

## MULTIPHOTON IONIZATION STUDIES OF IRON

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### ABSTRACT

The dissociation of  $\text{Fe}(\text{CO})_5$  by laser irradiation produces iron atoms for multiphoton ionization studies. Monitoring  $^{56}\text{Fe}^+$ , wavelength ionization spectra were taken in three dye wavelength regions and the observed transitions tabulated. The most intense lines were used to record the mass spectra of the  $\text{Fe}(\text{CO})_5$ . Dominating the spectra were the iron isotope ions with  $\text{Fe}(\text{CO})^+$  and  $\text{Fe}(\text{CO})_2^+$  present at about 1% of the  $^{56}\text{Fe}^+$ . The most intense wavelength for iron ionization was at 277.7 nm, which represents a non-ground state transition.

### INTRODUCTION

Laser multiphoton ionization (MPI) techniques are finding increasing application in physical and analytical chemistry. Lasers allow efficient and precise probing of both molecular [1,2] and atomic [3,4] spectroscopic states. These spectral characteristics, which are so beneficial in diagnostic studies [5], also serve as particular advantages in analytical considerations [6–8]. In both the molecular and atomic regimes, the sensitivity and specificity of laser MPI techniques offer great potential enhancement of analytical capability. By use of a tunable dye laser, a single specific transition may be pumped, creating maximum analytical selectivity. The reputed ability to ionize nearly 100% of the species of interest in a given volume [9] has important sensitivity considerations. The more conventional ionization methods operate at much lower efficiencies.

Organometallic compounds present the opportunity for both molecular and atomic spectroscopic studies. Multiphoton ionization techniques have been applied to numerous such compounds [10–12], usually with the intent of examining dissociation/ionization mechanisms. Metal carbonyls, which are readily dissociated by laser radiation, also absorb additional photons to

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produce ionization of the free metal atoms [13–15]. Mass spectra taken at moderately low laser power show the singly charged metal ion to be the dominant species, even for cases where the absorption of 10–15 laser photons is required for the ionization sequence [16].

This study was initiated with an interest in exploring by MPI the relative sensitivity of laser-initiated iron transitions in certain readily available spectral regions. Volatile iron organometallic compounds were selected as a convenient means to produce upon dissociation a replenishable free atom reservoir for subsequent laser photoionization.

## EXPERIMENTAL

Figure 1 shows a schematic diagram of the apparatus used. A Nd:YAG laser (Quanta-Ray \* DCR-1A) was used at its second harmonic (532 nm) or third harmonic (355 nm) to pump a tunable, frequency-doubled dye laser (Quanta-Ray PDL-1). The dye laser could be scanned over the wavelength range of a given dye by means of a stepping motor control. The desired wavelength region was reached by frequency-doubling the output of the dyes R590 \*\* (540–590 nm) and Coumarin 500 \*\* (480–520 nm). Raman shifting was also used to reach other wavelengths of interest.

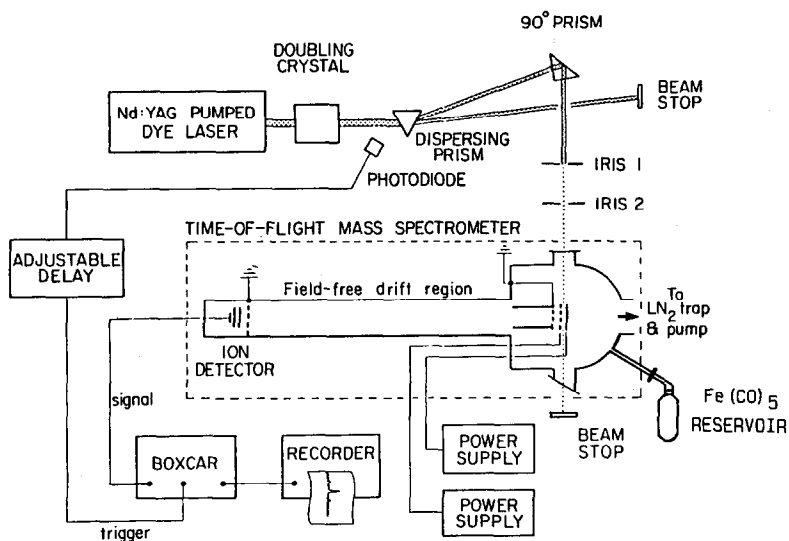


Fig. 1. Schematic diagram of the instrumentation used for the multiphoton ionization studies (as modified from ref. 2).

\* Quanta-Ray, Inc., Mountain View, CA 94043.

\*\* Exciton Chemical Co., Dayton, OH 45431.

The time-of-flight mass spectrometer used was previously designed and built in this laboratory [2]. Ions are produced by directing the appropriate laser wavelength through quartz windows into the source. A very low vapor pressure of the analytical compound is introduced through a heated leak valve from glass vials containing the pure compound. A microchannel plate electron multiplier (Varian \* model 8992-2) sends a signal to a boxcar integrator (PAR \*\* model 162) which drives a strip chart recorder. The collimated laser beam had a diameter of 3–5 mm and delivered approximately 4 mJ per pulse at peak of the dye gain.

## RESULTS AND DISCUSSION

Atomic multiphoton ionization studies require access to an atomic population which is stable and reproducible. For study, iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , was first selected because it is known to photodissociate readily in the gas phase to produce free iron atoms [9,15]. Iron pentacarbonyl exhibits a broad molecular absorption spectrum [17] below 310 nm, a region which can be reached by frequency-doubled laser output. Resonant frequencies in this same spectral region also produce iron atomic absorption. With a sufficient photon flux at a favorable iron transition, multiphoton ionization is observed. Thus, photons of a single energy can produce both dissociation of the carbonyl and subsequent ionization of the liberated metal atoms.

Iron has nearly 5000 spectral lines [18] covering the UV and visible regions. One wishes to identify the most sensitive line for MPI, but it would require many dyes and much time to evaluate thoroughly the rich iron spectrum. Attention was focused on the UV region for optimum carbonyl dissociation. Within this constraint, three wavelength regions were explored: 275–285 nm obtained by frequency-doubling the dye R590; 247–254 nm obtained by anti-Stokes Raman shifting (1st line) with  $\text{H}_2$  the frequency-doubled R590 output; and 264–274 nm obtained by frequency-doubling Coumarin 500.

A wavelength was selected at the power maximum of the R590 dye (280 nm) and a mass spectrum taken of iron pentacarbonyl at  $5 \times 10^{-8}$  torr (background of  $2 \times 10^{-8}$  torr). While this spectrometer was not primarily designed for analytical purposes, the high sensitivity of iron to laser ionization was reflected in the very small vapor pressure required to yield a significant iron spectrum. The spectrum was dominated by isotopes of atomic iron, with minor contributions from such species as  $\text{Fe}(\text{CO})^+$  and  $\text{Fe}(\text{CO})_2^+$ . The latter were typically two orders of magnitude below the  $^{56}\text{Fe}^+$

\* Varian, Electro-Optics Division, Palo Alto, CA 94303.

\*\* EGG, Princeton Applied Research, Princeton, NJ 08540.

intensity. Although atomic iron ions are the predominant ionic species, iron polycarbonyl photofragments have been reported to be the major neutral components in similar studies [9]. The  $\text{Fe}(\text{CO})_n$  bond strengths have been reported [19]. Other workers [20] have shown single photon dissociation of  $\text{Fe}(\text{CO})_5$  to yield  $\text{Fe}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_3$ , and  $\text{Fe}(\text{CO})_2$  in the ratio of 0.10:0.35:0.55. A recent report [21] showed the effect of laser pulse energy on mass spectra produced from  $\text{Fe}(\text{CO})_5$ . Another study [22] described stimulated emission from atomic iron states during the dissociation of  $\text{Fe}(\text{CO})_5$  by focused 248 nm radiation.

The use of a tunable dye laser as the ionization source adds another dimension to the obtainable mass spectra. Ionic species which are wavelength-sensitive, i.e. vary in intensity as a function of the applied laser wavelength, will yield wavelength ionization spectra which change as the laser is scanned over a given dye output. By monitoring mass spectrometrically the  $^{56}\text{Fe}^+$  ion while scanning the dye laser from 275 to 285 nm, the wavelength ionization spectrum shown in Fig. 2 was obtained. A great deal of line structure was observed, rising out of a shallow continuum background. The lines in Fig. 2 arise from iron atomic transitions where the tunable laser radiation is absorbed by resonant states, thus leading to sharp increases in the  $^{56}\text{Fe}^+$  signal as multiphoton ionization occurs. For photons of this energy, it has been estimated [9] that the absorption of at least four photons is necessary to produce  $\text{Fe}^+$  from  $\text{Fe}(\text{CO})_5$ . Given the photon flux and MPI reports of 10–15 photon absorption [16], a four-photon process would seem quite feasible.

Calibration of our laser allowed wavelength determination to  $\pm 0.01$  nm. By comparing the observed lines with standard optical spectral tabulations [18,23], identification could be made of each iron transition leading to  $\text{Fe}^+$  production. Tables 1–3 show the lines observed in the experiments in the three spectral regions. With rare exceptions, the lines matched known iron transitions and line assignments were made.

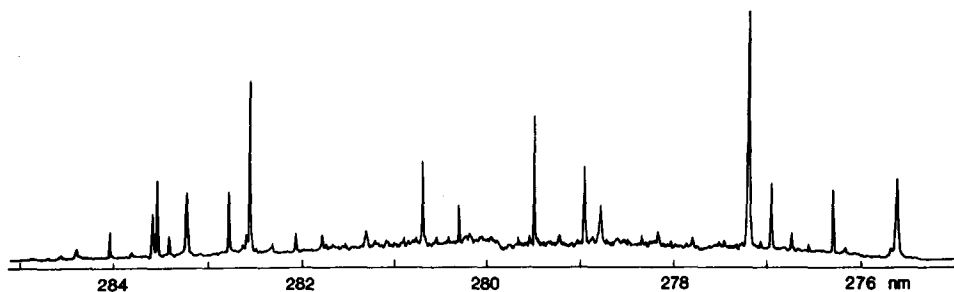


Fig. 2. Wavelength ionization spectrum of iron pentacarbonyl taken for  $^{56}\text{Fe}^+$ .

TABLE 1

Transitions observed in the 275–285 nm region using R590 dye

Observed	Literature	Line assignment
274.99	275.01	$a^5D_3-y^5P_3$
275.62	275.63	$a^5D_3-y^3F_4$
276.30	276.31	$a^5F_2-w^3F_3$
276.55	--	--
276.74	276.75	$a^5F_4-w^5D_4$
276.96	276.97	$a^5F_5-y^5G_4$
277.20	277.72	$a^5F_5-z^5H_5$
278.78	278.79	$a^3F_4-x^3G_5$
278.96	278.98	$a^3G_5-t^3F_4$
279.00	295.01	$a^5D_4-z^3G_4$
280.32	280.32	$a^5D_3-z^3G_3$
280.70	280.70	$a^5F_4-z^5H_5$
281.78	281.79	UA
282.07	282.08	$a^5D_3-z^5G_2$
282.32	282.33	$a^5F_3-y^5G_3$
282.56	282.57	$a^5D_4-z^3G_5$
282.78	282.79	$a^5D_3-z^3G_4$
283.23	283.24	$a^5F_3-y^5G_4$
283.42	283.42	$a^5F_3-x^3G_3$
283.54	283.55	$a^5D_4-z^5G_4$
283.59	283.60	$a^3F_3-x^3G_4$
283.81	283.81	$a^5F_2-y^5G_2$
284.04	284.40	$a^5D_3-z^5G_3$
284.39	284.40	$a^3F_2-y^5G_3$

Notation: --, line not found in the literature; UA, line unassigned.

In the 275–285 nm region, the most intense line was at 277.21 nm, which does not arise from a ground state transition. In conventional analytical atomic absorption, it is the ground states which are most heavily populated and the use of the corresponding transitions leads to maximum analytical sensitivity. Three ground state transitions in this wavelength regime are reported: 279.50 nm (0–35, 768  $\text{cm}^{-1}$ ), 282.57 nm (0–35, 379  $\text{cm}^{-1}$ ), and 283.54 nm (0–35, 257  $\text{cm}^{-1}$ ). Each appears in the wavelength ionization spectrum as a medium to strong line, but the 277.21 nm (6928–42, 992  $\text{cm}^{-1}$ ) is far more intense and can be used to detect smaller iron concentrations. There are also other non-ground state transitions which offer comparable sensitivity to the three ground state transitions. This suggests that the laser dissociation of  $\text{Fe}(\text{CO})_5$  produces free iron atoms with significant populations in excited states. The 277.21 nm line is not reported [24] as being of value in conventional atomic absorption. In comparing ion signal intensities, one must also consider the power level of the laser at those

TABLE 2

Transitions observed in the 246–254 nm region using anti-Stokes shifting with H<sub>2</sub> of the R590 dye

Observed	Literature	Line assignment
247.67	247.67	$a^5F_2 - v^5F_1$
247.96	247.98	$a^5D_2 - x^5F_2$
248.33	248.33	$a^5D_4 - x^5F_2$
248.52	248.51	UA
248.60	248.60	$a^5F_4 - w^5G_4$
248.63	248.64	$a^5D_4 - y^7P_3$
248.66	248.67	$a^5F_3 - v^5F_4$
248.70	248.71	$a^5F_1 - v^5F_1$
248.74	248.74	$a^5D_2 - z^5S_2$
248.81	248.81	$a^5D_3 - x^5F_4$
249.00	248.99	$a^5F_1 - x^3P_2$
249.07	249.06	$a^5D_2 - x^5F_3$
249.26	249.26	$a^5F_3 - x^3G_3$
249.28	249.29	UA
249.40	249.40	$a^5F_1 - v^5F_3$
249.43	249.43	$a^5F_5 - z^3H_5$
249.45	249.45	$a^5F_4 - z^1G_4$
249.59	249.59	$a^5F_5 - z^3H_6$
249.65	249.65	$a^5F_4 - w^5G_5$
249.89	249.89	$a^5D_3 - y^7P_4$
249.96	--	--
250.11	250.11	$a^5D_4 - x^5D_3$
250.15	--	--
250.17	250.17	$a^5F_4 - x^3F_4$
250.80	250.79	$a^5F_3 - w^5G_4$
250.88	250.88	$a^5F_2 - x^3G_3$
250.90	--	--
251.08	251.08	$a^5D_3 - x^5D_2$
251.23	251.24	$a^5D_3 - y^7P_3$
251.37	251.38	UA
251.58	251.59	$a^3F_3 - u^3D_2$
251.62	251.63	$a^5F_4 - z^3H_4$
251.65	251.66	$a^5F_3 - z^1G_4$
251.71	--	--
251.76	251.77	$a^5F_2 - w^5G_3$
251.81	251.81	$a^5D_2 - x^5D_1$
251.96	251.96	$a^5F_1 - w^5G_2$
252.10	252.10	UA
252.19	252.19	$a^5F_4 - w^3D_3$
252.25	252.25	$a^5F_4 - z^3H_5$
252.28	252.29	$a^5D_4 - x^5D_4$
252.74	252.74	$a^5D_3 - x^5D_3$
252.92	252.91	$a^5D_2 - x^5D_2$
253.07	253.07	$a^5D_2 - y^7P_3$

TABLE 2 (continued)

Observed	Literature	Line assignment
253.29	253.29	$a^5F_3-x^3F_2$
253.52	253.51	UA
253.69	253.63	$a^5F_3-w^3D_2$
253.75	253.75	$a^3F_4-u^3G_5$

Notation: --, line not found in the literature; UA, line unassigned.

absorbing wavelengths. Over the wavelength range shown in Fig. 3, 275–285 nm, the R590 dye output peaks at 280 nm and falls off to much lower intensities (order of magnitude reduced) at 275 and 285 nm. The sensitivity of the 277.21 nm line thus does not arise from being at the maximum dye power.

TABLE 3

Transitions observed in the 266–273 nm range using frequency-doubled Coumarin 500 dye

Observed	Literature	Line assignment
266.04	266.04	$a^5F_2-y^3G_3$
266.12	266.12	$a^5F_2-x^3D_1$
266.21	266.21	$a^5F_3-x^3D_2$
266.68	266.68	$a^5F_5-v^5D_4$
266.79	266.79	$a^5D_2-y^3D_3$
267.32	267.32	$a^5F_1-x^3D_1$
267.91	267.91	$a^5F_5-w^5F_5$
268.05	268.05	$a^5F_2-x^3D_2$
268.09	268.09	$a^3F_3-v^3G_3$
268.92	268.92	$a^5F_4-v^5D_3$
268.98	268.98	$a^3F_3-y^3H_4$
269.01	269.01	$a^5F_4-v^5D_3$
269.22	269.23	$a^3F_4-w^3F_4$
269.26	269.27	$a^5F_1-x^3D_2$
269.42	269.42	$a^5D_3-y^3F_2$
269.50	269.50	$a^5F_5-w^5F_4$
269.70	269.70	$a^3F_3-v^3G_4$
269.92	269.91	$a^5F_4-v^5D_4$
271.06	271.05	$a^3F_2-v^3G_3$
271.90	271.90	$a^5D_4-y^5P_3$
272.10	272.09	$a^5D_3-y^5P_2$
272.20	272.20	$a^3F_4-y^1G_4$
272.36	272.36	$a^5D_2-y^5P_1$
272.50	272.50	$a^5F_3-v^5D_4$
272.53	272.53	$a^3F_3-w^3F_3$

At wavelength regions between the line transitions, a low intensity continuum is observed which follows the dye power curve in intensity. These ions arise from non-resonant MPI, an effect which can be exaggerated by focusing the laser radiation (the power density increasing  $\sim 50\text{--}100\times$ ) rather than using a collimated beam. Under these conditions, the spectrum begins to lose its line-like characteristics and takes the form of small broadened lines arising from a deep continuum.

While the 277.21 nm line is the best analytical line in the 10 nm region scanned, this clearly covers only a very small portion of the UV-visible range over which the thousands of iron transitions are distributed. Given the time constraint of this project, it was not feasible to study carefully all the iron transitions of interest. Two other regions were explored, however. Using Courmarin 500 dye, the laser was scanned over 264–274 nm. The resulting wavelength ionization spectrum showed sharp line spectra similar to Fig. 3, but no line was found to be more intense than the 277.21 line. The strongest line by far in this region is the 271.90 nm line, a transition which is also one of the stronger atomic absorption spectroscopy lines, originating in a ground state ( $0\text{--}36, 767\text{ cm}^{-1}$ ). The other region examined was 247–254 nm, which was reached with the first anti-Stokes line of the  $\text{H}_2$  Raman-shifted, frequency-doubled R590 dye output. This was of interest because it encom-

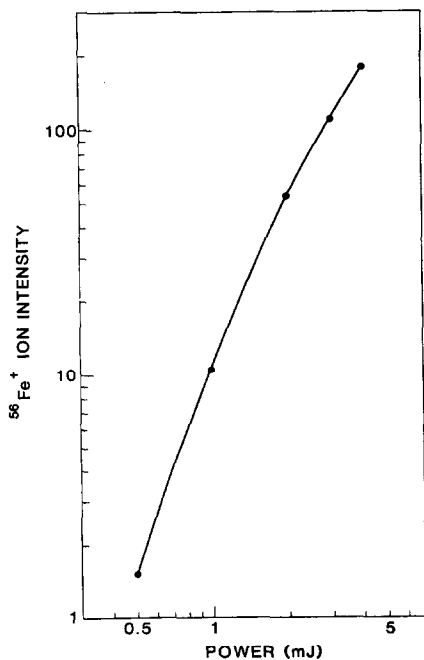


Fig. 3. Effect of dye laser power on  $^{56}\text{Fe}^+$  ion intensity. Wavelength = 277.21 nm.



passes the nominally most sensitive analytical line [24], 248.33 nm, which is used for atomic absorption spectrometry. Use of this wavelength does yield a strong  $^{56}\text{Fe}^+$  signal, but, because of the reduced power levels resulting from the Raman shifting, the 277.21 nm unshifted line actually gave better sensitivity. This points out one of the procedural difficulties in MPI, that of having available a suitable dye to yield the specific wavelength at a sufficient power level needed for a given study. It is possible that a more sensitive line than the one at 277.21 nm could be found in a more extensive wavelength study, but this transition was suitable for this work and was used for all subsequent experiments.

In addition to  $\text{Fe}(\text{CO})_5$ , 1,1'-dimethylferrocene was selected for study as a comparison compound. Mass spectra and wavelength ionization spectra were taken under conditions close to those for  $\text{Fe}(\text{CO})_5$ . The 1,1'-dimethylferrocene decomposed readily in the laser beam and yielded a mass spectrum by MPI which was dominated by the atomic iron isotopic ions. A parent ion peak of the 1,1'-dimethylferrocene was found at an intensity of 3% that of  $^{56}\text{Fe}^+$ . The wavelength ionization spectrum is not repeated here due to its similarity to the  $\text{Fe}(\text{CO})_5$  results; a highly structured spectrum was seen with maximum sensitivity at 277.21 nm. A wavelength ionization scan for the 1,1'-dimethylferrocene parent ion showed no structure, however. Ion intensity was uniform across the 275–285 nm region used.

### *Power studies*

The dye laser power applied to the ionization source could be varied smoothly over an order of magnitude by adjustment of the flashlamp pulse energy. Figure 3 shows the effect of such power variation on the production of  $^{56}\text{Fe}^+$  at 277.21 nm. The response tends to bend over at higher laser power, suggesting an eventual saturation leveling. Using a focused laser beam, a plot similar to Fig. 3 shows more extensive bending but never completely levels off. Four mJ represented the maximum power attainable with this system, preventing an extension of the plot.

### CONCLUSIONS

Laser multiphoton ionization of iron from iron pentacarbonyl arises from ground state or near-ground state transitions. The many sensitive lines of iron allow flexibility in choice of dyes and selection of analytical wavelength. Iron appears to offer high sensitivity for detection by MPI. The means of atomization employed may influence line selection by causing certain non-ground states to be heavily populated.

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