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6 October 1995

Chemical Physics Letters 244 (1995) 213–217

CHEMICAL PHYSICS LETTERS

Direct formation of a state-selected excited state of Fe atoms by multiphoton dissociation of $Fe(CO)_5$ at atomic transition frequencies

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Received 1 June 1995; in final form 31 July 1995

Abstract

When an unfocused laser beam with narrow linewidth whose frequency matches exactly an atomic transition line of the Fe atom was passed through a gas mixture containing $Fe(CO)_5$, atomic emissions from the state-selected excited state of Fe atoms were observed. The power dependence of the emission intensities as well as excitation and fluorescence spectra suggested that the state-selected excited state Fe atoms are generated by one-photon absorption of the ground state Fe atoms formed by two-photon dissociation of $Fe(CO)_5$ within a single laser pulse.

1. Introduction

Multiphoton dissociation (MPD) of metal carbonyls or organometallic compounds has been investigated by many groups [1–9], because MPD of these compounds is not only an interesting subject for studying photodissociation mechanisms, but also it provides a useful way to generate well-defined pulses of metal atoms in the gas phase without high temperature sources. Most of the MPD experiments, however, were done using a focused laser beam, and the product states of the bare metal atoms which are detected by atomic fluorescence [1–4] or multiphoton ionization techniques [5–9] were found to be distributed among the various electronic states. The formation of many different excited species of metal atoms from the MPD of metal carbonyls using a focused laser beam was an obstacle to apply this technique to study chemical kinetics of a specified excited state of refractory metal atoms with a one-color laser, although it generates well-defined pulses of metal atoms at low temperature.

In this work, we report direct formation of a state-selected excited state of Fe atoms from the MPD of $Fe(CO)_5$ using an unfocused UV laser pulse. When the $Fe(CO)_5$ sample is irradiated with a frequency doubled dye laser output at a frequency which matches exactly the corresponding atomic transition line, relatively strong fluorescence from the specified excited state of Fe atoms is observed. Although many of the optically allowed excited states locating at 25000–35000 cm^{-1} above the ground state term are found to be generated by this method, results for the generation of the y $^5D^o_J$ state are presented specifically in this Letter since the Einstein *A* coefficients for both the y $^5D^o_J \rightarrow a\,^5D_{J'}$ and y $^5D^o_J$

SSDI 0009-2614(95)00925-6

$\rightarrow a\,^5F_{J'}$ transitions are large and those absorption and emission lines are easily identified [10]. The energy dependence of the fluorescence intensities showed that this is a three-photon process: two-photon dissociation followed by one-photon absorption within a single laser pulse.

2. Experimental method

A detailed experimental setup has been reported elsewhere [11,12]. Briefly, the MPD/LIF cell was made of a 2 l pyrex bulb and two pairs of 1 inch pyrex O-ring joints were attached for the laser beam path and to connect to the gas handling vacuum rack. The ports for the fluorescence detection were made by attaching 1.5 inch pyrex tubes to the bulb and cutting the arms with a glass saw as close as possible to the bulb. The sample gas (0.5% $Fe(CO)_5$ in Ar) was premixed and stored in a storage bulb in the vacuum rack. The gas mixture was slowly flowed through the cell and the total pressure in the cell was maintained at 0.2–0.3 Torr while taking the fluorescence and excitation spectra. The flow rate (≈ 0.5 mmol/min) was controlled by adjusting the openings of the inlet needle valve and exit teflon valve. Then, the unfocused UV laser pulses (0.3–0.6 mJ/pulse with 0.4 cm^2 spotsize) obtained from the frequency doubling of the dye laser output were passed through the cell. The linewidth of our laser (Quantel YG681-TDL 60 with NBP and DGO) was narrow (< 0.1 cm^{-1}) enough to excite a single spin–orbit state selectively. The pulse shape of our laser is a Gaussian shape with 8 ns fwhm. For the excitation spectra, the laser was scanned in the 298.0–308.0 nm region and the fluorescence from the $y\,^5D_J^o \rightarrow a\,^5F_{J'}$ ($J' = J$, $J \pm 1$) transitions appearing in the 382.5–387.8 nm region was detected at 90° with respect to the laser beam direction with a Hammamatsu R928 photomultiplier (PM) tube and a band pass filter set. However, the fluorescence spectra to investigate formation of other excited states were obtained by using a 50 cm monochromator (Spex 1870c) equipped with a holographic grating and a Hammamatsu R928 photomultiplier tube. The signal from the PM tube was digitized with a transient digitizer (Tektronix 7912HB) and transferred to a laboratory computer for signal averaging and storage.

3. Results

Schematic energy levels of the chemical species [5,13–15] relevant to this work are shown in Fig. 1. A typical excitation spectrum obtained by scanning the laser in the 298.3–300.9 nm region and monitoring all the emissions from the $y\,^5D_J^o \rightarrow a\,^5F_{J'}$ transitions appearing in the 382.5–387.8 nm region is plotted in Fig. 2. The pulse energy of the laser was 0.6 mJ/pulse and the beam diameter was about 7 mm measured from the burned spot on a photosensitive film. The beam was quite homogeneous and the burn pattern showed no hot spots. Those numbers on the top of each peak indicate the total angular momentum J for the lower ($a\,^5D_J$) and upper ($y\,^5D_J^o$) states, respectively. The excitation spectrum clearly shows four well-resolved peaks corresponding to the $\Delta J = -1$ transitions. When the laser was scanned in the 301.5–306.0 nm region, relatively strong fluorescences were also observed only when the laser frequency matched exactly the $y\,^5D_J^o \leftarrow a\,^5D_{J'}$ atomic transition line. Very weak emissions corresponding to the $z\,^3P_J^o \leftarrow a\,^5D_{J'}$ transitions were identified dur-

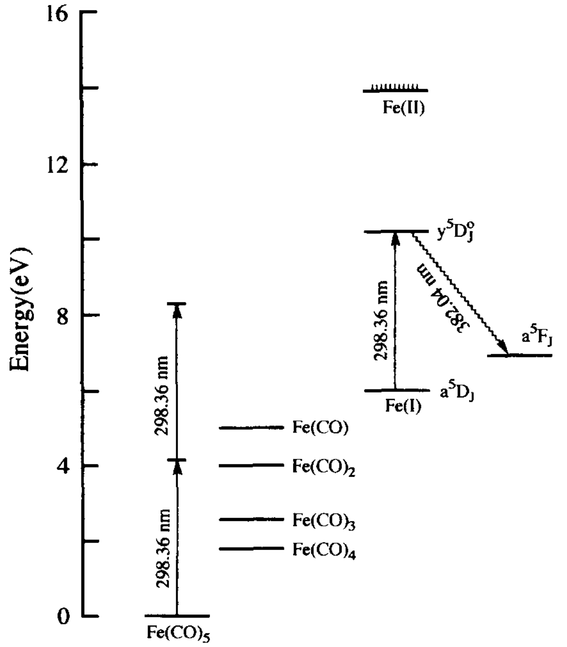

Fig. 1. Schematic energy level diagram showing the relative energies of each species from the ground state $Fe(CO)_5$. The Fe–CO bond energies are taken from Refs. [5,14,15].

ing the scan of the laser in this region, but they are not shown in Fig. 2. We also investigated the laser energy dependence of the fluorescence intensities for the y $^5D_3^o \leftarrow$ a $^5D_4$ atomic transition. When the laser pulse energies were very low (0.15–0.6 mJ/pulse), the fluorescence intensities were found to be proportional to the cube of the laser pulse energy as shown in the inset of Fig. 2. The slope of the plots for the fluorescence intensities versus laser power densities, however, decreased as the laser power densities increased due to partial saturation effects. The energy dependence of the fluorescence intensities suggested that the y $^5D_J^o$ state of Fe atoms were generated by a three-photon process.

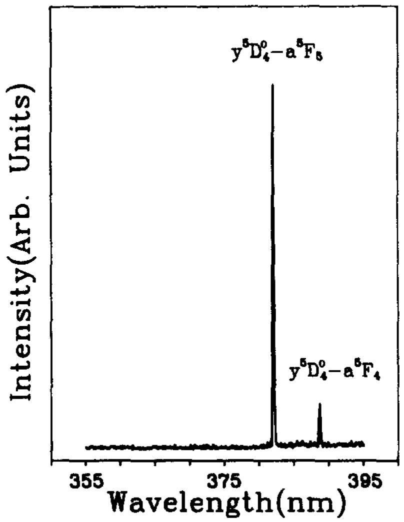

Fig. 3. A typical fluorescence spectrum obtained from 0.2 Torr of 0.5% Fe(CO)$_5$. The laser wavelength was set at 305.91 nm corresponding to the y $^5D_4^o \leftarrow$ a $^5D_3$. Only the fluorescences from the laser excited level were observed at low pressure.

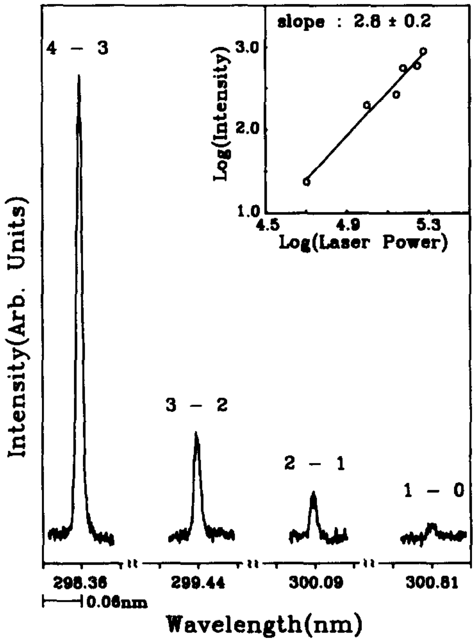

Fig. 2. A typical excitation fluorescence spectrum obtained from 0.3 Torr of 0.5% Fe(CO)$_5$ in Ar. The laser was scanned in the 298.3–300.9 nm range and the fluorescence appearing in the 382.5–387.8 nm region was monitored using a PM tube/band pass filter set. The numbers on top of each peak indicate J for the lower and upper level, respectively. The laser pulse energy dependence of the fluorescence intensities are shown in the inset.

Fig. 3 shows a typical fluorescence spectrum obtained by directing the 305.91 nm beam to the cell containing 0.2 Torr of 0.5% Fe(CO)$_5$ in Ar and scanning the monochromator in the 355–395 nm region. The strong emissions correspond to those from the laser excited level. We also scanned the monochromator in the various spectral regions to look for any fluorescence signal, but no emissions from other excited states lying above the y $^5D_J^o$ state were observed. Furthermore, no fluorescence was observed when the laser frequency was detuned by 0.04 nm from the atomic transition line. If the y $^5D_J^o$ levels were formed by a simultaneous three-photon process, fluorescences from other excited states should have been observed. In addition, detuning of the laser frequency by 0.04 nm may not be so critical for the observation of the fluorescence from the y $^5D_J^o$ state if the ground state Fe atoms were not involved in the excitation process. Thus, it can be concluded that the y $^5D_J^o$ levels are formed by one-photon absorption from the ground state Fe atoms generated by two-photon absorption of Fe(CO)$_5$ within a single laser pulse.

We have also investigated the possible formation of a ^5F_J and a ^3F_J states which are located 7000–13000 cm^{-1} above the ground state. If these states were formed during the photodissociation step, the emissions from x $^5D_J^o \rightarrow$ a $^5D_{J'}$ and x $^3D_J^o \rightarrow$ a $^3P_{J'}$ transitions could be observed when the laser wavelength was tuned to the x $^5D_J^o \leftarrow$ a $^5F_{J'}$ and x $^3D_J^o \leftarrow$ a $^3F_{J'}$ transitions in the 305–310 nm region. Indeed, very weak emissions from the x $^5D_J^o \rightarrow$ a $^5D_{J'}$ transitions in the 250–255 nm region were observed, when the laser frequency was tuned to the x $^5D_J^o$ ← a $^5F_{J'}$ transitions in the 305–310 nm region. However, the emission intensities from the x $^5D_J^o$ state were less than two orders of magnitude smaller than those from the y $^5D_J^o$ state. Since the absorption coefficients for the x $^5D_J^o$ ← a $^5F_{J'}$ transitions are similar in magnitude to those for y $^5D_J^o$ ← a $^5D_{J'}$ transitions [10], the a $^5F_{J'}$ state seemed not to be formed in appreciable amounts under the present experimental conditions. We were not able to detect any fluorescence originating from the x $^3D_J^o$ states, and the a ^3F_J state seemed not to be formed.

4. Discussion

The experimental results observed in this work are certainly quite different from those of previous reports which were obtained by using a focused laser beam [1–3]. Waller and Hepburn [15] and Yardley and co-workers [16] studied the photofragmentation dynamics of $Fe(CO)_5$ in detail using unfocused UV laser pulses and reported that the photofragmentation of $Fe(CO)_5$ follows a sequential mechanism. Waller and Hepburn have also shown that substantial amounts, i.e. 0.2–0.3 eV/CO fragment on the average, of the initially deposited energies are taken away by the CO fragments. Since the two-photon energies in this work correspond to ≈ 2.25 eV excess from the complete dissociation energies of $Fe(CO)_5$, only the a ^5D_J and a ^5F_J states can be formed, considering the energy partitioning between the photofragments. In fact, we were not able to detect any evidence for the formation of higher-lying states than the a ^5F_J state, and the results of this work are consistent with the sequential mechanism.

It is interesting that the intensity from the y $^5D_3^o$ ← a $^5D_4$ excitation in Fig. 2 is much stronger than those from other fine structure components, even though the laser pulse energy was kept constant during the experiments. Since the Einstein A coefficients for the observed y $^5D_J^o$ → a $^5F_{J'}$ transitions are not much different from each other [12], the different peak intensities suggest the populations of the Fe atoms in the different spin–orbit states of the ground state term are substantially different. While the two-photon energies corresponding to the y $^5D_3^o$ ← a $^5D_4$ and y $^5D_0^o$ ← a $^5D_1$ atomic transitions are 67014 and 66468 cm^{-1}, respectively, the sum of the five Fe–CO bond energies is about 48900 cm^{-1}. Since the difference in the two-photon energies corresponding to the y $^5D_3^o$ ← a $^5D_4$ and y $^5D_0^o$ ← a $^5D_1$ atomic transitions is 546 cm^{-1}, which is much smaller than the difference (≈ 18000 cm^{-1}) between the two-photon energy and dissociation energy of $Fe(CO)_5$, the different photon energies seemed not to be the dominant factor for the different peak intensities in the spectrum. We have also investigated the $\Delta J = 0$ transitions in the 301.7–302.2 nm region, where the two-photon energies for the y $^5D_1^o$ ← a $^5D_1$ atomic transition are 132 cm^{-1} larger than those for the y $^5D_4^o$ ← a $^5D_4$ transition. The same trend was found. Therefore, the different peak intensities in Fig. 2 are not due to the difference in the photon energies. Furthermore, collisional relaxation among the intramultiplet levels after dissociation is also very unlikely, because the dissociation and atomic excitation occur within the single laser pulse (≈ 8 ns). Thus, the different peak intensities in Fig. 2 imply that the formation of a $^5D_4$ atoms is favored at the photodissociation step of $Fe(CO)_5$ under the present experimental conditions.

The peak intensities in the excitation spectrum could be related to the relative populations of the Fe atoms in the ground term, since it was obtained by observing the total fluorescence from the y $^5D_J^o$ → a $^5F_{J'}$ transitions at the same laser pulse energies. Even though an unfocused laser beam was used in this experiment, the excitation process could be assumed to be saturated at higher laser pulse energies. Then the fluorescence intensities (I_F) from the upper levels depend on the number of atoms in the lower levels. The intensity ratio does not seem to follow the degeneracy ratio of the spin–orbit levels found by Grant and co-workers [7] when $Fe(CO)_5$ in a molecular beam was photolyzed using a focused laser beam. Instead, it appears to follow a Boltzmann distribution. If the populations in the lower levels were to follow the Boltzmann law, the number of atoms in each level is given by

$$I_F \propto N_i = g_i \exp(-E_i/kT). \qquad (1)$$

When the $\ln(I_F/g_i)$ versus E_i is plotted, where the E_i are the energies of the fine structure components, it revealed a linear dependence as shown in Fig. 4.

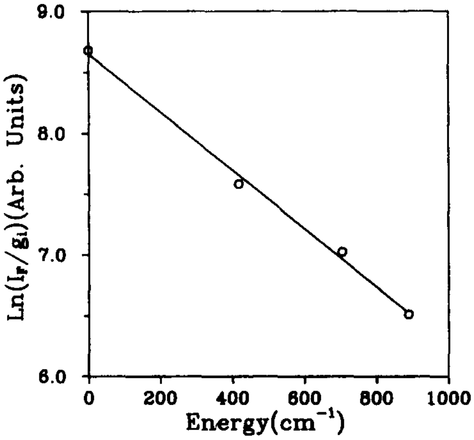

Fig. 4. Relative populations versus the energy of the intramultiplet levels in the ground state of Fe atoms formed by photodissociation of $Fe(CO)_5$. A least square fit to the data yielded the effective temperature of 650 ± 100 K.

One of the plausible explanations for the observed excitation spectrum is that the decomposition reaction of the precursor molecule (presumably one of the $FeCO^*$ states) might be slow under the present experimental conditions [17]. If the dissociation reaction is slow and the potential energy surface of this precursor state is crossed by those repulsive state potentials arising from Fe($a\,^5D_J$) and CO, formation of the lower energy levels could be favorable. It is found that the effective temperature for the Boltzmann distribution corresponds to 650 ± 100 K from the magnitude of the slope in Fig. 4. This temperature is very low compared with those obtained from the MPD of $Cr(CO)_6$ by using a focused laser beam [2,3]. The low effective temperature obtained from Fig. 4 further supports the sequential dissociation mechanism since the excess energy could be taken away in succession by the light CO fragment leaving less energy on the heavier fragment containing Fe atoms.

In this work, we have shown that the direct generation of a state-selected excited species of Fe atoms is possible by the two-photon dissociation of $Fe(CO)_5$ followed by one-photon absorption of the ground state Fe atoms using an unfocused one-color laser beam at a frequency which matches exactly the atomic transition line. Since the optical spectra of the $Fe(CO)_5$ shows continuum absorption in the 200–350 nm region [18], the ground state Fe atoms are expected to be generated by a laser beam whose frequencies do not match the atomic transition frequency. It would also be interesting to look at the formation and the distributions among the intramultiplet levels of the ground state term using the pump and probe method with two-color lasers.

Acknowledgements

This work is financially supported in part by KOSEF through the Center for Molecular Science, and in part by RIST and the Ministry of Education (BRSI-94-3438) through the Basic Science Research Program.

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