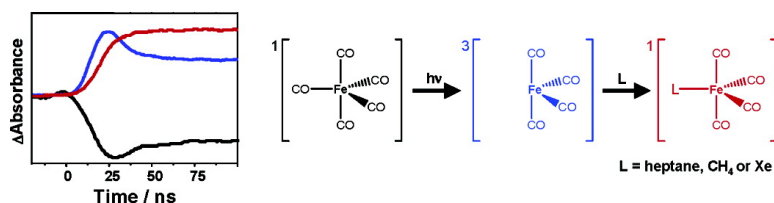Article

Unraveling the Photochemistry of Fe(CO) in Solution: Observation of Fe(CO) and the Conversion between Fe(CO) and Fe(CO)(Solvent)

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Unraveling the Photochemistry of Fe(CO)$_5$ in Solution: Observation of Fe(CO)$_3$ and the Conversion between ^{3}Fe(CO)$_4$ and ^{1}Fe(CO)$_4$(Solvent)

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Abstract: The photochemistry of Fe(CO)$_5$ (**5**) has been studied in heptane, supercritical (sc) Ar, scXe, and scCH$_4$ using time-resolved infrared spectroscopy (TRIR). ^{3}Fe(CO)$_4$ (^{3}**4**) and Fe(CO)$_3$(solvent) (**3**) are formed as primary photoproducts within the first few picoseconds. Complex **3** is formed via a single-photon process. In heptane, scCH$_4$, and scXe, ^{3}**4** decays to form ^{1}**4·L** (L = heptane, CH$_4$, or Xe) as well as reacting with **5** to form Fe$_2$(CO)$_9$. In heptane, **3** reacts with CO to form ^{1}**4·L**. The conversion of ^{3}**4** to ^{1}**4·L** has been monitored directly for the first time (L = heptane, k_{obs} = 7.8($\pm$0.3) $\times$ 10^7 s^{-1}; scCH$_4$, 5($\pm$1) $\times$ 10^6 s^{-1}; scXe, 2.1($\pm$0.1) $\times$ 10^7 s^{-1}). In scAr, ^{3}**4** and **3** react with CO to form **5** and ^{3}**4**, respectively. We have determined the rate constant (k_{CO} = 1.2 $\times$ 10^7 dm^3 mol^{-1} s^{-1}) for the reaction of ^{3}**4** with CO in scAr, and this is very similar to the value obtained previously in the gas phase. Doping the scAr with either Xe or CH$_4$ resulted in ^{3}**4** reacting with Xe or CH$_4$ to form ^{1}**4·Xe** or ^{1}**4·CH$_4$**. The relative yield, [^{3}**4**]:[**3**] decreases in the order heptane > scXe > scCH$_4$ $\gg$ scAr, and pressure-dependent measurements in scAr and scCH$_4$ indicate an influence of the solvent density on this ratio.

Introduction

The photochemistry of Fe(CO)$_5$ has been studied intensely, with applications ranging from photocatalysis and synthesis[1] to coherent control of gas-phase reactions.[2] There is considerable interest in the implication of crossing between different spin surfaces in transition metal chemistry.[3] Fe(CO)$_5$ has been widely investigated as a model system in organometallic photochemistry,[4] using techniques such as matrix isolation, flash photolysis, time-resolved infrared spectroscopy (TRIR), and electron diffraction. However, there still remain intriguing questions regarding the mechanism of Fe(CO)$_5$ photolysis.

In low temperature (12 K) matrices, Poliakoff and Turner showed that UV photolysis of Fe(CO)$_5$ (^{1}**5**,[5] Scheme 1) generated C_{2v} symmetric ^{3}Fe(CO)$_4$ (^{3}**4**).[6-8] Prolonged irradiation

Scheme 1. Photochemistry of Fe(CO)$_5$ in CH$_4$ and Xe Matrices, Adapted from Ref 5
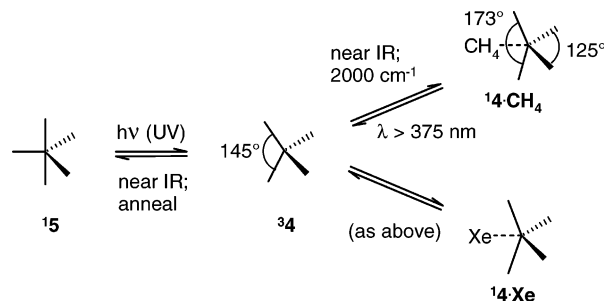
also generated C_{3v} symmetric Fe(CO)$_3$ (**3**).[9] In Ne and Ar matrices, near-IR irradiation or annealing the matrix could cause the reaction of ^{3}**4** with CO to regenerate Fe(CO)$_5$ (^{1}**5**). In Xe and CH$_4$ matrices, ^{3}**4** could be converted to ^{1}Fe(CO)$_4$·L (^{1}**4·L**, L = Xe or CH$_4$) by near- or mid-infrared radiation. The gas-phase photochemistry of Fe(CO)$_5$ has been probed at room temperature using TRIR, a combination of UV flash photolysis and fast IR detection.[10-13] Fuss and co-workers investigated the

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reactivity of Fe(CO)$_4$ by pumping with femtosecond UV pulses and detecting with time-of-flight mass spectrometry.[14] Ultrafast time-resolved electron diffraction was used by Zewail and co-workers to determine the gas-phase structure of ^{1}Fe(CO)$_4$ (**^{1}4**),[15] which was found to be almost identical to the structure determined from early matrix work.[6] In solution, **^{1}4·L** (L = benzene, cyclohexane) was characterized by Grevels and co-workers using μs-TRIR.[16–18] They recently proposed,[18] for the first time, that Fe(CO)$_3$(solvent) (**3·L**, L = cyclohexane) is formed in solution. Neither the spin state (singlet or triplet) of **3·L** nor the number of solvent molecules or matrix atoms (one or two) attached to it (L) is known. The formation of **3** is unusual, since in the condensed phase (matrix and solution) it is normally expected that metal carbonyls will only lose one CO group following excitation; i.e., only Fe(CO)$_4$ should be formed in solution.[19] However, the absorption of *one* photon may provide sufficient energy to eject more than one CO in a stepwise process, and this is often observed in the gas phase (i.e., generation of Fe(CO)$_n$ fragments, $n = 4-1$).[20–22] From the above-mentioned experimental work and theoretical investigations, it was suggested that for the photoreaction of Fe(CO)$_5$ a singlet pathway has to be given preference (**^{1}5** → [**^{1}5**]* → [**^{1}4**]* → **^{3}4**) as opposed to a triplet pathway (**^{1}5** → [**^{1}5**]* → [**^{3}5**]* → **^{3}4**).[4,14] In solution this means that hot **^{1}4** (i.e., [**^{1}4**]*) does not form an intermediate complex with the solvent but rather forms **^{3}4** which undergoes a slow triplet–singlet conversion, generating the solvent complex (**^{1}4·L**, L = solvent molecule). An ultrafast TRIR experiment by Harris and co-workers revealed that, in heptane solution, **^{3}4** is formed within 33 ps and is long-lived up to 660 ps.[23] Neither the formation of **^{1}4·L** nor **3·L** was observed. In the microsecond TRIR experiments, **^{1}4·L** and **3·L** were observed within the rise time of the Mülheim TRIR apparatus (ca. 0.4 μs) but no **^{3}4** was found.[18] Consequently, a comparably slow reaction of **^{3}4** with solvent to form **^{1}4·L** has to be assumed, but this has never been directly monitored.

Some intriguing questions remain regarding the photochemistry of Fe(CO)$_5$ in solution. What is the time scale for the conversion of ^{3}Fe(CO)$_4$ to ^{1}Fe(CO)$_4$(solvent), and how quickly is Fe(CO)$_3$(solvent) formed? In this paper we report the results of our investigation into the time scale of the **^{3}4** to **^{1}4·L** conversion and the rate of formation of **3·L** in conventional and supercritical fluids using fast and ultrafast TRIR.

Experimental Section

The Nottingham ns-TRIR apparatus has been described elsewhere.[24] In these experiments, a pulsed Nd:YAG laser (Quanta-Ray GCR-12*S*; 266 nm) initiates the photochemical reactions and the transient IR absorption bands are monitored using a cw IR source (Mütek diode laser) and a fast HgCdTe (MCT) detector.[25] The change in IR absorbance at one particular IR frequency is measured following excitation, and IR spectra are built up on a "point-by-point" basis by repeating this measurement at different infrared frequencies. The picosecond TRIR studies were performed on the PIRATE facility in the Rutherford Appleton Laboratory, details of which are described elsewhere.[26] Briefly, a part of the output from a 1 kHz, 800 nm, 150 fs, 2 mJ Ti:Sapphire oscillator and regenerative amplifier was used to pump a white light continuum seeded BBO OPA (β-barium borate optical parametric amplifier). The signal and idler produced by this OPA were difference frequency mixed in a type I AgGaS$_2$ crystal to generate tuneable mid-infrared pulses (ca. 150 cm^{-1} fwhm, 1 μJ). The 267 nm pump pulses were the third harmonic of the 800 nm regenerative amplifier output. Changes in infrared absorbance were recorded by normalizing the outputs from a pair of 64-element MCT linear-infrared array detectors on a shot-by-shot basis. Normally, several thousand shots were averaged for one delay time. 300 lines/mm gratings were used in spectrographs to achieve a spectral resolution of approximately 4 cm^{-1} in the 2200 cm^{-1} region. The Fe(CO)$_5$ concentration was adjusted to $10^{-3}-10^{-4}$ mol dm^{-3}. Different path lengths (ca. 0.5–1 mm for ultrafast experiments; 1–15 mm for the nanosecond point-by-point experiments) were used to ensure that the UV absorbance at the particular laser excitation wavelength and the maximum IR absorbance at the position of the ν(CO) absorption bands were below unity. *n*-Heptane (Aldrich HPLC grade, referred to as heptane throughout the text) was distilled from CaH$_2$ and degassed prior to use, and Ar (99.994%, BOC), CH$_4$ (99.995%, BOC), Fe(CO)$_5$ and CO (Aldrich), and Xe (99.995%, Spectragases) were used as supplied.

Results and Discussion

(a) Picosecond and Nanosecond TRIR Studies of Fe(CO)$_5$ in Heptane. Selected spectra from picosecond TRIR experiments with 267 nm excitation in heptane under CO (2 atm) are shown in Figure 1b. The two parent Fe(CO)$_5$ bands are bleached instantaneously, and there are new broad transient peaks apparent at lower wavenumbers after the first 5 ps. As is often observed in picosecond TRIR experiments performed upon metal carbonyls, these bands narrow and blue-shift, producing three clearly resolved transient ν(CO) bands at 1988, 1967, and 1926 cm^{-1}. The shift of the ν(CO) bands over the first 50 ps is consistent with a vibrational cooling of the newly formed species. The cooling time is similar for all three bands and is estimated to be ca. 10 ps.[27] The ν(CO) bands at 1988 and 1967 cm^{-1} can readily be assigned to **^{3}4** by comparison with the previous matrix isolation[9] and picosecond TRIR results,[23] whereas the band at 1926 cm^{-1} is due to **3·heptane**.[9,18] The ultrafast formation of **3·heptane** is unexpected, since in solution the excess energy which remains in a molecule following the ejection of one CO group is normally lost to the solvent rather than leading to loss of a second ligand. We have examined this question further by performing power-dependent TRIR measurements. We found that there was a linear dependence between the yield of **3·heptane** and **^{3}4** and the laser power. This strongly

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(27) Band areas and line widths at half-height were estimated by multi-Lorentzian curve fitting of the spectral points. The change in line width was then fitted to a first-order exponential decay function.
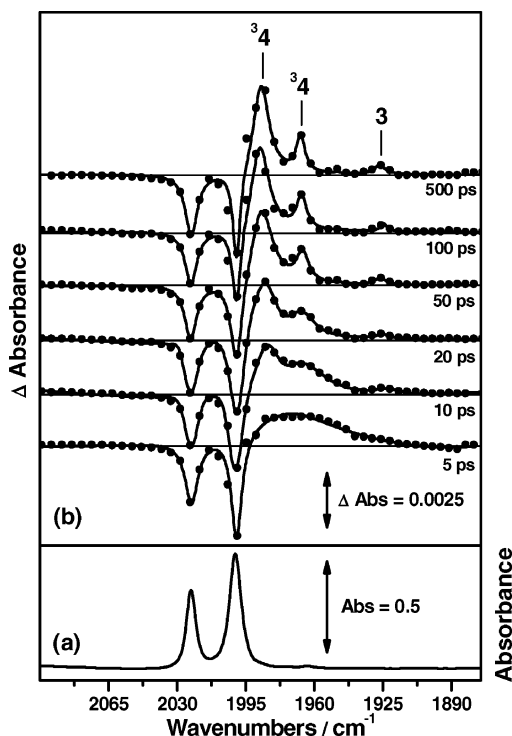
Figure 1. (a) FTIR spectrum and (b) TRIR spectra obtained between 5 and 500 ps following irradiation (267 nm) of a solution of Fe(CO)$_5$ in heptane saturated under 2 atm of CO.

supports a single-photon process where Fe(CO)$_5$ loses two CO ligands to generate **3·heptane** within the first 5 ps. An even weaker A$_1$ ν(CO) mode for **3·heptane** is expected at around 2036 cm^{-1},[9] but it is hardly discernible in our experiments (band positions are summarized in Table 1). Both **^{3}4** and **3·heptane** are stable up to 1 ns. From Figure 2, it can be seen that the TRIR spectrum obtained after 25 ns is similar to the 500 ps spectrum in that the vibrational bands due to **^{3}4** (1989 and 1969 cm^{-1}) and **3·heptane** (1926 cm^{-1}) are clearly present. However, an additional band at ca. 1950 cm^{-1} becomes apparent. As the bands at 1989, 1969, and 1926 cm^{-1} decay, many new absorption bands appear (see the 150 ns spectrum in Figure 2). In light of Grevels' microsecond TRIR work,[16,18] the new ν-(CO) peaks at 2083 cm^{-1} (A$_1$), 1989 cm^{-1} (B$_1$), 1973 cm^{-1} (A$_1$), and 1953 cm^{-1} (B$_2$) are unambiguously assigned to the singlet complex, **^{1}4·heptane**.

The formation of Fe$_2$(CO)$_8$ (**8**) and Fe$_2$(CO)$_9$ (**9**) is responsible for the other new absorption bands and is consistent with the previously published microsecond TRIR studies. **^{3}4** decays at the same rate as **^{1}4·heptane** is formed (Figure 3, Table 2). The decay of **^{3}4** and **3·heptane** is complex, since both of these species can react with CO in addition to forming **9** and **8**.[28] However, the decay rate of **^{3}4** is an order of magnitude faster than that of **3·heptane**. We have repeated the nanosecond TRIR experiment in the presence of argon (2 atm) instead of carbon monoxide, and it was found that the rate for the conversion of **^{3}4** ($k_{\text{obs}} = 8.1(\pm1.2) \times 10^7$ s^{-1}) into **^{1}4·heptane** ($k_{\text{obs}} = 7.5(\pm1.0) \times 10^7$ s^{-1}) was unchanged. Changing the Fe(CO)$_5$ concentration (from 6.6×10^{-4} to 5.5×10^{-3} mol dm^{-3}) did not affect the rate of the **^{3}4** to **^{1}4·heptane** conversion.

The lifetime of **3·heptane** was found to be dependent on both the CO and starting Fe(CO)$_5$ concentrations. Thus, **3·heptane** reacts with CO to generate **^{1}4·heptane** and with unphotolyzed Fe(CO)$_5$, forming **8**. These results are complementary to the previously published picosecond and microsecond TRIR data, since neither of these experiments were performed on a time scale that allowed the conversion of **^{3}4** to **^{1}4·heptane** to be monitored. The formation of **^{1}4·heptane** from the reaction of **3** with CO occurs on a slower time scale than the conversion of **^{3}4** to **^{1}4·heptane** and contributes to ca. 10% of the total formation of **^{1}4·heptane** in the presence of CO. In the absence of CO on the nanosecond time scale, **^{1}4·heptane** was observed to form solely from **^{3}4**. However, a close inspection of Figure 1 reveals that there is an additional, small peak at ca. 1950 cm^{-1}, and this possibly indicates that a *small* fraction of **^{1}4·heptane** is formed as an initial photoproduct. In other words, a small amount of the originally formed **^{1}4** could be directly converting into **^{1}4·heptane** rather than crossing over to form **^{3}4**. However, the possibility that this absorbance is due to some other minor photoproduct cannot be ruled out.

A conversion of **^{3}4** into **^{1}4·heptane** is consistent with the early matrix isolation work of Poliakoff and Turner, in which they demonstrated[6] that coordination of Xe or CH$_4$ to the Fe(CO)$_4$ moiety could be observed. However, no such coordination occurred following photolysis of Fe(CO)$_5$ in Ar matrices. We have recently used a combination of TRIR and supercritical fluids to characterize organometallic noble gas complexes in solution at room temperature.[29] This approach gives a unique opportunity to explore whether **^{1}4·L** can be formed in more weakly coordinating solvents such as Xe or Ar. In particular, the use of supercritical fluids may allow us to probe the role of vibrational relaxation on the formation of Fe(CO)$_3$ (**3**) from initially formed Fe(CO)$_4$ (**4**), since supercritical solvents have a significant effect on vibrational relaxation rates for metal carbonyls. For example, the vibrational relaxation lifetime of the $\nu = 1 \rightarrow 0$ ν(CO) transition in W(CO)$_6$ varies significantly as the solvent is changed from *n*-hexane (140($\pm$20) ps)[30] to scAr (1200 ps).[31]

(b) Picosecond and Nanosecond TRIR Studies of Fe(CO)$_5$ in Supercritical Xe (scXe). Selected TRIR spectra obtained following 267 nm photolysis of Fe(CO)$_5$ in scXe in the presence of CO are shown in Figure 4. The two parent ν(CO) bands are slightly blue-shifted relative to their positions in heptane. There are three bands clearly visible after the initially formed photoproducts have undergone vibrational cooling. The 1993 and 1972 cm^{-1} bands can be readily assigned to **^{3}4** in scXe, and the vibrational band at 1931 cm^{-1} is tentatively ascribed to **3·Xe**. The vibrational relaxation rates for **^{3}4** and **3·L** in scXe are slightly longer (ca. 25 ps) than those obtained from the aforementioned heptane experiments. **^{3}4** and **3·Xe** in scXe are stable up to 1 ns. It is interesting to note that there is relatively more **3·L** produced in scXe. The ratio[32] of [**^{3}4**]:[**3·L**] is ca. 5:1 in scXe compared to 17:1 in heptane. The TRIR spectrum obtained 25 ns after irradiation (Figure 5) is analogous to the spectrum at 500 ps. The bands at 1992 and 1973 cm^{-1} show

(28) The bands from dimers in the experiment are of very low intensity compared to the band from **^{1}4·heptane**. The intensities of dimer bands can be enhanced by increased Fe(CO)$_5$ concentration.

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Table 1. ν(C−O) IR Band Positions (cm^{-1}) of Iron Carbonyl Species

complex	conditions[g]	ν(CO) band positions (cm^{-1})	complex	conditions[g]	ν(CO) band positions (cm^{-1})
Fe(CO)$_5$ (**15**)	vapor	2032, 2018[a]	Fe(CO)$_3$(solv) (**3·L**)	scXe	1931[c]
	Ar matrix	2025, 2010, 2005, 1998[b]		heptane	1926[c]
	Xe matrix	2023, 2000, 1996, 1994[b]		cyclohexane	1926[f]
	CH$_4$ matrix	2025, 2003sh, 2001, 1996[b]	Fe$_2$(CO)$_8$ (**8**)	vapor	2046, 2016, 1982[a]
	scAr	2030, 2009[c]		Ar matrix	2042, 2009, 1987vw, 1979w
	scXe	2025, 2004[c]		scAr (Xe doped)	2045[c]
	heptane	2023, 200 [c]		scXe	2043[c]
^{3}Fe(CO)$_4$ (**^{3}4**)	vapor	2000, 1984[a]		heptane	2035[c]
	Ar matrix	1996, 1992, 1973[d]		cyclohexane	2036, 2004[f]
	Xe matrix	1989, 1983, 1967[b]	Fe$_2$(CO)$_9$ (**9**)	Ar matrix	2066, 2038, 2018w, 1855w
	CH$_4$ matrix	1992, 1985, 1967 [b]		scAr (Xe doped)	2067[c]
	scAr	1999, 1980[c]		scXe	2061[c]
	scXe	1993, 1972[c]		heptane	2057[c]
	heptane	1988, 1967[c]		cyclohexane	2056, ∼2020, 1826[f]
^{1}Fe(CO)$_4$(solv) (**^{1}4·L**)	Xe matrix	2085w, 1990, 1984, 1952[b]	Fe(CO)$_3$ (**3**)	vapor	1950[a]
	CH$_4$ matrix	2090w, 1998, 1984, 1954[b]		Ar matrix	2042w, 1936[b]
	cyclohexane	2084w, 1986, 1970, 1950		Xe matrix	2036w, 1927[b]
	scAr (Xe doped)	-, 1998, 1980, 1966[c]		CH$_4$ matrix	2040w, 1930[b]
	scXe	2085w, 1990, 1974, 1961[c]		scAr	1940[c]
	heptane	2083w, 1989, 1973, 1953[c]			

[a] Reference 12. [b] Reference 9. [c] This work. [d] Reference 38. [e] Reference 16. [f] Reference 18. [g] Matrix 12 K, fluids 298 K.
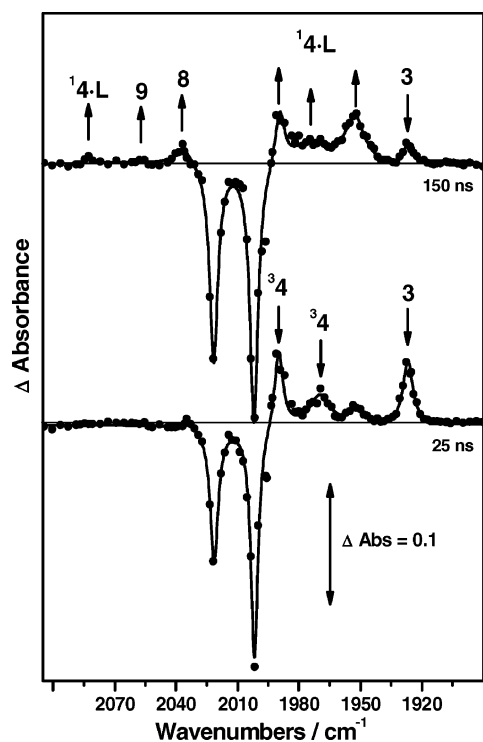
Figure 2. TRIR spectra obtained 25 ns and 150 ns following excitation (266 nm) of a solution of Fe(CO)$_5$ in heptane saturated under 2 atm of CO.

the presence of **^{3}4**, and the band at 1931 cm^{-1} is assigned to **3·Xe**. At 200 ns, these bands have decayed and several new ν(CO) bands are formed. Three of these bands (1990, 1974, and 1961 cm^{-1}) can be assigned to **^{1}4·Xe** by comparison with matrix isolation studies[7,9] and the analogous experiments carried out in heptane, which were described above. **^{3}4** decays at the same rate as **^{1}4·Xe** forms ($k_{obs} = 2.0(\pm0.2) \times 10^7$ s^{-1}). By direct comparison of the nanosecond traces in the region 2030−2090 cm^{-1}, a fourth, very weak ν(CO) absorption of **^{1}4·Xe** was found by a single trace experiment at 2085 cm^{-1}, which is, however, to small to be visible in the transient spectrum. Bands due to **8** and **9** in scXe were also observed to form as **^{3}4** and **3·Xe** decay (Table 1). Close examination of the picosecond TRIR spectra
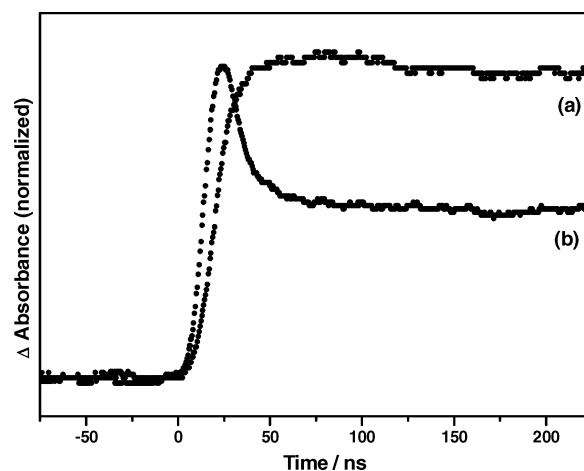
Figure 3. TRIR traces obtained following irradiation (266 nm) of a solution of Fe(CO)$_5$ in heptane saturated under 2 atm CO showing (a) the formation of **^{1}4·heptane** at 1953 cm^{-1} and (b) the decay of **^{3}4** overlapped with the formation of **^{1}4·heptane** at 1989 cm^{-1}.

Table 2. Rates of Decay of ^{3}Fe(CO)$_4$ (**^{3}4**) and Fe(CO)$_3$(solvent) (**3·L**) and Formation of ^{1}Fe(CO)$_4$(solvent) (**^{1}4·L**) in the Solvents, scAr, scXe, scCH$_4$, or Heptane (All Data at 298 K)[a]

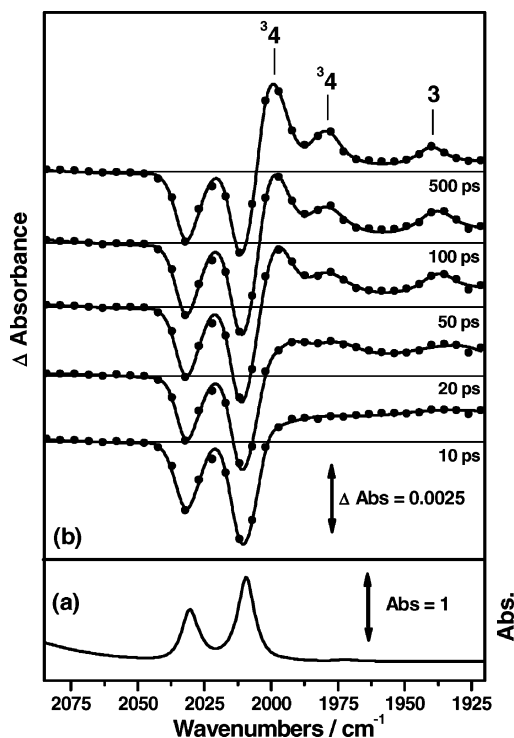| process	solvent	k_{obs} (s^{-1})
decay of **^{3}4**	scAr (CO doped)	5.3×10^6
	scXe (CO doped)	2.2×10^7
	scCH$_4$ (CO doped)	$6.2(\pm0.6) \times 10^6$
	heptane (CO saturated)	$8.1(\pm0.7) \times 10^7$
	heptane (Ar saturated)	$8.1(\pm1.2) \times 10^7$
decay of **3**	scAr (CO doped)	7.2×10^8
decay of **3·L**	scXe (CO doped)	5.3×10^7
	heptane (CO saturated)	$8.5(\pm1.0) \times 10^6$
	heptane (Ar saturated)	$1.99(\pm0.02) \times 10^6$
formation of **^{1}4·L**	scXe (CO doped)	2.0×10^7
	scCH$_4$ (CO doped)	$4.4(\pm0.4) \times 10^6$
	heptane (CO saturated)	$7.6(\pm0.1) \times 10^7$
	heptane (Ar saturated)	$7.5(\pm1.0) \times 10^7$

[a] The heptane solutions have been saturated at 30 psi.
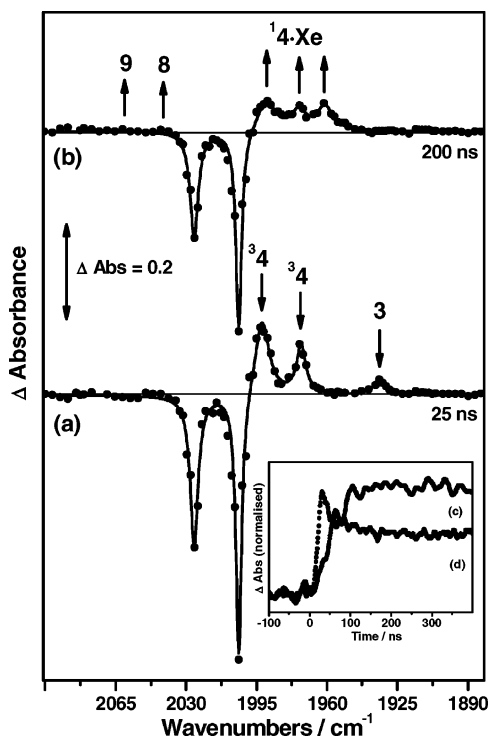
shows that, analogous to the experiments in heptane, there is a small peak (at ca. 1959 cm^{-1}) apparent at early time, possibly suggesting a rapid formation of a small amount of **^{1}4·Xe** in the first few picoseconds following excitation.
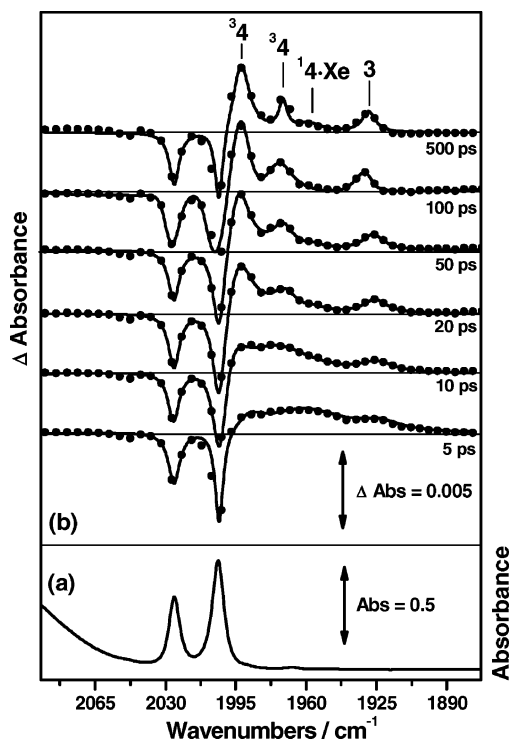
Figure 4. (a) FTIR spectrum and (b) TRIR spectra obtained between 10 and 500 ps following excitation (267 nm) of $Fe(CO)_5$ in scXe (1500 psi) doped with CO (30 psi).

Figure 5. TRIR spectra obtained at (a) 25 ns and (b) 200 ns after excitation (266 nm) of an $Fe(CO)_5$ solution in scXe (1500 psi) doped with CO (30 psi). TRIR traces showing (c) the formation of $^1Fe(CO)_4Xe$ (^{1}**4·Xe**) at 1961 cm^{-1} and (d) the decay of $^3Fe(CO)_4$ (^{3}**4**) overlapped with the growth of ^{1}**4·Xe** at 1990 cm^{-1}.

It is clear from these results that the basic photochemistry is similar in scXe and heptane in that both ^{3}**4** and **3·L** are formed within 5 ps and ^{3}**4** decays to form ^{1}**4·L**, whereas **3·L** decays to form ^{1}**4·L** and **8**.[33] The yield of **3·L** is increased and the

Figure 6. (a) FTIR spectrum and (b) selected TRIR spectra obtained between 10 and 500 ps after irradiation (267 nm) of $Fe(CO)_5$ in scAr (4500 psi) doped with CO (30 psi).

vibrational cooling rate is slower in scXe. Also, the lifetime of ^{3}**4** is longer in scXe. It is tempting to conclude that the more strongly coordinating heptane ligand is driving a faster conversion from ^{3}**4** to ^{1}**4·L**. We have investigated this further by performing TRIR experiments in scAr.

(c) Picosecond and Nanosecond TRIR Studies of Fe(CO)₅ in Supercritical Ar (scAr). Selected spectra from the picosecond TRIR investigation in scAr solution in the presence of CO are shown in Figure 6. In scAr, the rate of vibrational cooling is slower and bands which are readily assigned to ^{3}**4** and $Fe(CO)_3$ (**3**) sharpen at a much longer time delay relative to the experiments in scXe and heptane. Again the observed vibrational cooling times of ^{3}**4** and **3** are very similar (ca. 60 ps). The yield of **3** is higher in scAr, but a precise[34] ratio of [^{3}**4**]:[**3**] is difficult to estimate, since **3** is not stable and starts to decay before the vibrational relaxation is complete, see Figure 7. A value of 3:1 is obtained from the early time spectra. The lifetime of **3** ($\tau = 0.3$ ns) is much shorter than that in scXe ($\tau = 18$ ns) or heptane ($\tau = 117$ ns).[34] A possible explanation is that the strength of the Fe−solvent bond in the solvent coordinated species (**3·L**) increases in the order Ar ≪ Xe <

(33) Under CO, ^{3}**4** decays rapidly to form ^{1}**4·heptane**. The formation of ^{1}**4·heptane** from **3** was observed in a CO-saturated heptane solution of **5** resulting in a biphasic rise of ^{1}**4·heptane**. Rapid formation of ^{1}**4·heptane** was followed by a further slow growth which matched the decay of **3**. Under Ar, the formation of ^{1}**4·heptane** only occurred from the decay of ^{3}**4**. A reaction of ^{3}**4** with CO cannot be assumed due to the fact that **5** does not recover after the vibrational cooling has ceased and while the triplet−singlet conversion takes place. The formation of **8** starts within the first 40 ns, whereas the formation of **9** takes place within the first 1 μs. Compared with ^{1}**4·heptane**, only small fractions of **8** and **9** are formed while triplet singlet conversion takes place.

(34) In this work, the spectra 100 ps after the laser flash are used to estimate the intensity ratio, [^{3}**4**]: [**3·L**] or [^{3}**4**]: [**3**], respectively. At this time, we have assumed that there is a minimum contribution from vibrationally excited states. However, it must be noted that **3** has started to decay in scAr. The ratios obtained ranged from 3:1 in scAr to 5:1 in scXe to 17:1 in heptane.
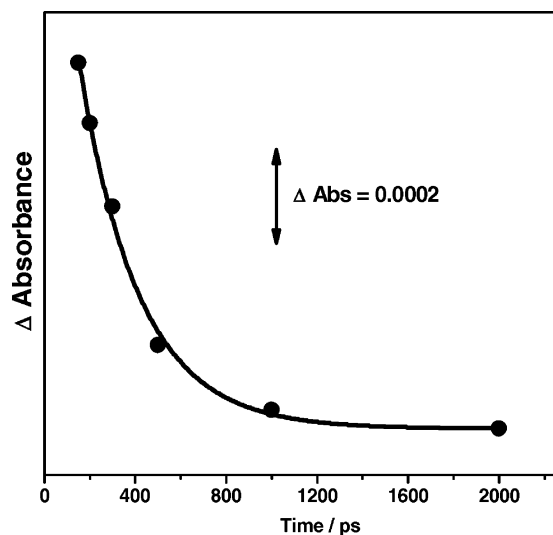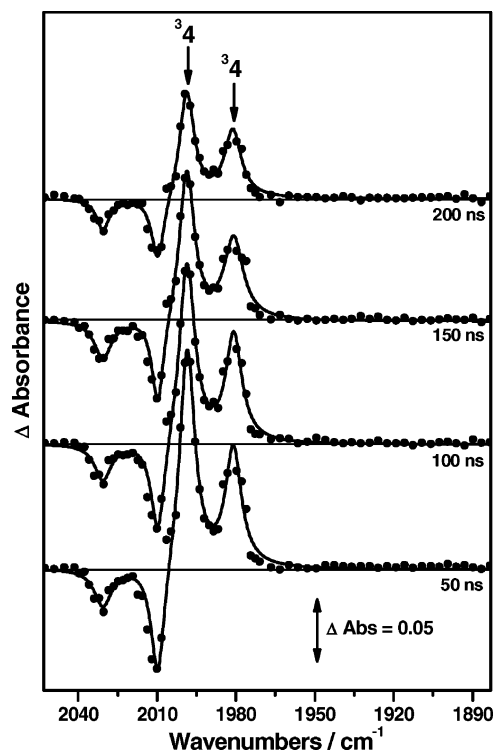
Figure 7. Change in intensity of the IR band centered at 1940 cm^{-1} between 0.1 and 2.0 ns after 267 nm excitation of Fe(CO)$_5$ in scAr (4500 psi) doped with CO (30 psi). Each data point represents the integral under the Lorentzian curve fitted transient peak. The curve represents a fit according to a first-order rate law for the decay of Fe(CO)$_3$ (**3**).

heptane. The long lifetime of **3** in heptane and scXe casts little doubt on the assignment of the solvated species, **3·heptane** and **3·Xe**. However, the coordination of Ar to **3** is more tentative. We have repeated the experiment at a much higher CO concentration (200 psi). This causes **3** to decay much more rapidly ($\tau = 50$ ps). Using five points at different CO partial pressures (30−200 psi), we have obtained an estimate for the bimolecular rate constant ($k_{CO} = 3.2(\pm 0.9) \times 10^{10}$ dm^3 mol^{-1} s^{-1}) for the reaction of **3** with CO in scAr. This value is an order of magnitude lower than the expected diffusion controlled rate ($k_{dif} = 2.0 \times 10^{11}$ dm^3 mol^{-1} s^{-1}), which suggests that **3** is solvent coordinated even in scAr solution. In scAr, **3** reacts with CO to form **³4**. Nanosecond TRIR spectra of Fe(CO)$_5$ in scAr following photolysis in the presence of CO are shown in Figure 8. **³4** is much longer lived in scAr ($\tau \approx 1$ μs). There was no evidence for the formation of the singlet solvated species **¹4·Ar** from **³4**.[35] **³4** decays ($k_{obs} = 5.2(\pm 0.5) \times 10^6$ s^{-1}) at the same rate as **¹5** is reformed ($k_{obs} = 4.5(\pm 0.5) \times 10^6$ s^{-1}) (see Figure 9), and the formation of **8** and **9** was not detected in scAr. The decay rate of **³4** in scAr depends linearly on the CO concentration (see inset in Figure 9), and this allows an estimation for the reaction rate of **³4** with CO in scAr ($k_{CO} = 1.2 \times 10^7$ dm^3 mol^{-1} s^{-1}). This value is similar to that obtained by Weitz and co-workers (3.1×10^7 dm^3 mol^{-1} s^{-1}) for the reaction between **³4** and CO in a gas phase study using Ar buffer gas.[11]

Although these studies show that Fe(CO)$_5$ has different photochemistries in scAr and scXe, it does not prove conclusively that the conversion is solely due to coordination of Xe to the metal center. Therefore we have repeated our TRIR experiments in scAr doped with Xe to probe this reaction further.

(d) Picosecond and Nanosecond TRIR Studies of Fe(CO)$_5$ in Supercritical Ar Doped with Xe. TRIR spectra obtained

(35) Close inspection of the picosecond TRIR spectra reveals an additional peak at 1969 cm^{-1} which decays rapidly ($\tau = 730(\pm 60)$ ps). It is tempting to assign this to rapidly decaying **¹4·Ar**. This would be consistent with the observation that in other solvents a small amount of **¹4·heptane** or **¹4·Xe** appears to be produced in the first few picoseconds. However, such an assignment must remain as very tentative.
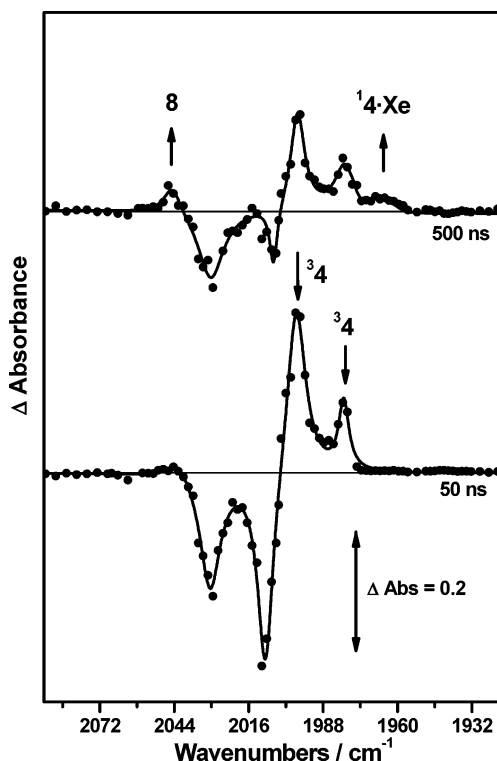
Figure 8. TRIR spectra obtained at 50, 100, 150, and 200 ns after irradiation (266 nm) of Fe(CO)$_5$ in scAr (4500 psi) doped with CO (30 psi).
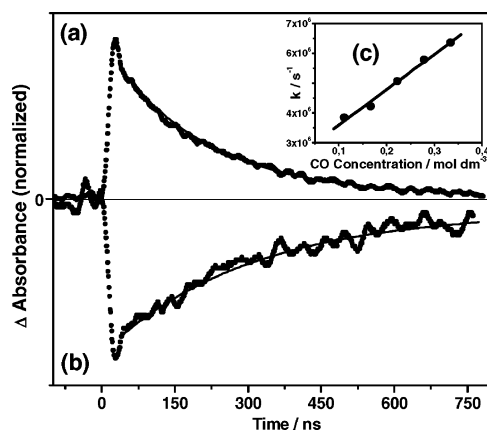
Figure 9. TRIR traces corresponding to the ³Fe(CO)$_4$ (**³4**) decay at 1980 cm^{-1} (a) and the recovery of Fe(CO)$_5$ (**¹5**) at 1998 cm^{-1} (b) obtained from the experimental results shown in Figure 8. (c) The CO concentration-dependent decay rate of **³4** is shown.

50 ns and 500 ns after excitation of Fe(CO)$_5$ in scAr doped with Xe, and a small amount of CO are shown in Figure 10. The parent bleaches are at very similar positions to those observed in pure scAr. The TRIR spectrum obtained after 50 ns shows that new bands are formed at 1998 and 1980 cm^{-1}, which are assigned to **³4** in the Xe−Ar mixture. These bands decay to form **¹4·Xe** (1998, 1980, and 1966 cm^{-1}), by comparison with the experiments carried out in pure scXe. **¹4·Xe** grows at the same rate as **³4** decays. Bands due to **8** and **9** are also detected in the Xe−Ar mixture (see Table 1), but the band of **9** is too small to become visible in the spectrum in Figure 10. In the presence of Xe *and* CO, **³4** can react to form either **¹5** or **¹4·Xe**. We have repeated this experiment, keeping the Xe concentration constant (450 psi) at two CO pressures (10 and 30 psi). We find that the rate of conversion between **³4**

Figure 10. TRIR spectra obtained at 50 ns and 500 ns after excitation (266 nm) of Fe(CO)$_5$ in scAr (4500 psi) doped with Xe (400 psi) and CO (30 psi).
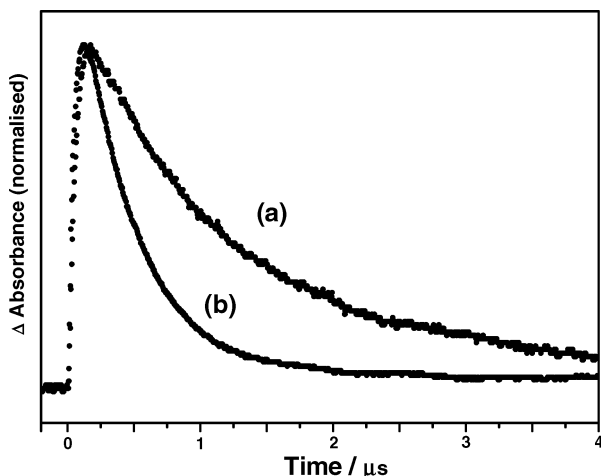

Figure 11. TRIR traces showing the formation and decay of ^{1}Fe(CO)$_4$Xe (^{1}**4·Xe**), monitored at 1966 cm^{-1} following irradiation (266 nm) of Fe(CO)$_5$ in scAr, doped with Xe (450 psi) and (a) 10 psi of CO or (b) 30 psi of CO. The overall pressure was 5000 psi.

and ^{1}**4·Xe** is identical (k_{obs} = 2.0(±0.2) 10^7 s^{-1}) at both CO concentrations. However, the lifetime of ^{1}**4·Xe** increases as the CO concentration is lowered, Figure 11. Although the Xe doped experiments strongly suggest that it is the coordinating ability of solvents, which is responsible for the conversion of ^{3}**4** to ^{1}**4·Xe**, it does not exclude the possibility that the additional Xe could be acting as a "heavy atom", facilitating the triplet−singlet conversion. The use of supercritical fluids again gives us an opportunity to test this theory by doping scAr with CH$_4$ rather than Xe. The photochemistry of Fe(CO)$_5$ in pure scCH$_4$ was very similar to that observed in heptane and scXe. TRIR experiments in scAr (4500 psi) doped with CH$_4$ (400 psi) show that ^{3}Fe(CO)$_4$ decays (k_{obs} = 4.6(±0.5) × 10^6 s^{-1}) to form
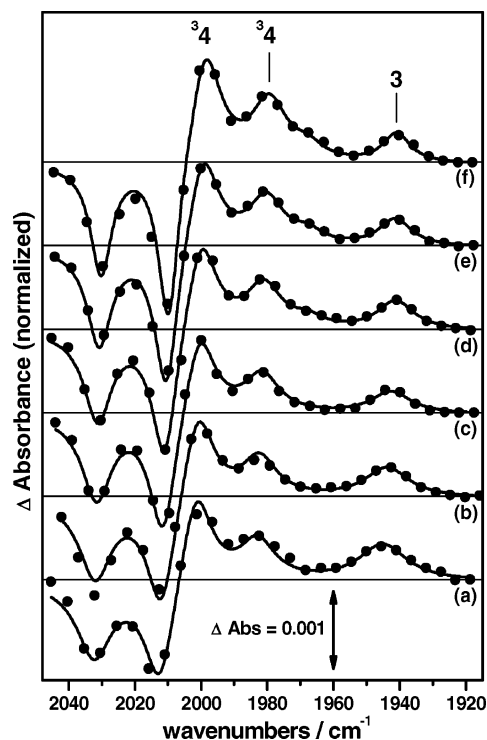
Figure 12. TRIR spectra obtained 150 ps after 267 nm excitation of Fe(CO)$_5$ in scAr, doped with 30 psi of CO at different overall pressures. The fit curves result from a multicomponent analysis of the six spectra at 1550 (a), 2140 (b), 2840 (c), 3450 (d), 4330 (e), and 5550 (f) psi. The spectra are normalized with the sum of the areas of the parent bleaches.

^{1}Fe(CO)$_4$(CH$_4$) in the mixed CH$_4$−Ar solvent, thus suggesting that a "heavy atom" effect is not being observed.[36]

(e) Exploring the Solvent-Dependent Yield of Fe(CO)$_3$ (3). The yield of Fe(CO)$_3$ (**3** in scAr and **3·L** in scXe, scCH$_4$, and heptane) relative to ^{3}**4** was found to be solvent dependent. The ratio [^{3}**4**]:[**3**] increases in the order scAr (3.5:1 at 1500 psi) < scCH$_4$ (4:1 at 3500 psi) < scXe (5:1 at 1500 psi) < heptane (17:1). One possible explanation is that **3** is formed from a vibrational excited state of Fe(CO)$_4$, i.e., Fe(CO)$_3$ is only generated when Fe(CO)$_4$ is vibrationally excited ([^{1}**4**]* or [^{3}**4**]*), and the yield of **3** depends on the vibrational relaxation rate. Another contribution to the relative yield of **3** and ^{3}**4** might be the solvent cage affecting the ratio of [^{3}**4**]:[**3**]. ^{3}**4** would not be expected to react with CO in the cage to form ^{1}**5**. It is possible that **3** could react with CO to form ^{3}**4** and that the nature of the solvent cage would then have a direct effect on the out-of-cage ratio of [^{3}**4**]:[**3**].

In supercritical fluids, the solvent concentration can be changed. A series of experiments at different pressures have been carried out to investigate the effects of Ar and CO concentration on the reaction mechanism of Fe(CO)$_5$ photolysis. We have performed picosecond TRIR experiments starting with a partial pressure of ca. 30 psi CO. As the total pressure was dropped from 4500 to 1500 psi, the [^{3}**4**]:[**3**] ratio decreased from 7:1 to 3.5:1. At the same time, **3** became longer lived (τ changes from 0.5 to 1.2 ns), which is consistent with the lower CO concentration. In a separate experiment at a fixed CO pressure of 30 psi, the total pressure was varied from 1600 to 5600 psi

(36) In the scAr doped with CH$_4$ experiment, we have observed a band growth at 1964 and 2086 cm^{-1}, which can be assigned to ^{1}**4·CH$_4$** by comparison with the previous matrix IR results. These bands are not observed in the experiment in pure scAr.

Scheme 2. UV Photolysis of Fe(CO)₅ in Solution (Heptane, scCH₄, scXe, and scAr)ᵃ

ᵃ Reactions which have major contribution are indicated by thick arrows. The dashed line is a tentative suggestion based upon a small band observed at early time.

by adding Ar to the mixture. Figure 12 shows TRIR spectra obtained at a range of pressures. The ratio changes significantly, and this is consistent with the solvent cage affecting the out-of-cage yield of **3**. However, it is also possible that the change in pressure is significantly affecting the vibrational relaxation rates. Unfortunately, analysis of the lower pressure data proved problematic, since both band position and width changed with pressure and accurate vibrational relaxation rates were not obtained.[37] We have repeated such experiments in scCH₄ and also found that the [**³4**]:[**3**] ratio had changed from 3:1 (1300 psi) to 6:1 (4300 psi) even though the observed vibrational relaxation is faster (ca. 10 ps).

Conclusions

We have provided direct evidence for the conversion of photogenerated triplet Fe(CO)₄ (**³4**) to singlet Fe(CO)₄(solvent) (**¹4·L**) (L = CH₄, Xe and heptane) in conventional and supercritical solution (Scheme 2). The existence of the solvent complexes of Fe(CO)₃ (**3·L**) and Fe(CO)₄ (**¹4·L**) was demonstrated in solution for all solvents except scAr. In scAr, we have no evidence for the formation of **¹4·Ar**.

The conversion of **³4** to **¹4·Ar** was not observed in scAr, but there is tentative evidence for the formation of **¹4·Ar** in the first few picoseconds. In coordinating solvents, **3·L** reacts with CO to form **¹4·L**, whereas, in scAr, **3** reacts with CO to form **³4**. The relative yield of [**³4**]:[**3**] is solvent and pressure dependent. The next challenge is to elucidate fully the formation of ³Fe(CO)₄ and Fe(CO)₃(solvent) in solution.

(37) The problem arises from the restricted number of spectral points compared to the number of bands in the spectral region of interest. This is combined with the especially broad and overlapped bands that are obtained at low pressure, thus preventing a quantitative analysis.
(38) Poliakoff, M. *Chem. Phys. Lett.* **1981**, *78*, 1–3.