MELDOLA MEDAL LECTURES*

II $Fe(CO)_4$

By M. Poliakoff
DEPARTMENT OF INORGANIC CHEMISTRY, THE UNIVERSITY OF NEWCASTLE UPON TYNE, NEWCASTLE UPON TYNE, NE1 7RU

> '*These Figures, although only approximate on account of the very small quantities of the substance . . . make it very probable that the iron compound is iron-tetracarbonyl,* $Fe(CO)_4$, *analogous to nickel-tetra-carbonyl,* $Ni(CO)_4$.'
>
> L. Mond and F. Quinke
> (*J. Chem. Soc.*, 1891, 604)

1 Introduction

The preparation of $[Fe(CO)_4]$ was first claimed eighty-seven years ago by Mond and Quinke. Although the compound was later shown to be $[Fe(CO)_5]$, $[Fe(CO)_4]$ has since been suggested as an important intermediate in photochemical and thermal substitution reactions of $[Fe(CO)_5]$ and its derivatives.[1] All attempts to detect its transient existence in solution or the gas phase have so far been unsuccessful. In particular, the work of the late E. A. Koener von Gustorf and his co-workers indicates that $[Fe(CO)_4]$, if implicated, is remarkably reactive in solution.[2] Their flash photolysis experiments on solutions of $[Fe(CO)_5]$ suggested that the lifetime of $[Fe(CO)_4]$ was less than the time scale of their apparatus, 1μs. $[Fe_3(CO)_{12}]$ was formed rapidly, $< 100\ \mu$s, *via* an unidentified intermediate, possibly $[Fe_2(CO)_8]$. On the other hand, flash photolysis of $Fe(CO)_5$ in the gas phase leads to the formation of Fe atoms.[3] In this lecture I describe the role of matrix isolation in the characterization of $[Fe(CO)_4]$ and show that, apart from its formula, it has little in common with $[Ni(CO)_4]$.

The technique of matrix isolation has been reviewed extensively elsewhere.[4] In the form discussed here, unstable species are prepared by photolysis of a stable molecule, trapped in a large excess of inert solid at low temperatures (*e.g.* solid Ar at 20K). The unstable fragments are usually sufficiently dilute in the

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* These lectures were delivered in April 1978 at the Annual Chemical Congress, University of Liverpool.

[1] M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.

[2] E. A. Koerner von Gustorf, N. Harritt, and J. M. Kelly, unpublished results.

[3] A. B. Callear and R. J. Oldman, *Nature*, 1966, **210**, 730; *Trans. Faraday Soc.*, 1967, **63**, 2888.

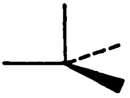
[4] See for example 'Vibrational Spectroscopy of Trapped Species', ed. H. E. Hallam, Wiley, London, 1973.

matrix to prevent any polymerization. Once prepared, the fragments can be studied spectroscopically. I.r. spectroscopy has been the most important technique in the case of $[Fe(CO)_4]$, although u.v.-visible spectroscopy and magnetic circular dichroism, m.c.d., have also played a significant part. In the following sections, I describe how $Fe(CO)_4$ was prepared and its structure determined, the use of m.c.d. to demonstrate its paramagnetism, and its photochemical reactions induced by u.v., visible, and i.r. radiation.

2 Preparation and Structure of $[Fe(CO)_4]$

The pioneering work of Sheline and co-workers demonstrated that u.v. photolysis of $[Fe(CO)_5]$ in frozen hydrocarbon solutions at 77K resulted in the formation of unidentified $[Fe(CO)_x]$ species.[5] Rest confirmed that similar results[6] could be obtained in solid Ar at 20K, and Newlands and Ogilvie found that $[Fe(CO)_4(C_2H_4)]$ and $[Fe(CO)_4(C_2H_2)]$ could be produced by u.v. irradiation of $[Fe(CO)_5]$ in Ar matrices containing ethylene or acetylene.[7] More extensive studies by Poliakoff and Turner showed that u.v. photolysis of $[Fe(CO)_5]$ in a large number of different matrices gave rise to molecular CO and an unstable $[Fe(CO)_4]$ species which had at least three i.r. bands in the 'C—O stretching' region of the spectrum.[8]

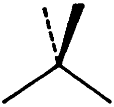
The presence of these three bands eliminates tetrahedral or square planar structures for $[Fe(CO)_4]$, as a T_d or D_{4h} molecule should have only one i.r. active C—O stretching mode. A number of other possible structures, which have more than one i.r. active C—O stretching mode are shown by structures (1)—(3). A recurrent problem in matrix isolation is caused by a series of different phenomena, usually called 'matrix splittings',[4] which often result in the presence of two or more closely spaced bands where only one is expected. Unfortunately, the presence of such 'matrix splittings' in the spectrum of $[Fe(CO)_4]$ meant that there was not enough information in the spectra to prove conclusively which of these



C_{3v}

ν_{CO} $(2a_1 + e)$

(1)



D_{2d}

$(b_2 + e)$

(2)

C_{2v}

$(2a_1 + b_1 + b_2)$

(3)

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[5] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1963, **84**, 3589; *ibid.*, 1964, **85**, 1013.

[6] A. J. Rest and J. J. Turner, Proceedings of the 4th International Conference on Organometallic Chemistry', Bristol, 1969.

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

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

three structures was correct. There was some circumstantial evidence that [$Fe(CO)_4$] had a C_{3v} structure (1), but more information was required.[8]

This additional information was provided by the use of ^{13}CO isotopic enrichment,[9] a technique which has been described in detail elsewhere.[10] The method is based on two observations; (i) that a mixture of [$M(^{12}CO)_{x-y}(^{13}CO)_y$] molecules will have more i.r. active bands than [$M(^{12}CO)_x$] itself, and (ii) that although two molecules, [$M^1(^{12}CO)_x$] and [$M^2(^{12}CO)_x$] having different structures, may have similar i.r. spectra in the C—O stretching region, the isotopic mixtures [$M^1(^{12}CO)_{x-y}(^{13}CO)_y$] and [$M^2(^{12}CO)_{x-y}$ $(^{13}CO)_y$] will have i.r. spectra that differ substantially both in the frequency and the relative intensities of the bands. The prediction of these frequencies and intensities is particularly simple for metal carbonyls as the C—O stretching vibrations can be treated as if they were totally uncoupled from the other vibrations in the molecule.[10] Initial predictions are made using approximate force constants calculated from the frequencies of the unenriched [$M(^{12}CO)_x$] molecule and bond angles and relative dipole moment derivatives which reproduce the correct band intensities of [$M(^{12}CO)_x$]. Subsequently force constants can be optimized using all of the observed [$M(^{12}CO)_{x-y}(^{13}CO)_y$] frequencies and an appropriate 'least-squares' method. Surprisingly, the spectra of partially substituted molecules, [$M(^{12}CO)_{x-y}$ $(^{13}CO)_y$], appear to be less affected by matrix splittings than those of the [$M(CO)_x$] molecules containing only one isotope.[9]

Figure 1(a) shows the i.r. spectrum of ^{13}CO-enriched [$Fe(CO)_4$], obtained by u.v. photolysis of ^{13}CO enriched [$Fe(CO)_5$] in an SF_6 matrix,[9] and the spectra predicted for a C_{2v} structure with bond angles 140° and 115° and a C_{3v} structure are shown in Figures 1(b) and 1(c), respectively. It is clear that the C_{2v} spectrum is in much closer agreement with the observed spectrum than is the C_{3v} spectrum. Similarly the fit for this C_{2v} structure is better than for a D_{2d} structure or a C_{2v} geometry with different bond angles. Since a constant linewidth has been assumed for all the bands in the predicted spectrum, there is not a perfect agreement between the intensities in the observed spectrum and that predicted for the C_{2v} structure. Nevertheless the agreement is sufficient to show that [$Fe(CO)_4$] has a C_{2v} geometry. The detailed assignment of bands has been confirmed using i.r. lasers,[11] (see below).

Bond angles are calculated from the relative intensities of i.r. bands, by assuming that the dipole moment change associated with the stretching of a particular C—O bond is collinear with that bond and by making the usual double harmonic approximation. The calculated bond angles vary slightly from one matrix to another; SF_6 (144°, 114°), Ar (147°, 120°), and CH_4 (150°, 120°) but the differences are within an experimental error of ± 5° caused by uncertainties in the measurement of band intensities.[9] Although there is the possibility of a

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[9] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

[10] J. K. Burdett, H. Dubost, M. Poliakoff, and J. J. Turner, in 'Advances in I.R. and Raman Spectroscopy', ed. R. J. H. Clark and R. Hester, Heyden, London, 1976.

[11] B. Davies, A. McNeish, M. Poliakoff, and J. J. Turner, *J. Amer. Chem. Soc.*, 1977, **99**, 7573.

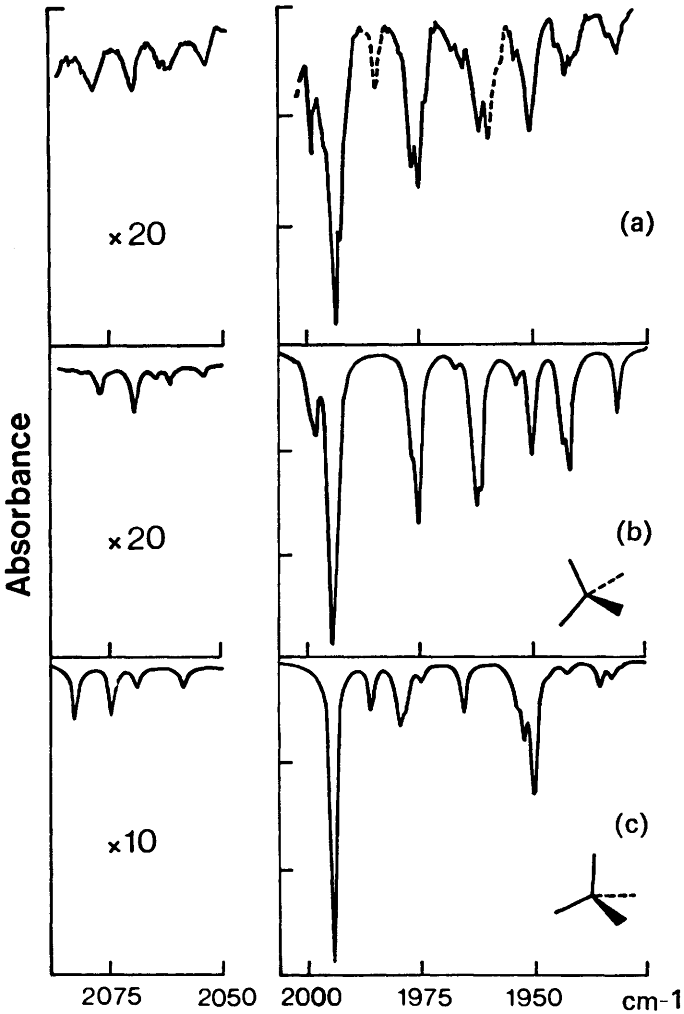

Figure 1 (*a*) *I.r. spectrum of* [$Fe(CO)_4$] *with* ^{13}CO *enrichment* (40%) *in an* SF_6 *matrix at* 35K. (– – – – –) *Bands due to unphotolysed* [$Fe(CO)_5$]; (*b*) *calculated spectrum for a* C_{2v} *geometry* (see 3) *with bond angles of* 140° *and* 115°; (*c*) *calculated spectrum for a* C_{3v} *geometry* (see 1) *with a bond angle of* 105° *between axial and basal groups. The calculated spectra have been redrawn from ref.* 9, *Figure* 1, *assuming Lorentzian lineshapes and a constant halfwidth of* 1.5 cm^{-1}

systematic error in the bond angles, it is clear that [$Fe(CO)_4$] is substantially distorted from a tetrahedral geometry.

Experiments in Ar matrices suggest that this distortion of [$Fe(CO)_4$] is not caused by interaction with the CO molecule ejected from the parent [$Fe(CO)_5$] molecule during photolysis.[8] If [$Fe(CO)_5$] is irradiated with u.v. light for a few seconds, the i.r. spectra show that, for the majority of [Fe(CO)$_4$] molecules, there is interaction with the photoejected CO. After prolonged u.v. irradiation the majority of [Fe(CO)$_4$] molecules no longer interact. Apart from subtle changes in the matrix splittings, there is no difference in the C—O stretching bands of the interacting and non-interacting [Fe(CO)$_4$] molecules, and hence their structures must be the same.

Since [Fe(CO)$_4$] has the same C_{2v} geometry in a wide range of different matrices, it is unlikely that this structure is imposed on the molecule by the matrix. There can be no direct evidence to show that [Fe(CO)$_4$] has the same structure in solution or the gas phase at normal temperatures, since it has only been detected in matrices. Nevertheless in those cases where unstable molecules, *e.g.* CH$_3$, have been detected both in a matrix and in the gas phase (see p. 507), the structures have been the same.

3 Magnetic Properties of [Fe(CO)$_4$]

The observed bond angles of [Fe(CO)$_4$] (~145°, ~120°) are close to those predicted by Burdett (135°, 110°) for the minimum energy geometry of [Fe(CO)$_4$] in a *triplet* ground state.[12] Figure 2 is an MO diagram which illustrates the basis of Burdett's argument. [Fe(CO)$_4$] is a d^8 system. Tetrahedral [Fe(CO)$_4$], which necessarily has a triplet ground state, is Jahn–Teller unstable, Figure 2(a). Distortion will occur to the minimum energy geometry, Figure 2(b) and, for singlet [Fe(CO)$_4$], the distortion would continue to a square planar geometry, Figure 2(c). If [Fe(CO)$_4$] were a triplet, further distortion of the C_{2v} geometry, Figure 2(b), would be prevented by the rapid rise in energy of the highest energy *d*-orbital. Since [Fe(CO)$_4$] has this C_{2v} geometry, it is predicted to be paramagnetic.

This paramagnetism has been established using m.c.d. spectroscopy, a technique which has recently been applied to matrix isolation through the pioneering studies of Thomson and Grinter.[14] An m.c.d. spectrum measures the difference in absorption of left- and right- circularly polarized light by a sample placed in a strong magnetic field. The value of m.c.d. for detecting paramagnetic species lies in the fact that a paramagnet has a temperature dependent m.c.d. spectrum, while diamagnetic compounds do not.

The m.c.d. spectrum of [Fe(CO)$_5$], isolated in an Ar matrix,[15] does not change over the temperature range 5—25 K. U.v. photolysis produces substantial changes in the spectrum, in particular the m.c.d. signal becomes temperature dependent with an absorption maximum corresponding to a u.v. absorption band ($\lambda_{\max}$ = 325 nm)[8] of [Fe(CO)$_4$]. Thus [Fe(CO)$_4$] is almost certainly paramagnetic. The presence of a broad far-red–near-i.r. electronic transition, ($\bar{\nu}_{\max}$ 13000 cm^{-1}) is also consistent with a paramagnetic ground state.[11] For example, paramagnetic complexes of the isoelectronic Ni^{2+} ion have

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

[13] J. K. Burdett, unpublished calculations.

[14] I. N. Douglas, R. Grinter, and A. J. Thomson, *Mol. Phys.*, 1974, **28**, 1377.

[15] T. J. Barton, R. Grinter, A. J. Thomson, B. Davies, and M. Poliakoff, *J.C.S. Chem. Comm.*, 1977, 841.

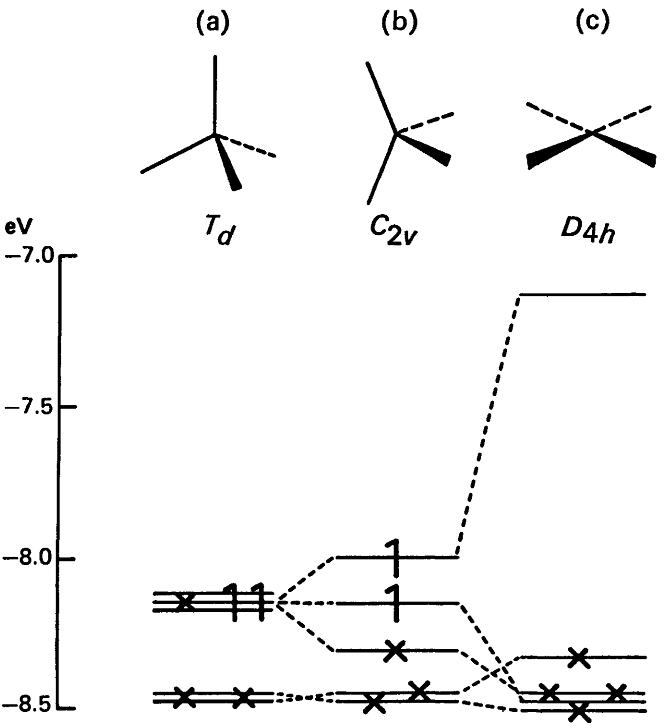

Figure 2 *The energy levels of the d orbitals of* [Fe(CO)$_4$] *in different geometries,* (*a*) *tetrahedral,* T_d; (*b*) C_{2v} *with bond angles of* 135° *and* 110°; *and* (*c*) *square planar,* D_{4h}. *The diagram is drawn to scale from the calculations,*[13] *summarized in ref.* 12

electronic transitions in the near-i.r., while diamagnetic Ni^{2+} complexes have no far-red–near-i.r. absorptions in this region.

[Fe(CO)$_4$] is therefore the first binary transition-metal carbonyl not to have a 'low spin' electronic ground state. It would clearly be interesting to know whether [Ru(CO)$_4$] and [Os(CO)$_4$] are similarly paramagnetic. No m.c.d. studies have been made on these compounds, but rather preliminary i.r. spectra suggest that [Os(CO)$_4$] is neither tetrahedral, nor square planar.[9] [Fe(CO)$_3$] (see below) is also predicted to be paramagnetic but unfortunately m.c.d. spectra are not yet available.

The paramagnetism of [Fe(CO)$_4$] could also explain many of its reactions in solution, for example rapid dimerization or insertion reactions,[16] similar to those of =CCl$_2$. Polymerization of [Fe(CO)$_4$] to form [Fe$_2$(CO)$_8$] and [Fe(CO)$_{12}$] can also be observed, when [Fe(CO)$_5$] is photolysed in concentrated matrices.[9]

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[16] C. S. Cundy, M. F. Lappert, J. Dubac, and P. Mazerolles, *J.C.S. Dalton*, 1976, 910.

4 U.v. Photochemistry—Dissociation

U.v. irradiation of $[Fe(CO_4)]$, produced photochemically from $[Fe(CO)_5]$, leads to further loss of CO and formation of $[Fe(CO)_3]$. ^{13}CO enrichment has been used to show that $[Fe(CO)_3]$ is a pyramidal C_{3v} molecule,[17] with a C—Fe—C bond angle of $\sim 108°$. The assignment of the bands has been described in detail elsewhere[10] and the theoretical reasons for this particular structure are discussed by Burdett in the preceding article (see p. 507). A most interesting aspect of this reaction is the difference in yield of $[Fe(CO)_3]$ in different matrices. Formation of $[Fe(CO)_3]$ is rapid in CH_4 or N_2, slow in Ar, and totally absent in SF_6. The explanation of these differences is unknown but it may well lie in the addition reactions of $Fe(CO)_4$ with CH_4 and N_2 matrices.

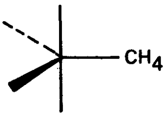
5 Near-I.R. Photochemistry—Addition Reactions

Photochemical addition reactions are found more frequently in matrices than in solution, merely because the photochemistry of co-ordinatively unsaturated molecules cannot be studied in solution. When $[Fe(CO)_4]$ is excited by near-i.r. radiation (13000—9000 cm^{-1}), the molecule undergoes a variety of addition reactions depending on the reactants available in the matrix.[9,11,*]

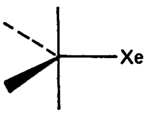
$$\text{Recombination } [Fe(CO)_4] + CO \xrightarrow{\text{near-i.r.}} [Fe(CO)_5] \qquad (1)$$

$$\text{Reaction } [Fe(CO)_4] + Q \xrightarrow[(Q\,=\,CH_4,\ Xe,\ N_2)]{\text{near-i.r.}} [Fe(CO)_4Q] \qquad (2)$$

The probable structures of the different $[Fe(CO)_4Q]$ species are shown in (4)—(6).



(4)



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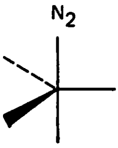

(6)

The geometry of the $Fe(CO)_4$ moiety in $[Fe(CO)_4CH_4]$ has been confirmed, using ^{13}CO isotopes,[9] to be C_{2v} with bond angles of 173.5° and 125°. Unfortunately no i.r. absorptions of co-ordinated CH_4 can be detected, because of the large excess of unbound CH_4 in the matrix. The most plausible modes of binding CH_4 to Fe are either a linear M—H—C bond similar to that found in the room temperature

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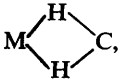
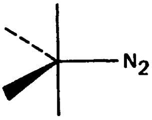
[*] These reactions were originally thought[9] to be caused by near-u.v. light corresponding to the 325 nm absorption of $[Fe(CO)_4]$. Later work has disproved this.[11] The near-i.r. radiation (13 000—9000 cm^{-1}) corresponds closely to the maximum intensity of the output from the source of an i.r. spectrometer. A filter, usually coated Germanium, is needed to remove radiation of this wavelength from the spectrometer beam to avoid $[Fe(CO)_4]$ being destroyed while a spectrum is run.[8]

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

crystal structures of Mo compounds[18] or a double H bridge,  analogous to the bonding[19] of BH_4^- in $[Mo(CO)_4BH_4]^-$. $[Fe(CO)_4(alkane)]$ complexes appear to be thermodynamically more stable than 'naked' $[Fe(CO)_4]$ as they are the only species detectable[9] after u.v. photolysis of $[Fe(CO)_5]$ in hydrocarbon glasses at 77K. The i.r. spectrum of $[Fe(CO)_4Xe]$ is so similar to that of $[Fe(CO)_4CH_4]$ that its structure is almost certainly the same. The compound is iso-electronic with the stable anion $[Fe(CO)_4I]^-$. $[Fe(CO)_4]$ does not react with Ar but recent work in Newcastle[20] suggests that it may react with Kr. Burdett has suggested[13] that the role of the CH_4 or Xe in these complexes is to stabilize the singlet state of $[Fe(CO)_4]$ but as yet no m.c.d. spectra are available to confirm this.

The structure of $[Fe(CO)_4N_2]$ has not been verified using ^{13}CO isotopes because the matrix splittings of the bands are too complex to make a detailed analysis possible.[9] By analogy with other $[M(CO)_xN_2]$ species, the N_2 group is almost certainly bonded end-on rather than sideways. Although the original experiments suggested a C_{3v} structure, both Burdett's MO calculations[13] and Timney's 'ligand effect' analysis[21] of the i.r. spectra predict a C_{2v} structure (7).



(7)

The electronic spectra of $[Fe(CO)_4]$ and '$[Fe(CO)_4Q]$' molecules are substantially different. $[Fe(CO)_4Q]$ species have bands in the region of 375 nm and no near-i.r. absorptions. $[Fe(CO)_4]$ can be regenerated from $[Fe(CO)_4Q]$ by photolysis with a filtered Hg arc, $\lambda > 375$ nm [reaction (3)]. The detailed mechanisms of all these processes are still unknown. However, sequential i.r. laser and near-i.r. irradiation (see below) suggests that the quantum yield for addition of CH_4 to $[Fe(CO)_4]$ in a CH_4 matrix is considerably higher than the quantum yield for addition of N_2 in an N_2 matrix.[22]

$$[Fe(CO)_5] \underset{\text{near-i.r.}}{\overset{\text{u.v.}}{\rightleftharpoons}} [Fe(CO)_4] \underset{\lambda\,>\,375\text{ nm}}{\overset{\text{near-i.r.}}{\rightleftharpoons}} [Fe(CO)_4Q] \qquad (3)$$

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

[19] S. W. Kirtley, M. A. Andrews, R. Bau, G. G. Grynkewich, T. J. Marks, D. L. Tipton, and B. R. Whitlesey, *J. Amer. Chem. Soc.*, 1977, **99**, 7154.

[20] K. P. Smith, unpublished results.

[21] J. A. Timney, *Inorg. Chem.*, submitted for publication.

[22] B. Davies, A. McNeish, M. Poliakoff, M. Tranquille, and J. J. Turner, *J.C.S. Chem. Comm.*, 1978, 36.

6 I.R. Laser Photochemistry

I.r. laser* irradiation at the frequency of a C—O stretching mode of $Fe(CO)_4$, ~ 1900 cm^{-1}, induces a variety of reactions, similar to those induced by near-i.r. radiation,[23] ~ 13000 cm^{-1} [reaction (4)]. When an isotopic $[Fe(^{12}CO)_{4-x}(^{13}CO)_x]$ mixture is used the difference between the i.r. laser and near-i.r. photochemistry becomes clear. With broad band near-i.r. radiation, all of the different $[Fe(^{12}CO)_{4-x}(^{13}CO)_x]$ species react. With the highly monochromatic i.r. laser, however, only the particular $[Fe(^{12}CO)_{4-x}(^{13}CO)_x]$ molecules, which have absorptions co-incident with the laser emission, undergo reaction and all the other $[Fe(^{12}CO)_{4-x}(^{13}CO)_x]$ molecules remain unaffected.[24] These laser-induced reactions involve the absorption of only a single photon of i.r. radiation by an individual molecule. This means that the activation energies for these processes must be < 1900 cm^{-1} or 23 kJ mol^{-1}.†

$$[Fe(CO)_4] + Q \xrightarrow[(Q\,=\,CO,\ Xe,\ CH_4)]{\text{i.r. laser } \nu_{CO}} [Fe(CO)_4Q] \qquad (4)$$

The most interesting laser-induced effects occur with $[Fe(CO)_4]$ produced in an Ar matrix by prolonged u.v. irradiation of $[Fe(CO)_5]$. Under these conditions the $[Fe(CO)_4]$ and photo-ejected CO molecules are too far apart in the matrix to recombine. I.r. laser irradiation promotes ligand exchange,[11] (Scheme 1)‡. In solution the two species (**7**) and (**8**) would be in rapid dynamic equilibrium but in the matrix at 20 K there is insufficient thermal energy for intramolecular rearrangement. Laser irradiation at the frequency of one of the C—O stretching absorption bands of (**7**) converts it into (**8**). Since molecules of (**8**) do not absorb at these frequencies, there is no reverse isomerization until the laser is retuned to coincide with the absorptions of (**8**). The high dilution of the matrix means that this ligand exchange must be intramolecular and the energy of a single i.r. photon, ~ 23 kJ mol^{-1}, is insufficient to cause the breaking of any Fe—CO bonds. A useful spin-off from this experiment is the ability to identify all of the C—O stretching bands belonging to a particular $[Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x]$ molecule. The results are in gratifying agreement with the original assignments.[9,11]

It is found that this intramolecular ligand exchange can also be induced by near-i.r. radiation,[11] Scheme 2. U.v. photolysis of $[Fe(^{12}C^{16}O)_{5-x}(^{13}C^{18}O)_x]$

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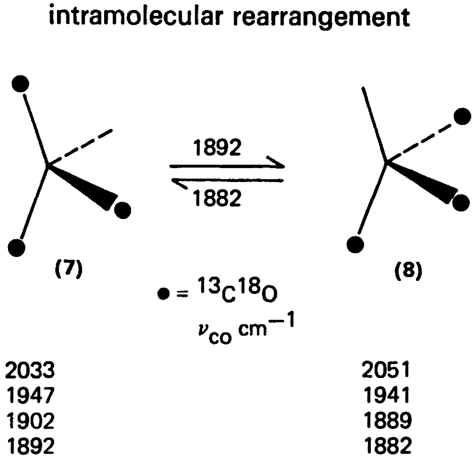
*These experiments used an Edinburgh Instruments c.w. CO laser.[11] This produces continuous, monochromatic radiation at one of a series of fixed frequencies, separated by ~4 cm^{-1}. The laser is tuned between these emission lines by a diffraction grating at one end of the laser cavity. Tuning is over the region 1950—1650 cm^{-1}. $^{13}C^{16}O$ or $^{13}C^{18}O$ enrichment of $[Fe(CO)_4]$ is required to bring the absorptions of $[Fe(CO)_4]$ into the tuning range of the laser.

†The activation energy for recombination with CO is probably extremely low as recombination takes place if the matrix is heated to only 40 K. The activation energy for reaction with CH_4 is presumably significantly higher because thermal reaction does not occur[9] up to 40 K.

‡ In Schemes 1–4 the numbers (in bold) of the isotopic isomers of $Fe(CO)_4$ correspond to those given in ref. 9.

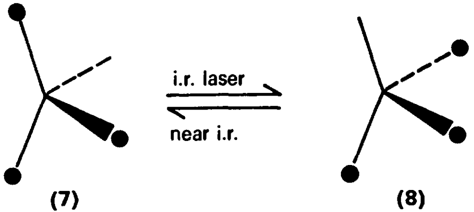
[23] B. Davies, A. McNeish, M. Poliakoff, M. Tranquille, and J. J. Turner, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 121.

[24] A. McNeish, M. Poliakoff, K. P. Smith, and J. J. Turner, *J.C.S. Chem. Comm.*, 1976, 859.



Scheme 1

necessarily produces equal quantities of (7) and (8). Since there are negligible isotopic shifts in the electronic transitions of [Fe(CO)$_4$], (7) and (8) will both absorb near-i.r. radiation and isomerize at the same rate. Thus the isomerization induced by near-i.r. radiation can only be detected after an i.r. laser has been used to alter the relative concentrations of (7) and (8).



Scheme 2

Burdett has provided a simple explanation of how electronic excitation of [Fe(CO)$_4$] could lead to intramolecular rearrangement.[11,13] The scheme is illustrated in Figure 3. Although the calculations are only approximate, they suggest that all $d \rightarrow d$ transitions of [Fe(CO)$_4$] should lie in the near-i.r. region of the spectrum. Absorption of near-i.r. radiation will produce electronically excited [Fe(CO)$_4$] still with a C_{2v} geometry, Figure 3(b).* This geometry would have a higher energy than the T_d geometry and so distortion would occur to this structure, which has all ligands equivalent, Figure 3(c). The T_d molecule is, in turn, unstable with respect to a C_{2v} geometry in the electronic ground state, and will distort, Figure 3(d).† This scheme is clearly a slight over-simplification since

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*Figure 3 has been drawn for one particular $d \rightarrow d$ transition, the same arguments can be applied to other transitions.

†Of course, the T_d structure could also distort back to Figure 3(a).

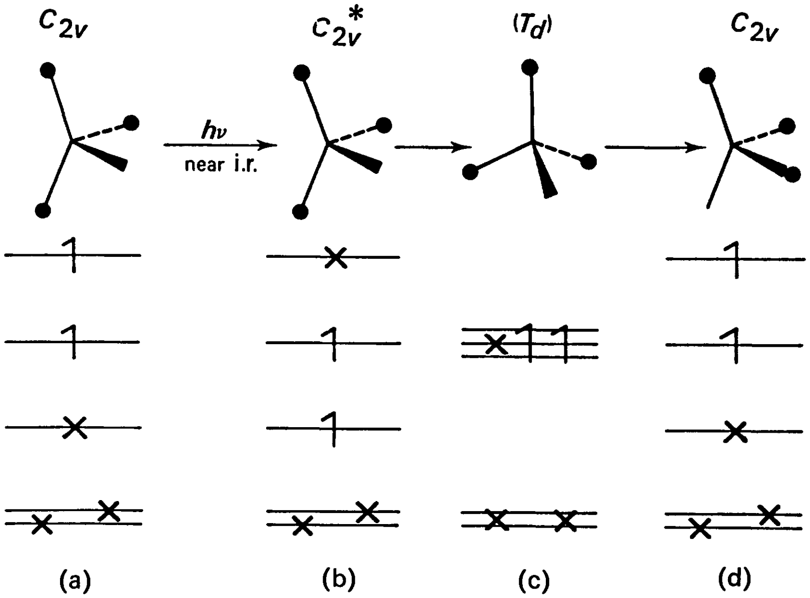

Figure 3 *Suggested pathway for electronic relaxation and intramolecular ligand exchange in* [Fe(CO)$_4$]. *The d-orbital energies*[14] *are as given in Figure* 2

the T_d molecule is Jahn–Teller unstable and must represent a local maximum on the potential energy surface. Nevertheless, this single mechanism provides a simple pathway for simultaneous electronic relaxation and intramolecular ligand exchange. Near-i.r. irradiation also promotes addition reactions (*q.v.*). It is probable that these reactions involve similar mechanisms to ligand exchange. Experiments suggest that reaction and rearrangement are competitive processes.[22]

The high selectivity of the i.r. laser induced isomerization of [Fe(CO)$_4$] allows us to make a detailed study of the permutational processes occurring during ligand exchange. This approach produces information analogous to that provided by dynamic n.m.r. techniques. The crucial experiment involves the interconversion of the three isomers of [Fe(^{12}C^{16}O)$_2$(^{13}C^{18}O)$_2$], (4), (5), and (6). There are two distinguishable isomerization pathways for these three isomers, as shown in Schemes 3 and 4. If, for a moment, the vacant co-ordination site of [Fe(CO)$_4$] is imagined to be a fifth ligand, then Scheme 3 corresponds to the *Berry Pseudo-rotation.* By default Scheme 4 is a *non-Berry Pseudo-rotation.* SF$_4$ which has the same symmetry as [Fe(CO)$_4$] has been shown, by means of d.n.m.r.,[25] to undergo thermal ligand exchange *via* the Berry pseudo-rotation, Scheme 3. The principal difference between Schemes 3 and 4 is that in Scheme 4, (10) isomerizes to (5), while in Scheme 3, (4) isomerizes to (6). The laser experiment illus-

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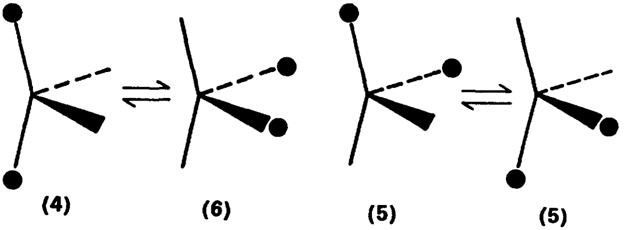
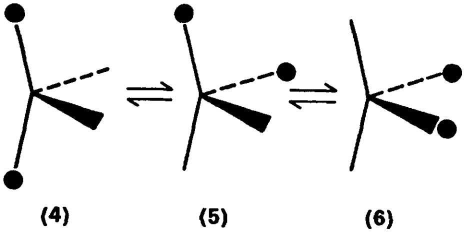
[25] W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muertterties, D. D. Traficante, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1975, **97**, 7023.


Berry Pseudo-rotation

Scheme 3


non-Berry Pseudo-rotation

Scheme 4

trated in Figure 4 distinguishes between these two possibilities. Laser irradiation of a band due to (**4**) causes an increase in the band due to (**5**) and no change in the band due to (**6**). The laser-induced ligand exchange in [$Fe(CO)_4$] is therefore the first known example of a non-Berry pseudo-rotation. Unfortunately it is not possible to extrapolate from a permutational mode to a precise mechanism. Nevertheless the results are inconsistent with C_{4v}, D_{4h}, D_{2d}, or T_d transition states, which would produce a Berry pseudo-rotation. The rearrangement is consistent with a C_s transition state or C_{3v} intermediate.[11] The difference between the rearrangement modes of [$Fe(CO)_4$] and SF_4 has been attributed to the energetic behaviour of the partially occupied metal *d*-orbitals during distortion of the [$Fe(CO)_4$] fragment.[11,13]

I.r. laser induced photochemistry has therefore revealed some very unusual properties of [$Fe(CO)_4$], which are unlikely to have been discovered by any other technique.

7 Conclusions

U.v. photolysis of matrix isolated [$Fe(CO)_5$] produces the reactive fragment [$Fe(CO)_4$] and molecular CO. A combination of i.r. spectroscopy and ^{13}CO enrichment has been used to show that [$Fe(CO)_4$] has a C_{2v} structure with bond angles of ~ 145° and ~ 120°. MO calculations predict that [$Fe(CO)_4$] should have a triplet ground state, and its paramagnetism has been confirmed using m.c.d. It is the first binary transition-metal carbonyl species which does not have a 'low spin' ground state. [$Fe(CO)_4$] loses CO on u.v. irradiation to form a pyramidal

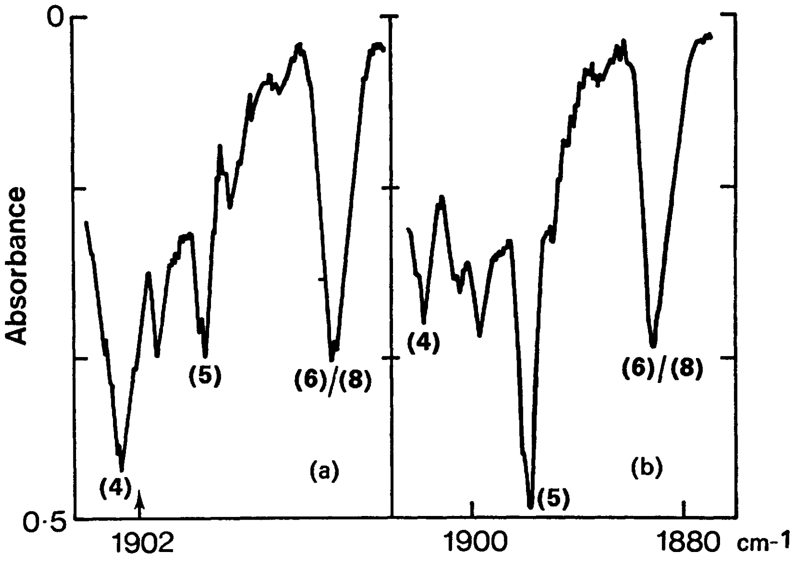


Figure 4 *I.r. spectra illustrating laser isomerization of isomer* (**4**) *of* [$Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$] *in an* Ar *matrix at* 20 K (see Schemes 2 and 4 for numbering of isomers)*:* (*a*) *before and* (*b*) *after* 25 min *i.r. laser irradiation at* 1902 cm^{-1}, *coincident with the band of* (**4**) (Reproduced by permission from *J. Amer. Chem. Soc.*, 1977, **99**, 7573.)

[$Fe(CO)_3$] fragment. The intuitively unexpected structures of [$Fe(CO)_3$] and [$Fe(CO)_4$] have provided valuable tests of theories for predicting the structures of transition-metal compounds.

[$Fe(CO)_4$] has a far-red–near-i.r. absorption band λ_{max} 770 nm due to $d \rightarrow d$ electronic transitions. Excitation of these transitions promotes addition reactions, most importantly with CH_4 to form [$Fe(CO)_4CH_4$]. This unusual complex has electronic and vibrational spectra which are significantly different from those of [$Fe(CO)_4$]. Although the exact nature of the $Fe \cdots CH_4$ bonding is still unclear, the strength of the interaction is sufficiently strong to produce substantial changes in the structure of the $Fe(CO)_4$ moiety. Similar addition reactions can be induced by irradiation of the C—O stretching modes of [$Fe(CO)_4$] using i.r. lasers.

I.r. lasers have also been used to promote intramolecular ligand exchange in [$Fe(CO)_4$], and to identify the permutational rearrangement mode involved. [$Fe(CO)_4$] is the first molecule known to undergo a so-called 'non-Berry pseudorotation', it is the first binary transition-metal carbonyl to have its rearrangement mode established, and it is the first time that such a mode has been identified without the use of dynamic n.m.r.

I thank the SRC for generous support and the Society of Maccabaeans for the award of the Meldola medal and prize. I am grateful to all my co-workers, particularly, Dr. R. N. Perutz, and my 'fellow medallist', Dr. J. K. Burdett, for their help and criticism and to Mr. R. Graham for his skill and ingenuity in building our apparatus. I am especially grateful to Professor J. J. Turner for all of the help, guidance, and encouragement that he has given to me throughout this work.