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# The Infrared Laser Induced Isomerization of Fe(CO)₄. The First Non-Berry Pseudorotation

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Abstract: A combination of matrix isolation and IR laser induced photochemistry has been used to identify the intramolecular ligand exchange process occurring in the highly reactive C_{2v} molecule Fe(CO)₄, which has a structure similar to SF₄. UV photolysis of Fe(CO)₅. ~40% enriched with $^{13}C^{18}O$, in an Ar matrix at 20 K generated a statistical mixture of the different isomers of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$. These isomers were distinguishable by their different IR absorption bands in the "C–O stretching" region. Irradiation of the matrix with a cw CO IR laser at a frequency corresponding to the absorption of one particular isomer of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ promoted the selective intramolecular rearrangement of this isomer, generating a nonstatistical distribution of $^{13}C^{18}O$. The permutational process occurring in this rearrangement could be identified directly from the interconversion of the three isomers of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$. The laser-induced ligand exchange in Fe(CO)₄ involves a non-Berry pseudorotation (permutational mode h_3^{ww}), and differs from the thermal rearrangement of SF₄, which involves the more familiar Berry pseudorotation (permutational mode h_4^{ww}). This difference can be rationalized using an angular overlap MO model. The photophysics of the laser rearrangement is briefly discussed. A broad asymmetric red/near-IR absorption, $\bar{\nu}_{max}$ 13 000 cm⁻¹, is reported for Fe(CO)₄. Irradiation with light, 13 000–9000 cm⁻¹, is shown to cause nonselective isomerization of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$. A possible mechanism is proposed for this near-IR isomerization.

Matrix isolation is a powerful method for studying intramolecular rearrangement processes.[1] The particular advantage of the technique is that molecules are held rigidly,[2] only rearranging when excited by either irradiating[1-3] or heating the matrix. In this paper we show how a combination of matrix isolation and IR laser induced photochemistry can be used to identify the rearrangement mode of the unstable C_{2v} molecule Fe(CO)₄.

The majority of selective IR laser induced reactions which have so far been reported occur in the gas phase. They involve individual molecules overcoming a high activation barrier by rapidly absorbing many low-energy photons, usually from a high-intensity (~10⁸ W/cm²) CO₂ laser beam. For example, the dissociation[4] of ³²SF₆ requires absorption of approximately 40 photons[5] at ~948 cm⁻¹. On the other hand, the energy barriers for reactions in low-temperature matrices are often relatively low and can be overcome by individual molecules absorbing only one IR photon. We recently described[6] how a low-power cw CO laser (~1 W/cm² at ~1925 cm⁻¹) promoted the reaction between Fe(CO)₄ and CH₄ at 20 K.

$$Fe(CO)_4 + CH_4 \xrightarrow{\text{IR laser}} Fe(CO)_4CH_4$$
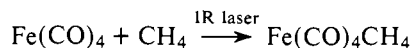
The reaction was remarkably selective. Using a sample of

Fe(CO)₄ enriched with ¹³CO it was possible to react selectively isomers of $Fe(CO)_{4-x}(^{13}CO)_x$ which differed only in the positions of the ¹³CO groups around the central Fe atom. It was this result which prompted the present study.

Fe(CO)₄ can be prepared[7] in an Ar matrix at 20 K by UV photolysis of Fe(CO)₅.

$$Fe(CO)_5 \underset{\text{Nernst}}{\overset{\text{UV}}{\rightleftharpoons}} Fe(CO)_4 + CO$$
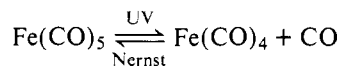
The Fe(CO)₅ is rapidly regenerated when the matrix is exposed to the unfiltered radiation from the Nernst glower of the IR spectrometer.[7] If, however, the Fe(CO)₄ is produced by *prolonged* UV photolysis of Fe(CO)₅, the reaction is only partially reversed by the Nernst glower.[7] There is substantial IR evidence[1,7] to suggest that this is the result of the photoejected CO molecule diffusing away from the Fe(CO)₄ fragment during the prolonged photolysis. The present experiments have been performed using this "irreversible" Fe(CO)₄.

The structure of Fe(CO)₄ was determined from the IR spectrum of the ¹³C¹⁶O enriched compound.[8] It has a C_{2v} structure, similar to SF₄, with bond angles of ~145 and ~120°. These bond angles are close to the angles 135 and 110° predicted by Burdett[9] for the minimum energy configuration of Fe(CO)₄ in the *lowest triplet state.* Very recent experiments

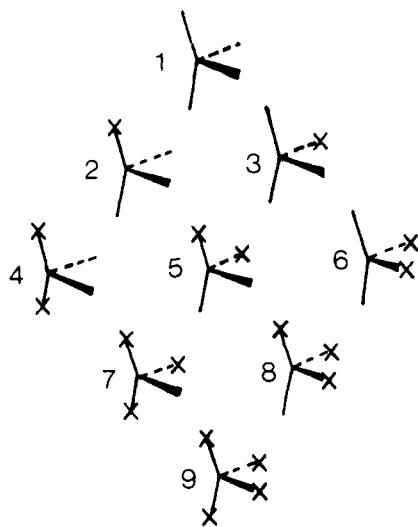**Figure 1.** The nine isomers of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$, showing the numbering used in this paper, X represents $^{13}C^{18}O$.

have used magnetic circular dichroism measurements to show that, in an Ar matrix, $Fe(CO)_4$ is indeed paramagnetic.[10]

Isotopic CO enrichment of $Fe(CO)_4$ produces the nine different $Fe(CO)_{4-x}(*CO)_x$ molecules illustrated in Figure 1. In these experiments, we have used $^{13}C^{18}O$ enrichment because this isotope gives good overlap between the IR absorptions of $Fe(CO)_4$ and the output of the CO laser, and because it maximizes the separation between the IR bands of the different $Fe(CO)_{4-x}(*CO)_x$ species. The wavenumbers of these IR bands are given in Table I. Those which overlap with the CO laser are shown in bold type.

Experimental Section

Redistilled $Fe(CO)_5$ was enriched with $^{13}C^{18}O$ (Prochem 92.5% ^{13}C, 98% ^{18}O) by UV photolysis of an isopentane solution under an atmosphere of $^{13}C^{18}O$, using the procedure described[3] for Cr-$(CO)_5CS$. Although substantial quantities of $Fe_2(CO)_9$ are still formed, the method appears to be considerably more effective than the gas-phase photolysis method[8] which had previously been used for the ^{13}CO enrichment of $Fe(CO)_5$. The long irradiation time of $\sim$3 h ensured that the isotopic enrichment is statistical. BOC "grade X" Ar was used for the matrices.

IR spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer, using a spectral slit width of $\sim$0.9 cm^{-1}. The IR source was a 1500K Opperman source with a total output power over all wavelengths of 75 mW at the sample position. All spectra were recorded using a polished Ge filter in the sample beam to remove radiation with wavelength $<$2 μm. The UV photolysis lamp and low-temperature apparatus have been described previously.[8]

The laser was an Edinburgh Instruments PL3 cw CO laser, the detailed design of which has been described elsewhere.[12] The laser can produce output with a line width $\ll$0.001 cm^{-1}, at any one of a series of frequencies, separated by $\sim$4 cm^{-1}, in the region 1932–1680 cm^{-1}. An intracavity diffraction grating is used to select the output frequency. For the photolysis of $Fe(CO)_4$, the laser was run at $\sim$255 K with an output power of 1.5–3 W (1919–1880 cm^{-1}). At these powers laser action occurs simultaneously on more than one V $\rightarrow$ V transition of CO and laser output is produced at two or three closely spaced frequencies; see Table II. The separation of these laser lines is less than the slit width of the IR spectrometer and, for our purposes, the laser may be considered to be monochromatic. The laser beam was partially focused by a 50-cm concave mirror to a beam diameter of 2 cm, a size similar to that of the matrix.

An automatic temperature controller, Air Products Model APD-B, was used to maintain the matrix at 20 K, about 8 K above the lowest temperature of the apparatus. The temperature controller can compensate for changes in the thermal load on the cooler, and prevented any overall temperature rise of the matrix during laser irradiation.

Table I. Wavenumbers (cm^{-1}) of Bands of the Nine Possible Molecules of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ [a]

Unsubstituted	
1	
(2092.8)[a]	
1995	
1988.5	
1973	

Monosubstituted	
2	**3**
2074.5	(2082.8)
(1991.2)	1995
1973	(1915.9)
1919	**1899**

Disubstituted		
4	**5**	**6**
(2051.8)	2062.5	(2072.6)
1973	1989[b]	1995
(1936.6)	(1924.8)	(1916.1)
1902	**1894**	**1882**

Trisubstituted	
7	**8**
(2032.5)	2051
(1946.5)	(1941.0)
1902	(1898.9)
1892	**1882**

Tetrasubstituted
9
(1996.9)
1902
(1898)
1882

[a] The molecules are numbered as in Figure 1. Wavenumbers in bold type overlap with CO laser lines, those in italics were observed to change intensity during laser irradiation, and those in parentheses are calculated. Calculated values for bands predicted to be weak or obscured by other absorptions, using the force constants, nm^{-1}, k_1 1658.0, k_2 1617.2, k_{11} 50.8, k_{12} 40.5, k_{22} 42.7 (see ref 8) and effective reduced mass ratios R_{eff1} 0.954335, and R_{eff2} 0.953668 (see ref 11). [b] Poorly resolved shoulder.

Table II. Wavenumbers (cm^{-1}) of the Different CO Laser Lines Used in These Experiments

Line identification	Wavenumber[a]	
7-6 P(17)	1918.98	
6-5 P(23)	1918.58	1919[b]
8-7 P(11)	1917.88	
7-6 P(21)	1901.96	1902[b]
8-7 P(15)	1901.76	
8-7 P(16)	1897.65	1898[b]
7-6 P(22)	1897.62	
8-7 P(17)	1893.68	1894[b]
7-6 P(23)	1893.25	
8-7 P(20)	1880.90	
9-8 P(14)	1880.34	1881[b]
7-6 P(26)	1879.97	

[a] Wavenumbers calculated using Dunham coefficients from ref 13. [b] Wavenumbers used in the text to refer to this group of lines.

Rearrangement Schemes for $Fe(CO)_4$

Klemperer, Muetterties, Whitesides, and co-workers have classified the possible site exchange processes in a C_{2v} four-coordinate molecule which are detectable by dynamic nuclear magnetic resonance.[14] Their study was based on SF$_4$, which has the same symmetry as $Fe(CO)_4$. These processes are listed in Table IIIA, using the numbering shown in **10**. The NMR

h_3^{ww}
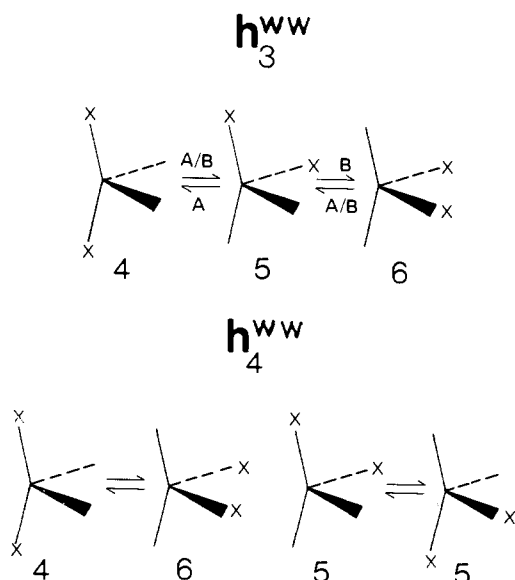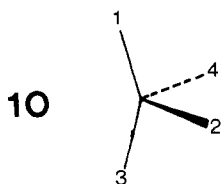

h_4^{ww}

Figure 2. The IR distinguishable ligand exchange processes, h_3^{ww} and h_4^{ww}, applied to the isomers of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$. Note that both processes A and B of h_3^{ww} convert **4** or **6** into enantiomers of **5**. A and B are not equivalent for **5**.

Table III

A. NMR Detectable Intramolecular Exchange Schemes[a] for a 4-Coordinate C_{2v} Molecule, e.g., SF_4

Rearrangement mode	Representative permutation[b]
h_3^{ww}	= (12) (non-Berry pseudorotation)
h_4^{ww}	= (12) (34) (Berry pseudorotation)

B. IR Detectable Intramolecular Exchange Schemes for an Isotopically Disubstituted 4-Coordinate C_{2v} Molecule, e.g., $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$

Rearrangement mode	Representative permutatuon
h_3^{ww} A	= (12)
B	= (34)
h_4^{ww}	= (12) (34)

[a] Taken from ref 14. [b] See **10** for numbering of groups.

10

results[14] show that the uncatalyzed ligand exchange in SF_4 proceeds via h_4^{ww}. If the vacant coordination site is treated as a fifth ligand, h_4^{ww} is equivalent to the Berry pseudorotation with the vacant site acting as the pivot ligand. Similarly, h_3^{ww} corresponds to a non-Berry pseudorotation.

Dynamic intramolecular ligand exchange processes cannot be studied by conventional IR spectroscopy because the time scale of the technique is always much faster than any exchange process. In our matrix experiments we are examining a system where thermal exchange processes are frozen out.[1,2] Once a molecule has been isomerized by laser irradiation, it apparently remains fixed in its new configuration indefinitely. Under these conditions, the isotopic labeling of the CO groups in $Fe(CO)_4$ enables us to follow the stereochemistry of rearrangement processes from the changes in the "C–O stretching" region of
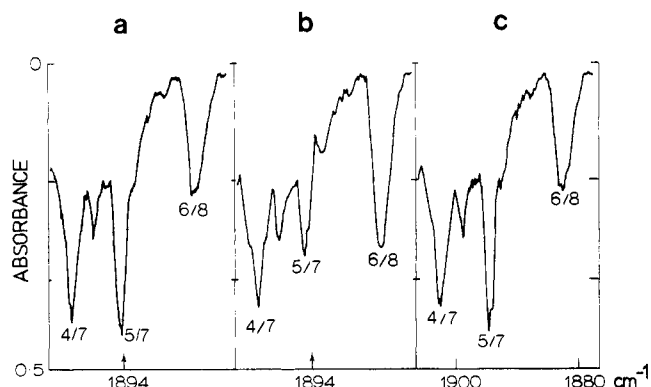

Figure 3. IR spectra of "irreversible" $Fe(CO)_4$ with ~40% $^{13}C^{18}O$ enrichment in Ar at 20 K ($Fe(CO)_4$:Ar ~ 1:4000). Bands are assigned to isomers of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$ using the numbering of Figure 1. Note the overlapping and coincident bands of different isomers. The bands **4/7** and **6/8** also contain a small contribution from **9**. (a) After 15 min irradiation with the unfiltered spectrometer beam to remove "reversible" $Fe(CO)_4$. (b) After 20 min irradiation with CO laser at 1894 cm^{-1}. (c) 2 min exposure to the unfiltered spectrometer beam.

the IR spectrum. It is, however, only the interconversion of the isomers of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$, **4, 5,** and **6,** which can show any spectroscopic differences between the possible intramolecular rearrangement modes. This is because there are three disubstituted isomers and a particular isomer can undergo two possible isomerizations while the mono- or trisubstituted species have only two isomers and one possible isomerization.

The rearrangement processes detectable in our experiment are listed in Table IIIB. These are somewhat different from the NMR distinguishable processes, Table IIIA, because h_3^{ww} is split into two processes A and B. Figure 2 illustrates the operation of these rearrangements on **4, 5,** and **6.** The principal differences between h_3^{ww} and h_4^{ww} are: (1) under h_3^{ww}, **4** cannot rearrange *directly* to **6**; (2) under h_4^{ww}, **5** can only rearrange into itself and not into **4** or **6.** If $Fe(CO)_4$ rearranged via a C_{3v} intermediate, the process would follow h_3^{ww}. If it rearranged via a D_{4h}, C_{4v}, or D_{2d} intermediate, h_4^{ww} would be followed. If, however, the rearrangement involved a T_d intermediate, a combination of h_3^{ww} and h_4^{ww} would be observed. IR laser photochemistry allows us to distinguish between these possibilities.

Results

Figure 3a shows part of the IR spectrum of irreversible $Fe(CO)_4$ enriched with 40% $^{13}C^{18}O$, in an Ar matrix at 20 K. The $Fe(CO)_4$ has a statistical distribution of $^{13}C^{18}O$, since it was generated from $Fe(^{12}C^{16}O)_{5-x}(^{13}C^{18}O)_x$ which itself contained a statistical distribution of $^{13}C^{18}O$. Irradiation with the CO laser at 1894 cm^{-1} produced substantial changes in the relative intensities of the bands, Figure 3b. Exposure of the matrix to the unfiltered IR spectrometer beam rapidly regenerated the original spectrum,[15] Figure 3c. The laser clearly had the following effect:

Laser at 1894 cm^{-1} **5** and **7** destroyed, **6** and **8** produced

but the overlap of the bands makes it impossible to separate the isomerization of di- and trisubstituted species. There were also changes in other parts of the "C–O stretching" region. For example, the experiment illustrated in Figure 4 shows that the 1894 cm^{-1} laser line causes **5** to decrease and **8** to increase. Table I indicates other bands which changed in intensity during laser irradiation.

These experiments demonstrate the following points:

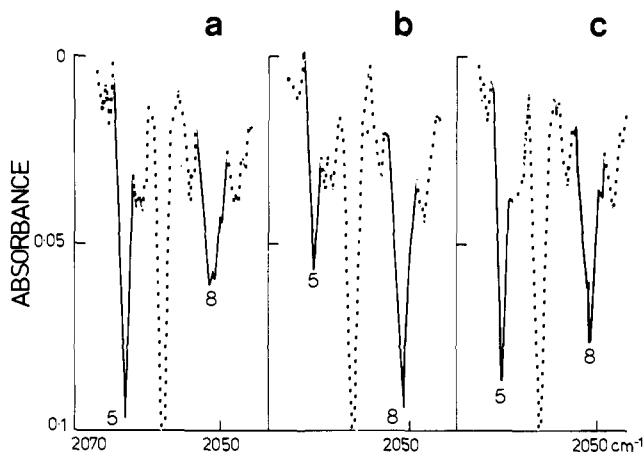(1) The laser causes *selective* isomerization of the different $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ species.

Figure 4. IR spectra of "irreversible" $Fe(CO)_4 \sim 40\%$ $^{13}C^{18}O$ enrichment Ar/20 K. The numbering of the bands refers to Figure 1. The bands shown in broken lines are due to $Fe(CO)_5$. (a) After laser irradiation 1881 cm^{-1}, 30 min. (b) After laser irradiation 1894 cm^{-1} 30 min. (c) After 2.5 min exposure to the unfiltered spectrometer beam.
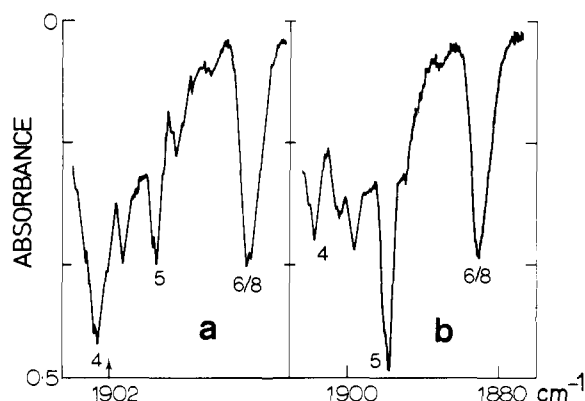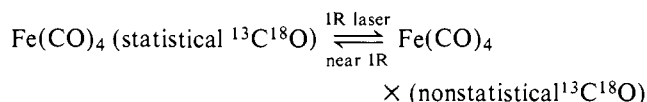

Figure 5. IR spectra illustrating laser isomerization of isomer **4** of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$. (a) After 35 min laser irradiation at 1894 cm^{-1} to isomerize **7** to **8** (see text). (b) After 25 min laser irradiation at 1902 cm^{-1}, coincident with the band of **4**.

(2) Laser irradiation produces a nonstatistical distribution of $^{13}C^{18}O$ among the isomers of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$.

(3) Exposure to the IR source of the spectrometer restores the statistical distribution of $^{13}C^{18}O$. By filtering the spectrometer beam with a series of cutoff filters, we have shown that this isomerization is caused by near-IR radiation in the region 13 000–9000 cm^{-1}, corresponding to the previously unreported broad red/near-IR absorption of $Fe(CO)_4$, $\bar{\nu}_{max}$ 13 000 cm^{-1} (770 nm). Thus the near-IR isomerization provides a convenient way of returning the sample to its original state at any stage of the experiment.

$$Fe(CO)_4 \text{ (statistical } ^{13}C^{18}O) \underset{\text{near IR}}{\overset{\text{IR laser}}{\rightleftharpoons}} Fe(CO)_4$$

$$\times \text{ (nonstatistical} ^{13}C^{18}O)$$

The identification of the rearrangement mode of $Fe(CO)_4$ was hindered in these experiments by the laser promoting isomerization of both di- and trisubstituted species. Fortunately this problem could be overcome as follows. One laser frequency was used to isomerize the interfering trisubstituted molecule, **7**, and then the isomerization of the disubstituted species was studied with a different laser frequency.

The results of this experiment are shown in Figure 5. The matrix was first irradiated at 1894 cm^{-1} to isomerize **7** into **8**, Figure 5a. Irradiation of the band at 1902 cm^{-1}, now almost entirely due to **4**, caused an increase in the band due to **5** but
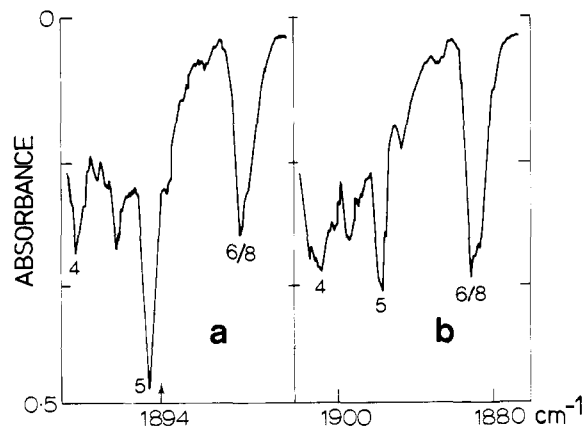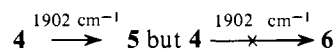

Figure 6. IR spectra illustrating laser isomerization of isomer **5** of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$. (a) After 25 min laser irradiation at 1902 cm^{-1} (see Figure 5). (b) After 25 min laser irradiation at 1894 cm^{-1}.

no change in the band assigned to **6**, Figure 5b. Other bands due to **5**, at 2062.5 and 1989 cm^{-1}, also increased during the laser irradiation; see Table I.

$$4 \xrightarrow{1902 \text{ cm}^{-1}} 5 \text{ but } 4 \xrightarrow{1902 \text{ cm}^{-1}} \times \rightarrow 6$$

(It is interesting than the laser appears to "burn a hole" in the irradiated band[16] (Figure 5b), so that the band does not decrease in intensity uniformly across its width. This point will be discussed in detail elsewhere.[17]) Isomer **5**, which had just been produced from **4**, was now rearranged using the 1894 cm^{-1} laser line, Figure 6. It can be seen that as the bands due to **5** decreased, there was an increase in the bands due to both **4** and **6**.

$$5 \xrightarrow{1894 \text{ cm}^{-1}} 4 + 6$$
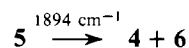
In the case of **4**, the "hole", produced in the band by irradiation with the laser at 1902 cm^{-1}, is partially filled in. The increase in the band due to **6** was substantially less than that of the band due to **4** (Figure 6b). This is because the band assigned to **6** is a b_2 mode while the band due to **4** is a b_1 mode, and the extinction coefficient of the b_2 mode of $Fe(CO)_4$ is only $\frac{2}{3}$ that of the b_1 mode.[8] Other bands due to **4** and **6**, at 1973 (**4**) and 1995 cm^{-1} (**6**), also increased in intensity (not illustrated; see Table I). During the laser irradiations in Figures 5 and 6, there was negligible change in the intensities of the bands assigned to any mono- or trisubstituted species (e.g., the bands at 2075.5 (**2**) or 2051 cm^{-1} (**8**)). *Thus all the changes observed were caused by interconversion of the different disubstituted $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$ species.* Laser irradiation at 1881 cm^{-1} (not illustrated) promoted the isomerization.

$$6 \xrightarrow{1881 \text{ cm}^{-1}} 5$$
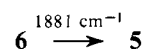
Other laser frequencies promoted the interconversion of **2** and **3**. All the observed laser-induced isomerizations are summarized in Figure 7.

We can draw the following conclusions from the results of these experiments.

(1) The rearrangements of **4**, **5**, and **6** are exactly what would be expected for h_3^{ww} (Figure 2) and are inconsistent with either h_4^{ww} or a combination of h_3^{ww} and h_4^{ww}.

(2) Although symmetry does not require that **5** should rearrange to **4** and **6** with equal probability, the spectra suggest that, when **5** rearranges, similar amounts of **4** and **6** are formed. This implies that the $^{13}C^{18}O$ groups are merely acting as labels and do not affect the course of the rearrangement significantly.

(3) The growth and decay of bands, assignable to particular isomers of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$, are in gratifying agreement with our original interpretation[8,18] of the IR spectrum of $^{13}C^{16}O$ enriched $Fe(CO)_4$; see Table I.
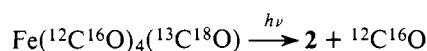
(4) The powerful combination of matrix isolation and IR laser irradiation represents the only existing experimental method which could have been used to follow these isomerizations.
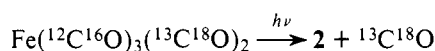
Discussion

The Rearrangement Mode of $Fe(CO)_4$. Before these results can be taken as conclusive evidence for the *intramolecular* rearrangement mode of $Fe(CO)_4$, it must be shown (a) that no dimeric $(Fe(CO)_4)_2$ species participates in the rearrangement, (b) that the rearrangement does not involve exchange with the CO molecule, ejected from the parent $Fe(CO)_5$ during UV photolysis, or (c) that dissociation to $Fe(CO)_3$ does not occur.

(a) Matrix isolation has been used to investigate the dimers of SF_4 and their role in ligand-exchange processes.[19,20] In our experiments, however, the dilution, ($Fe(CO)_5$:Ar, 1:4000) was at least ten times higher than the highest dilution used for SF_4,[19] and under these conditions the concentration of dimeric species is negligible.[8]

(b) A particular isomer of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ must be formed by ejection of either $^{12}C^{16}O$ or $^{13}C^{18}O$ from the appropriately $^{13}C^{18}O$ substituted molecule of $Fe(CO)_5$. For example:

$$Fe(^{12}C^{16}O)_4(^{13}C^{18}O) \xrightarrow{h\nu} 2 + {}^{12}C^{16}O$$

or

$$Fe(^{12}C^{16}O)_3(^{13}C^{18}O)_2 \xrightarrow{h\nu} 2 + {}^{13}C^{18}O$$

Thus the matrix contains two types of molecules of **2**, either with $^{12}C^{16}O$ or with $^{13}C^{18}O$ close to them. Any rearrangement process wihch involved exchange of bound and photoejected CO groups would require a substantial proportion of the irradiated molecules to change the number of coordinated $^{13}C^{18}O$ groups, e.g., **2** → **1, 4, 5,** or **6**. The observed isomerizations are totally inconsistent with such an exchange process, as there is no evidence for any change in the number of coordinated $^{13}C^{18}O$ groups during laser irradiation. Furthermore, in the case of reversible $Fe(CO)_4$, where there is interaction[7] with the photoejected CO, laser irradiation causes regeneration of $Fe(CO)_5$ with little or no isomerization of the $Fe(CO)_4$.[17]

(c) Dissociation of $Fe(CO)_4$ to $Fe(CO)_3$ is unlikely because the isomerization appears to involve absorption of only one photon (see below), and the energy of one photon at 1880 cm^{-1}, equivalent to 22.5 kJ mal^{-1}, is much less than the mean enthalpy of disruption for an Fe–CO bond,[21] 118 kJ mol^{-1}.

Thus the laser-induced ligand exchange in $Fe(CO)_4$ is almost certainly an intramolecular process. The rearrangement proceeds via scheme h_3^{ww}. This laser-induced rearrangement mode is different from the thermal exchange process,[14] h_4^{ww}, in liquid SF_4. Thus $Fe(CO)_4$ provides the first known example of a *non-Berry pseudorotation.*

Is this unusual rearrangement mode of $Fe(CO)_4$ peculiar to Ar matrices, and is it the result of exciting particular C–O stretching vibrations of the molecule? Attempts to carry out the isomerization in CH_4 and Xe matrices have failed because $Fe(CO)_4$ reacts with the matrix to form $Fe(CO)_4CH_4$ and $Fe(CO)_4Xe$. However, laser-induced isomerization of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ does occur in N_2 matrices.[17] The experiments show that the isomerization **4** ⇌ **5** is occurring but, unfortunately, "matrix splittings" make it difficult to
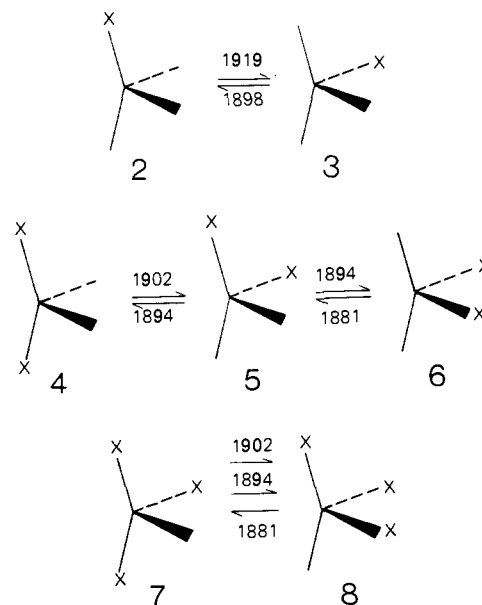

Figure 7. The observed laser induced isomerizations of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ species. X represents the $^{13}C^{18}O$ group. Note that experiments cannot distinguish between the different enantiomers of **5**.

eliminate the possibility that **4** → **6** is occurring simultaneously. Nevertheless, it is clear that the non-Berry pseudorotation (i.e., **4** ⇌ **5**) is not confined to Ar matrices. All of the isomerizations have been achieved by excitation of vibrations, the normal coordinates of which always involve the out-of-phase stretching of C–O bonds. Unhappily, it has not yet been possible for us to discover whether the non-Berry pseudorotation is the result of exciting these asymmetrical vibrations of $Fe(CO)_4$, as all of the symmetrical C–O stretching vibrations lie outside the tuning range of a cw CO laser, operating near room temperature. It should, however, be possible to test this point using a different type of laser.

Although it is not possible to deduce a unique mechanism from a permutational rearrangement mode, one can draw some conclusions about the symmetry of the intermediates or transition states involved in the rearrangement. The observed isomerization of $Fe(CO)_4$ is inconsistent with a C_{4v}, D_{4h}, D_{2d}, or T_d transition state. It is, however, consistent with a C_{3v} intermediate or C_s transition state. By contrast, the thermal intramolecular fluorine exchange in SF_4 is inconsistent with a C_{3v} intermediate or C_s transition state and consistent with any of the other symmetries.

Although there is no proof that the thermal rearrangement mode of $Fe(CO)_4$ would necessarily be the same as the observed laser-induced rearrangement, recent MO calculations suggest a genuine difference between the thermal rearrangement modes of $Fe(CO)_4$ and SF_4. Burdett has used his angular overlap model[9] to compare the relative energies of different geometries of $Fe(CO)_4$. Although the energy differences are quite small, his results[22] show that a C_{3v} geometry, with a bond angle of 100° between axial and radial CO groups, has a lower energy than any C_{4v}, D_{4h}, D_{2d}, or T_d structure for $Fe(CO)_4$ in a triplet electronic state. The selection rules, derived by Stanton and McIver,[23] mean that this C_{3v} geometry cannot be a transition state and that a lower energy C_s geometry may be involved in the isomerization. Nevertheless, Burdett's calculations suggest that, for $Fe(CO)_4$, an h_3^{ww} rearrangement should have a lower activation energy than any h_4^{ww} process. Similar calculations[24] for ligand exchange in SF_4 indicate an h_4^{ww} mode with a C_{4v} transition state with an F–S–F_{trans} bond angle of 145°. The difference is primarily caused by the energetic behavior of the partially occupied metal d orbitals on distortion of $Fe(CO)_4$.

The Near-IR Isomerization of Fe(CO)₄. Our experiments have also demonstrated that near-IR radiation, 9000–13 000 cm^{-1}, isomerizes Fe(CO)₄. The process is highly efficient. For example, the isomerization, illustrated in Figures 3b and 3c, required less than 2 min of irradiation. The isomerization differs from the laser-induced rearrangement in that it involves an electronic excitation. The isomerization is caused by absorption of light corresponding to the broad asymmetric band, λ_{max} 770 nm. Unfortunately this band cannot as yet be identified with a particular d–d transition, since Burdett's MO calculations[9,22] suggest that the splitting of the d orbitals, **11**, in C_{2v} Fe(CO)₄ is such that all d → d transitions will lie in the far-red/near-IR region of the spectrum. It is interesting that the isoelectronic paramagnetic 16-electron compounds Fe(RN=C(R')C(R')=NR)₂ also show far-red/near-IR absorptions.[25] An electronically excited state of C_{2v} Fe(CO)₄ would be of higher energy than higher symmetry isomers (e.g., T_d) in the ground state, **11**. Distortion of the excited C_{2v}

d. ORBITAL SPLITTING OF Fe(CO)₄
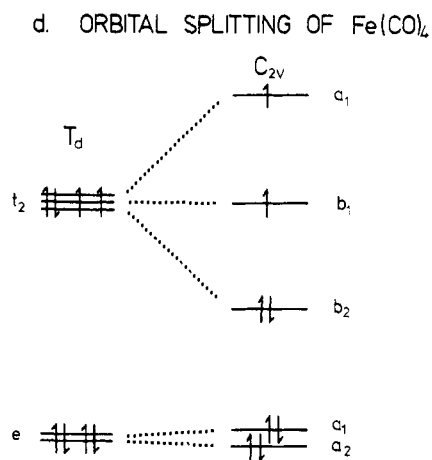
11

molecule to a higher symmetry isomer might therefore provide a smooth pathway both for relaxation of the excited electronic state and ligand exchange.

$$\text{Fe(CO)}_4 \ (C_{2v})_{\text{excited}} \rightarrow \text{(e.g., } T_d)_{\text{ground state}} \longrightarrow (C_{2v})$$
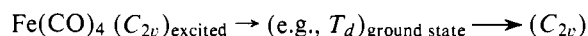
Because the near-IR isomerization is unselective, there is, unfortunately, no experimental evidence to show what the geometry of this intermediate might be. We have, however, shown that similar relaxation pathways for the lowest electronic excited states of Cr(CO)₅, and Cr(CO)₄, will explain all the observed low-temperature photochemistry of these species.[26]

The reactions of Fe(CO)₄ with CO, N₂, and CH₄ are all promoted by radiation from the unfiltered source of an IR spectrometer[8] and it is now clear that all these reactions must also involve near-IR excitation of Fe(CO)₄. This suggests that isomerization of Fe(CO)₄ may well form an integral part of these reactions.

The Photophysics of the Laser-Induced Isomerization of Fe(CO)₄. The laser-induced isomerization of Fe(CO)₄ raises two interesting questions; firstly, how many IR photons are required to promote the rearrangement, and secondly, how efficient is the energy transfer from the excited C–O and M–C stretching modes to the combination of C–M–C bending modes which allows rearrangement?

Multiphoton excitation of a particular molecule could occur either by an excited molecule absorbing further photons, or by V → V transfer between excited molecules.

$$(V = 1) \xrightarrow{h\nu'} (V = 2) \text{ etc.}$$

or

$$(V = 1) + (V = 1) \rightarrow (V = 2) + (V = 0) + \Delta E$$
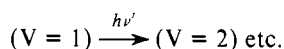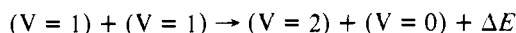
The first process occurs in the gas-phase decomposition of SF₆ by a CO₂ laser[4,5] but it is only significant at very high power densities (>10⁷ W/cm²). In the present experiments not only will the *large* anharmonicity,[27] ~30 cm^{-1}, in the C–O stretching vibrations make the process unlikely, but also the laser power density is far too low (<10 W/cm²). Relaxation from V = 1 will almost certainly occur far more quickly than absorption of a second photon.

The second process, intermolecular V → V transfer, has been observed by Dubost and Charneau[28] during IR laser irradiation of matrix isolated CO. In particular, irradiation of $^{12}C^{16}O$ in a mixture of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ led to fluorescence of *all three* isotopic species.[28] Thus, in the case of Fe($^{12}C^{16}O$)₄₋ₓ($^{13}C^{18}O$)ₓ, any intermolecular V → V process would be expected to destroy the selectivity of the isomerization. Furthermore, the rate of the isomerization was, at least qualitatively, linearly dependent on the incident laser intensity. This implies that a single molecule requires absorption of only one photon to undergo isomerization, since any multiphoton process would show a highly nonlinear dependence.

Since kT is small at these temperatures the laser photon energy gives an approximate upper limit of 1880 cm^{-1}, or 22.5 kJ/mol, for the activation energy for the isomerization of Fe(CO)₄. This is quite close to 27 kJ/mol, the energy difference between C_{2v} and C_{3v} Fe(CO)₄ predicted by Burdett,[22] although the calculated value is probably sensitive to the parameterization, which is used. However, the activation energy for the rearrangement of Fe(CO)₅ has been estimated[29] to be only ~4 kJ/mol and the barrier for Fe(CO)₄ might well be even lower.

Comparison of the approximate numbers of near-IR and IR photons absorbed by the Fe(CO)₄ and the rates of the near-IR and laser-induced isomerizations indicate that the laser-induced rearrangement must be several orders of magnitude less efficient than the near-IR isomerizations. Furthermore, the rate of laser-induced isomerization was significantly slower than that of the laser-induced regeneration[17] of Fe(CO)₅ from "reversible" Fe(CO)₄. Thus the quantum yield for the laser-induced ligand exchange appears to be extremely low.

In the gas phase energy transfer from one vibrational mode to another does not generally occur in an isolated molecule but requires intermolecular collisions. In the matrix there are no collisions between Fe(CO)₄ molecules and thus the matrix itself must play a role in the intramolecular V → V transfer. Little is known about energy transfer in matrix isolated molecules as large as Fe(CO)₄.

Brus and Bondebey have recently studied intramolecular energy transfer processes in a series of elegant experiments,[30] involving the UV/visible fluorescence of somewhat smaller matrix isolated molecules. In one experiment, a laser was used to populate the excited state *stretching* modes of CN₂ but emission was only observed from the *bending* mode of the excited state.[31] Thus, even in a matrix isolated *triatomic* molecule, intramolecular energy transfer from high to low frequency vibrations is very efficient. Their experiments are consistent with the theories[32] that the rate of energy transfer from a vibrationally excited molecule into the phonon bands of the matrix depends inversely on the energy separation. Since the "C–O stretching" vibrations (~1900 cm^{-1}) are far removed from lattice phonons (<50 cm^{-1}), direct energy transfer from the C–O stretching vibrations of Fe(CO)₄ to the matrix should be very inefficient. Furthermore, our experiments[17] suggest that, qualitatively, there is little difference in the rates at which "reversible" Fe(CO)₄ reacts with CO in an Ar matrix and in a SF₆ matrix where $2\nu_3$, ~1880 cm^{-1}, is almost resonant

with the b_2 C–O stretching vibration of $Fe(^{13}C^{18}O)_4$, 1884 cm^{-1}.

These results suggest that, in the matrix, the principal relaxation mode of vibrationally excited $Fe(CO)_4$ molecules should be energy transfer from the high frequency C–O stretching modes to the lower energy M–C stretching and bending modes. However, subsequent energy transfer from these low energy modes to the Ar lattice may well be more rapid than energy transfer from one bending mode to another. This might explain the low efficiency of energy transfer to the particular C–M–C bending mode or modes responsible for the isomerization of $Fe(CO)_4$. Alternatively, the low efficiency might indicate that more than one quantum of bending energy is required to overcome the activation barrier for isomerization. Nevertheless, whatever the explanation for the low efficiency, it is clear that *intramolecular* energy transfer leading to ligand exchange is far more efficient than the equivalent *intermolecular* energy transfer between different $Fe(^{12}C^{16}O)_{4-x}$-$(^{13}C^{18}O)_x$ species.

Conclusions

These experiments have allowed us to identify the permutational process which occurs during the laser-induced intramolecular ligand exchange in $Fe(CO)_4$. Thus for the first time there is a technique which provides an alternative to DNMR for identifying intramolecular rearrangement modes in fluxional molecules. The two methods differ in that DNMR looks at molecules which exchange thermally and continuously while, in the matrix, molecules only rearrange when irradiated with the laser. Since laser irradiation only provides an upper limit for activation energies, DNMR is clearly preferable for quantitative measurements. On the other hand, matrix isolation can be used to study highly unstable molecules and those which do not contain any magnetic nuclei. (The nuclear spin of ^{13}C used in our experiments is purely coincidental.) Although it is not yet clear that laser-induced ligand exchange processes are necessarily the same as those which would occur thermally, the combination of matrix isolation and IR lasers appears highly promising for the study of intramolecular rearrangements.

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(15) A small reduction occurred in the intensity of the band at 1902 cm^{-1} (4/7 in Figure 3) relative to the band at 1894 cm^{-1} (5/7), when the sample was allowed to stand in the dark overnight. The original intensity was immediately restored by brief irradiation with the Nernst glower. This band in fact consists of several components which cannot be resolved at the spectrometer slit widths used in this experiment. The intensity change is attributed to some small thermal change in this fine structure.
(16) This "hole burning" indicates inhomogeneous broadening of the bands. This means that the bands of irreversible $Fe(CO)_4$ are, in reality, the unresolved envelope of a series of narrow bands, presumably due to $Fe(CO)_4$ molecules in different matrix sites.
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(18) There is a misprint in Table 2 of ref 8, which lists the observed and calculated wavenumbers for $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{16}O)_x$ species in Ar at 20 K. The band at 1950.79 cm^{-1} should be assigned to 7 and the band at 1929.42 cm^{-1} to 8. As predicted by our analysis[11] of the C–O factored force field method, the force constants were slightly different form those obtained by $^{13}C^{16}O$ substitution and the standard deviation was somewhat greater ($^{13}C^{18}O$ 1.0 cm^{-1}, $^{13}C^{18}O$ 0.33 cm^{-1}). The poorer agreement between observed and calculated wavenumbers for $^{13}C^{16}O$ was also due in part to the broadness of the bands which hindered the accurate measurement of band positions.
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