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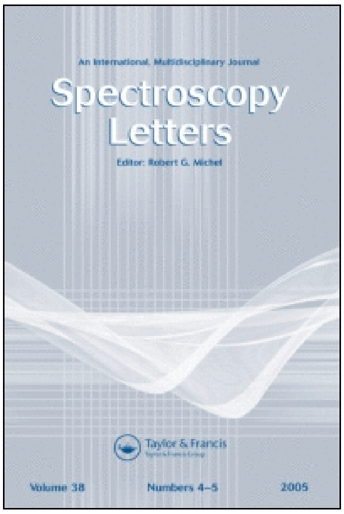

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MULTIPHOTON DISSOCIATION OF IRON CARBONYLS: EMISSION FROM ATOMIC IRON

Key words: multiphoton dissociation, fluorescence, iron carbonyls

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ABSTRACT

The third harmonic of the Nd:YAG laser is used to photodissociate $Fe(CO)_3L$, where L = C_4H_6 or C_6H_8. The resulting emission is analyzed and observed to originate from high lying states of atomic iron. Iron ions are concurrently produced at laser energies as low as 20 μJ pulse^{-1}. The nature of the emission spectrum is dependent upon the total pressure and the nature of any added background gas. The photochemistry is analyzed using an RRKM treatment, which indicates that the absorption of two photons by $Fe(CO)_3L$ leads to production of FeL with a small excess energy. Ground state Fe production occurs upon absorption of an additional photon. In competition with this process would be the absorption of additional photons leading to the observed Fe atomic levels with "intermediate" energy. High energy states observed in the emission spectrum could be accessed by absorption of three photons by FeL. In all three reaction channels, the atomic states could be populated by multiple curve crossings. Such high levels of excitation are constant with the observation of J-independent populations in many of the electronic states and the absence of a Boltzmann temperature for the distribution of atomic iron electronic states.

INTRODUCTION

The mechanism of the photodissociation of carbonyl complexes has been the subject of a number of studies.[1-10] We have recently reported on the multiphoton dissociation of a series of iron tricarbonyl complexes.[3] In that study, the initial excitation involved two-photon pumping of the Fe → π^* CO transition. REMPI was employed to characterize the state distribution of the atomic iron after photodissociation. The results indicated that only the three lowest electronic levels were populated, that the ground state multiplet was statistically populated and that the relative populations of the two electronic states were dependent upon both the total bond energy of the complex and the density of states of the organic ligand. In a later RRKM study[11], we probed the mechanism of the dissociation process and concluded that ground state, unsaturated molecular fragments were produced via a statistical, stepwise process with the final Fe states resulting from further direct excitation to a dissociative channel.

In this paper, we report the Fe emission spectrum resulting from photodissociation of the $Fe(CO)_3C_4H_6$ and $Fe(CO)_3C_6H_8$ molecules. Unlike the earlier study, initial excitation involved the ligand field (d_{xy}, $d_{x2-y2} \rightarrow d_{z2}$) transition, so that sequential, single photon processes were involved in all of the reported photochemistry. The emission spectrum was recorded as a function of the total sample cell pressure. Additional spectroscopic measurements were employed to study to ultimate fate of the photofragments.

EXPERIMENTAL

The experiments were performed in a static gas cell with a standard "Tee" configuration and containing 300 mtorr of the sample as measured with a MacLeod gauge. The cell was fitted a pair of stainless steel parallel plate electrodes so that fluorescence and ionization measurements could be made simultaneously. High purity helium, argon or nitrogen (Air Products) were used as background gases at pressures up to 300 mtorr. Degassed samples of the organometallics (Strem Chemical) were used without further purification. All photo-excitation was accomplished using the third harmonic (355 nm) of a Nd:YAG laser focused into the cell by means of a 15 cm focal length lens. The laser intensity was recorded using a surface calorimeter positioned at the exit window of the cell. Emission spectra were recorded using a system consisting of a 0.25 m MacPherson monochromator, a Hammamatsu R663 photomultiplier and a Stanford Research

Systems Gated Integrator. The spectrometer was under the control of a microprocessor which scanned the grating and acquired the spectra. The monochromator was capable of recording wavelengths into the vacuum ultraviolet, but the emission was limited to the region from 250 to 600 nm and no emission was observed at wavelengths greater than approximately 500 nm. Ionization current was usually recorded by an electrometer, although the gated integrator was also used for this task.

RESULTS

The gas phase absorption spectra of the tricarbonyl iron complexes were reported in our earlier work.[3] For both the butadiene and hexadiene complexes, these spectra consist of an intense band with a maximum at ~47,000 cm^{-1} that has been assigned to an Fe → π^* CO transition and a weaker shoulder with a maximum at approximately 35,000 cm^{-1} that was assigned to the (d_{xy}, $d_{x2-y2} \rightarrow d_{z2}$) ligand field transition. The photolysis energy in this study was such that irradiation occurred in the long wavelength tail of the ligand field transition and the initial excitation was assumed to be single-photon. Photolysis produced both excited neutral fragments and ions at all laser intensities down to 20 μJ $pulse^{-1}$. The energetics[12] of excitation at 355 nm are schematically represented in Figure 1. It may be seen that, in the simplest energetic terms, production of atomic iron requires a minimum of two photons, formation of $Fe(CO)_3L^+$ requires at least the energy of three photons and the production of Fe^+ involves absorption of at least four photons at the wavelength employed. Time-of-flight mass spectrometric results indicated that the major ionic product was Fe^+; the only substantial peak was readily assigned to the major isotope of iron. A small peak at m/z 54 was assigned, by means of the ratio of the two peaks, to a minor isotope of iron. The ligand ions, $C_4H_6^+$ and $C_6H_8^+$, were not observed in the mass spectrum.

Emission Spectra. A typical fluorescence spectrum, in the 200 to 350nm and 360 to 500nm regions, resulting from photolysis of $Fe(CO)_3C_4H_6$ at 355 nm (~30 μJ $pulse^{-1}$) is shown in Figure 2. All of the features observed in these spectra may be assigned to transitions of neutral iron atoms.[13-15] No molecular features, either from CO or from organic fragments, were observed under these experimental conditions. A cursory comparison of the emission lines observed in this work, over the spectral range from 250 to 500nm, with those observed in an iron arc

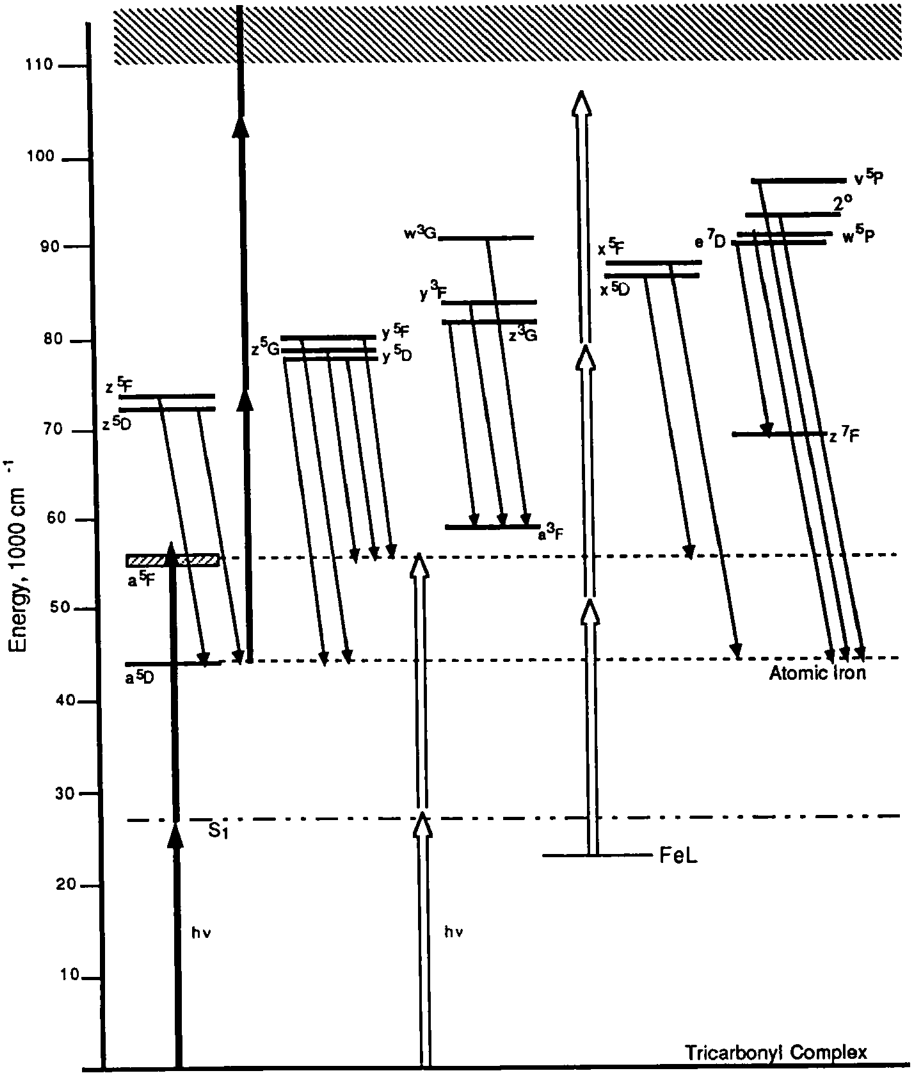

FIG. 1. Schematic energy level diagram for the iron tricarbonyl-Fe-Fe$^+$ system irradiated at 355nm.

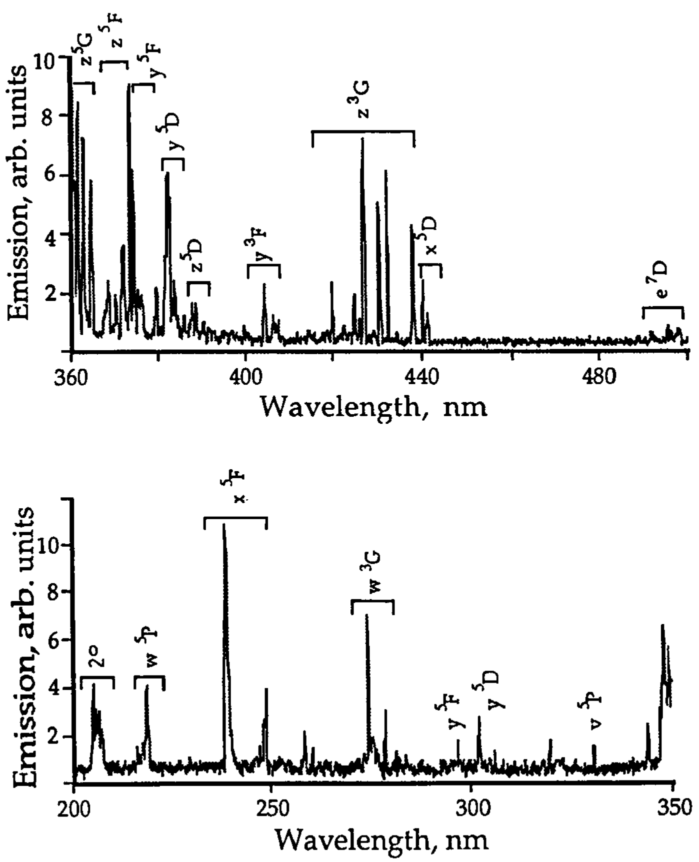

FIG. 2. Emission spectrum resulting from the photolysis of $Fe(CO)_3C_4H_6$ at 355nm. The laser intensity was 160 μJ pulse^{-1} and the pressure of the sample was 300 mtorr with 130 mtorr of argon added.

spectrum indicates that many of the same features appear, but with different intensities.[13-16] The vast majority of the lines observed in the spectrum represent transitions involving p-electrons within the quintet manifold. The relative intensities of the spectral lines were dependent upon the total sample pressure in the sample cell increasing linearly with carbonyl pressure to 600mtorr. The spectra were identical, except for the intensities, whether the hexadiene or the butadiene complex was used as the source of iron atoms. The observed transitions involve upper states with energies in the range from approximately 25,000 cm^{-1} to 48,000

cm^{-1}. These states all have odd parity. With a single exception, $e^7D \rightarrow z^7F$, the transitions terminate on one of the three lowest electronic states, all of even parity and arising form the ground electronic (a^5D) configuration, $3d^6\,4s^2$, or the first excited (a^5F, a^3F) configuration, $3d^7\,4s$. A complete listing of the electronic configurations of the excited states is presented in Table 1.

The spectral intensities may be used, along with the Einstein coefficients, to determine the relative populations of the electronically excited states. For a statistical excitation process, the Boltzmann relationship holds and a plot of the populations, corrected for degeneracy, as a function of electronic energy should be linear with a slope related to the temperature. The populations of the various J-states within an particular electronic state are approximately equal and the average population for a given electronic state may be employed in any discussion of the electronic temperature. The electronic populations observed in this study are not fit by linear equations and are non-Boltzmann.

Studies of the time dependence of the fluorescence signal at a number of wavelengths indicate that all of the upper states of the observed transitions are populated coincident with the laser pulse and that no delayed emission is present in this system. The maximum fluorescence intensity is reached within 5ns of the laser pulse. The laser intensity dependence of the fluorescence was observed at a number of wavelengths using laser pulse energies as low as 20μJ and as large as 200μJ. The log-log plots of fluorescence vs. laser intensity indicate that some of the excitation steps leading to the fluorescent states are saturated even at the lowest laser energy. This is reflected in slopes of unity for all such plots. One possibility is that the laser intensity dependence reflects only the initial one-photon absorption in the wings of the ligand field transition. The absorption spectra indicate that this is a weakly allowed, one-photon transition.

As is clear form Figure 1, the energies of a number of the upper states are sufficiently great that two photons are required to populate them from $Fe(a^5D_J)$. Others may be populated by single photon excitation provided that the photochemically prepared quantum state of the iron atom is not the ground state. In this simple case, the proposed laser energy dependence requires the assumption that dissociation of the iron complex is effected by sequential two photon absorption. The validity of this assumption will be addressed in the following section.

TABLE 1

Observed Fe Emission Lines and Pressure Effects in $Fe(CO)_3C_4H_6$ and $[Fe(CO)_3C_6H_8]$ Multiphoton Dissociation

Observed Transition	He	Ar	N_2
$(3d^5\,4s^2\,4p)\ w^5P \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	+[+]	+[+]
$(3d^6\,4s\,4p)\ x^5F \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	+[+]	+[+]
$(3d^7\,4p)\ v^5P \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	-[-]	-[+]
$(3d^6\,4s\,4p)\ y^5F \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	+[+]	-[+]
$(3d^7\,4p)\ y^5D \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	+[+]	-[+]
$(3d^6\,4s\,4p)\ z^5D \rightarrow a^5D\ (3d^6\,4s^2)$	-[-]	-[-]	-[ ]
$(3d^6\,4s\,4p)\ z^5F \rightarrow a^5D\ (3d^6\,4s^2)$	-[-]	-[-]	-[ ]
$(?)\ 2^0 \rightarrow a^5D\ (3d^6\,4s^2)$	+[+]	+[ ]	+[+]
$(3d^7\,4p)\ z^5G \rightarrow a^5F\ (3d^7\,4s)$	-[-]	+[+]	+[-]
$(3d^7\,4p)\ y^5F \rightarrow a^5F\ (3d^7\,4s)$	-[-]	-[-]	-[-]
$(3d^7\,4p)\ y^5D \rightarrow a^5F\ (3d^7\,4s)$	-[-]	-[-]	-[-]
$(3d^6\,4s\,4p)\ x^5D \rightarrow a^5F\ (3d^7\,4s)$	-[-]	+[+]	-[ ]
$(3d^7\,4p)\ w^3G \rightarrow a^3F\ (3d^7\,4s)$	+[+]	+[+]	+[+]
$(3d^7\,4p)\ y^3F \rightarrow a^3F\ (3d^7\,4s)$	-[-]	+[+]	-[ ]
$(3d^6\,4s\,4p)\ z^3G \rightarrow a^3F\ (3d^7\,4s)$	-[-]	+[+]	+[-]
$(3d^6\,4s\,5s)\ e^7D \rightarrow z^7F\ (3d^6\,4s\,4p)$	-[-]	+[+]	-[ ]

Ion Formation. The ion current was monitored simultaneously with the fluorescence measurements reported above. A current was observed at all laser intensities. A laser multiphoton mass spectrum indicated that the current was due to Fe^+. Since the experiments were carried out at a single wavelength, it was not possible to directly ascertain the electronic states involved in the multiphoton production of ions. However, our previous studies[3,11] have indicated that production of any one of the three lowest electronic states of Fe rapidly leads to formation of ions even at laser energies as low as 10 μJ per pulse. None of the fluorescence transitions observed in the study could be assigned to transitions in the ion manifold.

Deposition. In any experiment involving organometallic complexes, there is the possibility of the formation of a metal film at the windows and/or the deposition of a fine powder inside the cell. Film production was observed, was independent of gas mixture and increased with increasing laser energy. The semi-transparent film was assumed to be iron. Production could be prevalent for all sample mixtures and constant vigilance was required to ensure that any film that developed on the input window did modify the final spectroscopic or ionization results. The laser intensity through the sample was constantly monitored to eliminate the effects of the film production and, for most experiments, the laser energy was maintained at the minimum possible so that the laser energy was constant throughout the recording of a particular spectrum. Interestingly, the powder deposition process was found to be dependent upon the nature of the organometallic and on added background gases. The butadiene complex led to more substantial powder deposition and the addition of He increased the yield of the powder. Addition of nitrogen led to a reduction in powder production. Several attempts were made to analyze the powder by solid probe mass spectrometry. However, the material proved to be involatile.

DISCUSSION

The ions observed at all laser energies may be attributed to the further excitation of the states produced by one or two photons. These are allowed transitions with large transition moments and are readily saturated even at low laser intensities.[3] The proposed reaction mechanism leading to ions is indicated by the solid up-pumping arrows in Figure 1.The dissociation pathway leading to formation of the excited iron atoms reported in this study is more complex. Several different mechanisms may be proposed. A previous study involving excitation in the charge transfer band utilized RRKM calculations to differentiate between direct production of Fe via an explosive process and sequential loss of the four ligands.[11] A similar study, relevant to production of iron atoms in the current process, was conducted here. Since the time scale of importance is that upon which fluorescence is observed (5 ns), a number of scenarios may be eliminated. Single photon absorption leading to loss of the three carbobyl groups is predicted to be too slow for observation on the experimental time scale, regardless of whether the decomposition occurs sequentially or explosively since the rate constants are 10^{7} s^{-1} and 10^{-5} s^{-1}, respectively. Decomposition to directly produce the ground electronic state iron atoms via a statistical process is much too slow to be observed whether the process follows absorption of either two ($k = 10^{-7}$ s^{-1}) or three ($k = 10^{2}$ s^{-1}) photons. Similar difficulties are encountered with a two photon absorption, sequential dissociation mechanism, $k = 10^{5}$ s^{-1}. However, a mechanism in which the complex absorbs three 355nm photons and sequentially dissociates is predicted to occur on the experimental time scale ($k = 10^{9}$ s^{-1}). In this scenario, the excited states of the iron atom would be populated by two photon excitation of the ground state atoms initially produced. There is no known quantum state at the one photon energy level, but the u^3H electronic state is resonant with the energy of two photons. This transition would violate both spin selection rules (not unusual for iron atoms) as well as the orbital angular momentum selection rules. Previous studies have indicated that the latter were generally obeyed in the iron excitation manifold.[1-10] Examination of the emission lines indicated that the u^3H state was not observed. Iron is known to exhibit a large number of infrared transitions that may readily populate the lower electronic states observed in this study by a cascading process from the upper levels; however, the lifetimes of these infrared emitting states are generally longer than the 5ns required for the observed fluorescence to reach its maximum value, and we conclude that such a reaction pathway is unlikely.

Finally, a series of steps is postulated leading to, first the formation of the coordinatively unsaturated FeL after two photons are absorbed, and then, formation of ground state Fe subsequent to absorption of a third photon, Scheme 1.
The rate constant is of the correct order of magnitude, $k = 3.8 \times 10^{8}$ s^{-1}, but the issue of the mechanism of population of the higher electronic states remains. In a previous study[3], the mechanism of formation of the ground state iron atoms was

$$\mathrm{Fe(CO)_3L} + h\nu \rightarrow \mathrm{Fe(CO)_3L^*} \rightarrow \mathrm{Fe(CO)L^*} + 2\mathrm{CO} + h\nu \rightarrow$$
$$\mathrm{FeL} + 3\mathrm{CO} + h\nu \rightarrow \mathrm{Fe(a^5D_J)} + 3\mathrm{CO} + \mathrm{L}$$

Scheme 1. Postulated Reaction mechanism for Iron tricarbonyls.

postulated to be a hybrid process involving sequential, statistical loss of the carbonyl ligands to produce a triplet unsaturated FeL fragment. Absorption of additional energy by this fragment resulted in the formation of iron atoms in the three lowest electronic states by a curve crossing process from the excited state molecular fragment. The forbidden nature of excitation from the lower electronic states as well the lack of a one photon transition from the lowest electronic states of the iron atom at 355nm indicates that the excited state emission may not arise from excitation in the atomic ladder, but rather from excited states of the unsaturated complex. Application of the earlier model would indicate that the absorption of two photons by $\mathrm{Fe(CO)_3L}$ leads to production of FeL with a small excess energy. Further decomposition of this unsaturated fragment may occur by any one of a set of competing pathways. Ground state Fe production would be expected upon absorption of a single photon. In competition with this process would be the absorption of additional photons with subsequent channel opening for a number of the observed Fe atomic levels with "intermediate" energy. Finally, the high energy states observed in the emission spectrum could be accessed by absorption of three photons by FeL. In all three reaction channels, the atomic states could be populated by multiple curve crossings. Such high levels of excitation are constant with the observation of J-independent populations in many of the electronic states and the absence of a Boltzmann temperature for the distribution of atomic iron electronic states.

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