 000) was very similar to that in methane, although the photolysis was rather less efficient due to the 'snowy' matrix. The results can be summarized in equation (6).

$$\begin{tikzcd}
{[Fe(CO)_5]} \arrow[r, shift left, "\text{Hg arc}"] & {[Fe(CO)_4]} \arrow[l, shift left, "\text{Nernst}"] \arrow[r, shift left, "\text{Hg arc}"] \arrow[d, shift left, "\text{Nernst}"] & {[Fe(CO)_3]} \arrow[l, shift left, "\text{Nernst}"] & (6) \\
& (W) \arrow[u, shift left, "\lambda > 375\text{ nm}"] & &
\end{tikzcd}$$

Wavenumbers for $[Fe(CO)_4]$, $[Fe(CO)_3]$, and (W) are given in Table 6. The bands assigned to (W) always increased and decreased with the same intensity ratio. Although no ^{13}CO experiments were done, comparison of the wavenumbers and photochemistry of (W) and $[Fe(CO)_4Q]$ strongly suggests that (W) is $[Fe(CO)_4Xe]$. Formation of the latter is not altogether surprising since it is isoelectronic with the well established anion $[Fe(CO)_4I]^-$,[20] and the nobility of the noble gases is considerably tarnished.

On photolysis of $[Fe(CO)_5]$ in a krypton matrix (1 : 8 000) a weak band was observed at 1 948 cm^{-1}, in addition to those of $[Fe(CO)_4]$ and $[Fe(CO)_3]$. This band disappeared on Nernst-glower irradiation at the same rate as $[Fe(CO)_4]$ and was *possibly* due to a very unstable compound $[Fe(CO)_4Kr]$. These observations mean that there is no photochemical way of distinguishing between the bands of '$[Fe(CO)_4Kr]$' and $[Fe(CO)_4]$, making ^{13}CO-substitution experiments almost impossible to interpret.

---

[13] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, 1966.

[14] M. A. Graham, R. N. Perutz, M Poliakoff, and J. J. Turner, *J. Organometallic Chem.*, 1972, **34**, C34.

[15] R. N. Perutz and J. J. Turner, unpublished work.

[16] F. A. Cotton, T. LaCour, and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754.

[17] N. Harritt, J. M. Kelly, and E. A. Koerner von Gustorf, personal communication.

[18] J. M. Kelly and E. A. Koerner von Gustorf, unpublished work.

[19] G. Cardaci, *Inorg. Chem.*, 1974, **13**, 368.

[20] E. W. Abel, I. S. Butler, and C. R. Jenkins, *J. Organometallic Chem.*, 1967, **8**, 382.

Photolysis of [Fe(CO)$_5$] *in Hydrocarbon Glasses at* 77 K.—Some years ago Sheline and his co-workers described results of u.v. photolysis of [Fe(CO)$_5$] in a frozen glass (1 : 4, isopentane : methylcyclohexane) at 77 K.[21] We repeated their experiments and observed additional bands not previously reported. Table 6 compares the wavenumbers of bands produced in the glass, with those seen in methane and xenon matrices. It is clear that the bands reported by Sheline are closer in frequency to those of [Fe(CO)$_4$Q] than to [Fe(CO)$_4$] itself, suggesting that the compound formed by photolysis is [Fe(CO)$_4$(glass)]. Since the glass is, like methane, a hydrocarbon, it would be expected to form similar compounds. Prolonged u.v. photolysis produced two more bands (Table 6). Irradiation with the Nernst glower caused these bands to disappear rapidly, with accompanying growth in the [Fe(CO)$_4$(glass)] bands. These two bands are reasonably assigned to an [Fe(CO)$_3$] species in the glass.

In contrast to the behaviour of [Fe(CO)$_4$(CH$_4$)] and [Fe(CO)$_4$Xe] at 20 K, irradiation with $\lambda > 375$ nm did not remove the bands assigned to [Fe(CO)$_4$(glass)]. This is either because [Fe(CO)$_4$(glass)] is photochemically more stable than [Fe(CO)$_4$] or, perhaps more probably, because thermal reaction of [Fe(CO)$_4$] with hydrocarbons occurs more readily at 77 than at 20 K.* Unfortunately it was not possible, using our apparatus, to cool hydrocarbon glasses to 20 K to see if [Fe(CO)$_4$] itself could be isolated at this temperature. These experiments show that interaction between a carbonyl fragment and the hydrocarbon glass may well be significant at 77 K and care is required when comparing results of photolysis in glasses with those in rare-gas matrices. On the other hand, it could be argued that since most solution photochemistry takes place in hydrocarbon solvents such interactions with the glass or methane will produce more realistic models of photochemical intermediates in solution.

Reactions in Concentrated Matrices: Polymerization.—On melting the hydrocarbon glass, Sheline and his co-workers[21] observed a band at 1 834 cm^{-1} which they assigned to [Fe$_2$(CO)$_9$], perhaps produced by reaction of [Fe(CO)$_4$] {strictly [Fe(CO)$_4$(glass)]} with [Fe(CO)$_5$]; [Fe(CO)$_4$] is indeed thought to be an intermediate in photochemical formation of [Fe$_2$(CO)$_9$] and [Fe$_3$(CO)$_{12}$].[22] We showed elsewhere that photolysis of [Mo(CO)$_6$] in matrices at concentrations even as low as 1 in 1 000 can produce measurable quantities of polynuclear carbonyl complexes [Mo$_a$(CO)$_b$] in addition to much greater quantities of mononuclear fragments.[14]

Table 8 summarizes results of photolysis of [Fe(CO)$_5$] in methane (1 : 1 000). The data suggest that photolysis in a moderately concentrated matrix produces bands assignable to both [Fe$_2$(CO)$_8$][23] and [Fe$_3$(CO)$_{12}$].[24] We have previously shown that [Fe$_2$(CO)$_9$] is extremely photosensitive in low-temperature matrices, losing CO to produce [Fe$_2$(CO)$_8$], but when such matrices are annealed the reverse reaction to produce [Fe$_2$(CO)$_9$] occurs.[23] Table 8 shows that the new bands which appeared on annealing the concentrated matrix are reasonably assigned to [Fe$_2$(CO)$_9$]. These results are consistent with [Fe(CO)$_4$] being an intermediate in photochemical formation of polynuclear iron carbonyl compounds.

TABLE 8

Wavenumbers of bands produced on photolysis of [Fe(CO)$_5$] in concentrated methane matrices (1 : 1 000) at 20 K and assigned to polynuclear iron carbonyl compounds

After u.v. photolysis[a]	[Fe$_3$(CO)$_{12}$][b]	[Fe$_2$(CO)$_8$][b]
2 057s	2 058	2 058
2 053s[c]	2 053	
2 042vs		2 042—2 040
2 037s	2 036	2 034
2 022s		
d		
1 867w	1 871—1 862	1 867
1 823br,m	1 833—1 828	1 826—1 820
After annealing to 35 K	[Fe$_2$(CO)$_9$][b]	
2 065s	2 066	
d		
1 845m	1 855—1 845	

[a] The matrix appeared faintly green and [Fe$_3$(CO)$_{12}$] itself is a dark green compound. [b] Argon and nitrogen matrices of [Fe$_3$(CO)$_{12}$] (ref. 24) and [Fe$_2$(CO)$_{8\text{ and }9}$] (ref. 23). Only appropriate bands have been listed. [c] A broad band was observed at this wavenumber in hydrocarbon glasses containing high concentrations of [Fe(CO)$_5$]. [d] The region 2 040—1 930 cm^{-1} was severely complicated by exceedingly intense bands of [Fe(CO)$_x$] species.

CONCLUSION

These experiments indicate that in most matrices [Fe(CO)$_4$] has a C_{2v} structure with approximate bond angles of 145 and 120°, which may well represent the structure of the 'free' molecule. We have already shown that [Fe(CO)$_3$] has a pyramidal C_{3v} structure, and this, together with the distortion of [Fe(CO)$_4$], throws considerable doubt on the theory that carbonyl fragments always adopt the most symmetrical structure. The differences between the photochemical behaviour of matrix-isolated [Fe(CO)$_5$] and that of other metal carbonyl compounds is due, at least in part, to the properties of [Fe(CO)$_4$]. U.v. absorption bands of this fragment make it possible to observe photochemical reactions which in other carbonyls are prevented by overlapping bands. Nevertheless, [Fe(CO)$_4$] appears to be extremely reactive. More specifically, we have shown in this paper an apparently significant interaction

---

* *Added in Proof:* Spectra obtained independently (J. D. Black and P. S. Braterman, personal communication) show a band at 1 961 cm^{-1}, after photolysis ($\lambda > 290$ nm) of [Fe(CO)$_5$] in an isopentane–methylcyclohexane glass at 77 K. This band may well be due to uncomplexed [Fe(CO)$_4$].

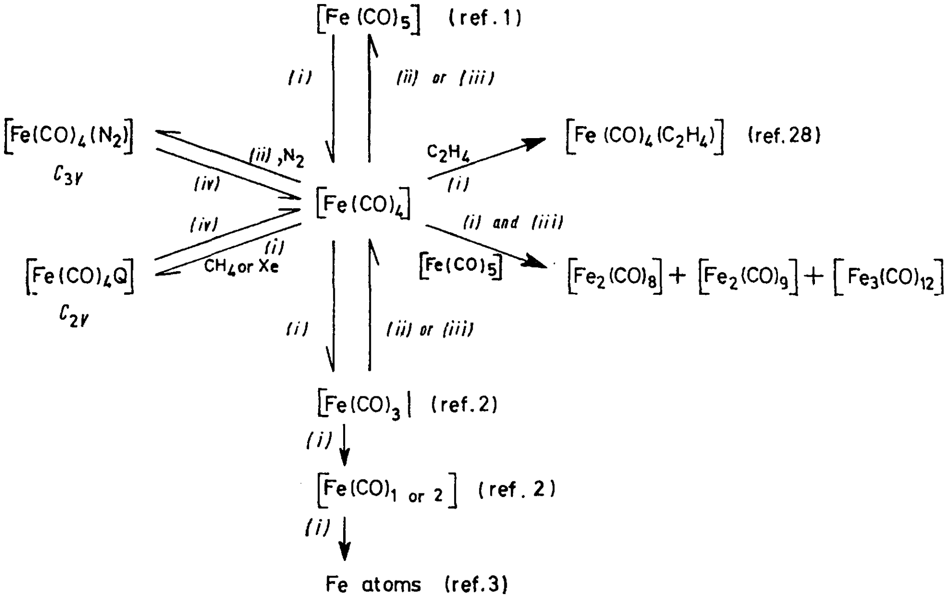
[21] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1962, **84**, 3589; 1963, **85**, 1013.

[22] E. Koerner von Gustorf and F.-W. Grevels, personal communcation.

[23] M. Poliakoff and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2403.

[24] M. Poliakoff and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 654.

between [$Fe(CO)_4$] and CH_4, Xe, or hydrocarbon molecules. This suggests that interactions between carbonyl fragments and solvent molecules should not necessarily be ignored when considering mechanisms of solution reactions. The principal reactions of matrix-isolated [$Fe(CO)_4$] can therefore be summarized.



(*i*) U.v. photolysis; (*ii*) ' Nernst-glower ' photolysis ($\lambda > 320$ nm); (*iii*) annealing matrix; and (*iv*) $\lambda > 375$ nm.

EXPERIMENTAL

All experiments were carried out with an AC-3L Cryotip Joule–Thomson liquifier, or CS-202 Displex closed-cycle helium refrigerator, both manufactured by Air Products, which have been described elsewhere.[3,23] All matrix i.r. spectra were recorded using a modified Grubb–Parsons Spectromajor spectrometer [23] calibrated with CO_2, DCl, and DBr. Wavenumber reproducibility, as estimated from spectra of DCl, was $\pm 0{\cdot}2$ cm^{-1}. The Spectromajor resolution was better than 0·5 cm^{-1} (*i.e.* it resolved the $D^{79}Br$–$D^{81}Br$ rotational doublets at *ca.* 1 900 cm^{-1}).

Hydrocarbon glasses were prepared according to ref. 9 using purified solvents, and their i.r. spectra were recorded on a Perkin-Elmer 257 spectrometer calibrated with DCl. U.v. spectra were recorded using a Perkin-Elmer 356 spectrometer.[3] All matrices were deposited using the pulsed technique,[25] except SF_6 which was ' sprayed on ' slowly. All matrix gases were ' Grade X ' (B.O.C.) except for SF_6 (Cambrian Gases) and were used without further purification. The compound [$Fe(CO)_5$] was commercial grade, redistilled. ^{13}CO Enrichment was achieved by gas-phase photolysis [3] of [$Fe(CO)_5$] in the presence of 90% ^{13}CO (Prochem) using the method of Crichton and Rest.[26] Initially we believed that the isotopically substituted molecules produced in this way were not statistically scrambled,[2] but further analysis of the spectra showed the scrambling to have been very good. The compound [$Os(CO)_5$] was prepared by high-pressure reaction of CO and OsO_4 in the absence of solvent.[27]

The u.v. photolysis source was a Phillips HPK 125 medium-pressure mercury arc, with a 4 cm quartz filter filled with deionized water. Light ($\lambda > 375$ nm) was obtained by using a Balzer ' Calflex C ' filter. Visible light was filtered from the Nernst-glower beam using a polished germanium disc (OCL1 Coatings Ltd.). All calculations were made on a Hewlett–Packard 2000E computer.

APPENDIX

Assignment of [$Fe(CO)_4$] *Bands in* SF_6 *Matrices*.—A C_{3v} tetracarbonyl compound should show three bands ($2A_1 + E$) and the spectrum of [$Fe(^{12}CO)_4$] was originally assigned: A_1 *ca.* 2 090 (too weak to see); E 1 999·1, and A_1 1 994·1 (split by matrix); and A_1 1 974·3. Although a C_{3v} carbonyl compound has four C–O force constants (two stretching and two interaction) it is possible, by guessing a frequency for the invisible A_1 band and using Bor's force-constant approximations for [$Fe(CO)_4L$] compounds,[29] to predict frequencies for ^{13}CO isotopically substituted [$Fe(CO)_4$]. However, the agreement with observed frequencies was not good enough to make a detailed assignment of the bands, nor did the predicted intensities agree with experiment. The spectrum in Figure 1(*c*) was calculated with force constants $f_{\text{axial}} = 16{\cdot}40$, $f_{\text{radial}} = 16{\cdot}36$, $f_{a,r} = 0{\cdot}52$, and $f_{r,r} = 0{\cdot}305$ mdyn Å^{-1}, corresponding to $\cos\beta = 0{\cdot}3$ (see ref. 29) which gave the best frequency prediction.* The bond-angle and dipole-derivative ratios were chosen to give band intensities close to the observed values (Table 4).

However a C_{2v} geometry (Figure 2) with five force constants (two stretching and three interaction) was successful. Approximate force constants were obtained by guessing a high-frequency A_1 band (2 090 cm^{-1}) and using the approximation $f_{11} = f_{22}$. {The conventional Cotton–Kraihanzel approximation is $f_{11} = f_{11} = 2f_{22}$, but the force constants of

---

* 1 mdyn Å^{-1} = 100 N m^{-1}.

[25] M. M. Rochkind, *Spectrochim Acta.*, 1971, **A27**, 547; R. N. Perutz and J. J. Turner, *J.C.S. Faraday II*, 1973, **69**, 452.

[26] O. Crichton and A. J. Rest, *Inorg. Nuclear Chem. Letters*, 1972, **9**, 391.

[27] F. Calderazzo and F. L'Eplatenier, *Inorg. Chem.*, 1967, **6**, 1220.

[28] M. J. Newlands and J. F. Ogilvie, *Canad. J. Chem.*, 1971, **49**, 343.

[29] G. Bor, *Inorg. Chim. Acta*, 1967, **1**, 81.

cis-$[Fe(CO)_4I_2]$ [30] suggested that in the present case $f_{11} = f_{22}$ would be more appropriate.} The bands were assigned: (2 090 A_1); 1 994·1 B_1; 1 999·1 A_1; and 1 974·3 B_2.

Reversing the assignment of B_1 and B_2 merely exchanged the labels '1' and '2' on the force constants. These approximate force constants enabled bands in the spectrum of ^{13}CO-enriched $[Fe(CO)_4]$ to be assigned to one or other of the nine substituted molecules (Figure 2). These wavenumbers were then entered in a least-squares refinement of the force constants, which minimized the square of the error between observed and calculated wavenumbers.[15] Each wavenumber was only entered once even though it may have been assigned to more than one molecule. The full results are shown in Table 1. Errors are larger for bands in the region 2 090—2 040 cm^{-1} than for those at lower frequencies, because the low intensity of these bands made accurate wavenumber measurement more difficult. (The force constants have been quoted to more significant figures than strictly justified by the data to enable others to repeat our calculations.)

Treatment of Split Bands.—The bands of $[Fe(^{12}CO)_4]$ in argon and methane matrices, and $[Fe(^{12}CO)_4(CH_4)]$, showed splittings due to 'matrix effects'. Surprisingly, bands of the partially ^{13}CO-substituted molecules were much less split and the high-frequency bands (2 090—2 040 cm^{-1}) were not split at all. The splittings were largest for $[Fe(^{12}CO)_4(CH_4)]$ where annealing experiments suggested that the splittings were due to different matrix sites. For this molecule, three different approximations were made in the force-constant refinement: first, average wavenumbers of the split bands were entered; secondly, the split bands were totally omitted; and thirdly, bands were assigned, on the basis of the annealing experiments, to two 'different' unsubstituted molecules which were refined separately. Superposition of these two spectra reproduced the observed band pattern quite closely. The results of these calculations are shown in Table 7 and it can be seen that all three approximations give similar force constants. This implies that the exact wavenumbers of the split bands are exceedingly sensitive to the values of the force constants, while those of the unsplit bands are much less sensitive. Thus considerable uncertainty (*ca.* 2 cm^{-1}) in the positions of the split bands will only have a small effect on the accuracy of the force-constant calculation.

Calculation of Bond Angles.—It has been shown that an estimate of the bond angles of metal carbonyl compounds can be made from the intensities of the CO absorption bands.[31] For $[Fe(CO)_4]$ one can measure the intensities of three of the bands and in addition one can estimate that the high-frequency A_1 band $\leqslant 1/100$ of the intensity of the low-frequency A_1 band. For $[Fe(CO)_4(CH_4)]$ all four intensities could be measured. Since the exact concentration of $[Fe(CO)_4]$ was not known, the intensities are relative rather than absolute and the three intensity ratios allow only three molecular parameters to be calculated. In these circumstances we chose the two bond angles and the ratio of the MC–O group dipole moment derivatives.

If the intensities of the i.r. bands are I'_{A_1}, I_{A_1} (low frequency), I_{B_1}, and I_{B_2}, the intensity ratios can be defined as $I_{A_1}/I_{B_1} = x^2$, $I_{A_1}/I_{B_2} = y^2$, and $I_{A_1}/I'_{A_1} = z^2$. Then, if the normal co-ordinate of the low-frequency A_1 mode is written as in equation (A.1), the bond angles are

$$Q_{A_1} = (a/2)(r_1 + r_2) - (b/2)(r_3 + r_4) \qquad (A.1)$$

given by (A.2) and (A.3) where θ_1 is the angle between

$$\tan(\theta_1/2) = (za^2 + zb^2)/2^{\frac{1}{2}}(za + b)x \qquad (A.2)$$

$$\tan(\theta_2/2) = (za^2 + zb^2)/2^{\frac{1}{2}}(zb - a)y \qquad (A.3)$$

groups (1) and (2) and θ_2 the angle between (3) and (4). The ratio of the dipole moment derivatives of groups (1) and (2), μ_1, and groups (3) and (4), μ_2, is as in equation (A.4).

$$\frac{\mu_1}{\mu_2} = \frac{(za + b)\cos(\theta_2/2)}{(zb - a)\cos(\theta_1/2)} \qquad (A.4)$$

There are two possible solutions for the bond angles. The 'in-phase' solution takes the positive square root of z^2, and the 'out-of-phase' uses the negative value. Taking negative values for x or y does not produce new solutions but alters the sign of the bond angles; μ_1/μ_2 must always be positive. Since the eigenvectors $a/2$ and $b/2$ are dependent on the force field, the calculated bond angles will also be so dependent. Fortunately, using a ratio of 1 : 100 for the intensities of the A_1 bands of $[Fe(CO)_4]$, the 'in-' and 'out-of-phase' solutions (Table 4) are very close together and the angles lying between these two solutions can be shown to correspond to smaller ratios of the intensities of the two A_1 bands.

Relative intensities of i.r. bands were measured by weighing tracings of the bands, taken from absorbance spectra. Using several different measurements the average error for the ratio of intensities obtained in this way was ±10%; it must be stressed that this was the random error, and the results may be subject to substantial systematic errors. It will be noticed that the dipole-derivative ratio acts as an 'error sink' and quite large changes in relative intensities of the bands produce relatively small changes in bond angle. Errors were estimated by calculating bond angles for all possible combinations of the extreme values of the intensities of the bands. Details of the method of predicting intensities of ^{13}CO-substituted molecules [as in Figure 1(*b*)] using calculated bond angles will be given elsewhere.[15]

We thank the S.R.C. for support, Mr. P. A. Breeze, Dr. J. K. Burdett, and Mr. R. N. Perutz for their assistance with computing and permission to use results in advance of publication, Messrs. W. Bruce and P. Jackson for their collaboration on the hydrocarbon glass experiments, Professor E. W. Abel, Dr. P. S. Braterman, Dr. E. A. Koerner von Gustorf, Professor J. Lewis, and Dr. B. P. Straughan for their help, and Dr. M. J. Ware for a sample of $[Fe(CO)_4PH_3]$.

[4/397 *Received*, 10*th May*, 1974]

---

[30] I. S. Butler and H. K. Spendjian, *J. Organometallic Chem.*, 1969, **18**, 145.

[31] L. M. Haines and M. B. H. Stiddard, *Adv. Inorg. Chem. Radiochem*, 1969, **12**, 53.