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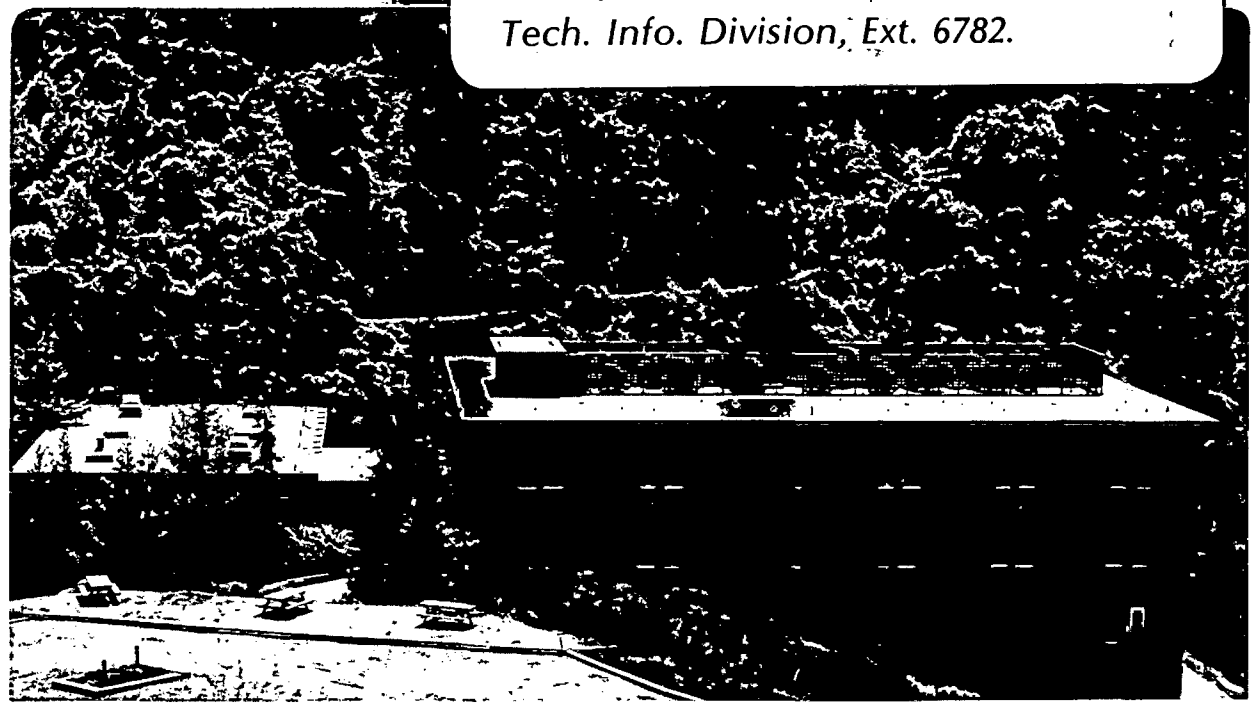
Fe\* EMISSION YIELD AND PHOTOIONIZATION OF Fe(CO)<sub>5</sub>  
BY VUV RADIATION

David V. Horák and John S. Winn

August 1982

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Fe\* Emission Yield and Photoionization  
of Fe(CO)<sub>5</sub> by VUV Radiation

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**Abstract**

A crossed VUV photon-Fe(CO)<sub>5</sub> molecular beam experiment was used to study the Fe\* emission and the Fe(CO)<sub>5</sub> photoionization yields induced by VUV photons in the 9 to 21 eV range. Fe emission from quintet spin states was observed, and the total Fe\* fluorescence quantum yield was modeled over the 9 to 14 eV range by a restricted degrees of freedom statistical dissociation model first used to explain Fe fluorescence produced by metastable rare gas collisions. Over this range, absolute cross-sections for dissociation into neutrals, dissociation into fluorescing neutrals, and photoionization were determined.

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## Introduction

Metal carbonyl photochemistry is generally discussed<sup>1</sup> in terms of a single metal-ligand bond rupture or, at most, of two or three such ruptures. In solution phase, or in solid matrices, the chemical consequences of this photochemistry range from simple ligand substitution to photoclustering (or declusterification) to photocatalysis. Virtually all such studies have employed photon sources in the near UV or visible region, corresponding to photon energies in the range 2-5 eV. Since single metal carbonyl bond energies are typically 1-1.5 eV, one does not expect all metal-ligand bonds to be broken by single photon absorption in this wavelength range.

In contrast, a number of experiments have demonstrated that all such bonds can be broken if sufficient energy is transferred quickly enough. Thus, metastable atom electronic energy transfer can break all metal-ligand bonds in a single collision<sup>2</sup>; multiple UV photon absorption can similarly produce free atoms (or ions)<sup>3</sup>; electron impact dissociation can extensively fragment a metal carbonyl<sup>4</sup>; and, of primary concern in this paper, single VUV photon absorption can produce free metal atoms from isolated metal carbonyls<sup>5</sup>.

We report here crossed VUV-molecular beams experiments which elucidate in some detail the fate of iron pentacarbonyl subjected to VUV photolysis. In brief, we have measured the VUV absorption cross-section, the photoionization quantum yield, and the fluorescence quantum yield for  $\text{Fe}(\text{CO})_5$  irradiated throughout the 9.5-14 eV/photon energy range. We also show that our results are

consistent with a restricted statistical dissociation model first advanced<sup>2</sup> to explain the metastable atom electronic energy transfer dissociation. We also confirm the previous reports<sup>5</sup> of spin selectivity in the Fe atom fluorescence spectrum.

### Experimental

The experimental technique used was that of crossed photon and Fe(CO)<sub>5</sub> molecular beams<sup>6</sup>. Visible fluorescence was monitored in a direction perpendicular to the plane of these beams, and total (mass-undifferentiated) photoion production was monitored by an ion collector as described below.

The VUV photon source was a cold cathode discharge lamp with a 300mm x 6mm ID capillary. The lamp was operated with H<sub>2</sub> to produce the pseudo-continuum emission from ca. 850 to 1650 Å and with He, Ne, and Ar to produce the intense atomic resonance lines at 584 Å (He), 736 and 744 Å (Ne), and 1048 and 1067 Å (Ar). Wavelengths were selected with a 1m VUV monochromator operated with slits which passed a 10 Å bandwidth of radiation.

The selected photon beam next entered a chamber containing the Fe(CO)<sub>5</sub> molecular beam. Due to the generally low flux of VUV radiation available from discharge lamps, this chamber was designed to allow as large a molecular beam flux as possible while maintaining a collisionless environment and protecting the monochromator from Fe(CO)<sub>5</sub> contamination. (The entire VUV photon path, from lamp to molecular beam, was windowless.) A cross-sectional view of this chamber through the photon-molecular beam plane is shown in Fig. 1. Extensive liquid nitrogen cryopumping

and a system of cold baffles were used to confine  $\text{Fe}(\text{CO})_5$  to this chamber.

The  $\text{Fe}(\text{CO})_5$  beam was semi-effusive. A reservoir of  $\text{Fe}(\text{CO})_5$  at  $\sim 40$  torr supplied a 6.4mm nozzle opening and produced a beam flux into the chamber of  $6.7 \times 10^{20}$  molecules/sec, corresponding to the consumption of 13g of  $\text{Fe}(\text{CO})_5$  per minute. This flow was turned on and off (not pulsed) by a solenoid valve (not shown in Fig. 1). The amount of VUV absorption by the beam was monitored by a sodium salicylate scintillator and a photomultiplier.

Visible and near UV fluorescence was monitored in the direction normal to Fig. 1. A quartz window passed this radiation onto an RCA C31034 photomultiplier (for total fluorescence measurements) or through a 0.25m monochromator and then onto the photomultiplier (for dispersed fluorescence measurements). The data collection electronics are shown schematically in Fig. 2. The experiment ran under the control of a small Commodore PET microcomputer which gathered scintillator intensity and fluorescence intensity while controlling the beam on/off valve<sup>7</sup>.

Photoion current was collected on a copper electrode mounted to, but electrically insulated from, the beam nozzle. This electrode (not shown in Fig. 1) was biased at -96V, a value which was found to be more than enough to saturate the photoion current at steady and reproducible values.

The absolute beam density was measured by recording the near UV absorption spectrum of the beam. A low pressure  $\text{D}_2$  lamp and the Hg 2537 Å line were used as light sources. These sources were directed through the beam onto the fluorescence photo-

multiplier, an arrangement which allowed the UV and VUV absorption properties of the beam to be measured simultaneously.

### Results and Analysis

First, we describe the VUV absorption spectrum of  $\text{Fe}(\text{CO})_5$ . In the near UV, the gas phase absorption spectrum rises smoothly to a maximum photon absorption cross-section of about  $0.6 \text{ \AA}^2$  near 2000  $\text{\AA}$ . Yardley, et al.<sup>8</sup>, have investigated the single photon fragmentation dynamics of  $\text{Fe}(\text{CO})_5$  at three laser wavelengths (352, 248, and 193 nm) throughout this region.

By comparing the VUV absorption to the near UV absorption properties of our beam, we have measured the VUV photon absorption cross-section over the 900 to 1300  $\text{\AA}$  region, as is shown in Fig. 3. This region is of greatest relevance to the dissociation process of primary concern here. Note that the maximum VUV absorption cross-section,  $2 \text{ \AA}^2$ , is appreciably larger than the  $0.6 \text{ \AA}^2$  value at 2000  $\text{\AA}$ .

Next, we describe the visible fluorescence which accompanies VUV photolysis of  $\text{Fe}(\text{CO})_5$ . Hellner, et al.<sup>5</sup>, irradiated  $\text{Fe}(\text{CO})_5$  in a cell with Ar resonance radiation (1048 and 1067  $\text{\AA}$ ) and observed atomic iron emission from the quintet spin manifold of Fe. F center formation in the LiF window separating their Ar lamp from the  $\text{Fe}(\text{CO})_5$  and the gradual deposition of an Fe film on their observation window precluded them from making quantitative statements about the relative intensities of these atomic emissions.

In our beam experiment, the emission intensity was too weak to allow us to disperse the fluorescence at high resolution. We



were able, however, to record the dispersed fluorescence at a resolution of about 15 Å FWHM using Ar and Ne resonance radiation. A comparison was made of these spectra with spectra recorded at the same resolution but using a flowing afterglow apparatus<sup>2</sup> and metastable Ar and Ne atoms as energy carriers. This comparison confirmed the presence of emission from the quintet manifold of Fe. No further attempts were made to study the VUV wavelength dependence of the dispersed fluorescence spectrum.

The majority of the remainder of this paper will therefore be concerned with the total, undispersed fluorescence quantum yield over the wavelength range to which our detector was sensitive, i.e., 2000-8500 Å. The relative quantum yield for fluorescence (QF), which is the relative number of fluorescent photons detected divided by the relative number of VUV photons absorbed, corrected for scattered light and dark count contributions, is shown on a semilogarithmic scale in Fig. 4. Curve A and the five discrete points (corresponding to the rare gas resonance line data) are the experimental results. Curve B will be discussed below. The error bars at the high energy end of the hydrogen lamp excited data (Curve A) correspond to the large statistical errors in this region due to the greatly diminished lamp output below about 950 Å (13eV). The statistical error at lower energies is everywhere  $\lesssim 3\%$ . The rare gas resonance line data were recorded during one experiment and were therefore correctly scaled relative to each other. By normalizing these points to the hydrogen lamp data at the two Ar line

positions, the entire data set was scaled to one consistent range. Curve A is the result of several overlapping and repeated scans. The structure shown in this curve is probably due to numerical errors introduced by the highly structured H<sub>2</sub> lamp spectrum and is not necessarily real.

These data show the following trend. From an apparent threshold near 10eV, the quantum yield for fluorescence rises smoothly over nearly five orders of magnitude to a plateau or maximum value somewhere in the 14 to 18 eV range. It is this trend which will be the focus of our discussion below.

The total photoion yield throughout this wavelength range, plotted as the ratio of the photoion current to the relative number of photons absorbed, is shown in arbitrary units on a semilogarithmic scale in Fig. 5. As with the fluorescence yield data, the structure near 10.8eV in Fig. 5 is probably an artifact due to the highly structured hydrogen lamp output in this region. Again, the quantum yield rises smoothly from a minimum near 10eV. Photoion current measurements were not made at the rare gas resonance lines.

### Discussion

The following points should be kept in mind when considering these data. First, we have measured only the photoion yield and the fluorescence Fe atom yield. Presumably other dark channels result from VUV photolysis. Table I lists the energies of all relevant neutral and ionized product channels, relative to ground state Fe(CO)<sub>5</sub> and assuming ground state products. One sees that

ionization is occurring at photon energies below 10eV, and that neutral atomic Fe in its ground state is a likely product. Second, the observed fluorescing states were found to be from only the quintet manifold. These states have very short radiative lifetimes in comparison to some of the septet levels observed with metastable atom excitation<sup>2</sup>. However, we are confident that had the septet levels been populated, we would have observed them. Our confidence is based on the viewing area of our photomultiplier, the radiative lifetimes of these states, and the velocity of Fe(CO)<sub>5</sub> in our room temperature semi-effusive beam. Moreover, septet emission was seen in beam experiments<sup>9</sup> which crossed Fe(CO)<sub>5</sub> with a metastable argon atom beam, and a simple correction to the intensities of those emissions (based on the ratio of observing time to radiative lifetime) gave excellent agreement<sup>9a</sup> to the flowing afterglow spectra of Hartman, et al.<sup>2</sup>.

The discussion of these data will therefore be based on the following assumptions, each of which will be justified below.

1. The fate of each excited Fe(CO)<sub>5</sub> is either ionization (to an unspecified ion state) or dissociation into Fe (in any quintet state, including the <sup>5</sup>D ground state) and five CO fragments in their ground electronic states.
2. Dissociation into neutrals is far more likely than is photoionization in the 10-14 eV range.
3. The production of any given Fe state is proportional to a restricted density of product states, calculated on the basis of the total energy available to the products.
4. Dissociation occurs by either the simultaneous rupture

of all five metal-ligand bonds or the rapid sequential rupture of these bonds on a time scale which precludes imparting a net impulse to the central Fe atom.

Assumptions 3 and 4 form the basis of the restricted degree of freedom statistical dissociation model applied successfully<sup>2</sup> by Hartman, et al., to the Fe and Ni emission intensities from Ar\*, Ne\* and He\* collisions with Fe(CO)<sub>5</sub> and Ni(CO)<sub>4</sub>. The essence of this model involves the following steps. First, a certain amount of energy is transferred to the carbonyl. Next, some fraction of this energy may be thought of as contributing to the metal-ligand bond ruptures. Finally, the desired Fe state is produced at a rate proportional to the density of CO states at the remaining energy, assuming CO's translate in one dimension, vibrate as free CO's, and do not receive rotational excitation as a result of the dissociation. The picture is one of a radial dissociation of all CO's along the equilibrium Fe-C-O direction. In applying this model to the data presented here, the additional restriction of quintet spin selectivity must be used.

By assuming that the rate of production of a given Fe state is proportional to a density of product states, one is most fundamentally using the data to measure the rate of increase of this density of states with energy. The dynamic information comes from choosing a plausible set of degrees of freedom which is consistent with this measured rate of increases. The data of Hartman were most consistent with that set of degrees of freedom mentioned above. Similarly, if the dispersed fluorescence data of Hellner are assumed to be untainted by the systematic effects

of F center formation and Fe film deposition, one finds<sup>6</sup> that they are also more consistent with these restricted degrees of freedom than with a model allowing all degrees of freedom<sup>10</sup> to be active.

To confirm the dynamic information assumed by this model would require a measurement of the translational spectra of the CO and Fe products. In fact, this model predicts a curious fate for the Fe translational motion. Imagine an experiment in which an effusive beam of  $\text{Fe}(\text{CO})_5$  is dissociatively photolyzed to Fe. The translational spectrum of  $\text{Fe}(\text{CO})_5$  would be characterized by a Maxwell-Boltzmann distribution of velocities at the source temperature, say 300K. The model assumes no net impulse is imparted to the Fe atom (or equivalently, that the Fe remains stationary in the center of mass velocity space of  $\text{Fe}(\text{CO})_5$ ). After photodissociation, the Fe atoms would have the same velocity spectrum they had as carbonyls. But if one were to describe this velocity spectrum by a temperature, the temperature would be lower than 300K by the factor 56/196, which is the Fe to  $\text{Fe}(\text{CO})_5$  mass ratio. In effect, one would have produced a beam of Fe atoms at a temperature of 85.7K.

We apply this model to the data in Fig. 4 in the following way. We first calculate as a function of total excitation energy the theoretical ratio of the probability that iron in any quintet state is produced to the probability that iron in any observable (i.e., fluorescing) state is produced. In order to use this ratio in a later calculation, the wavelength dependent quantum efficiency of the detecting photomultiplier is included in the

calculation of the probability for producing a fluorescing iron state. This ratio is parametrically dependent on the total metal-ligand dissociation energy,  $E_D$ , and it is most sensitive to  $E_D$  at the lower excitation energies, where fewer fluorescing states are available<sup>11</sup>. This ratio varies from ca.  $10^6$  at 10eV excitation energy to ca.  $10^2$  at 14eV.

If this theoretical ratio is divided by the experimental relative quantum yield for fluorescence, a constant value should be obtained at all excitation energies. In Fig. 6, we show this ratio for a variety of values of  $E_D$ . Before discussing those values, we point out that the quantum yield for fluorescence used to make Fig. 6 was the dashed curve in Fig. 4 (labeled curve B). This interpolated curve was drawn smoothly through curve A (the true data) from regions of low statistical error (below 12eV) to the similarly accurate Ne excited points (near 17eV). The curve falls well within the statistical uncertainty of the  $H_2$  lamp excited data in their region of greatest uncertainty, a region which is also least sensitive to the model.

As for the value of  $E_D$ , Fig. 6 shows that  $E_D = 6.10\text{eV}$  gives the constant ratio of ratios expected. Varying  $E_D$  by as little as 0.05eV (which is only 1 kcal/mole) produces a decidedly non-horizontal curve, especially near threshold. Cotton, Fisher, and Wilkinson determined  $E_D$  to be  $138.3 \pm 1.7$  kcal/mole ( $5.997 \pm 0.074$  eV) by thermochemical means while Distefano<sup>13</sup> reported an average Fe-CO bond energy of  $1.25 \pm 0.03$  eV in his photoionization study of  $Fe(CO)_5$ . Our value is between these two and within the error limits of each. Thus, the statistical model is

consistent with the known energetics of  $\text{Fe}(\text{CO})_5$  dissociation.

We have assumed dissociation into neutrals to be the dominant channel. As Table I shows, ionization (including dissociative ionization) competes with neutral dissociation in this energy range. If we assume that our experimental quantum yield for fluorescence is in agreement with the theoretical model in all respects except for the inability of the model to include ionization, then the difference between the theoretical quantum yield for fluorescence and the experimental yield should predict the observed quantum yield for photoionization. This comparison is made in Fig. 7, where the photoionization data of Fig. 5 are replotted and compared to this relevant difference at a variety of  $E_D$  values. Not only is the general trend correct, but also the value  $E_D = 6.10\text{eV}$  is once again consistent with the data.

We now turn to the absolute magnitude of the cross-sections leading to these various products (neutrals, fluorescing neutrals, and ions). We will focus on a photon energy of  $10.6\text{eV}$  ( $1170\text{\AA}$ ); absolute values at other wavelengths can be derived from the figures. First, a lower estimate of the VUV photon flux was made by considering the fraction of VUV photons absorbed, the detected UV photon flux, the theoretical branching ratio between all neutrals and all detected fluorescing neutrals, and the detection efficiency of our apparatus<sup>14</sup>. This estimate gave a flux of  $3 \times 10^{11}$  VUV photons/sec, which is a reasonable magnitude for our lamp design and large VUV monochromator slit sizes. To produce the observed photoion current at  $1170\text{\AA}$ , a VUV photon flux of only  $2 \times 10^{10} \text{ sec}^{-1}$  would be required, if every absorbed photon

lead to one photoion. Hence, photoionization is a less likely event than is dissociation into neutrals (at this energy).

Using this flux estimate, we conclude that the cross-section for neutral dissociation at 1170Å is  $1.3 \pm 0.2 \text{ \AA}^2$  (i.e., essentially the entire absorption cross-section; see Fig. 1), while the cross-section for photoionization is between 0.003 and 0.006  $\text{\AA}^2$ . The cross-section for fluorescing neutrals production at this wavelength is between  $2.0 \times 10^{-4}$  and  $1.4 \times 10^{-4} \text{ \AA}^2$ .

We are hesitant to extend our model beyond an excitation energy of around 14eV. At higher energies,  $\text{Fe}^+$  can be produced directly, and the possibility of excited  $\text{Fe}^+$  states at appropriately higher energies cannot be ruled out. Without an explicit model for the ionization channels, and some clear way to place these channels in competition with neutrals production, one can only speculate about the branching ratios at, for instance, the He resonance line at 21eV. Probably any sort of restricted statistical model (such as a restricted RRKM or QET theory) could be used to explain the branching ratios among the various ionization fragments, much in the way Yardley, et al., explained neutral  $\text{Fe}(\text{CO})_5$  fragmentation at lower photon energies. The real question remains one of placing ionization and neutral dissociation in their proper competition.

#### Concluding Remarks

There have now been many reports of many processes which lead to metal carbonyl dissociation and/or ionization. Table II summarizes those which have studied  $\text{Fe}(\text{CO})_5$  in particular. The



general picture is that dissociation and/or ionization will result if sufficient energy is transferred from virtually any energy carrier in a sufficiently brief time. The subtle differences center around the spin multiplicities observed in the excited atomic iron fluorescence. Metastable excitation produces all spin multiplicities; multiphoton excitation produces only triplet and quintet spins; single photon VUV photolysis produces only quintet spin states; the fluorescence from electron impact is being studied in this laboratory<sup>15</sup> and will be reported in a later publication. Preliminary data indicate electrons also produce only quintet emission.

Setting this spin differentiation puzzle aside for the moment, the most pressing dynamical question involves the rate of release of CO ligands and the energy deposition among all nascent product states. The most pressing spectroscopic question is the nature of the highly excited electronic states which are, on the one hand, the first receptors of the transferred energy and, on the other hand, the states from which dissociation and/or ionization subsequently derives. A related question is the branching ratio of neutrals to ions as a function of energy over the range in which both are observed. Snyder, et al.<sup>9b</sup>, reported an ionization cross-section of  $\sim 20 \text{ \AA}^2$  for Ar\* induced processes at  $\sim 190 \text{ meV}$  average collision energy. They also indicated that at  $\sim 40 \text{ meV}$ , a value more representative of room temperature, the ionization cross-section was larger. Comparing this value ( $\sigma$  (ionization)  $> 20 \text{ \AA}^2$ ) to the rate constants for Fe fluorescence production reported by Hartman, et al.<sup>2</sup>, ( $\sigma$  (fluorescence)  $\sim 1 \text{ \AA}^2$ )

gives a ratio  $\approx 20$ . For VUV photolysis, we have found this ratio to be in the range 20-40 for photon energies comparable to that of Ar\*. (It must be kept in mind that Fe production in all states far outweighs Fe fluorescence production or ionization in the energy range below  $\sim 14\text{eV}$ ). This comparison indicates that ionization and neutral dissociation in single energy deposition experiments compete after the fact, i.e., one method of energy deposition does not prepare a decaying state appreciably different from another, at least in this respect. This conclusion cannot be made with certainty for multiphoton experiments which can consist of a variety of simultaneous and sequential absorptions, depending on the laser pulse duration and energy fluence.

The dynamic question of sequential versus simultaneous ligand release in the energy range above roughly 8eV is probably no more than semantic, given the time scales for dissociation at these energies. If the initial excited electronic state of  $\text{Fe}(\text{CO})_5$  is totally metal-ligand repulsive (at the geometry of ground state  $\text{Fe}(\text{CO})_5$ ), then the release is clearly simultaneous with no net impulse imparted to Fe. Such a picture is analogous to ordinary photodissociation to a repulsive state, for which the dynamics are largely governed by relative masses and the probability, by Franck-Condon factors. These dynamics, however, are not in accord with the statistical model, nor do they provide a ready means of producing the variety of excited Fe states which are observed.

If the initial excited electronic state does not rapidly,

spontaneously, and adiabatically dissociate into Fe + 5CO, then it may well intersystem cross to any of a number of dissociative excited states which undergo unimolecular dissociation. Since the rate of dissociation at these energies is  $\approx 10^{12} \text{ sec}^{-1}$  for the ground electronic state (compare the restricted RRKM calculations of Ref. 8b, their Fig. 7 in particular), there is little or no time for ligand rearrangement, and all metal-ligand bonds break at essentially the same rate. The states to which intersystem crossing occurs in this picture are those which ultimately correlate to the observed products, viz. 5CO ( $X \ ^1\Sigma^+$ ) + Fe (any observed electronic state). The rate of unimolecular dissociation from excited electronic states is difficult to estimate without spectroscopic information (geometries, force constants, etc.) on these states, but rates of  $\sim 10^{12} \text{ sec}^{-1}$  would not be surprising. Dissociation rates must be on this order, since dissociation into neutrals competes favorably with autoionization (either photoionization or Penning ionization, as discussed above).

Finally, we comment on the amazing variety of Fe atom spin selectivities exhibited by these processes. One photon yields one spin manifold; one collision yields many; many photons yield several, but not all. While  $\text{Fe}(\text{CO})_5$  and  $\text{CO}(X \ ^1\Sigma^+)$  are singlets, it is clear that spin is not conserved in any of these processes, yet each selects initial excited molecular states which appear to have varying abilities to couple to product states of varying spin multiplicities. Whether the multiphoton experiments are best described as simultaneous absorption of more than one photon

(with concomitantly different selection rules from single photon absorption) or as a sequential absorption at a rate faster than, but close to, the dissociation or internal conversion rates depends critically on the laser fluence and pulse duration.

#### Acknowledgements

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Table I. Dissociation and Ionization Threshold Energies for  $\text{Fe}(\text{CO})_5$ 

Product Channel	Threshold Energy (eV) (Relative to $\text{Fe}(\text{CO})_5$ )	Reference
$\text{Fe}(\text{CO})_4 + \text{CO}$	2.4 (2.1) <sup>b</sup>	a
$\text{Fe}(\text{CO})_3 + 2\text{CO}$	2.6	a
$\text{Fe}(\text{CO})_2 + 3\text{CO}$	4.0	a
$\text{Fe}(\text{CO}) + 4\text{CO}$	5.0	a
$\text{Fe} + 5\text{CO}$	6.1	see text
$\text{Fe}(\text{CO})_5^+ + e^-$	8.0	4, 13
$\text{Fe}(\text{CO})_4^+ + \text{CO} + e^-$	8.8	4, 13
$\text{Fe}(\text{CO})_3^+ + 2\text{CO} + e^-$	9.8	4, 13
$\text{Fe}(\text{CO})_2^+ + 3\text{CO} + e^-$	10.7	4, 13
$\text{Fe}(\text{CO})^+ + 4\text{CO} + e^-$	11.5	4, 13
$\text{Fe}^+ + 5\text{CO} + e^-$	14.2	4, 13

<sup>a</sup>P. C. Engelking and W. C. Lineberger, J. Am. Chem. Soc. 101, 5569 (1979).

<sup>b</sup>As determined by laser pyrolysis: G. P. Smith and R. M. Laine, J. Phys. Chem. 85, 1620 (1981).

Table II. Summary of Fe(CO)<sub>5</sub> (g) Dissociation Processes

Energy Carrier	Observed Products <sup>a</sup>	Technique	Reference
Rg*	1,3,5,7Fe*	Flowing afterglow	2
	5,7Fe*	Beam, single collision	9a,b
	Fe(CO) <sub>n</sub> <sup>+</sup>	Beam, n=5-0	9b
Ar* ( <sup>1</sup> P)	5,7Fe*	Bulb, VUV photosensitized	5b
hν (UV)	Fe(CO) <sub>n</sub>	Bulb, chemical trapping, n=4-1	8
nhν (UV)	3,5Fe*	Bulb, multiphoton	3a
	Fe(CO) <sub>n</sub> <sup>+</sup>	Beam, multiphoton, n=0,1	3b
	Fe(CO) <sub>n</sub> <sup>+</sup>	Multiphoton photo- ionization cell	3c
hν (VUV)	<sup>5</sup> Fe*	Bulb	5a
	<sup>5</sup> Fe*, Fe(CO) <sub>n</sub> <sup>+</sup>	Beam	this work
	Fe(CO) <sub>n</sub> <sup>+</sup>	Mass spectrometry, n=5-0	13
e-	Fe(CO) <sub>n</sub> <sup>+</sup>	Mass spectrometry, n=5-0	4,9b

Figure Captions

<sup>a</sup> The notation is as follows: Fe\* indicates atomic fluorescence detected (spin multiplicity indicated by superscripts); Fe(CO)<sub>n</sub> and Fe(CO)<sub>n</sub><sup>+</sup> indicate carbonyl fragments detected over the range of n noted.

Fig. 1. Cross-section of beam interaction chamber: (A) - VUV monochromator exit arm, (B) - exit slit, (C-F) - cryopump optical baffles, (G) - cryopump body, (H) - beam nozzle, (I) - scintillator and scintillation PMT, (J) - cryopump stand-off supports, (K) - liquid nitrogen feed tubes, (L) - chamber vacuum wall, (M) - cryopump housing cover plate. The cryopump is copper; the vacuum walls are stainless steel.

Fig. 2. Detection and beam control electronics. The beam solenoid was operated at a reduced voltage and was air cooled to inhibit thermal decomposition of  $\text{Fe}(\text{CO})_5$ .

Fig. 3.  $\text{Fe}(\text{CO})_5$  total absorption cross-section.

Fig. 4. Total quantum yield for fluorescence (QF) versus incident VUV photon energy. Curve A shows the results from the  $\text{H}_2$  lamp source. The discrete points are for rare gas resonance line sources. Error bars near 14eV are statistical (one standard deviation) and shrink to  $\lesssim$  3% at photon energies below 12eV. Curve B is an interpolation discussed in the text.

Fig. 5. Photoionization quantum yield versus incident VUV photon energy. The discrete points are the data, which have been connected by straight line segments. The structure near 11eV is probably not real.

Fig. 6. The ratio of the neutral (N) to fluorescing neutrals (F) yield divided by the quantum yield for fluorescence (interp. QF, curve B of Fig. 4) plotted versus photon energy. Each curve is labeled by the value of  $E_D$  used in its calculation. Over this energy range, photoionization is a minor channel.

Fig. 7. Predicted photoionization yields for various  $E_D$  values versus photon energy compared to observed photoionization yields (see Fig. 5).



References

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10. The all degrees of freedom model allows for full CO rotation and three dimensional translation as well as Fe translation.
11. The adiabatic threshold for observing the lowest strongly fluorescing quintet state of Fe is 9.3eV, corresponding to production of the  $z\ ^5D_4^o$  state of Fe.
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14. The collection efficiency calculation included the geometrical viewing solid angle, the detector quantum efficiency, and electronic factors. Not included were unknown loss factors due to the two quartz windows in the optical path, but these factors would be near unity.
15. B. C. Hale and J. S. Winn, to be published.

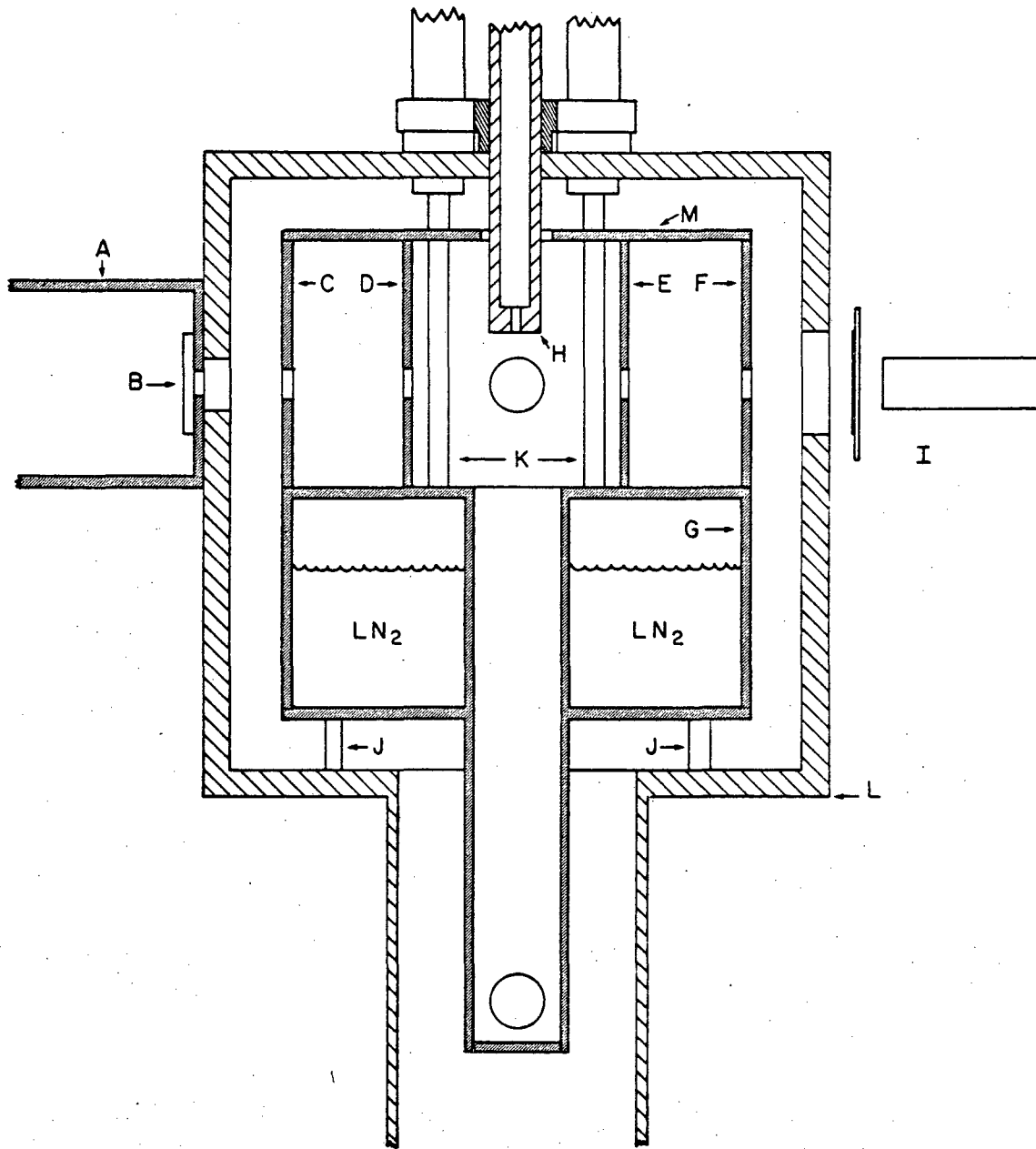
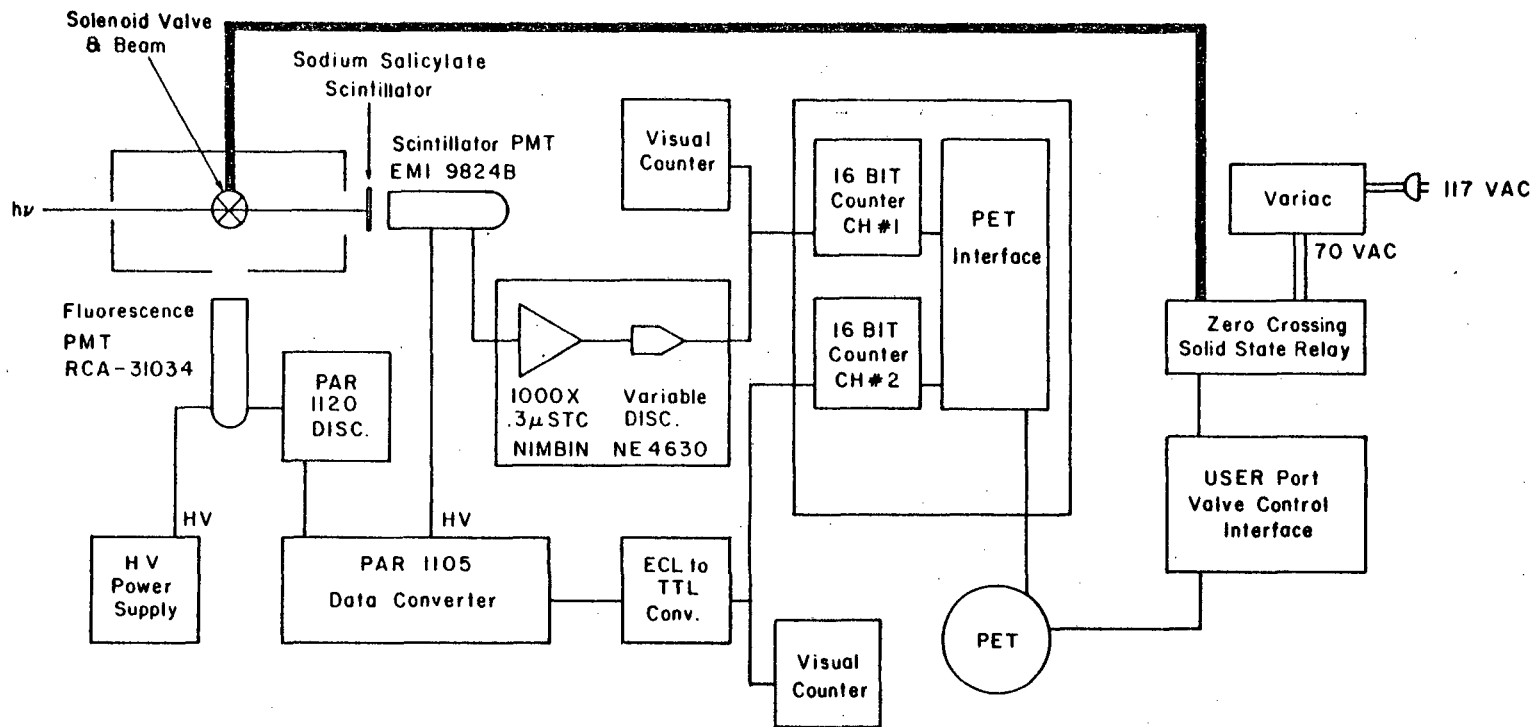
700  $\mu$ /s

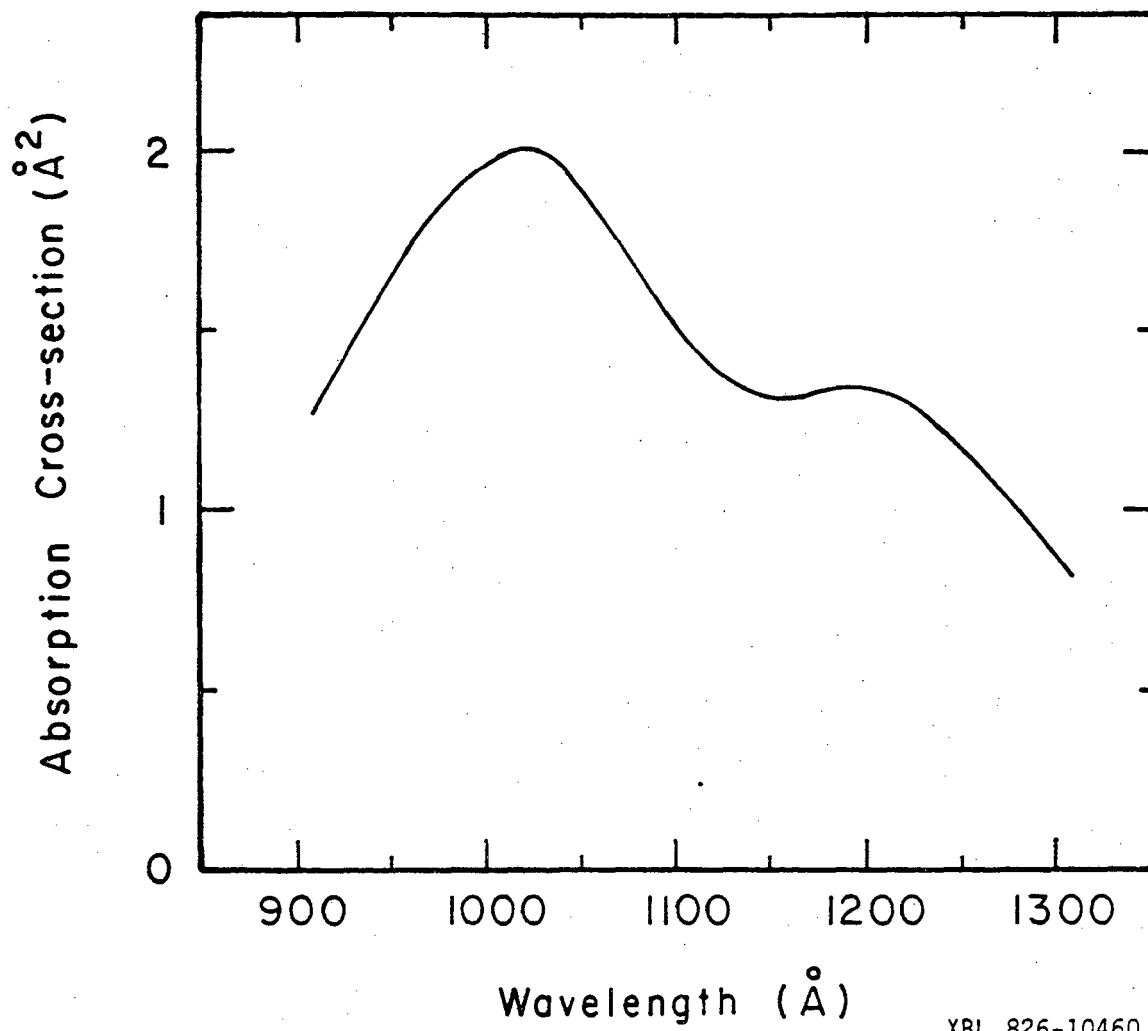
Figure 1

XBL 826-10414



XBL 826-10417

Figure 2



XBL 826-10460

Figure 3

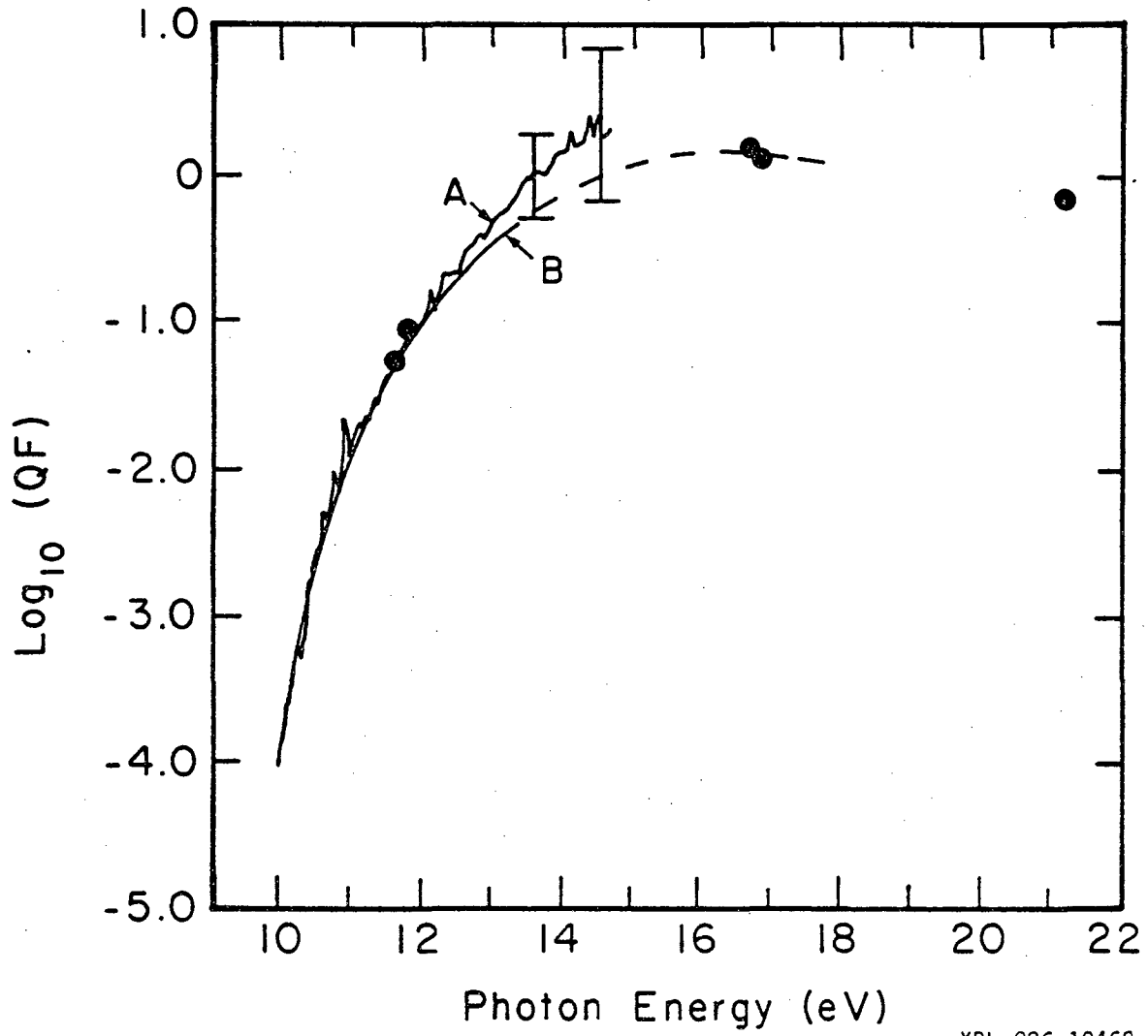
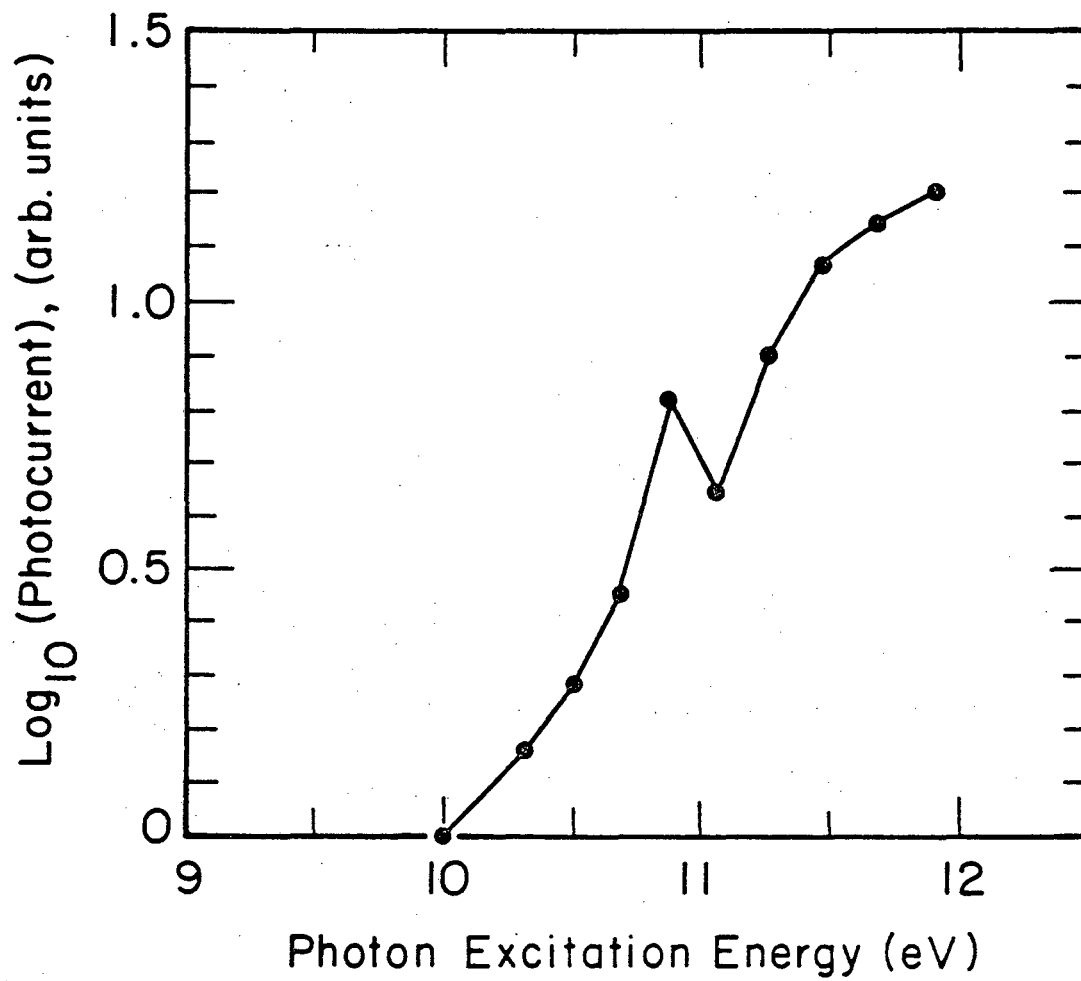


Figure 4

XBL 826-10462



XBL 826-10413

Figure 5

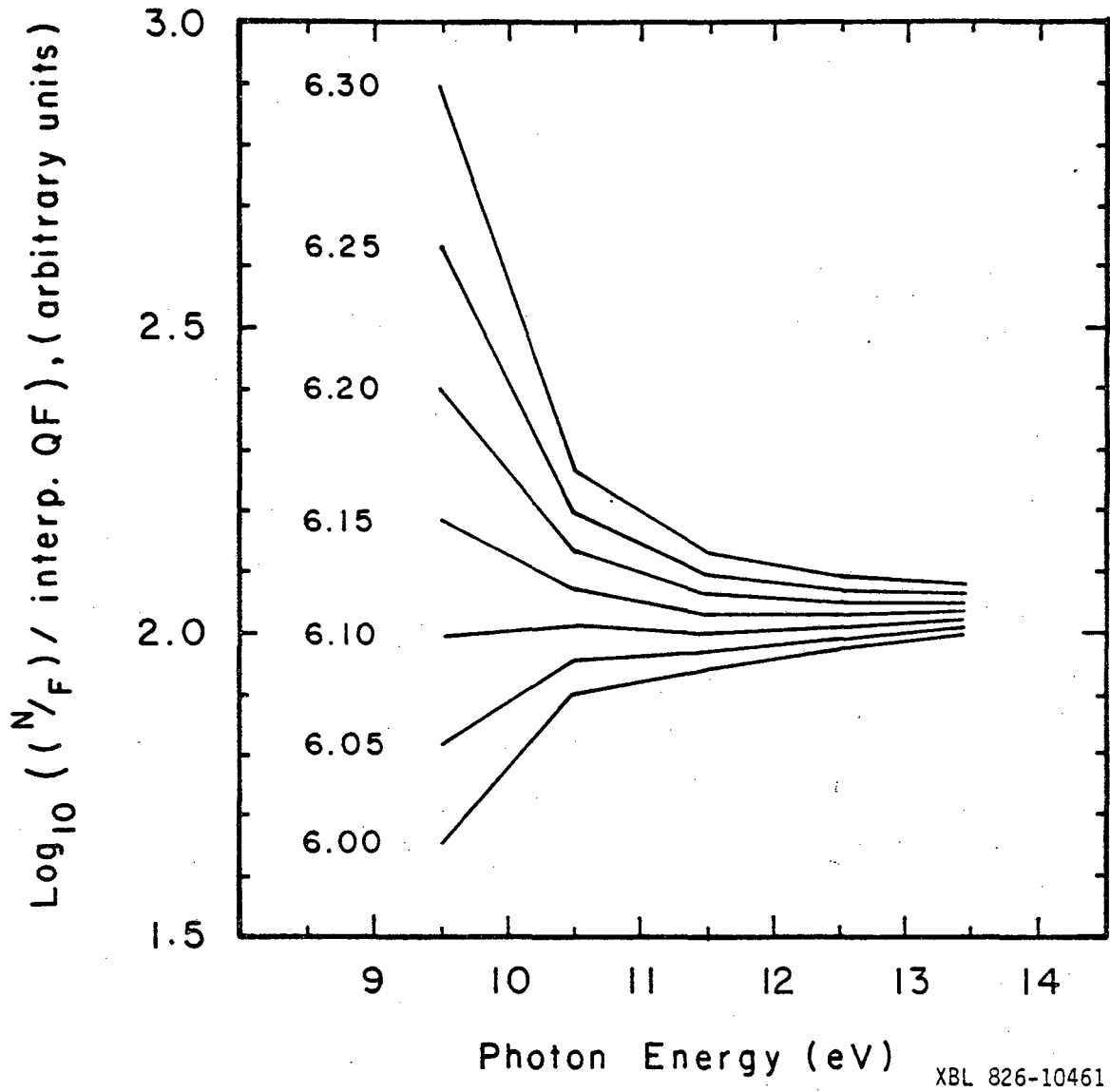
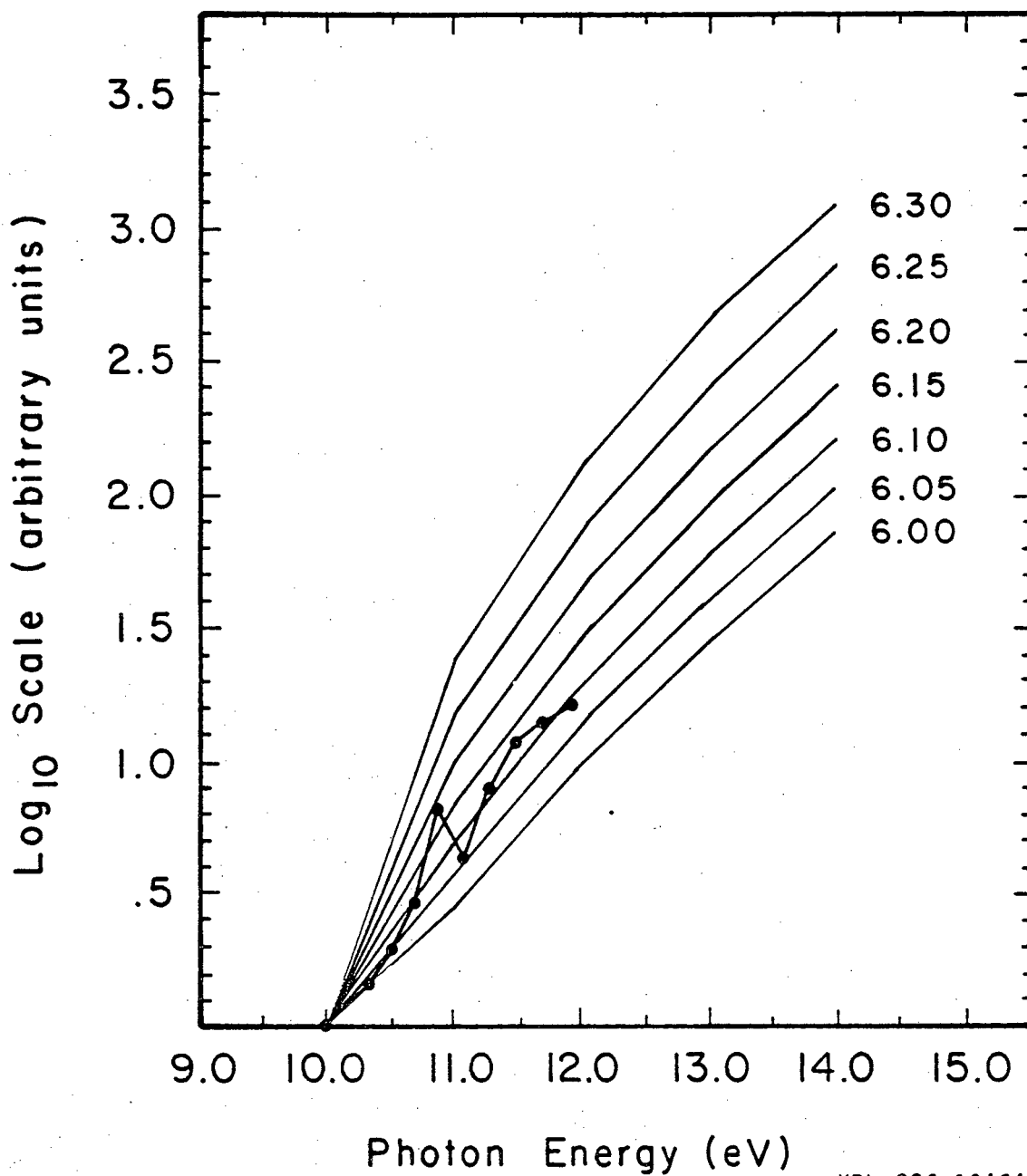


Figure 6

XBL 826-10461





XBL 826-10464

Figure 7

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