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Note

Ultrafast studies of metal–metal bond cleavage in $Fe_3(CO)_{12}$ in solution ☆

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Abstract

The ultrafast dynamics following metal–metal bond breaking in $Fe_3(CO)_{12}$ have been investigated. Following excitation at 590 nm, the ground state $Fe_3(CO)_{12}$ is converted to a coordinatively unsaturated isomer with bridging COs, $Fe_3(CO)_{12}$(unsat.), within the instrument response of 1.5 ps. The unsaturated isomer then returns to the ground state with an exponential time constant of 150 ps. This rate of isomerization back to the ground state implies a barrier of 4.3 kcal mol^{-1}. This is in agreement with the results of Cotton and Hunter who put an upper limit of 6 kcal mol^{-1} on the isomerization of $Fe_3(CO)_{12}$ from an all terminal structure to a bridging structure. A portion (20%) of the excited molecules do not return to the ground state on the time scale of this experiment (<1 ns). This is attributed to fragmentation of $Fe_3(CO)_{12}$ to mono- and dinuclear species. Faster disappearance of the $Fe_3(CO)_{12}$(unsat.) at longer wavelengths indicates that fragmentation is promoted by excess vibrational energy.

Keywords: Metal–metal bond cleavage; Iron complexes; Carbonyl complexes; Cluster complexes

The structure and dynamics of $Fe_3(CO)_{12}$ have been under investigation for over 60 years. The solid state structure was intensely investigated by many groups throughout the 1950s, 60s and early 70s [1], but proved difficult to determine because of disorder in the crystal caused by intramolecular rearrangement. One of the primary investigators of this system was F.A. Cotton. In 1974, Cotton and Troupe [2] refined the structure originally proposed by Wei and Dahl [3]. This work showed that in the solid state, the three iron atoms form an isosceles triangle with two COs bridging across the asymmetric side of the triangle. The results of Cotton and Troupe showed the two CO bridges to be highly asymmetric, and based on this, they proposed that the barrier between an all terminal CO configuration and a CO bridging configuration is low and nearly flat. The structure of $Fe_3(CO)_{12}$ in solution has also been a subject of much investigation. It is clear from the IR spectrum that the bridging character of $Fe_3(CO)_{12}$ is much reduced in solution as compared to the solid state [4]. This is also supported by more recent extended X-ray absorption fine structure (EXAFS) [5] which showed the primary structure in non-polar solution is an all terminal CO structure with a small contribution from a possible bridging isomer. Additionally, ^{13}C NMR studies by Cotton and Hunter on $Fe_3(CO)_{12}$ in solution [4] showed that there is rapid exchange between terminal and bridging COs, and based on low temperature studies they determined that the barrier between an all terminal and a bridging configuration must be $\leqslant 6$ kcal mol^{-1}. In this work the long wavelength (>560 nm) photochemistry of $Fe_3(CO)_{12}$ in cyclohexane is investigated. Initial results indicate that this bridging to terminal process, first investigated by Cotton and Hunter, may play an important role in the long wavelength photochemistry of $Fe_3(CO)_{12}$.

Triiron dodecacarbonyl undergoes cleavage of a metal–metal bond upon absorption of visible light [6,7]. The bond cleavage is a result of a direct $\sigma \rightarrow \sigma^*$ absorption which is centered at 600 nm. Isomerization, involving conversion of a terminal carbonyl group to

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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a bridging carbonyl group, has been shown to occur in low temperature matrices following metal–metal bond cleavage in $Fe_3(CO)_{12}$ [7]. The isomerization results in a coordinatively unsaturated intermediate $Fe_3(CO)_{12}$-(unsat.) which can, upon heating, convert back to ground state $Fe_3(CO)_{12}$ or fragment to produce mono- and dinuclear species. This conversion back to ground state $Fe_3(CO)_{12}$ accounts for the low quantum yield observed at this wavelength for the declusterification of $Fe_3(CO)_{12}$.

In order to understand the dynamics of the long wavelength excitation of $Fe_3(CO)_{12}$ in solution, picosecond pump-probe experiments have been carried out with 1 ps time resolution. The experimental details have been described elsewhere [8]. Briefly, 1 ps, 0.5 mJ pulses at 590 nm were used to excite the sample and transient absorption signals were measured using a continuum probe. The continuum was generated in a water cell and 10 nm FWHM bandpass filters were used for wavelength selection. The sample concentration was 1.5×10^{-3} M $Fe_3(CO)_{12}$ in deoxygenated cyclohexane. This solution was continuously flowed through an optical cell with a path length of 1 mm.

$Fe_3(CO)_{12}$ has a broad absorption centered at 600 nm which is attributed to a metal–metal $\sigma \rightarrow \sigma^*$ transition. Fig. 1 displays the absorbance change at 560 nm near the center of the $Fe_3(CO)_{12}$ absorption following excitation at 590 nm. The data show an instrument response limited decrease (note the negative *y*-axis) in the absorption of the sample followed by a recovery of the absorption which fits a single exponential decay with a time of 150 ± 20 ps. The bleach does not recover to the initial value, but exhibits an offset of approximately 20%.

Fig. 2 shows the absorbance change at 720, 760 and 800 nm following excitation at 590 nm. At all wavelengths the data show a transient absorption with a two component decay. The rise time of the absorbance is instrument response limited. The long component of the decay is 150 ± 15 ps and is independent of wavelength. The fast component is wavelength dependent with values of 14 ± 2, 9 ± 2 and 5.5 ± 2 ps at 720, 760 and 800 nm, respectively.

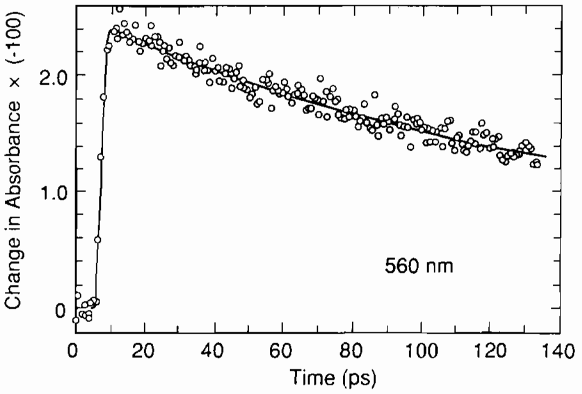

Fig. 1. Change in absorption at 560 nm following excitation at 590 nm (note the negative *y*-axis). The solid line represents a fit to a 150 ps single exponential decay.

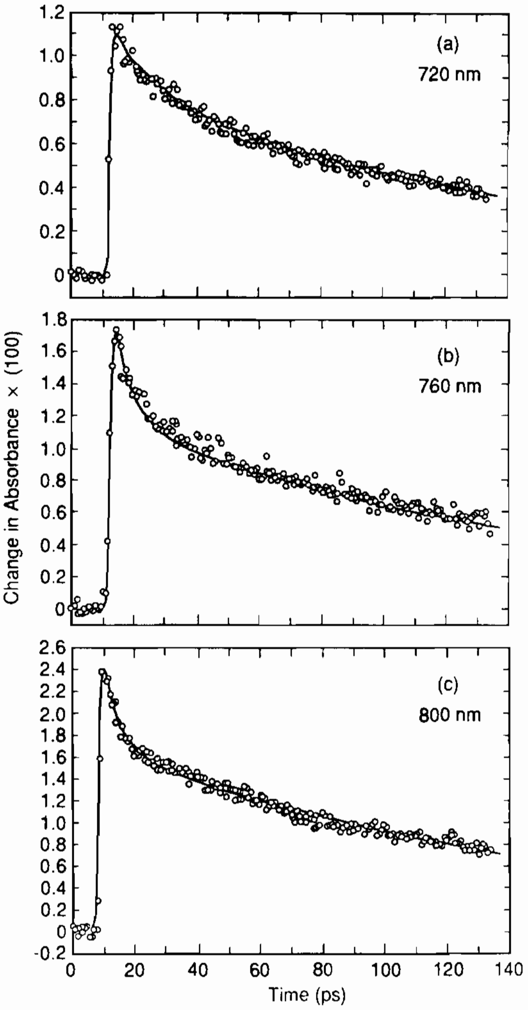

Fig. 2. (a) Change in absorption at 720 nm following excitation at 590 nm. The solid line is a fit to a biexponential decay with time constants of 14 and 150 ps. (b) Change in absorption at 760 nm following excitation at 590 nm. The solid line is a fit to a biexponential decay with time constants of 9 and 150 ps. (c) Change in absorption at 800 nm following excitation at 590 nm. The solid line is a fit to a biexponential decay with time constants of 5.5 and 150 ps.

In low temperature matrices the bridging isomer, $Fe_3(CO)_{12}$(unsat.), has been shown to have a broad featureless absorption to the red of the ground state $Fe_3(CO)_{12}$ [7]. Based on this work we assign the broad transient absorption to the red of the ground state absorption to the formation of $Fe_3(CO)_{12}$(unsat.). Therefore, the instrument response limited rise time in both the bleach and the red-shifted transient absorption indicates that $Fe_3(CO)_{12}$(unsat.) is formed in $\leqslant 1.5$ ps after excitation. The 150 ps component present in both the recovery of the ground state absorption at 560 nm and in the decay of the absorption of $Fe_3(CO)_{12}$(unsat.) at 720, 760 and 800 nm is attributed to the conversion of $Fe_3(CO)_{12}$(unsat.) back to ground state $Fe_3(CO)_{12}$.

From a simple Arrhenius description, the size of the barrier on going from the bridging isomer, $Fe_3(CO)_{12}$(unsat.), to the all terminal ground state can be estimated. Assuming a preexponential of 1×10^{13} (same as used by Cotton and Troupe [2]) and a rate of isomerization of 6.67×10^9 s^{-1} (1/150 ps) at 300 K, the height of the barrier is approximately 4.3 kcal mol^{-1}. This is well under the upper limit placed by Cotton and Hunter (6 kcal mol^{-1}) from NMR studies, but still chemically reasonable. Temperature dependent studies are currently planned to further examine this process.

The decay of the transient absorption at 720, 760 and 800 nm shows two components. The wavelength independent long component of 150 ps, as mentioned above, is assigned to the isomerization of $Fe_3(CO)_{12}$(unsat.) back to ground state $Fe_3(CO)_{12}$. The fast component is wavelength dependent and does not appear in the ground state bleach at 560 nm. This indicates that a fraction of the coordinatively unsaturated species, $Fe_3(CO)_{12}$(unsat.), is not returning to ground state $Fe_3(CO)_{12}$. Previous studies have shown that $Fe_3(CO)_{12}$(unsat.) can fragment to produce mono- and dinuclear species [7]. In light of this, the fast component is attributed to the fragmentation of $Fe_3(CO)_{12}$(unsat.) which also accounts for the observed incomplete recovery of the bleach at 560 nm.

The wavelength dependence of the fast component can be interpreted as probing $Fe_3(CO)_{12}$(unsat.) molecules with excess vibrational energy. It has been found in previous studies [9,10] that following excitation vibrationally excited molecules absorb to the red of the cooled species. Therefore, the faster decays at longer wavelengths correspond to species with more excess vibrational energy fragmenting faster than species with less vibrational energy.

In conclusion, the dynamics of metal–metal bond cleavage in $Fe_3(CO)_{12}$ have been investigated. Fig. 3 summarizes our results. A coordinatively unsaturated, carbonyl bridging intermediate, $Fe_3(CO)_{12}$(unsat.), which results from metal–metal bond cleavage and carbonyl rearrangement is formed within 1.5 ps. This intermediate can either fragment or convert back to ground state $Fe_3(CO)_{12}$. The fragmentation is promoted by excess vibrational energy and occurs in 5–15 ps. The isomerization back to the all terminal ground state structure occurs on a time scale of 150 ps which implies a barrier of 4.3 kcal mol^{-1}. Transient IR experiments which can probe the bridging carbonyl group in $Fe_3(CO)_{12}$(unsat.) are currently planned in order to better understand the details of the carbonyl rearrangement.

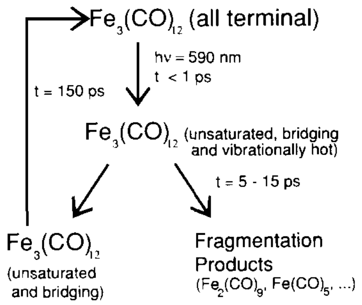

Fig. 3. Reaction scheme for the long wavelength photochemistry of $Fe_3(CO)_{12}$.

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