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PHOTOIONIZATION OF ORGANIC MOLECULES IN
DIELECTRIC LIQUIDS

A Dissertation

Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

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ABSTRACT

The photoionization threshold of organic molecules in dielectric liquids has been determined and the effect of the medium (solvent) on the ionization threshold and the molecular properties has been studied. Two different techniques, the integrated fluorescence technique and the laser two-photon ionization technique, were developed and utilized to determine the ionization threshold of molecules embedded in liquids. With the integrated fluorescence technique the ionization threshold of a fluorescing molecule was determined from the decline of the integrated fluorescence intensity, measured as a function of the excitation wavelength, caused by the presence of an electron attaching molecule. With the two-photon ionization technique the threshold was established from the onset of the conductivity current, measured as a function of the wavelength of a tunable-dye laser, in a solution of the molecule under study. Absorption properties of molecules in solution in the VUV region and the effect of the medium on them have also been studied utilizing an especially developed double-beam technique.

The first ionization thresholds, I_L^1 , of pyrene, N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) and fluoranthene in liquid media comprising a dielectric liquid-- n-pentane (n-P), n-hexane (n-H), n-heptane (n-Hp), isopentane (i-P), cyclopentane (c-P), neohexane (neo-H), cyclohexane (c-H), tetramethylsilane (TMSi)-- and an electron attaching compound (A)--perfluoro-normal-hexane (PFn-H), perfluorodimethyl-cyclo-butane (c-C₆F₁₂), perfluoro-methyl-cyclo-hexane

(c-C₇F₁₄), perfluoro-dimethyl-cyclo-hexane (c-C₈F₁₆)--at rather high concentrations were measured with the integrated fluorescence technique. The I_L^1 of pyrene and fluoranthene were found to be independent of the dielectric hydrocarbon liquids and the concentration of A used. The average value of the I_L^1 of pyrene and fluoranthene for all cyclic A's (c-C₇F₁₄, c-C₆F₁₂, c-C₈F₁₆) was 5.48 and 5.57 eV respectively and for the linear A(PFn-H) was 5.88 and 5.97 eV respectively. For both pyrene and fluoranthene the I_L^1 as determined with the cyclic A's was ~ 0.40 eV lower compared to its value for the linear A. The I_L^1 of TMPD in n-hexane was found to be 5.02 eV using PFn-H as A.

Laser two-photon ionization (TPI) spectroscopy was applied to determine the ionization threshold of TMPD and fluoranthene in n-pentane. The I_L^1 was found to be 3.88 ± 0.05 and 4.50 ± 0.05 eV respectively, i.e., 2.32 and 3.22 eV lower than the respective gas phase ionization potentials. The I_L^1 of TMPD in n-pentane was also measured by one-photon induced ionization and found to be 3.83 ± 0.02 eV in agreement with the two-photon I_L^1 value. For both molecules the TPI spectra showed distinct structure due to autoionization. For fluoranthene the TPI spectrum suggests that the molecule dissociates upon excitation in the vibrational progression of the first excited singlet state.

The absorption spectra of benzene, naphthalene, azulene, TMPD, pyrene and fluoranthene in PFn-H and n-pentane were measured in the VUV spectral region. The effect of the medium on the properties of the molecular states is discussed.

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CHAPTER 1

INTRODUCTION

1.1 General Considerations

The properties of a molecule embedded in a liquid are changed as a result of intermolecular interactions which are not experienced by a molecule in the gas phase at low pressures. Especially sensitive to the medium perturbation are charged-separated states such as: electron-ion pairs, free and quasi-free electrons, positive and negative ions, and Rydberg states.

The ionization threshold, I_L^1 , of a pure liquid or a molecule embedded in a liquid is closely associated with the effect of the medium on the aforementioned states. More importantly, it provides the basic quantity needed to quantify this effect and as such its knowledge is of basic interest. It has been known that the ionization threshold of a solute molecule is lowered relative to the gas-phase ionization potential, I_G^1 , but the kinetics and the energetics of the photoionization process are not yet well understood.

The object of this work is to measure the ionization threshold of a molecule embedded in a dielectric liquid and to examine the effect of the bulk properties of the dielectric liquids and electron attaching additives on I_L^1 . The effect of the medium on the molecular states in the VUV region is also examined. The understanding of the effect of the medium on the physicochemical properties of the molecules is the key in bringing physics closer to chemistry and both closer to the realism of biology.

1.2 Review of the Photoionization of Molecules in Dielectric Liquids

The history of the photoionization studies in the condensed phase started with the classical work of Lewis and coworkers (1942; 1943) on the photoionization of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in an EPA (Ether, Iospentane, Alcohol) glass. They proved that the product of irradiation of TMPD-containing EPA glass is the TMPD^+ radical known as Wuster's blue. This was the first demonstration of the photoionization of a molecule in the condensed phase.

The next important advancement in the photoionization studies was the spectroscopic identification of the trapped electron after irradiation of solid solutions (Linschitz and coworkers, 1954; Jortner and Sharf, 1962). The field attracted much attention during the nineteen sixties when systematic efforts began to elucidate the mechanisms involved in the condensed phase photoionization. Intensive studies were carried out on the electron photo-ejection from aromatic molecules in a variety of systems by many workers (Albrecht, 1970; Lesclaux and Joussot-Dubien, 1973; Bernas and coworkers, 1972a; 1972b; Delahay, 1976; Steen and Kongshaug, 1974).

The liquid-phase photoionization studies lag those in solids and low-temperature solid solutions, because of difficulties associated with the liquid phase. Some of these difficulties associated with the photoionization studies are:

- i) The lifetimes of transient species, such as excited singlet and triplet states and excited charge transfer complexes, are considerably shorter in the liquid phase than in the solid or gas phases. As a result, intense excitation is required to observe

transient products (Tamir and Ottolenghi, 1970; Potashnik and coworkers, 1969). The laser offered the appropriate tool for liquid phase photoionization studies.

ii) Local density fluctuations and diffusional processes taking place in liquid media may provide new photoionization mechanisms complicating the process.

iii) Reorientation effects may play a role in the photoionization process even though they are much slower than the electron-photoejection process.

It was as late as 1962 when for the first time the hydrated electron was spectroscopically identified by Hart and Boag from the transient absorption band peaking at 700 nm observed in water after irradiation with 1.8 MeV electron pulses. Grossweiner and Zwicker (1963) and Swenson and coworkers (1963) showed experimentally that the hydrated electrons are the primary product of the ultraviolet-light photolysis of aqueous solutions of aromatic compounds.

In condensed media the energy required to photoeject an electron from a neutral molecule is lowered by an amount ΔI given by the sum of the solvent polarization energies P^+ , P^- , the electron affinity of the capturing species, E_A , and the coulomb interaction energy, E_C , of the charged species

$$\Delta I \equiv I_G - I_L = P^+ + P^- + E_A + E_C \quad (1.1)$$

I_L and ΔI are strongly dependent on the nature of the solvent. Raz and Jortner (1969) proposed, for the case of impurity states in a liquid corresponding to correlated electron-hole pair with negligible "width" of the hole state, that the impurity energy gap, E_G ,

corresponds to the ionization potential of the impurity in the liquid medium. This energy gap is given by;

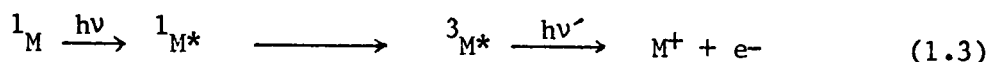
$$I_L = E_G = I_G + P^+ + V_0 \quad (1.2)$$

where P^+ is the medium polarization energy due to the positive hole and V_0 is the energy of quasi-free electron state corresponding to the bottom of the conduction band relative to the vacuum level. Relation (1.2) has been used extensively by many authors (Holroyd, 1972; Holroyd and Russell, 1974; Peterson and coworkers, 1975; Grand and coworkers, 1977; 1979; Bullot and Gauthier, 1977; Bernas and coworkers, 1980) to describe the photoionization energetics in liquid solutions.

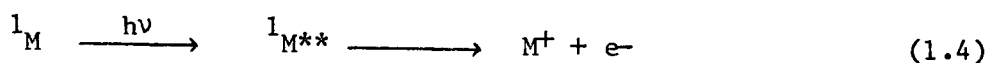
These studies showed that the crucial factor in understanding the primary processes and the energetics of the photoionization of a molecule in the condensed phase is the fate of the photoejected electron in the host medium. An implication of this is the difficulty of defining a liquid phase ionization potential. In contrast to the gas phase, where the lowest needed energy to eject the electron to infinity (zero potential energy) with zero kinetic energy is defined as the gas-phase ionization potential, the electron-medium system undergoes relaxation processes in the presence of the coulombic field of the parent positive ion which are evolving in time. Delahay (1971) suggested that the electron is created in an unbound state into the liquid and the dependence of the bound-unbound transition rate on photon energy, E_p , is of the form $E_p^{-3/8}$ for $E_p < 2E_{con}$ and E_p^{-3} for $E_p > 2E_{con}$ where E_{con} is the energy at the bottom of the continuum. On the other hand, Peterson and coworkers (1975), in order to

interpret their results on the photoionization of tetra-alkyl-paraphenylenediamines in hydrocarbon solutions, proposed an electron transfer mechanism from excited donor-molecule levels to fluid states. The above discussion indicates that the technique used to probe the photoionization process in liquids may be revealing different stages in the time evolution of the process according to the ultimate fate of the ejected electron. In a photoconductivity technique the photoionization is probed by the electrons which have escaped geminate recombination and propagated through the medium in its conduction band. In an electron scavenging experiment, such as the one in the present study, the electrons may be captured by the scavenger molecule at times shorter than the solvation time.

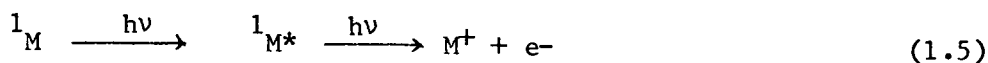
The group of organic amino-compounds has been used almost exclusively for photoionization studies. The gas-phase ionization potentials of some members of this group are in the range 5-7 eV (Nakato and coworkers, 1971). These compounds are expected to photoionize in liquids at photon energies at which most of the commonly used solvents are transmitting. In particular TMPD has been used extensively to study the effect of the medium on I_L . Different mechanisms have been proposed to explain data on TMPD photoionization in various solvents. Pillof and Albrecht (1966; 1968) reported dependence of the photocurrent on the square of the exciting light intensity in their flash-photolytic studies of TMPD in 3-methylpentane. They proposed a two-step biphotonic mechanism involving the lower triplet state as intermediate.



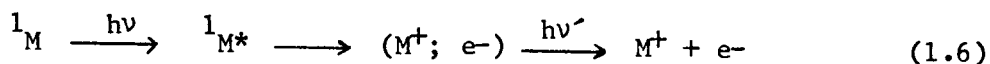
^1_M , $^1_{M^*}$, $^3_{M^*}$ represent the molecule in the ground state, the first excited singlet state and the lowest triplet state, respectively; M^+ is the positive ion, e^- the solvated electron and $h\nu$ and $h\nu'$ the two photons of different energies. Houser and Jarnagin (1970) demonstrated the presence of the biphotonic process (1.3) in the flash photoconductivity of TMPD in n-hexane from the oxygen effect and a kinetic analysis. Takeda and coworkers (1971) reported monophotonic ionization (1.4) of TMPD in tetramethylsilane (TMSi) for excitation energies above 4.3 eV.



where $^1_{M^{**}}$ represents the molecule in a superexcited singlet state (i.e. embedded in the ionization continuum). In a laser-induced conductivity of TMPD in 3-methylpentane and isopentane at 337.1 nm (Tamir and Ottolenghi, 1970) the photocurrent exhibited a square-law dependence on the laser intensity. Using piperylene as selective triplet quencher, it was shown that the triplet state was partly responsible for the biphotonic process (1.3) and suggested that the lowest excited singlet state plays the role of the intermediate according to:



Potashnik and coworkers (1969), in order to explain flash-photolytic results of TMPD in isopentane-isopropanol solution, suggested that a second photon is absorbed by a "semi-ionized" state in which the electron is strongly associated with the parent ion.



In all proposed photoionization mechanisms in solution involving more than one photon, even in the case of intense laser excitation, it was considered that the multiphoton process was taking place in consecutive steps with some transient species as intermediates. Two-photon absorption in one quantum act was proposed for the first time as the mechanism responsible in a laser-induced ionization of pyrene at a fixed wavelength (347.1 nm) in methanol and ethanol (Richards and coworkers, 1970)

Photoionization thresholds of TMPD in several dielectric liquids determined from photoconductivity measurements have been reported by Holroyd (1972). Holroyd and Russell (1974) measured the single-photon ionization quantum yield of TMPD in dielectric liquids. They found that I_L^1 is temperature-dependent, it increases as the temperature decreases, and attributed this to the dependence of P^+ and V_0 on the temperature. Peterson and coworkers (1975) studied the photoionization of alkyl-paraphenylenediamines in hydrocarbon liquids with a photoconductivity technique. They reported photoionization yields for TMPD in 2,2 dimethyl-butane extending down to 3.65 eV and exhibiting structure. The low-energy structure was attributed to the density of tail states of the fluid which may serve as acceptor states for the monophotonic process. The decrease of the photoionization yield for energies above 5.5eV was attributed to the onset of the third absorption band of TMPD around 6eV. Bullo and Gauthier (1977) studied the temperature dependence at the threshold energy of TMPD in eight hydrocarbon solvents using photoconductivity or recombination luminescence

measurements. They reported a linear increase of I_L^1 with decreasing temperature and found no correlation of the photoionization curve with the absorption spectrum. Kam-Chu-Wu and Lipsky (1977) reported that the fluorescence quantum yield of TMPD in liquid hydrocarbons decreases for excitation photon energies higher than the photoionization threshold and used an electron scavenging technique to determine the threshold. Bernas and coworkers (1980) and Grand and coworkers (1979) used electron scavenging technique by N_2O to determine the photoionization threshold of indole in tetramethylsilane and polar solvents. They reported that the electron affinity of the scavenger does not affect the value of the threshold. They suggested that the photoejected electron is promoted to a quasi-free state before being solvated or scavenged.

Some of the aforementioned findings are contradictory. For example, findings concerning the initial and final state of the photoejected electron in the liquid, the relation of the photoionization yield to the optical absorption spectrum of the molecule, the role of the electron attaching molecule, its electron affinity and capturing properties on the threshold of the solute molecule. This is a further indication of the experimental difficulties involved in the liquid photoionization studies as well as of the need for further experimental work.

1.3 Present Work

An attempt to elucidate some of the contradictions related to the photoionization in the liquid phase, exposed in the preceding section, and to investigate further the photoionization of a molecule embedded

in a dielectric liquid was undertaken in the present work. The problem of the photoionization threshold determination of a molecule in solution was approached with two different but complementary techniques.

The Integrated-Fluorescence Technique, and

The Laser Two-Photon Ionization Technique.

Each technique probed different aspects of the photoionization process. In the integrated fluorescence technique, applied to fluorescing solute molecules, the photoionization was probed by the effect of an electron attaching additive on the total fluorescence emitted by the solute upon excitation at various energies. For excitation energies below the solute ionization threshold the fluorescence quantum yield was independent of the excitation energy (Vavilov's law; Birks, 1970), for energies above the ionization threshold the fluorescence quantum yield did not change appreciably due to the high probability for geminate recombination (maximum quantum yield of ionization of TMPD in hydrocarbons is of the order of 10^{-3} ; Holroyd and Russell, 1974). The situation changes in the presence of an electron attaching additive. The geminate recombination is prevented by the electron attachment and the photoionization is manifested from the decline of the total fluorescence intensity with increasing excitation energy.

In the laser two-photon ionization technique, the solute molecule was ionized via a two-photon excitation and the final products detected were the electron and the positive ion in their final states in the liquid medium. The induced photocurrent was monitored as a

function of the laser wavelength. The so obtained two-photon ionization (TPI) spectrum, gave important spectroscopical information about the molecular properties and revealed photochemical molecular processes in solution.

The photoabsorption is the primary event in the photoionization process and the knowledge of the absorption properties of the molecule, under the same conditions as the photoionization studies, was necessary for the interpretation of the photoionization data. For this reason, we studied the absorption spectra of the molecules used in the photoionization studies (TMPD, fluoranthene, pyrene) and additionally benzene, naphthalene and azulene, in the VUV region and the effect of the solvent on their absorption bands.

For the present study the molecules TMPD, pyrene and fluoranthene were chosen. Their choice was based on several facts. All are very good fluorescing materials (the fluorescence quantum yield of pyrene is 0.65 and of fluoranthene is 0.25 in cyclohexane; Birks, 1970) necessary for the integrated fluorescent technique. The TMPD was exclusively used for photoionization measurements, for the reasons mentioned in the preceding section, and most of the conclusions concerning the photoionization processes in liquids have been based on measurements using this molecule. Pyrene is a cata-condensed aromatic hydrocarbon with a relatively low gas-phase ionization potential (7.41 eV). Fluoranthene has also a relatively low gas-phase ionization potential (7.72 eV) and is a non-alternant conjugated aromatic hydrocarbon with "peculiar" absorption and fluorescence characteristics (Heilbronner and coworkers, 1966; Michl, 1969; Kolc and

coworkers, 1974). It was considered as a prototype of two weakly interacting subsystems (namely, benzene and naphthalene). Both pyrene and fluoranthene are products of coal burning and synthetic fuel production and they are of great environmental interest. Saturated alkanes and tetramethylsilane were used as solvents and saturated perfluorocarbons as electron attaching compounds.

1.4 Outline of the Present Work

The present work consists of experimental studies on the photoionization of pyrene, TMPD and fluoranthene in dielectric liquids using the above mentioned techniques and absorption measurements on the same molecules and benzene, naphthalene and azulene in solution and in the VUV region. In CHAPTER 2 the apparatus and procedures used in the present experimental work are discussed.

In CHAPTER 3 results and analysis are presented for the photoionization of pyrene, TMPD and fluoranthene in several dielectric liquids using the integrated fluorescence technique.

CHAPTER 4 contains the results and analysis on the photoionization of TMPD and fluoranthene in *n*-pentane solutions studied by the laser two-photon ionization technique.

In CHAPTER 5 the values of the photoionization threshold of the molecules in liquid obtained with the two techniques are compared and the effect of the medium on the threshold is discussed.

In CHAPTER 6 the absorption spectra of benzene, naphthalene, azulene, TMPD, pyrene and fluoranthene in *n*-P and PFn-H in the VUV spectral region are presented. The effect of the solvent on the molecular states and especially on the Rydberg states is discussed.

Finally, in CHAPTER 7 a summary of the results is given and possible future studies are indicated.

CHAPTER 2

EXPERIMENTAL METHODS AND PROCEDURES

2.1 Introduction

Photoionization, photoabsorption and fluorescence spectroscopy provide important information on the interaction of electromagnetic radiation with molecular systems. These techniques have been used extensively to study molecular systems in the gas phase. Although the same techniques present more experimental difficulties when applied to the liquid phase, especially in the VUV region, they, nonetheless, can provide information on the properties of molecules embedded in liquids as well as on the properties of the bulk medium. In this chapter the experimental apparatus and procedures used in the present study are described and discussed.

Two different but complementary techniques were employed to study the photoionization of a molecule in solution. In the integrated fluorescence technique (IFT) as the probe of the photoionization was used the effect of an electron attaching molecule on the fluorescence intensity emitted by the solute molecule. The integrated fluorescence spectrum (integrated fluorescence intensity vs. excitation wavelength) for various concentrations of the electron attaching additive was the source of information on the process taking place upon excitation of the solute molecule. Instrumentation suitable for VUV spectroscopy was used in this technique.

In the laser two-photon ionization technique (also to be referred to as photoconductivity technique) the products of the photoionization process, namely electron and ion current, were directly observed. Utilizing a laser beam, the ionization of the solute molecule was induced via a two-photon absorption in one quantum act and the photocurrent intensity was measured as a function of the exciting laser wavelength. That way the two-photon ionization (TPI) spectrum of a molecule in solution was obtained. The two techniques differ in that different probes of the photoionization process were used, but both give complementary information about the energetics of the process.

The photoabsorption measurements were made by a double-beam technique. An especially constructed absorption cell and VUV transparent solvents enabled us to measure absorption spectra of aromatic molecules in solution for wavelengths down to 155 nm.

2.2 Integrated Fluorescence Technique

The apparatus employed in this technique is shown schematically in Fig. 2.1. It consists of the monochromatic light source assembly, the photoionization chamber containing the cell and the associated optical components, the detection electronics and vacuum systems.

The monochromatic light source utilizes a commercial hydrogen discharge lamp, a vacuum monochromator and a light chopper (Fig. 2.1). The H₂-lamp was operated at 10 torr pressure and ~ 15kV voltage. It can be operated without a window and with a quartz or a MgF₂ window mounted behind the entrance slit of the monochromator. The monochromator is a commercial half-meter Seya-Namioka instrument, with 1200 lines per mm grating blazed at 200 nm. The wavelength resolution

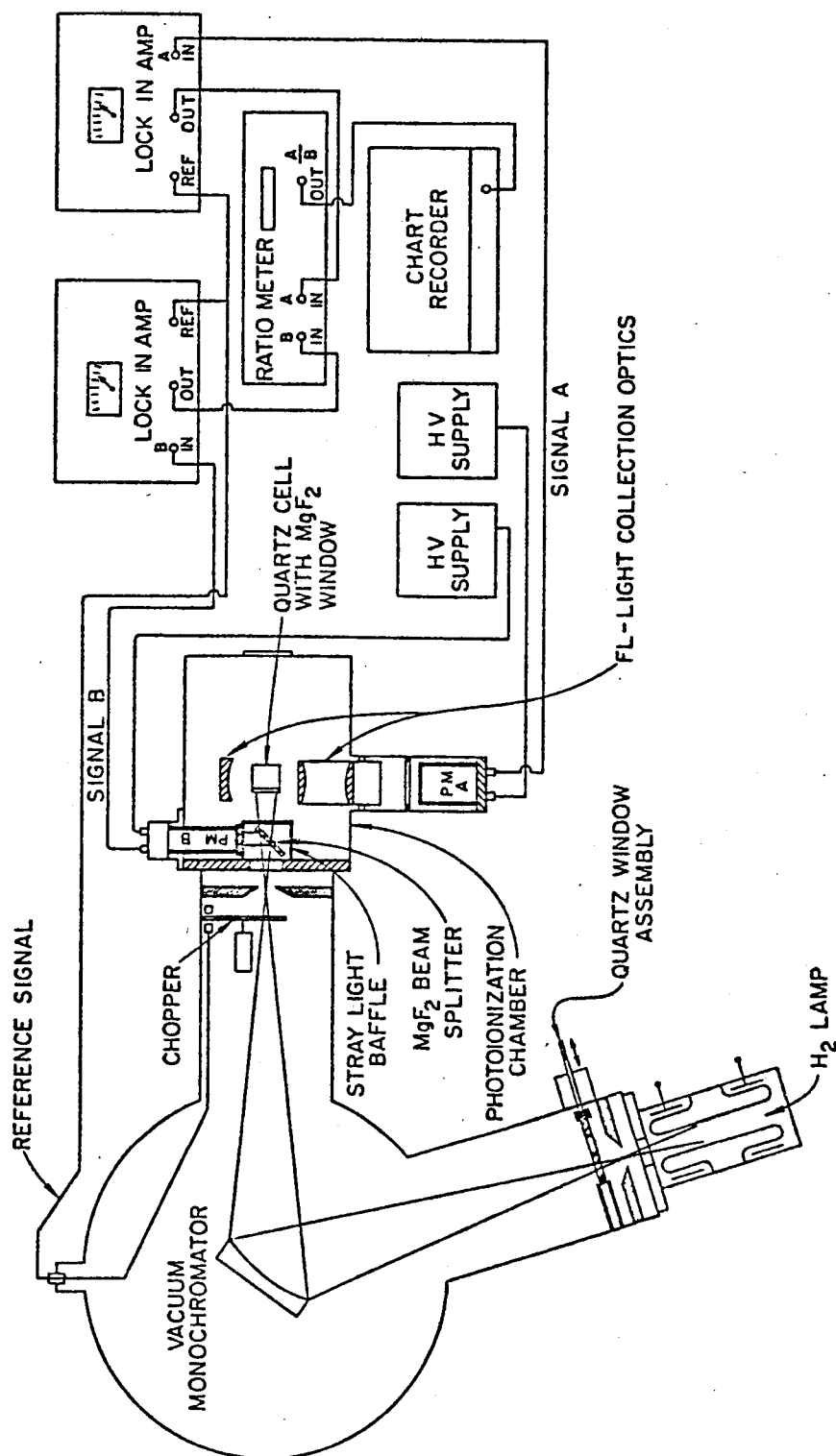


Fig. 2.1. Layout of the experimental apparatus of the integrated fluorescence technique.

of the instrument is ~ 0.6 nm in the spectral range of interest (160–300 nm). A custom made light chopper is located inside the monochromator in front of the exit slit and is operated at ~ 220 Hz. With a quartz window behind the entrance slit of the monochromator the operating pressure of the entire system (including the cell chamber) was less than $\sim 5 \times 10^{-6}$ torr. The excitation light beam is tunable over the spectral range from 120 to 300 nm and illuminates homogeneously the entire sample volume. Figure 2.2 gives in more detail the arrangement of the cell and the various optical components inside the photoionization chamber. The cell is located ~ 5 cm beyond the monochromator exit slit inside the photoionization chamber. The cell has a rectangular shape (inner dimensions 1 X 1 cm) and is made of suprasil with a 1 mm thick MgF_2 front window. It is mounted on a specially constructed holder which provides for accurate translation of the cell along the path of the excitation light. This allows alignment of the cell with respect to the detection optics and encloses it in such a way that only the illuminated volume of the liquid sample can be "seen" by the detection optics. A stray-light baffle has been located between the monochromator exit slit and the cell to eliminate the stray light.

The excitation light beam is split into two beams inside the sample chamber by a 1 mm thick MgF_2 window mounted at 45° with respect to the incident light beam. The transmitted beam, $I_T(\lambda)$, is used for the excitation of the sample and the reflected beam, $I_R(\lambda)$, is monitored with the photomultiplier B (Hamamatsu, type R647; Fig. 2.1) providing the signal B which is used for the correction of the sample

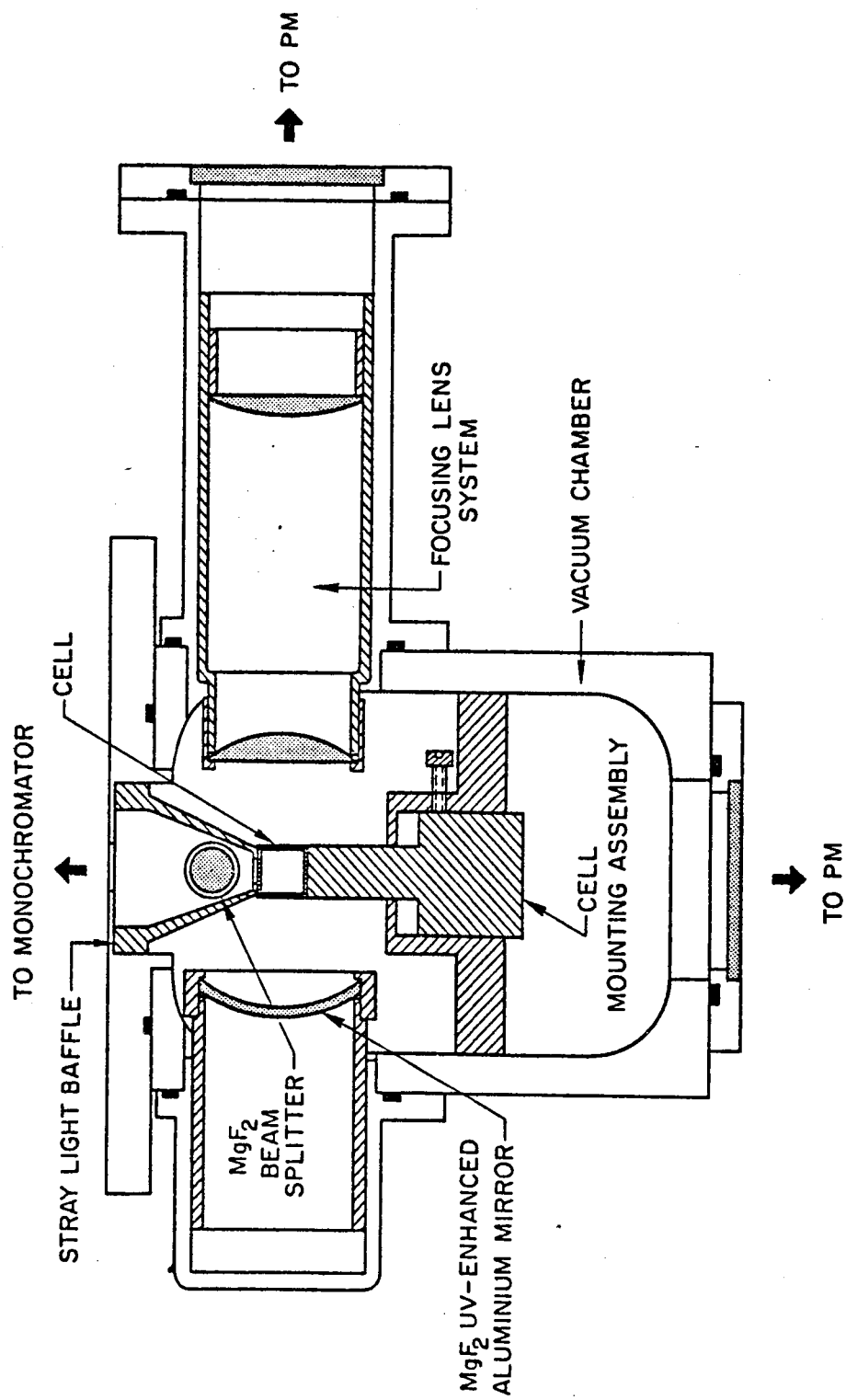


Fig. 2.2. Optical arrangements inside the photoionization chamber.

fluorescence signal registered simultaneously by the photomultiplier A (EMI, type 9558Q). The correction signal B is proportional to $I_R(\lambda)$. The front window of the photomultiplier B was coated with sodium salicylate in front of which was placed a 2 mm-thick MgF_2 window. Since the fluorescence quantum efficiency of sodium salicylate (Samson, 1967) and the refractive index of MgF_2 (Williams and Arakawa, 1979) are independent of λ_{exc} in the region of interest, the signal B is proportional to both $I_R(\lambda)$ and $I_T(\lambda)$ (which excites the sample). This has been confirmed experimentally. This "beam splitter technique" allowed us to correct the excitation spectra not only for the wavelength dependence of the intensity of the excitation light but also for the intensity fluctuations of the lamp and possible changes with time of the properties of the optical components.

The total fluorescence intensity from the solutions under study was observed as a function of λ_{exc} at 90° to the direction of the excitation light beam by means of a "confocal optical system." This consists of a spherical UV-enhanced front surface aluminum mirror and an $f/1$ suprasil lens. The liquid cell is mounted on the confocal point of the optical system and the fluorescence light is focused on the cathode of the photomultiplier A with an additional $\sim f/5$ suprasil lens. To test the optical system for "inner filter effects" (Parker, 1968) the excitation spectra of a 10^{-5} mol l^{-1} solution of pyrene in n-hexane were observed as a function of the position of the cell along the optical axis. No changes in the spectra were recorded as long as the cell was located inside the solid angle of observation defined by the optics. Similar results were obtained with concentrated solutions

(10^{-2} - 10^{-3} mol ℓ^{-1}) of TMPD. The solute photoionization threshold was determined at a fixed solute concentration and varying concentration of an electron attaching additive (see CHAPTER 3).

The electronics detection system (Fig. 2.1) consists of the two photomultipliers, two identical lock-in amplifiers [Princeton Applied Research (PAR) model HR-8], an analogue divider (ratiometer; PAR model 188) and a recorder. The output signals, A from photomultiplier A (PM-A) and B from photomultiplier B (PM-B), are fed into the preamplifiers of the two phase sensitive devices. In a phase-sensitive detection arrangement, such as the one used in the present experiments, the amplifier responds only to the component of the input signal which is in-phase with the reference signal provided independently by the chopper. The noise rejection capability of such an arrangement is improved over conventional detection systems so as variations in the A/B ratio of the order of 10^{-3} can be readily observed. The outputs of the lock-in amplifiers are fed into a ratiometer, with linearity better than 0.3% over a dynamic range of four decades, whose output is proportional to the ratio A/B of the signal A (integrated fluorescence) to the signal B (excitation intensity). By means of a computer-controlled digitizer, the obtained analog data were fed to a PDP-10 computer for analysis.

The obtained ratio $\frac{A}{B}(\lambda_{\text{exc}})$ is the integrated fluorescence intensity

$$I_F(\lambda_{\text{exc}}) \equiv \int F(\lambda_F) d\lambda_F$$

of the solute molecule normalized to the unit of the excitation intensity $I_0(\lambda_{\text{exc}})$. For a given wavelength of excitation, λ_{exc} , the signal

$A(\lambda_{\text{exc}})$ is proportional to the total fluorescence intensity $I_F(\lambda_{\text{exc}})$, viz.,

$$A(\lambda_{\text{exc}}) = k_1 \cdot I_F(\lambda_{\text{exc}}) \quad (2.1)$$

where k_1 is a constant.

The total fluorescence intensity $I_F(\lambda_{\text{exc}})$ is proportional to the intensity, $I_A(\lambda_{\text{exc}})$ of the absorbed light and the fluorescence quantum yield $\phi_F(\lambda_{\text{exc}})$, viz.,

$$I_F(\lambda_{\text{exc}}) = k_2 \cdot I_A(\lambda_{\text{exc}}) \cdot \phi_F(\lambda_{\text{exc}}) \quad (2.2)$$

where k_2 is a proportionality factor including, *inter alia*, the geometry factor, and

$$I_A(\lambda_{\text{exc}}) = I_T(\lambda_{\text{exc}}) \cdot [1 - 10^{-\epsilon_{\text{exc}}}] \quad (2.3)$$

where $I_T(\lambda_{\text{exc}})$ is the transmitted intensity through the beam splitter (see Fig. 2.1), ϵ is the molar extinction coefficient, c the solute concentration in moles per liter and x the optical path in cm. The transmitted intensity is given by:

$$I_T(\lambda_{\text{exc}}) \equiv k_3 \cdot I_0(\lambda_{\text{exc}}) \cdot T(\lambda_{\text{exc}}) \quad (2.4)$$

where $T(\lambda_{\text{exc}})$ is the transmittance of the MgF₂ beam splitter.

Equation (2.1) using Eqs (2.2), (2.3) and 2.4) becomes:

$$A(\lambda_{\text{exc}}) \equiv k_4 \cdot I_0(\lambda_{\text{exc}}) \cdot T(\lambda_{\text{exc}}) \cdot [1 - 10^{-\epsilon_{\text{exc}}}] \cdot \phi_F(\lambda_{\text{exc}}) \quad (2.5)$$

k_4 being a proportionality constant. The signal $B(\lambda_{\text{exc}})$ (see Fig 2.1) is proportional to $I_R(\lambda_{\text{exc}})$,

$$B(\lambda_{\text{exc}}) = k_5 \cdot I_R(\lambda_{\text{exc}}) = k_5 \cdot I_0(\lambda_{\text{exc}}) \cdot R(\lambda_{\text{exc}}) \quad (2.6)$$

where $R(\lambda_{\text{exc}})$ is the reflectance of the MgF₂ and k_5 is a constant independent of the spectral response of the B photomultiplier in the wavelength region of interest because we used sodium salycilate scintillator (Samson, 1967).

From Eqs (2.5) and (2.6) the ratio

$$\frac{A}{B}(\lambda_{\text{exc}}) = K \cdot \frac{T(\lambda_{\text{exc}})}{R(\lambda_{\text{exc}})} \cdot [1 - 10^{-\epsilon c x}] \cdot \phi_F(\lambda_{\text{exc}}) \quad (2.7)$$

was obtained and because $T(\lambda_{\text{exc}})$ and $R(\lambda_{\text{exc}})$ are independent of λ_{exc} in the wavelength region of interest (Williams and Arakawa, 1979) Eq. (2.7) becomes:

$$\frac{A}{B}(\lambda_{\text{exc}}) = K \cdot [1 - 10^{-\epsilon c x}] \cdot \phi_F(\lambda_{\text{exc}}) \quad (2.8)$$

Equation (2.8) indicates that the ratio $\frac{A}{B}(\lambda_{\text{exc}})$ is proportional to the fraction of the photons absorbed and the fluorescence quantum yield $\phi_F(\lambda_{\text{exc}})$ of the molecule under study.

Two extreme cases can be distinguished with regard to the present studies:

(i) Very dilute solutions

In this case

$$\frac{A}{B}(\lambda_{\text{exc}}) = K' \cdot \phi_F(\lambda_{\text{exc}}) \cdot \epsilon \quad (2.9)$$

where $K' = K \cdot 2.303 \cdot c x$.

Equation (2.9) indicates that $\frac{A}{B}(\lambda_{\text{exc}})$ should follow closely the variation of ϵ with λ_{exc} . Therefore the analysis of $\frac{A}{B}(\lambda_{\text{exc}})$ requires a correction for the fraction of the absorbed photons as a function of λ_{exc} and thus a knowledge of the absorption spectrum is necessary.

(ii) Very concentrated solutions

In this case, complete absorption of the excitation light is achieved and

$$\frac{A}{B}(\lambda_{\text{exc}}) \propto \phi_F(\lambda_{\text{exc}}), \quad (2.10)$$

(i.e. $\frac{A}{B}(\lambda_{\text{exc}})$ is independent of ϵ). To ensure this we conducted optical transmission measurements on 10^{-2} mol ℓ^{-1} solutions of pyrene in the liquids used. For such concentrated solutions the maximum light

penetration length was 150 μm for the excitation intensities used and in the wavelength region under consideration. Although situation (ii) simplifies matters considerably, concentrated solutions may not be possible to make because of solubility limitations.

In order to investigate the possible dependence of the fluorescence spectrum $F(\lambda_F)$ itself on λ_{exc} an additional 0.25 m monochromator (not shown in Fig 2.1) was positioned between the photoionization chamber and photomultiplier A. The fluorescence spectrum of a 10^{-4} mol ℓ^{-1} solution of TMPD in n-hexane was independent of λ_{exc} . We also conducted measurements of the fluorescence spectrum of pyrene in solution for the range of concentrations of the electron attaching molecules used and for different excitation wavelengths using the second harmonic of a tunable dye laser as excitation source. The fluorescence spectrum was found to be independent of λ_{exc} and of the concentration of the electron attaching additive in agreement with the spectrum reported by Berlman (1971).

The optical transmittance of the solvent-electron attaching molecule solutions was measured in a 150 μm thin MgF_2 absorption cell. At 190 nm the transmittance was found to be 95% for PFn-H (~ 1.50 mol ℓ^{-1} solution) and 75% for $\text{c-C}_6\text{F}_{12}$, $\text{c-C}_7\text{F}_{14}$ and $\text{c-C}_8\text{F}_{16}$ (~ 1.50 mol ℓ^{-1} solutions). At 200 nm the optical transmittance of the solutions was 100%. The solvent TMSi starts transmitting at $\lambda \sim 195$ nm and has $> 95\%$ transmittance at 210 nm. These experimental findings therefore imply that solvent absorption effects and consequently energy transfer processes between solvent and solute molecules should not have a significant effect on the determination of the solute ionization

threshold in the present study. All measurements were made at ambient temperature and in aerated solutions.

2.3 Laser Two-Photon Ionization Technique

The experimental apparatus used in this study has been described by Siomos and Christophorou (1980) and Siomos and coworkers (1979). Figure 2.3 shows schematically the apparatus for the photoconductivity measurements. It consists of a tunable light source, the photoconductivity cell, the electronic detection system and the vacuum and liquid purification assembly.

The light source, a tunable-dye laser pumped by a nitrogen laser (Molelectron UV 1000/DL 200), was operated with a repetition frequency at 25pps (pulses per second). The dye laser frequency was tuned to the spectral region of interest with the help of a 0.5m grating monochromator to within $\pm 0.1\text{nm}$. The bandwidth of the spectral distribution of the dye laser was 0.02 nm which is sufficient for photoionization studies in the liquid phase. To cover the wavelength region of interest (360–650nm) 17 different dyes, listed in Table 2.1, were used. The energy per pulse of this source was varied from 0.2 to $\sim 1\text{mJ}$ depending on the wavelength and the efficiency of the particular dye used. The dye-laser beam had a $\sim 1\text{mm}$ diameter after spatial filtering and was focused to a waist of $\approx 40\mu\text{m}$ diameter onto the photoconductivity cell which contained the solution of the molecule under study at a concentration of $\sim 5 \times 10^{-6} \text{ mol l}^{-1}$. This concentration corresponds to a particle density of $3 \times 10^{15} \text{ molecules cm}^{-3}$. For comparison the photon density of the laser beam corresponding to

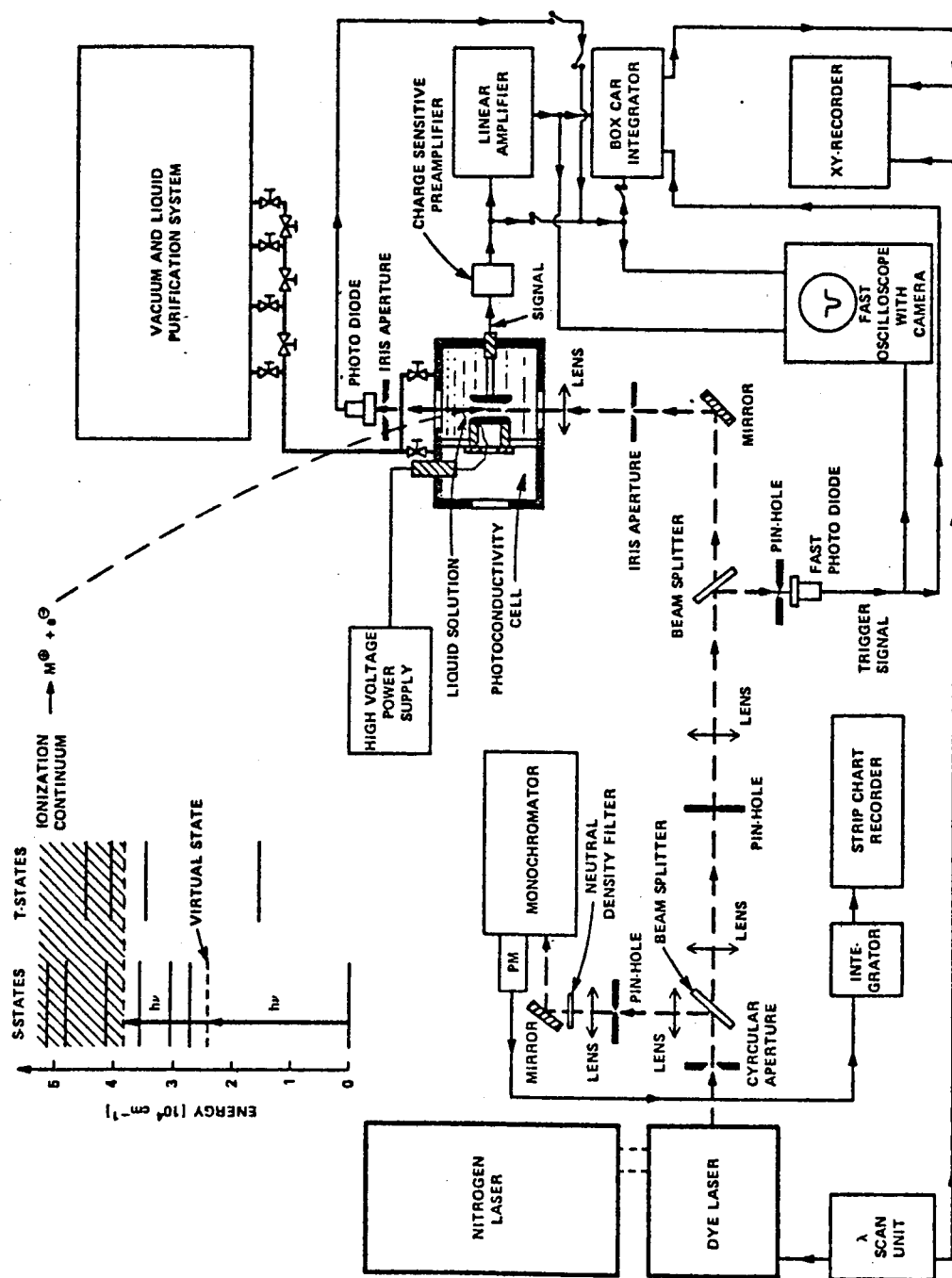


Fig. 2.3. Layout and principle of the laser two-photon ionization technique.

Table 2.1. List of Dyes Used in the Laser Two-Photon Ionization Technique

Name	Wavelength range (nm)
2-(4-Biphenyl)-5-phenyl-1,3,4-oxadiazole	360 - 386
4,4'-bis-butylacetoxy-terphenyl	373 - 399
2-(4'-Biphenyl)-6-phenylbenzoxazole	391 - 411
4,4'-diphenylstilbene	396 - 416
1,4-bis-(2-methylstyryl)benzene	411 - 430
Coumarin	420 - 457
Coumarin	428 - 465
7-diethylamino-4-methylcoumarin	440 - 478
Coumarin	453 - 495
7-diethylamino-4-trifluoro-methylcoumarin	460 - 517
Coumarin-500(fluorinated)	473 - 547
Coumarin-485(fluorinated)	490 - 562
Coumarin-540A(fluorinated)	515 - 583
Rhodamine 6G	568 - 605
Rhodamine B	594 - 643
Cresyl Violet Perchlorate	628 - 651
Cresyl Violet Perchlorate	641 - 687

radiation of 520 nm (2.38 eV per photon), 1mJ energy per pulse and reaction volume of 10^{-3} cm^3 (approximately the size of the solution volume irradiated by the laser beam) was $\sim 2.6 \times 10^{18}$ photons cm^{-3} which is ~ 3 orders of magnitude higher than the molecule density. Also the photon flux at the focal point for $\sim 6\text{ns}$ pulse duration was of the order of $\sim 10^{27}$ photons $\text{cm}^{-2}\text{s}^{-1}$. The laser beam was monitored before and after the photoconductivity cell with photodiodes of well-known spectral responsivity and was sampled with a boxcar integrator.

The photoconductivity cell is shown schematically in Fig. 2.4. It was made out of stainless steel and is divided into two parts which can be evacuated independently. The first part (high voltage chamber, 2 in Fig. 2.4) allows for the connection of the high-voltage source to the high voltage plate. It comprises a ceramic high-voltage feed-through (6 in Fig. 2.4), which is enclosed in a container of transformer oil. The second part of the cell (the liquid chamber, 1 in Fig. 2.4) consists of four suprasil quartz windows mounted in cross symmetry and two electrodes. The electrodes - 2 cm - diameter gold-plated stainless steel discs - are mounted in such a way that their separation can be changed continuously from 0 to 15 mm with an accuracy of 0.02mm by means of a micrometer (8 in Fig. 2.4). In the course of the present studies the electrodes were spaced 2mm apart and maintained at a potential difference of 3kV corresponding to an electric field of 15kVcm^{-1} . The liquid chamber provides connections to the high vacuum and the purification systems.

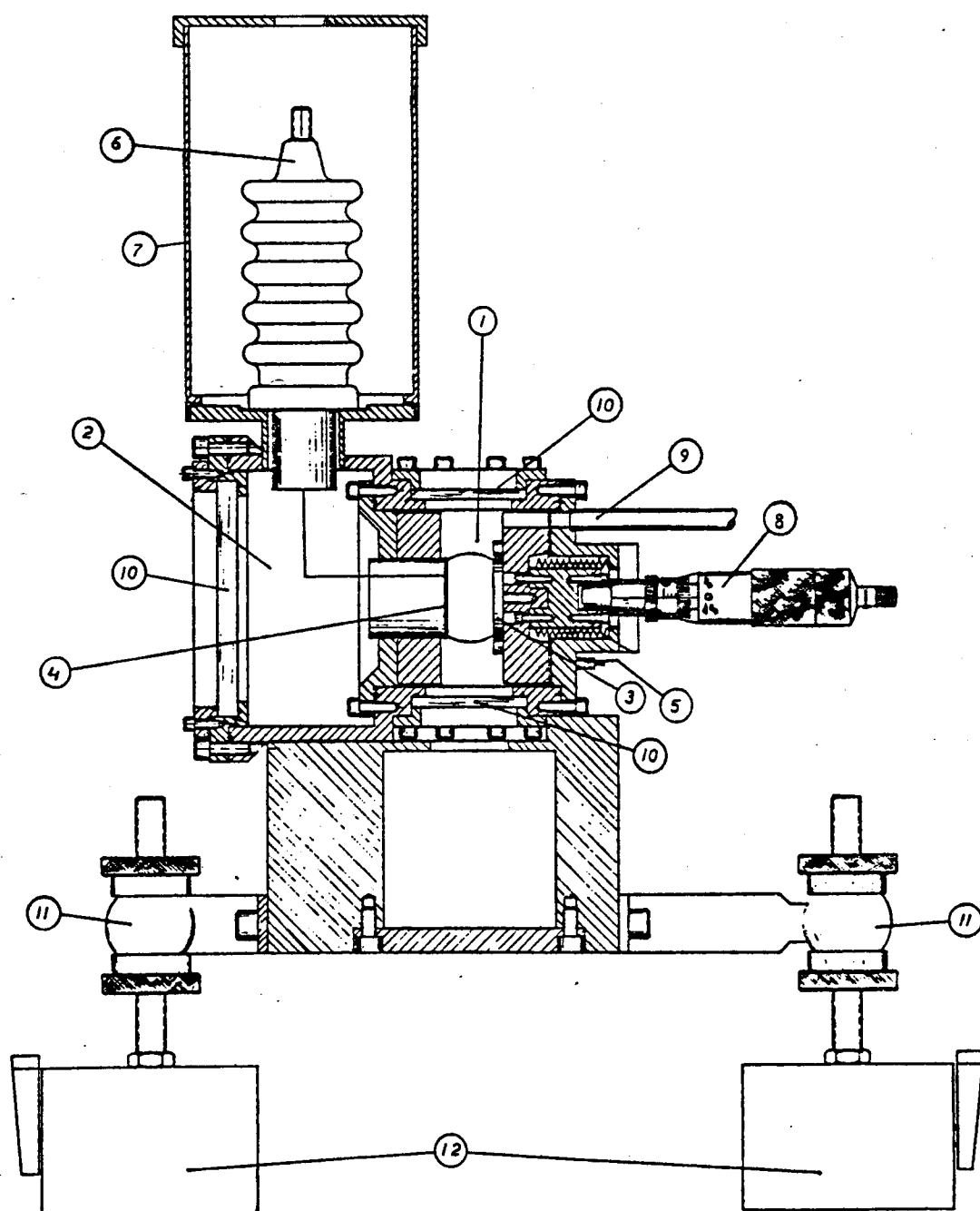


Fig. 2.4. Cross-sectional view of the liquid photocell.
 (1) liquid chamber, (2) high-voltage chamber, (3) adjustable collector electrode, (4) cathode, (5) signal output feedthrough, (6) high-voltage connector, (7) high-voltage oil container, (8) micrometer, (9) liquid inlet, (10) quartz windows, (11) three-point kinematic holder, (12) magnetic bases.

The purification system is a combination of three high-vacuum pump systems with different distillation steps and molecular filters (Fig. 2.5). A silica-gel column, activated at 300°C, is followed by an activated charcoal column at a temperature of 500°C. A system allowing for multiple freeze-pump-thaw cycles is used for the de-aeration of the solvent to a pressure of $\sim 10^{-7}$ torr. The solvent is finally stirred on a NaK alloy to remove traces of oxygen and water. In the final stage a gas chromatograph is attached to the purification system to monitor the purity of the solvent before its transfer to the photoconductivity cell.

The photoconductivity cell was equipped with a two-parallel plate charge-sensitive detector, which was coupled into a high input impedance ($\sim 100\text{M}\Omega$) preamplifier with a bandwidth of 200 MHz and gain of 20 (Fig. 2.6). It was chosen to provide fast response and maximum sensitivity. The signal, after amplification by a linear amplifier (TC-200), is averaged by a boxcar integrator (PAR, Model 162) operated in the single-point mode. In this mode (a block diagram is shown in the insert of Fig. 2.6) the boxcar integrator measures the mean amplitude of repetitive pulses by sampling for a time interval t_s (sampling time). Since the sampling time may be less than 1% of the repetition period the result after sampling must be held until the next sample is taken. This is accomplished by carefully choosing the gate time constant $t_g = R_g C_g$. The observed time constant in the output, t_{ob} , is longer because the charging circuit is inactive for most of the time-cycle. The observed time constant is given by:

$$t_{ob} = t_g / t_s \cdot f \quad (2.11)$$

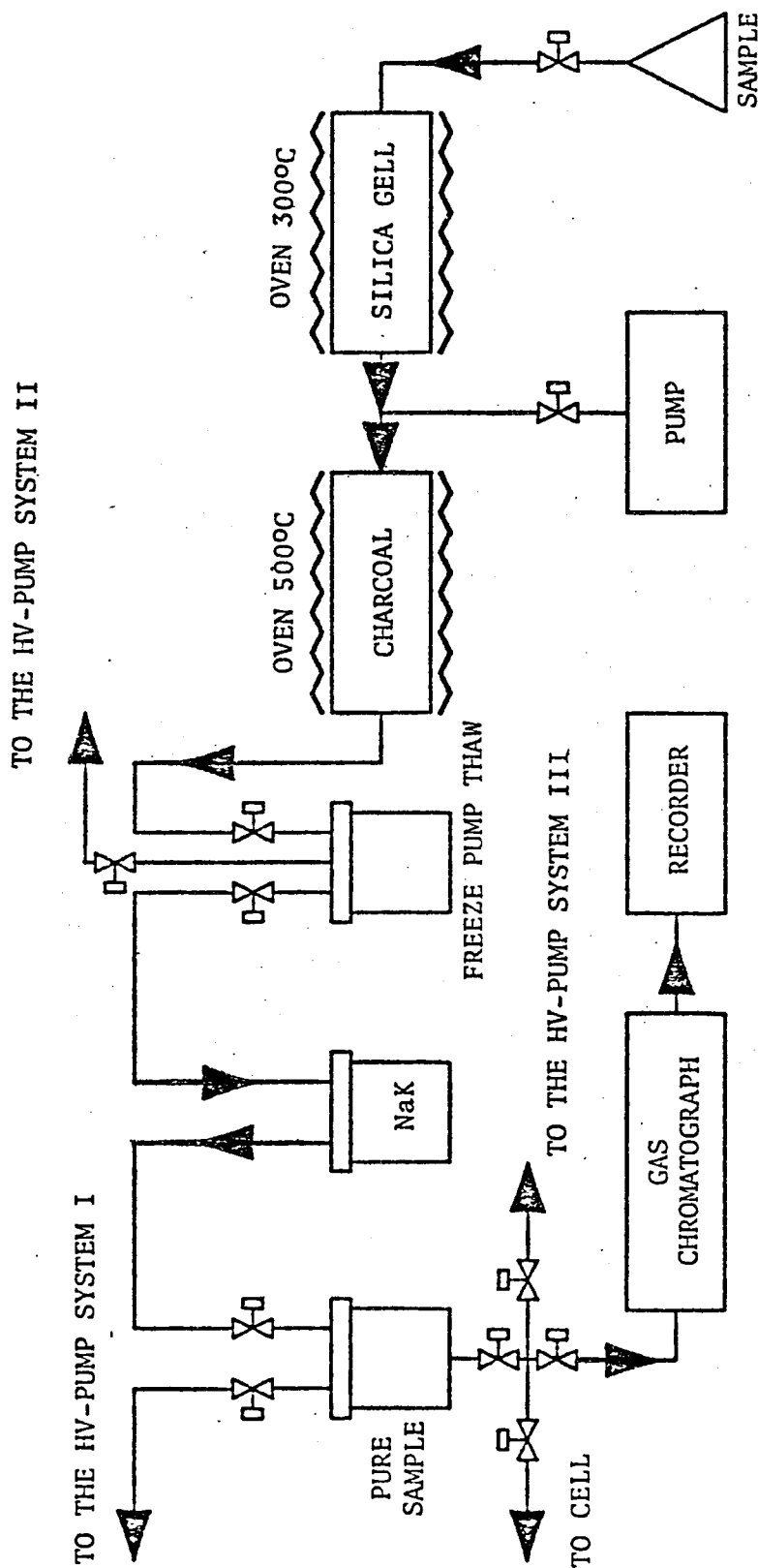


Figure 2.5. Purification system used in the laser two-photon ionization technique.

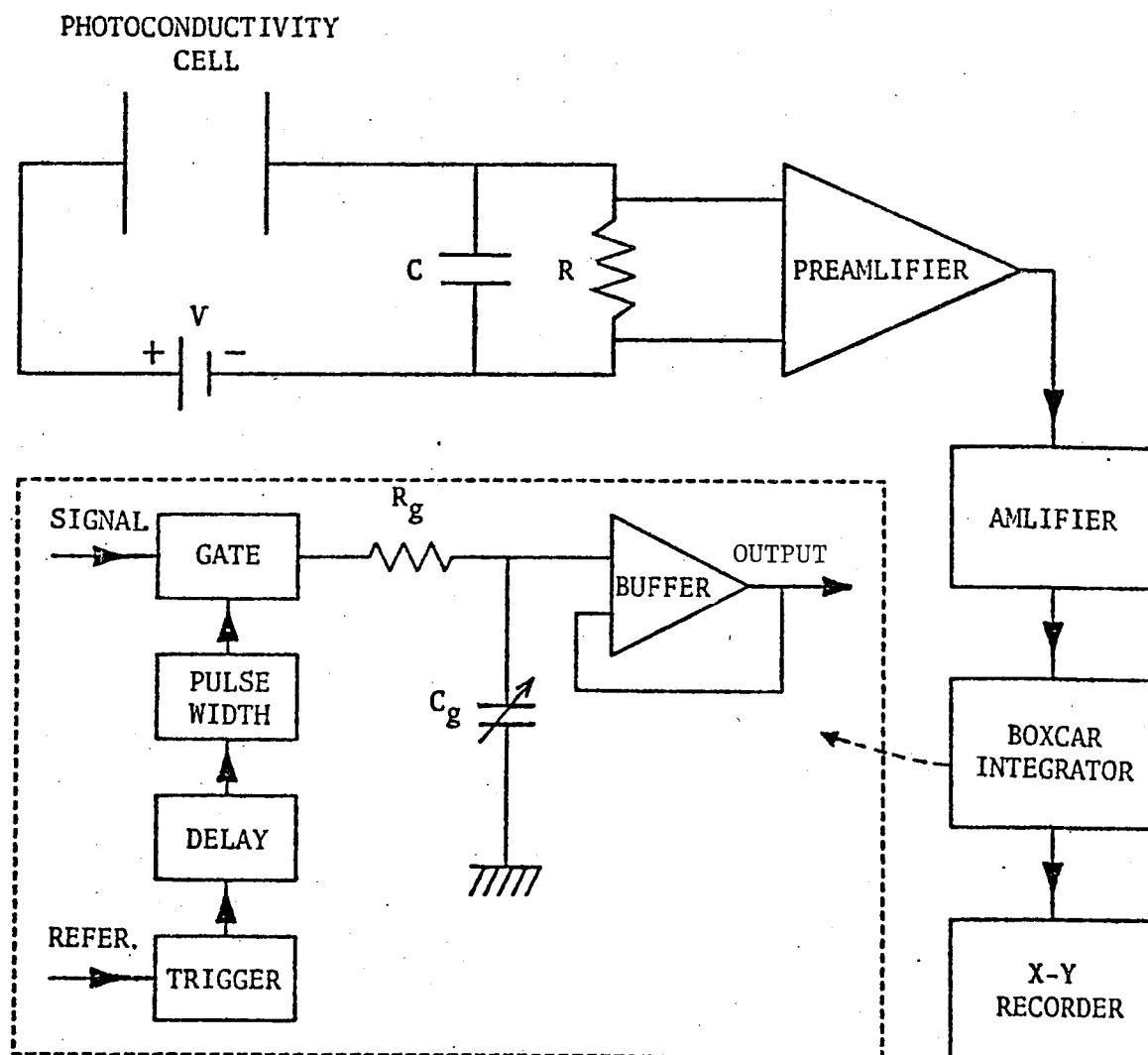


Fig. 2.6. Block-diagram of the detection system. Insert: block-diagram of the boxcar integrator in the single-point mode of operation.

where f is the repetition frequency. The signal-to-noise improvement ratio S is given by:

$$S = \sqrt{2t_{ob} \cdot f} = \sqrt{2t_g/t_s} \quad (2.12)$$

For the majority of our measurements $t_s = 500\text{ns}$, $f = 25\text{Hz}$ and $t_g = 100\mu\text{s}$. Then, from (2.12), the signal-to-noise ratio was improved by a factor of 20.

The photoconductivity signal obtained in this way was recorded as a function of the excitation (laser) wavelength. The laser intensity was simultaneously recorded as a function of the laser wavelength. The photoconductivity signal induced via a two-photon absorption and subsequent ionization of the solute molecule was expected to depend on the square of the laser intensity I_{laser} . The dependence of the two-photon-ionization (TPI) signal on the incident laser intensity I_{laser} has been checked experimentally for the case of pyrene (Siomos and Christophorou, 1980). The results are shown in Fig. 2.7. It was found that the TPI-signal had a functional dependence of the form $I_{\text{laser}}^{1.55}$, which agrees well with the theoretically calculated dependence of $I_{\text{laser}}^{3/2}$ (Abutyunyan and coworkers, 1970; Speiser and Jortner, 1976). The $I_{\text{laser}}^{3/2}$ dependence is observed with the onset of saturation of the two-photon process, due to purely geometrical effects in the region of a tightly focused laser beam.

The output signals of both integrators after digitalization were fed into a PDP-10 computer for analysis. The TPI-signal after

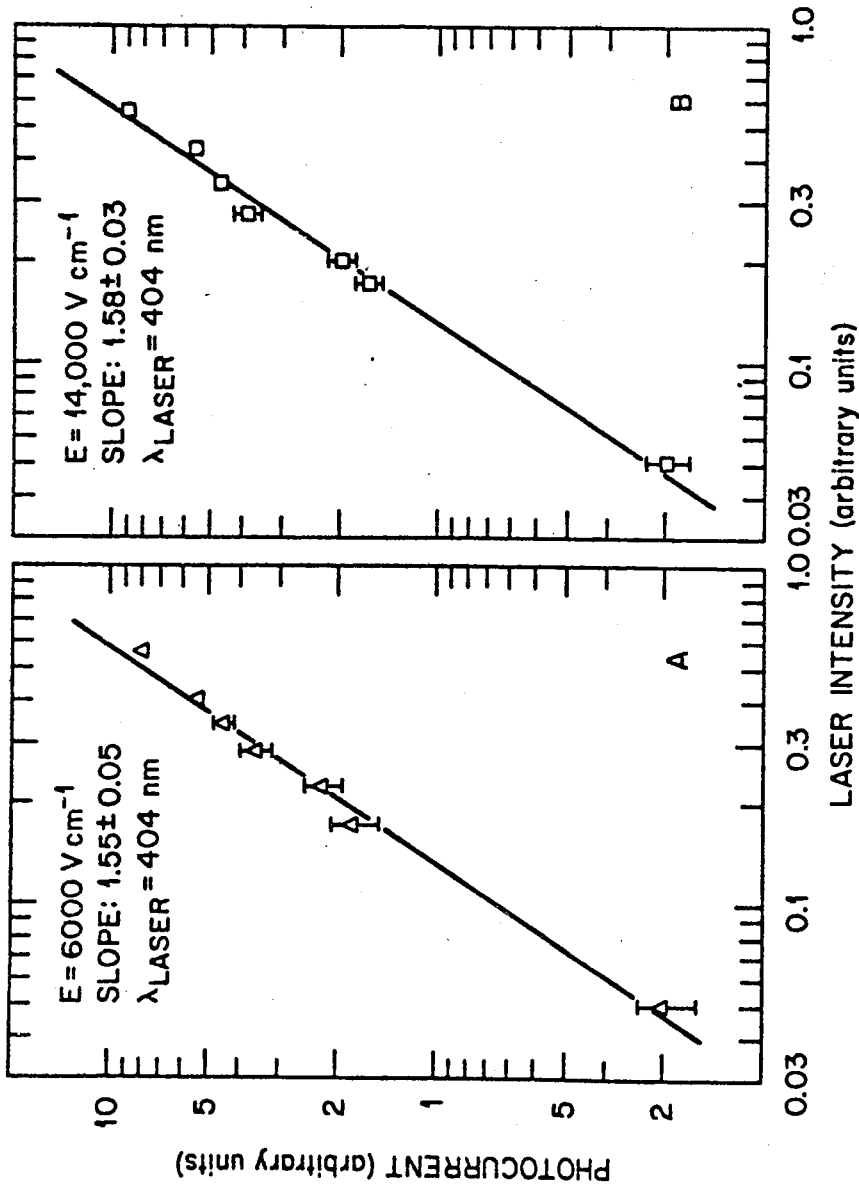


Fig. 2.7. Dependence of the two-photon ionization signal on the incident laser intensity. The applied field was 6 kV cm^{-1} (a) and 14 kV cm^{-1} (b). The solid lines through the experimental points were obtained by means of a least squares fitting procedure to $y = ax^b$. The $3/2$ dependence is associated (see text) with the onset of saturation of the two-photon ionization process. (Siomos and Christophorou, 1980).

intensity correction (division by the square of the light intensity⁺ after correction for the spectral responsivity of the photodiode) was plotted as a function of laser wavelength.

The system used in the laser two-photon ionization measurements (Fig. 2.3) was also used, with a slight modification, to measure the one-photon induced ionization current. For this, the apparatus was slightly modified to accommodate a frequency-doubling unit. The second harmonic of the dye-laser, generated in an angle-tuned KDP-crystal (Potassium Dihydrogen Phosphate), was in the wavelength range of 285 to 330 nm. In this wavelength range it was possible to measure the one-photon induced ionization (OPI) spectrum of TMPD in n-pentane near threshold, due to its low I_L^1 value.

2.4 VUV Absorption Spectroscopy in Solution

The apparatus employed in the VUV absorption spectroscopy is shown schematically in Fig. 2.8. It consists of the monochromatic light source assembly, the vacuum chamber with the absorption cell and the associated optics, and the detection-electronics and data handling systems. Parts of the instrumentation have been used for the integrated fluorescent measurements and have been described in section 2.2. In what follows we describe the modifications made for measurements of absorption spectra in solution.

⁺Division by $I_{\text{laser}}^{1.55}$ did not alter the distribution of the TPI spectrum.

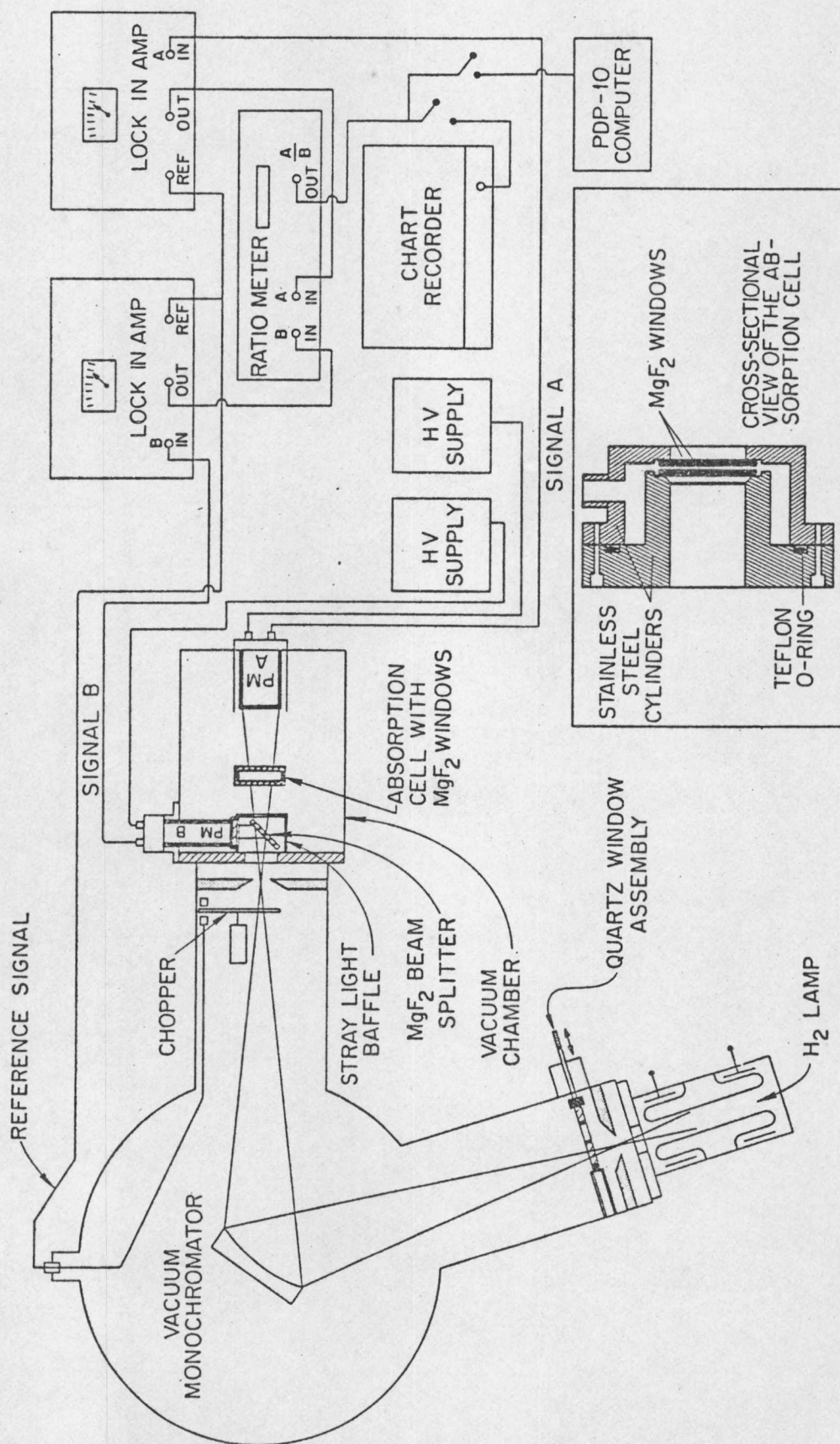


Fig. 2.8. Layout of the experimental apparatus. Insert: Cross section view of the absorption cell.

A hydrogen discharge lamp in conjunction with a half-meter Seya-Namioka-type monochromator was used as the excitation light source.

The absorption cell is made of two stainless steel cylinders equipped with 1-mm-thick MgF_2 windows and arranged as to form the cell when one is inserted into the other (see insert in Fig. 2.8). The thickness of the cell was measured interferometrically and found to be 150 μm . The absorption cell is mounted on a holder which allows for accurate positioning and alignment of the cell with respect to the exciting light beam and enclosed it in such a way that only the light illuminating the sample reaches the detection optics. In order to eliminate stray light, a stray-light baffle was located between the monochromator exit slit and the cell. The absorption cell was constructed for measurements in the VUV region. Therefore, its thickness was chosen on the basis of the transmission of the solvents used, the absorption properties of the molecules under study and their solubilities.

The excitation light beam (tunable over the energy region 30000 to $\sim 80000\text{ cm}^{-1}$; $\sim 330 - 125\text{ nm}$) is amplitude-modulated with a light chopper operating at $\sim 220\text{ Hz}$. The latter was located in front of the exit slit of the monochromator. The excitation light beam is split into two beams inside the vacuum chamber by means of a 1-mm-thick MgF_2 window placed at 45° with respect to the incident light beam. The reflected beam is monitored with the photomultiplier B (Hamamatsu R647), providing the signal B which is used for the correction of the transmission signal through the sample (a 3-mm-thick MgF_2 window is

placed in front of this photomultiplier to match the optical path to that of the transmitted beam). The transmitted beam used for the sample excitation is monitored with a solar-blind photomultiplier (EMI, G26H315). The detection-electronics and data handling system consists of two identical phase-sensitive amplifiers, a ratiometer, and a computer-controlled digitizer.

The present technique has several advantages over other methods used for VUV measurements (Korn and Braunstein, 1972; Schmitt and Brehm, 1966; Nihei and coworkers, 1968; Boursey and coworkers, 1971):

- (1) Spatial beam splitting is achieved by using a MgF_2 beam splitter, thus avoiding mechanically moving parts. The system is stable in time and the excitation light beam is constantly focused on the sample.
- (2) By monitoring the signal A (Fig. 2.8) transmitted through the sample with the solar-blind photomultiplier, the spectra obtained are free of any interference due to possible fluorescence of the molecules under study [aromatic hydrocarbons fluoresce at $\lambda > 280 \text{ nm}$ (Berlman, 1971)].
- (3) The recorded transmission spectra are corrected not only for the wavelength dependence of the intensity of the excitation light but also for the intensity fluctuations of the lamp and the possible changes with time of the properties of the optical components. The latter is of importance in the VUV region because the transmission of the optical materials used in this region (e.g., MgF_2) deteriorates with time for several reasons as, for example, deposition of oil on surfaces and color-center formation (Samson, 1967).
- (4) The detection system used is a phase-sensitive arrangement utilizing two identical amplifiers. The beam is amplitude-modulated at a relatively high frequency ($\sim 220 \text{ Hz}$) compared with flipper

mirror or rotating cell arrangements operating at frequencies of 7-12 Hz and 8 Hz, respectively (Korn and Braunstein, 1972; Schmitt and Brehm, 1966; Nihei and coworkers, 1968). In this way the signal-to-noise ratio is greatly improved so that changes in the transmission signal as low as 10^{-3} can be detected. The overall linearity of the detection system is better than 0.3% over a dynamic range of four decades.

Utilizing the apparatus described in the previous section we measured the corrected transmission signal

$$\left[\frac{A}{B}(\lambda) \right]_{\text{solvent}} \equiv F_0(\lambda) \text{ of the solvent}$$

and

$$\left[\frac{A}{B}(\lambda) \right]_{\text{solution}} \equiv F(\lambda)$$

of the solution to determine the transmittance of the solute from the ratio of the solution to the solvent transmission spectra. The signal $A(\lambda)$ is proportional to $I(\lambda)$, the intensity of the exciting light, $D(\lambda)$, the transmittance of MgF_2 , $S_A(\lambda)$, the spectral responsivity of the photomultiplier A and the transmittance, $T_0(\lambda)$ of the solvent or $T(\lambda)$ of the solution, viz.,

$$[A(\lambda)]_{\text{solvent}} = k_1 \cdot I(\lambda) \cdot D(\lambda) \cdot S_A(\lambda) \cdot T_0(\lambda). \quad (2.13)$$

The signal $B(\lambda)$ is proportional to $I(\lambda)$, the intensity of the exciting light, $R(\lambda)$, the reflectance of MgF_2 and $S_B(\lambda)$, the spectral responsivity of the photomultiplier B, viz.,

$$B(\lambda) = k_2 \cdot I(\lambda) \cdot R(\lambda) \cdot S_B(\lambda). \quad (2.14)$$

In (2.13) and (2.14) k_1 and k_2 are proportionality constants. From (2.13) and (2.14)

$$F_o(\lambda) = \frac{k_1}{k_2} \cdot \frac{D(\lambda)}{R(\lambda)} \cdot \frac{S_A(\lambda)}{S_B(\lambda)} \cdot T_o(\lambda), \quad (2.15)$$

and accordingly

$$F(\lambda) = \frac{k_1}{k_2} \cdot \frac{D(\lambda)}{R(\lambda)} \cdot \frac{S_A(\lambda)}{S_B(\lambda)} \cdot T(\lambda) \quad (2.16)$$

If we let $\epsilon(\lambda)$ be the extinction coefficient of the solute in $\ell \text{ mol}^{-1} \text{ cm}^{-1}$, $T_S(\lambda)$ its transmittance, c , the concentration in $\text{mol } \ell^{-1}$, and d the cell thickness in cm , we have

$$\epsilon(\lambda) = \log_{10} \left(\frac{1}{T_S(\lambda)} \right) / c \cdot d \quad (2.17)$$

And since

$$T_S(\lambda) = \frac{T(\lambda)}{T_o(\lambda)} = \frac{F(\lambda)}{F_o(\lambda)}, \quad (2.18)$$

$$\epsilon(\lambda) = \log_{10} \left(\frac{F_o(\lambda)}{F(\lambda)} \right) / c \cdot d \quad (2.19)$$

The division of the two transmission spectra (Eq. 2.18) results in a solute transmittance which is free of possible mismatching of the A and B channels[‡] (see Fig. 2.8). Therefore, the requirement for a flat "baseline" (Korn and Braunstein, 1972) is an intrinsic property of the experimental apparatus, in the present technique.

2.5 Materials

All hydrocarbons used for the present studies--n-pentane (n-p), n-hexane (n-H), n-heptane (n-Hp), cyclo-hexane (c-H), isopentane

[‡] In other double-beam techniques (Schmitt and Brehm, 1966) extensive care has to be exercised for a "perfect" matching of the two channels.

(i-P), neohexane (neo-H), cyclopentane (c-P) - were Phillips Research Grade (>99.98%) and they were purified further by stirring for ~24h with H_2SO_4 and then with BaCO_3 and dried out on a NaOH-pellets column. The solvent tetramethylsilane (TMSi) was of quoted purity of 99.99% and was used without further purification. The electron attaching compounds — perfluoro-normal-hexane (PFn-H) of purity 99%, perfluoro-dimethyl-cyclo-butane ($\text{c-C}_6\text{F}_{12}$), perfluoro-methyl-cyclo-hexane ($\text{c-C}_7\text{F}_{14}$) and perfluoro-dimethyl-cyclo-hexane ($\text{c-C}_8\text{F}_{16}$) each of quoted purity of 97%—were used as supplied. The solute molecules—pyrene and fluoranthene—were zone-refined to a purity better than 99.99% and the TMPD had a quoted purity of 98%+. They were used as supplied. The hydrocarbon solvents used in the laser two-photon ionization measurements were additionally treated with the purification system described in section 2.3 to remove traces of oxygen and water.

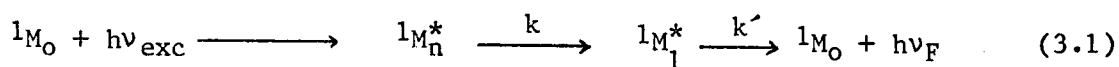
CHAPTER 3

PHOTOIONIZATION THRESHOLDS OF ORGANIC MOLECULES IN DIELECTRIC LIQUIDS DETERMINED WITH THE INTEGRATED FLUORESCENCE TECHNIQUE

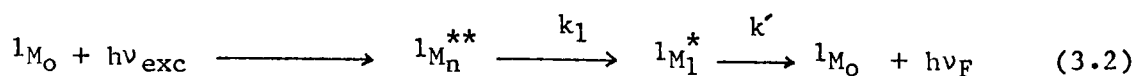
3.1 Introduction

The photoionization threshold of a fluorescent molecule in solution was established by monitoring its integrated fluorescence intensity, $I_F(\lambda_{exc})$, as a function of the excitation wavelength, λ_{exc} , or photon energy, $h\nu_{exc}$, and the concentration of an appropriate electron attaching compound.

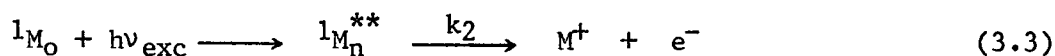
In organic photophysics two closely related generalizations have been in wide usage for decades: Vavilov's law "The fluorescence quantum efficiency is independent of the excitation wavelength for nonionizing radiation" (Birks, 1970), and Kasha's rule "The emitting electronic level of a given multiplicity is the lowest excited level at that multiplicity" (Kasha, 1950). When a fluorescent molecule in the ground electronic singlet state, $^1M_0$, is irradiated with a beam of photons of energy $h\nu_{exc} < I_L^1$, the molecule is excited in a higher singlet state $^1M_n^*$. After internal conversion, with a given rate constant, k , to the first excited singlet state $^1M_1^*$ it fluoresces with certain rate constant, k' , viz.



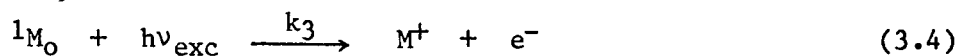
When the excitation photon energy $h\nu_{exc} > I_L^1$ a similar process



may still be possible; $1M_n^{**}$ is now a superexcited state, i.e. an excited state lying in the ionization continuum and k_1 the rate constant for the internal conversion from $1M_n^{**}$ to $1M_1^*$. However, superexcitation may lead to autoionization (indirect ionization) with a rate constant k_2 , viz.

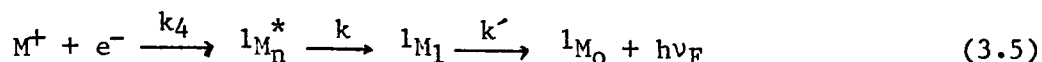


Indirect ionization (Eq. 3.3) in many cases predominates over direct ionization (Eq. 3.4) (see CHAPTER 4; Christophorou, 1971)



where k_3 is the rate constant for this process.

When, therefore, the excitation photon energy exceeds the ionization threshold energy, fluorescence would result primarily from the geminate recombination process with rate constant k_4



Implicit in Eq (3.5) is the assumption that the "spin correlation" has not been lost during the lifetime of the electron-ion pair. This has been indicated by the work of Brocklehurst (1969; 1974a; 1974b; 1976) and Brocklehurst and coworkers (1964; 1972).

If, however, "spin correlation" can be lost partially or totally, the recombination processes (3.5) will not lead to singlet excited states, but also to triplet states, T_n^* , and thus to a reduction in the

fluorescence intensity when $h\nu_{\text{exc}} > I_L^1$. Strong electric fields can be used to decorrelate the spins of the electron-ion pair.

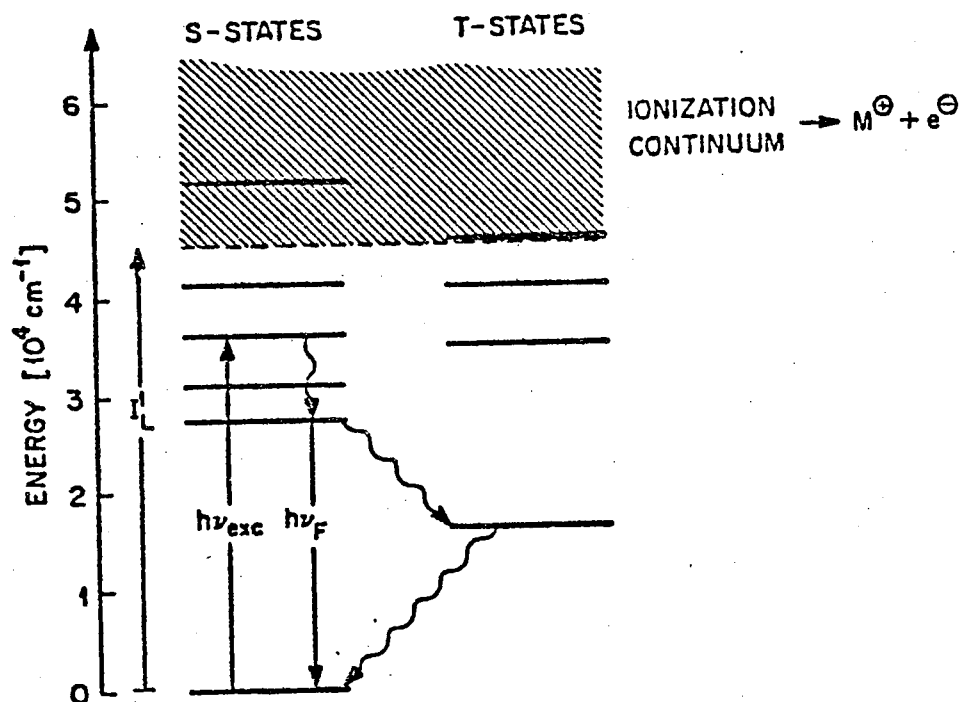
Alternatively, as it has been done in this work, one can prevent geminate recombination of the electron-ion pair by removing the e^- via electron attachment to an appropriately chosen electron attaching molecule A.



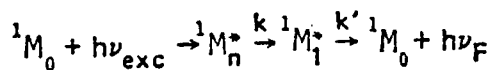
Fluorescence resulting from possible neutralization of M^+ , A^- ion pair would certainly be much less than that of geminate recombination.

Thus a reduction in the fluorescence yield for $h\nu_{\text{ex}} > I_L^1$ with increasing concentration of the electron attaching additive could allow a determination of the ionization threshold(s) of the fluorescent solute. In Fig. 3.1 the mechanisms involved in the excitation and ionization of a fluorescing molecule in dielectric liquids in the presence of an electron attaching additive are summarized.

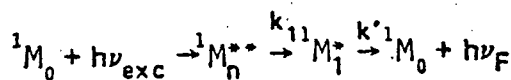
A serious consideration in choosing the electron attaching additives was their fluorescence quenching properties as well as their optical transmission properties. This becomes an especially serious problem when, as in the present study, one is after discrete discontinuities in $I_F(\lambda_{\text{exc}})$ identifiable with photoionization thresholds by means of electron attaching additives ("scavengers") which are often themselves strong quenchers of fluorescence. In such cases the choice of a strong electron scavenger which is a weak fluorescence quencher is highly desirable. In this regard, we found that the perfluorinated electron attaching molecules PFn-H, c-C₇F₁₄, c-C₆F₁₂ and c-C₈F₁₆ are



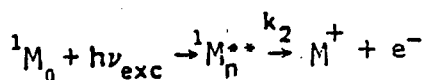
I $h\nu_{\text{exc}} < I_L^1$



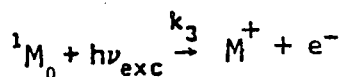
II $h\nu_{\text{exc}} \geq I_L^1$



INDIRECT IONIZATION



DIRECT IONIZATION



RECOMBINATION FLUORESCENCE $M^+ + e^- \xrightarrow{k_{41}} ^1M_n^* \xrightarrow{k_1} ^1M_1^* \xrightarrow{k'} ^1M_0 + h\nu_F$

ELECTRON ATTACHMENT



Fig. 3.1. Summary of the excitation and photoionization mechanisms of a molecule in solution in the presence of an electron attaching compound. The symbols are explained in the text.

preferable to chloroform; the latter has been used by Kam-chu-Wu and Lipsky (1977) in similar studies.

3.2 Photoionization of Pyrene in Dielectric Liquids

The first photoionization threshold of pyrene was measured with the integrated fluorescence technique in liquid media comprising a dielectric liquid and an electron attaching additive. The dielectric liquids were the six hydrocarbons n-hexane (n-H), n-pentane (n-P), n-heptane (n-Hp), isopentane (i-P), cyclopentane (c-P), neohexane (neo-H) and tetramethylsilane (TMSi). The electron attaching molecules used were the cyclic perfluorocarbons perfluoro-methyl-cyclohexane (c-C₇F₁₄), perfluoro-1,2-dimethyl-cyclo-butane (c-C₆F₁₂), perfluoro-1,3-dimethyl-cyclo-hexane (c-C₈F₁₆) and the linear perfluorocarbon perfluoro-normal-hexane (PFn-H). The concentration of A used was rather high; it was varied in steps of 0.25 mol ℓ⁻¹ and was in the range 0.25-1.50 mol ℓ⁻¹. The concentration of pyrene was 10⁻² mol ℓ⁻¹. Figure 3.2 shows typical integrated fluorescence intensity spectra of pyrene in liquid n-pentane. The integrated fluorescence intensity,

$$I_F(\lambda_{exc}) \equiv \int F(\lambda_F) d\lambda_F$$

corrected for the excitation light intensity is plotted vs the excitation wavelength for a 10⁻² mol ℓ⁻¹ solution of pyrene in liquid n-pentane in the absence of the A (curve 1), in the presence of PFn-H (curves 2-4) and in the presence of c-C₇F₁₄ (curves 5-7). All spectra were normalized at 270 nm. Any other normalization point in the wavelength range ~230-280 nm would have been equally appropriate.

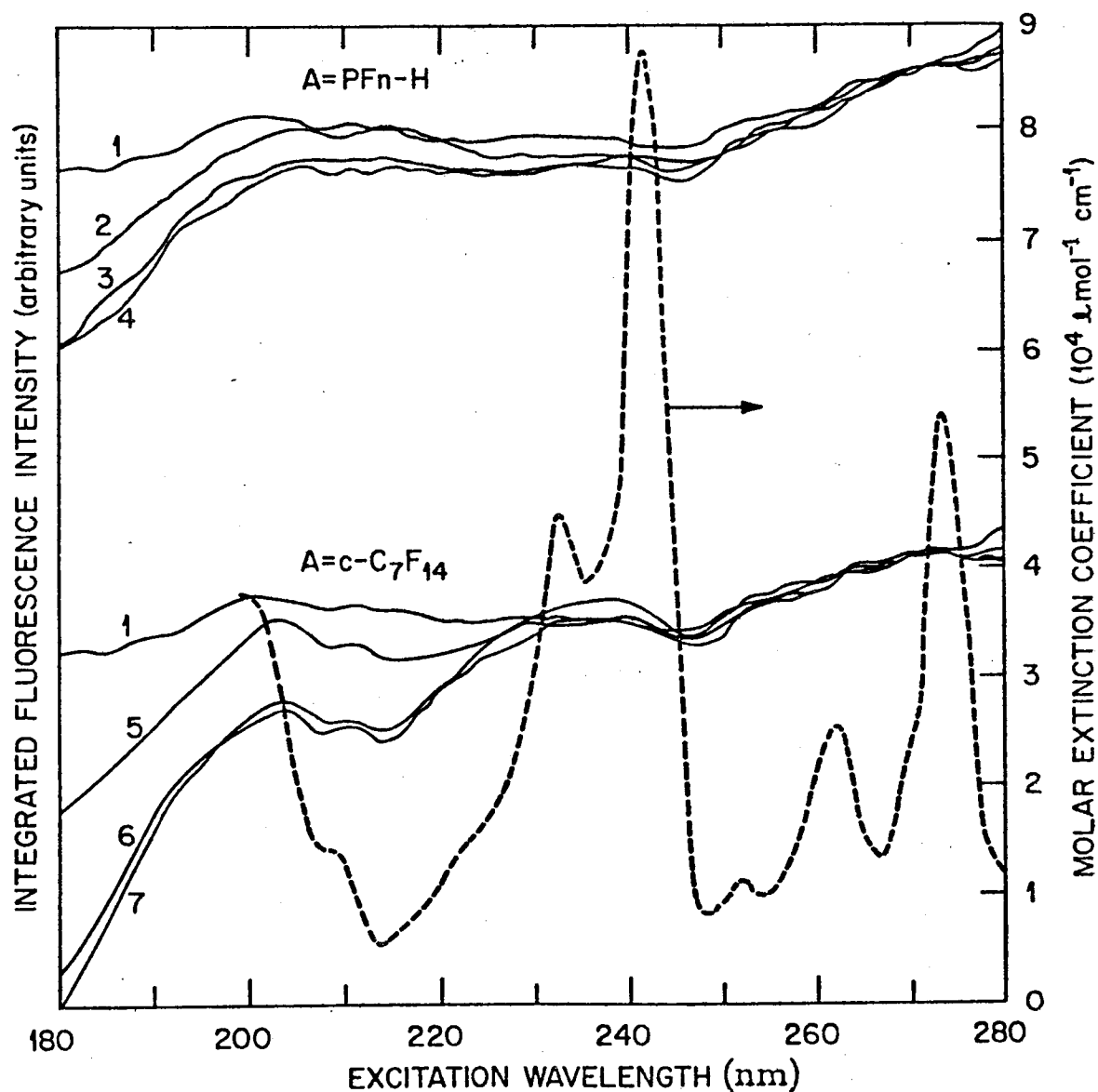


Fig. 3.2. Integrated fluorescence intensity vs excitation wavelength for a $10^{-2} \text{ mol l}^{-1}$ solution of pyrene in liquid n-pentane at room temperature. [A] (perfluoro-n-hexane): 0.0 mol l^{-1} (curve 1), 0.25 mol l^{-1} (curve 2), 1.01 mol l^{-1} (curve 3), 1.48 mol l^{-1} (curve 4), and [A] (perfluoromethyl-cyclohexane): 0.26 mol l^{-1} (curve 5), 1.04 mol l^{-1} (curve 6) and 1.51 mol l^{-1} (curve 7). The spectra were normalized at 270 nm. The dashed curve represents the absorption spectrum of pyrene.

These and similar spectra (not shown in the figure) at other pyrene concentrations as well as spectra presented in subsequent figures are free of the possible effects of light emission from the solvent, the sample cell, or the electron attaching additives. The detector signal under identical conditions for the empty cell, the cell filled with only the solvent or the cell filled with the solvent plus the electron attaching additive was flat over the entire range of λ_{exc} and much smaller (by a factor of 100) than for the fluorescent samples. The absorption spectrum of pyrene in n-P (see CHAPTER 5) is shown in the figure by the dashed curve. The $I_F(\lambda_{\text{exc}})$ for 10^{-2} mol ℓ^{-1} pyrene solutions is independent of the molar extinction coefficient variations and no correction for the fraction of photons absorbed as a function of λ_{exc} is necessary (see CHAPTER 2). For the PFn-H containing solutions, $I_F(\lambda_{\text{exc}})$ decreases considerably for $\lambda_{\text{exc}} < 210$ nm while for the c-C₇F₁₄-containing solutions this decrease starts around 230 nm. Similar results with those in Fig. 3.2 were obtained for all the solvents and all the electron attaching additives studied in this work.

The ratio $R_{[A]}(\lambda_{\text{exc}})$ of the $I_F(\lambda_{\text{exc}})$ function in the absence of A to that in the presence of A has been determined. Figures 3.3 and 3.4 show (solid lines) two typical examples for a 10^{-2} mol ℓ^{-1} solution of pyrene in liquid n-pentane at a PFn-H concentration of 1.01 mol ℓ^{-1} (Fig. 3.3) and at a c-C₇F₁₄ concentration of 1.04 mol ℓ^{-1} (Fig. 3.4). We assumed that the $R_{[A]}(\lambda_{\text{exc}})$ function consists of a number of linear parts. Under this assumption we calculated the function indicated by the long dashed lines in Figs. 3.3 and 3.4 by means of a least squares fitting procedure to the experimental curves (solid

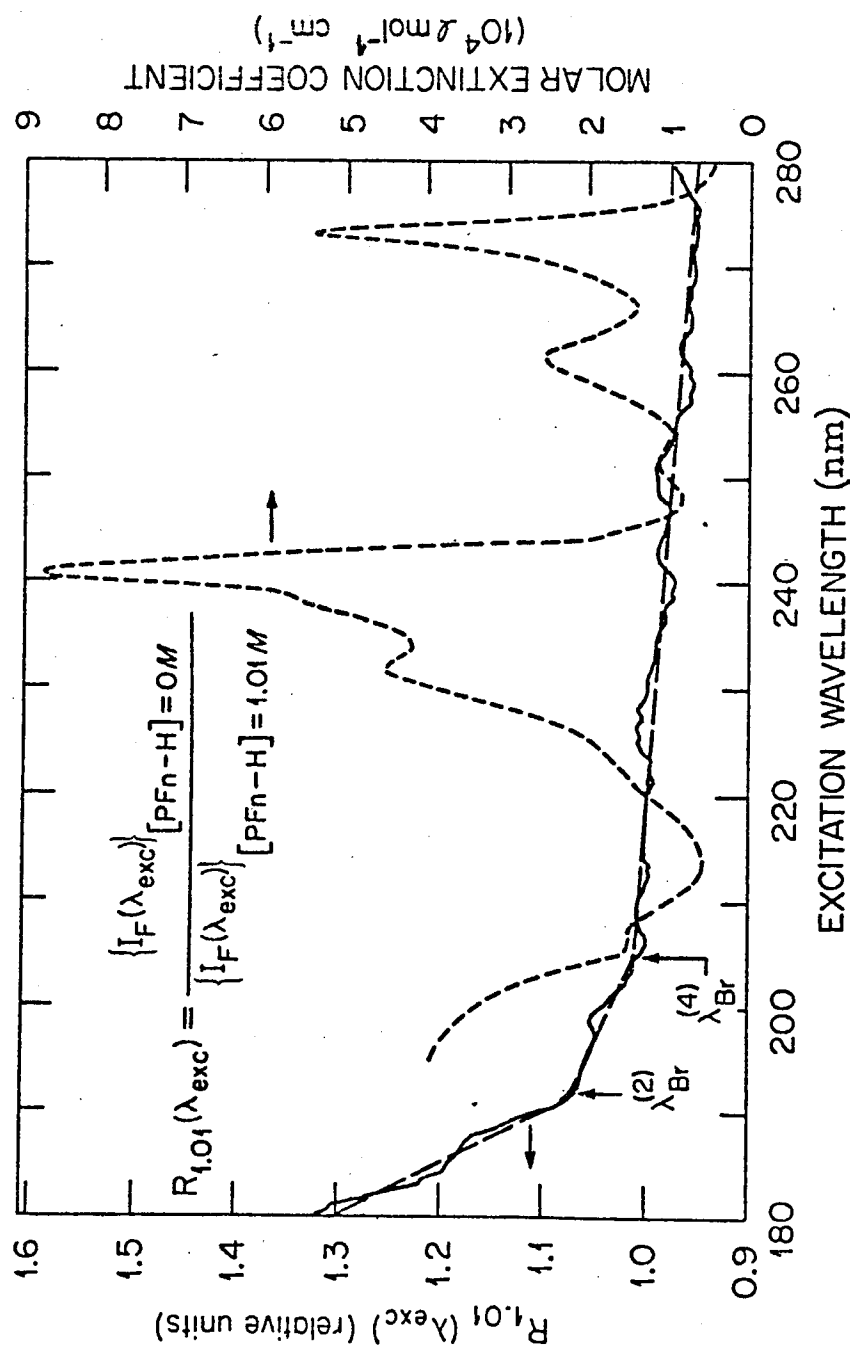


Fig. 3.3. The ratio of pyrene integrated fluorescence intensity ($10^{-2} \text{ mol } \ell^{-1}$ solution in n-pentane) in the absence of perfluoro-normal-hexane (the electron attaching compound) to that in the presence of $1.01 \text{ mol } \ell^{-1}$ of perfluoro-normal-hexane as a function of the excitation wavelength. The long dashed line (---) through the experimental data (solid line) was obtained by a least squares fitting procedure (see text). The pyrene absorption spectrum is represented by the (----) line. The symbol $M = \text{mol } \ell^{-1}$.

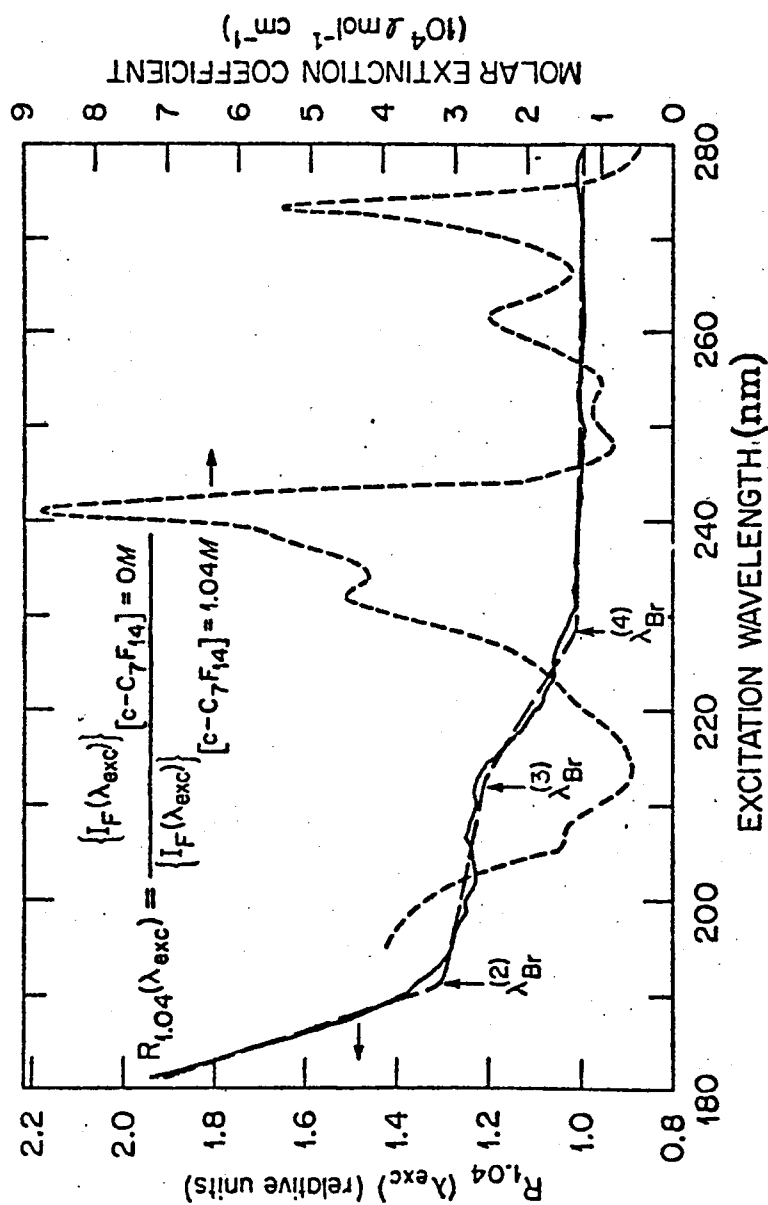


Fig. 3.4. The ratio of pyrene integrated fluorescence intensity ($10^{-2} \text{ mol l}^{-1}$ solution in n-pentane) in the absence of perfluoro-methyl-cyclo-hexane (the electron attaching compound) to that in the presence of 1.04 mol l^{-1} of perfluoro-methyl-cyclo-hexane as a function of the excitation wavelength. The long dashed lines (---) through the experimental data (solid line) are obtained by a least squares fitting procedure (see text). The pyrene absorption spectrum is represented by the (----) line. The symbol $M = \text{mol l}^{-1}$.

lines). This procedure which assumes linear fitting through segments of the $R[A](\lambda_{\text{exc}})$ function with the constraint that the function, but not its derivative, is continuous in going from one segment to the next, allows accurate location of the breaks, $\lambda_{\text{Br}}^{(n)}$ ($n = 2, 3, 4$) in the $R[A](\lambda_{\text{exc}})$ function. From such analyses the first ionization threshold I_L^1 , identified with $\lambda_{\text{Br}}^{(4)}$ in the Figs. 3.3 and 3.4 of pyrene in six hydrocarbon liquids and TMSi, using PFn-H and c-C₇F₁₄ as the A, were determined (Table 3.1).

In order to ensure that the decrease of the fluorescence intensity in the energy region above the ionization threshold, I_L^1 , is due to the role of A as an electron capturing agent--indicative of electron-ion pair formation--and not as a fluorescence quencher, we determined the ratios $R_c(\lambda_{\text{exc}} = 200)/R_c(\lambda_{\text{exc}} = 270)$ from data such as shown in Figs 3.3 and 3.4 for both electron attaching additives PFn-H and c-C₇F₁₄. These ratios were plotted in Fig. 3.5 as a function of the square root of the concentration, C, of A. The expected linear dependence of the ratio on the square root of the concentration of A (Piciulo and Thomas, 1978) is exhibited by both electron attaching additives. The intercepts and slopes of the linearly fitted curves through the experimental points, do not change if the ratios of the integrated fluorescence intensities are determined at other energies above and below I_L^1 , in the wavelength region from ~195 to 280 nm. The larger error bars and the smaller slope (by ~a factor of 2) for PFn-H compared to c-C₇F₁₄ are due to the fact that c-C₇F₁₄ is--as is expected from gaseous electron attachment data--a more efficient

Table 3.1. Values of the Photonionization Threshold for Pyrene in Dielectric Liquids

Liquid	$V_0(\text{eV})$	Dielectric Const.		Refractive Index at 20°C		Ionization Threshold ^a							
						$I_L^1(\text{eV})$		$\text{c-C}_7\text{F}_{14}$					
		°20°C		n_D^f	n_D^g 250nm	X	FFn-H	Y	X	Y	X	Y	
[CH ₃ - (CH ₂) ₄ - CH ₃] (n-Hexane)	0.00 ^b 0.04 ^b 0.10 ^b 0.16 ± 0.05 ^b	1.890 ^d	1.885 ^e	1.37506	1.433	5.97	0.12	5.99	0.03	5.43	0.11	5.43	0.03
[CH ₃ - (CH ₂) ₃ - CH ₃] (n-Pentane)	-0.01 ^b 0.01 ^b 0.04 ^b	1.843 ^d	1.844 ^e	1.3575		6.06 ± 0.04		6.04 ± 0.03		5.44 ± 0.05		5.46 ± 0.03	
[CH ₃ - (CH ₂) ₅ - CH ₃] (n-Heptane)		1.926 ^d	1.920 ^e	1.38777	1.45	5.80 ± 0.03		5.77 ± 0.03		5.46 ± 0.02		5.46 ± 0.03	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array}$ (Isopentane)										5.54 ± 0.05		5.50 ± 0.03	
$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \quad \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \end{array}$ (Cyclopentane)	-0.28 ^b -0.21 ^b -0.17 ^b	1.960 ^d	1.965 ^e	1.4065	1.484	5.80 ± 0.01		5.81 ± 0.03		5.51 ± 0.01		5.50 ± 0.03	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ (Neohexane)	-0.26 ^b -0.15 ± 0.03 ^c			1.3688		5.76 ± 0.21		5.92 ± 0.03		5.46 ± 0.04		5.50 ± 0.03	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{Si} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ (Tetramethylsilane)	-0.62 ^b -0.59 ^b -0.55 ^b			1.3585						5.51 ± 0.01		5.50 ± 0.03	

^aAll data on I_L^1 are for a pyrene concentration of 10^{-2} mol g^{-1}

X Mean values of I_L^1 for an A concentration range of 0.25-1.50 mol g^{-1}

Y values of I_L^1 for the highest concentration (1.50 mol g^{-1}) of A used.

^bR. A. Holroyd, R. L. Russell, J. Phys. Chem. **78**, 2128 (1974).

^cR. Schiller, Sz. Vass, and J. Mandics, Int. J. Radiat. Phys. Chem. **5**, 491 (1973).

^dS. O. Morgan and W. A. Yager, Ind. Engng. Chem. **32**, 1519 (1940).

^eG.W.C. Kaye, T. H. Laby, Tables of physical and chemical constants Longman, London, New York (1973).

^fHandbook of Chemistry and Physics (55 edition) CRC Press (1974-1975).

^gO.V. Sverdlova, Opt. Spectry. **6**, 223 (1959).

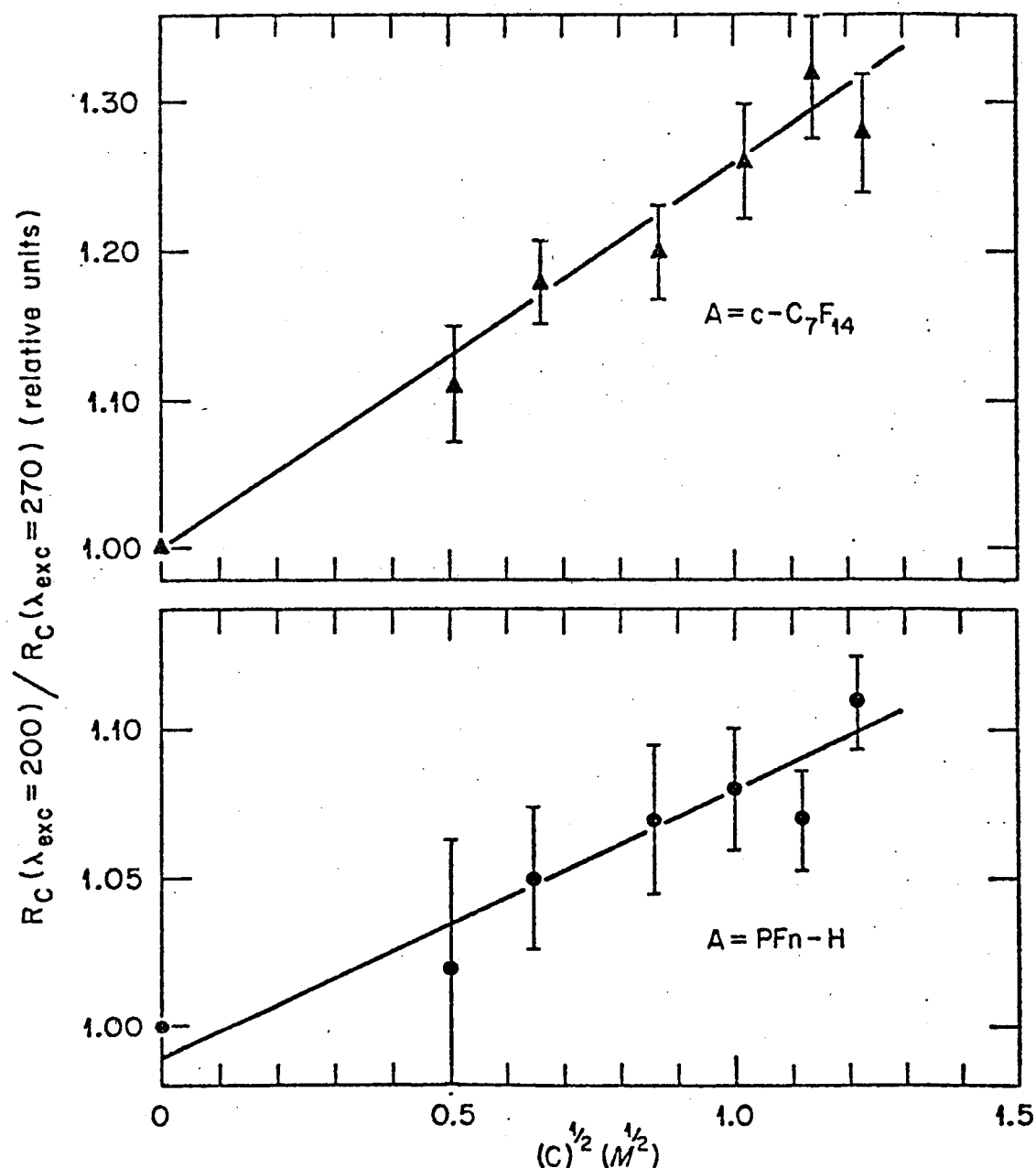


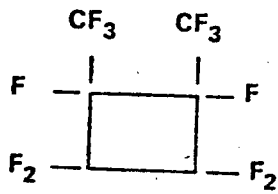
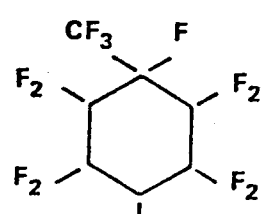
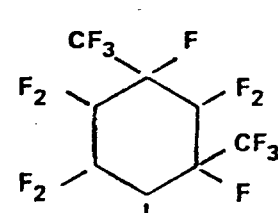
Fig. 3.5. The ratios of $R_C(\lambda_{exc} = 200)/R_C(\lambda_{exc} = 270)$ for different concentrations, C , of perfluoro-normal-hexane and perfluoro-methyl-cyclo-hexane vs the square root of the concentration, C , of A . The error bars give the mean standard deviation. The solid lines were obtained by a least squares fitting procedure through the experimental points. The symbol $M = \text{mol } \ell^{-1}$.

electron attaching molecule than PFn-H in these liquids (see discussion in Section 3.5).

In Table 3.1 (column 1) the hydrocarbon liquids used and TMSi are listed in order of increasing "sphericity". The more symmetrical the molecule, the more negative the corresponding ground state energy V_0 is, of the photoejected electron. In the same table columns 3 and 4 contain some useful physical constants for the hydrocarbon liquids. In columns 5 and 6 of Table 3.1 are listed the photoionization threshold values, I_L^1 , obtained for a 10^{-2} mol ℓ^{-1} solution of pyrene in seven different liquid media, using PFn-H (column 5) and c-C₇F₁₄ (column 6) as A. In each column two sets of values, X and Y, are given. Under X are listed the I_L^1 values corresponding to the mean value for six different concentrations of PFn-H and c-C₇F₁₄ in the range 0.25 and 1.50 mol ℓ^{-1} in 0.25 mol ℓ^{-1} steps. Under Y are listed the I_L^1 values for the highest concentration of A (~ 1.50 mol ℓ^{-1}). The errors given in X are the mean standard deviations, and the error listed in Y is the estimated error resulting from the uncertainties in the measurements of the excitation wavelength. The I_L^1 values for TMSi could not be measured in the case of PFn-H because of the absorption of TMSi at $\lambda < 210$ nm and the limited solubility of PFn-H in TMSi. The values of I_L^1 in liquid neohexane obtained using c-C₆F₁₂ and c-C₈F₁₆ agreed well with those obtained using c-C₇F₁₄ (see Table 3.2).

Finally in changing the solute (pyrene) concentration by one order of magnitude (from 10^{-2} to 10^{-3} mol ℓ^{-1}) no change in the values of the photoionization threshold was observed (Table 3.2).

Table 3.2. Values of I_L^1 for Pyrene in Neohexane Using Various Electron Attaching Additives

Electron Attaching Additive, A	Ionization Threshold ^a	
	I_L^1 (eV)	
	10^{-2} mol ℓ^{-1} Pyrene	10^{-3} mol ℓ^{-1} Pyrene
 (c - C ₆ F ₁₂)	5.45 ± 0.08	
 (c - C ₇ F ₁₄)	5.46 ± 0.04	5.49 ± 0.04
 (c - C ₈ F ₁₆)	5.39 ± 0.08	

^aMean values of I_L^1 for a concentration range of A of 0.25 - 1.50 mol ℓ^{-1} .

The I_L^1 data in Table 3.1 show four important findings: (i) The I_L^1 values of pyrene in the dielectric hydrocarbon liquids determined with this technique are higher than the I_L^1 of pyrene in n-P ($4.80 \pm 0.02\text{eV}$) determined with the TPI technique (Siomos and Christophorou, 1980). (ii) The I_L^1 values of pyrene in the dielectric hydrocarbon liquids used with PFn-H as the additive are higher than the I_L^1 values using c-C₇F₁₄ as A. (iii) For both electron attaching additives (PFn-H and c-C₇F₁₄) the I_L^1 values are independent of the nature and the "sphericity" of the molecules of the liquid medium in which the pyrene molecules are embedded, and (iv) the determined I_L^1 values are apparently independent of the concentration of A used ($>0.25 \text{ mol } \ell^{-1}$).

3.3 Photoionization of TMPD in n-Hexane

Figure 3.6 gives the integrated fluorescence intensity, corrected for the excitation light intensity, as a function of the excitation wavelength, λ_{exc} , for a dilute ($10^{-5} \text{ mol } \ell^{-1}$) and a concentrated ($10^{-2} \text{ mol } \ell^{-1}$) solution of TMPD in n-hexane. The two spectra were normalized at 280 nm. The $I_F(\lambda_{\text{exc}})$ excitation spectrum for the $10^{-2} \text{ mol } \ell^{-1}$ solution is independent of ϵ and no correction for the fraction of the absorbed photons is necessary. The $I_F(\lambda_{\text{exc}})$ for the $10^{-5} \text{ mol } \ell^{-1}$ solution in the range of 210-300 nm is practically a replica of the absorption spectrum and it must be corrected for the fraction of the absorbed photons as a function of λ_{exc} . The absorption spectrum of TMPD (see CHAPTER 5) in n-H is shown in Fig. 3.6 (dashed curve). The peak at $\sim 260 \text{ nm}$ corresponds to the second absorption band; a stronger absorption band exists at 200 nm. In Fig. 3.7

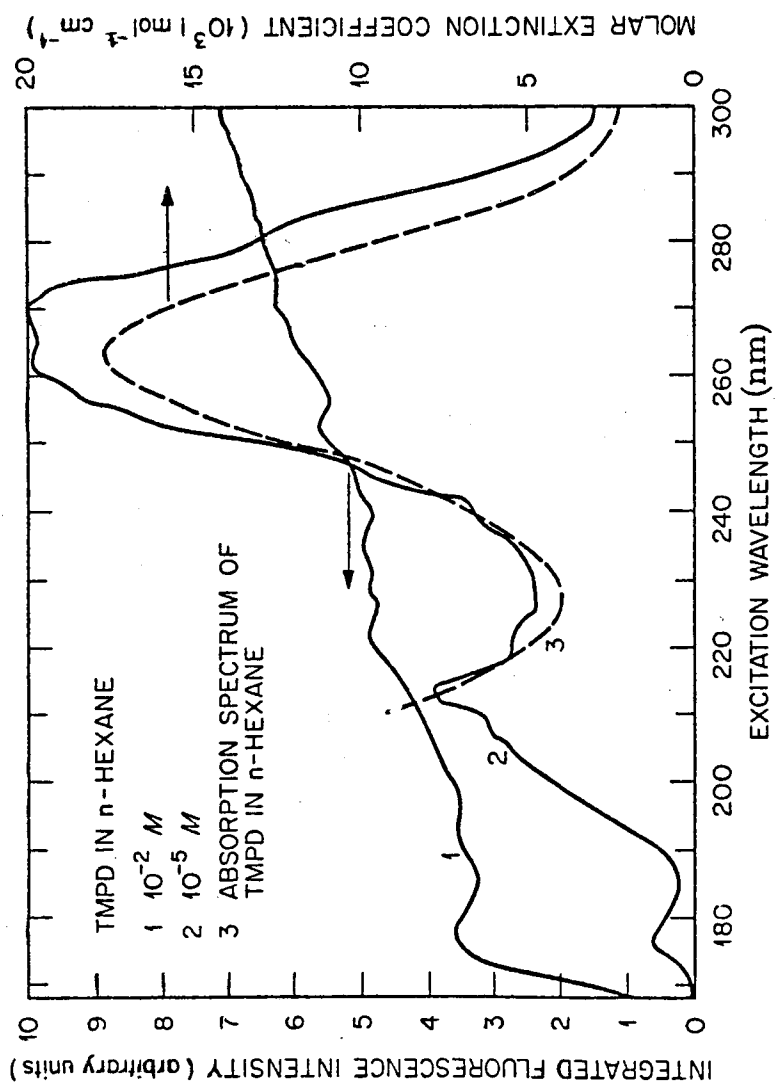


Fig. 3.6. Integrated fluorescence intensity (solid lines) for two concentrations of TMPD in liquid n-hexane at room temperature versus the excitation wavelength. The spectra were normalized at 280 nm. The dashed curve (3) is the absorption spectrum of TMPD in n-hexane. The symbol $M = \text{mol l}^{-1}$.

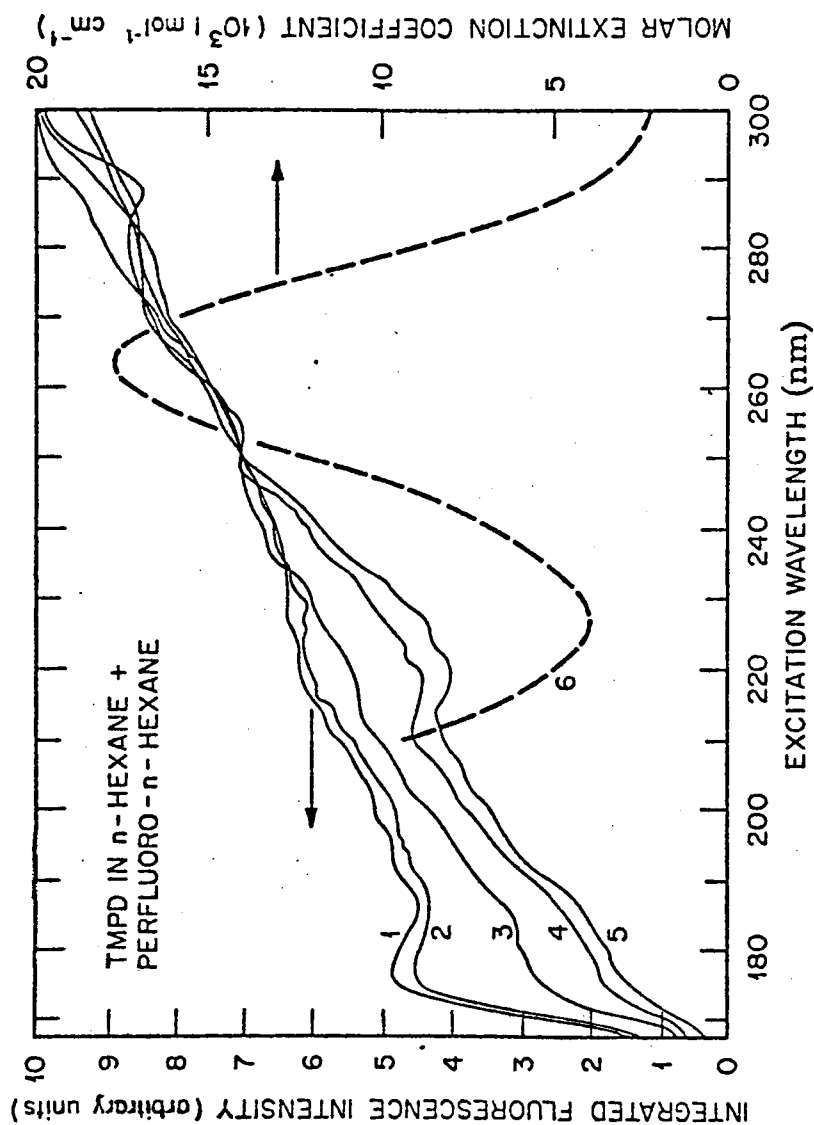


Fig. 3.7. Integrated fluorescence intensity (solid lines) for $10^{-2} \text{ mol l}^{-1}$ solution of TMPD in n-hexane (1) as a function of the excitation wavelength at 0.01 (2), 0.135 (3), 0.57 (4) and 1.25 mol l^{-1} (5), of perfluoro-normal-hexane. The spectra were normalized at 250 nm. The dashed curve (6) is the absorption spectrum of TMPD in n-hexane.

$I_F(\lambda_{exc})$ is shown for a 10^{-2} mol ℓ^{-1} solution of TMPD in n-H for 0, 0.01, 0.135, 0.57 and 1.25 mol ℓ^{-1} of PFn-H. All data were normalized at 250 nm although normalization at any wavelength between 250 and 300 nm would have been equally appropriate. It is seen that as the concentration of PFn-H increases, $I_F(\lambda_{exc})$ decreases, especially below ~ 235 nm. Above ~ 245 nm the $I_F(\lambda_{exc})$ shows little, if any, decrease with increasing concentration of PFn-H. Since the first absorption maximum of TMPD is at 320 nm and the second at 260 nm no noticeable decrease in $I_F(\lambda_{exc})$ is seen which coincides with these absorption maxima.

For the purpose of determining "the breaks" in the $I_F(\lambda_{exc})$ functions the ratio $R_{[A]}(\lambda_{exc})$ of the $I_F(\lambda_{exc})$ in the absence of A to that in the presence of A at concentration [A] was determined. Figure 3.8 shows a typical example for a 10^{-2} mol ℓ^{-1} solution of TMPD in n-H at a PFn-H concentration of 1.25 mol ℓ^{-1} . It is seen that although $R_{1.25}(\lambda_{exc})$ is practically flat down to ~ 250 nm, it increases at shorter wavelengths and shows evidence of structure. Using the same fitting procedure as in pyrene we were able to locate the discontinuity in $R_{1.25}(\lambda_{exc})$ at 246 ± 2.5 nm (5.03 ± 0.05 eV) as shown in Fig. 3.8. We identify this as the first ionization threshold, I_L^1 , of TMPD in n-H.

In order to ensure that this threshold determination is independent of the solute concentration we have treated the data of 10^{-3} mol ℓ^{-1} solution of TMPD in n-H with varying concentrations of PFn-H (Fig. 3.9) in a similar way to the 10^{-2} mol ℓ^{-1} solution data. The $I_F(\lambda_{exc})$ functions were normalized at 280 nm. They show no noticeable effect on the electron scavenger at $\lambda_{exc} > 270$ nm. They,

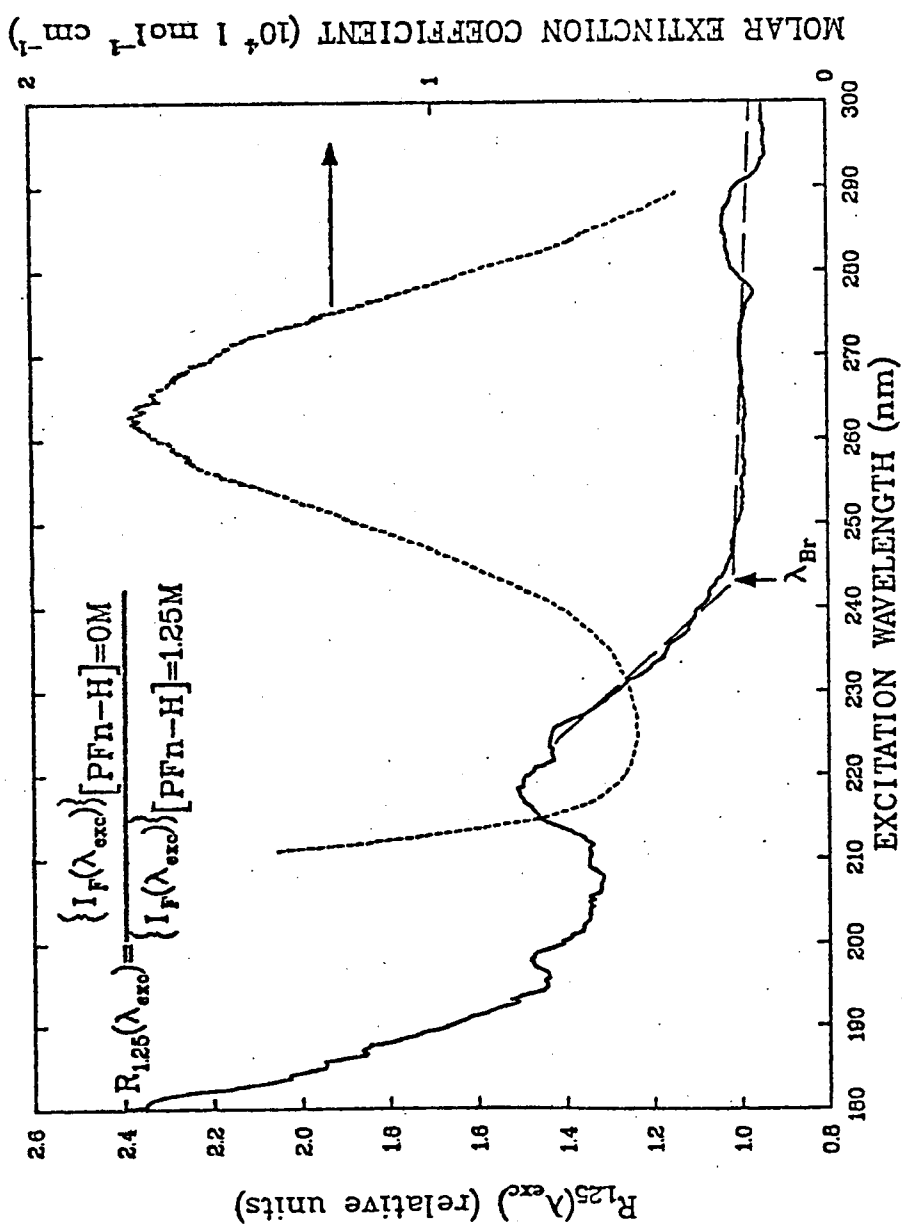


Fig. 3.8. The ratio of TMPD integrated fluorescence intensity ($10^{-2} \text{ mol l}^{-1}$ of TMPD in n-hexane) in the absence of perfluoro-normal-hexane to that in the presence of 1.25 mol l^{-1} of perfluoro-normal-hexane as a function of the excitation wavelength. The symbol $M = \text{mol l}^{-1}$.

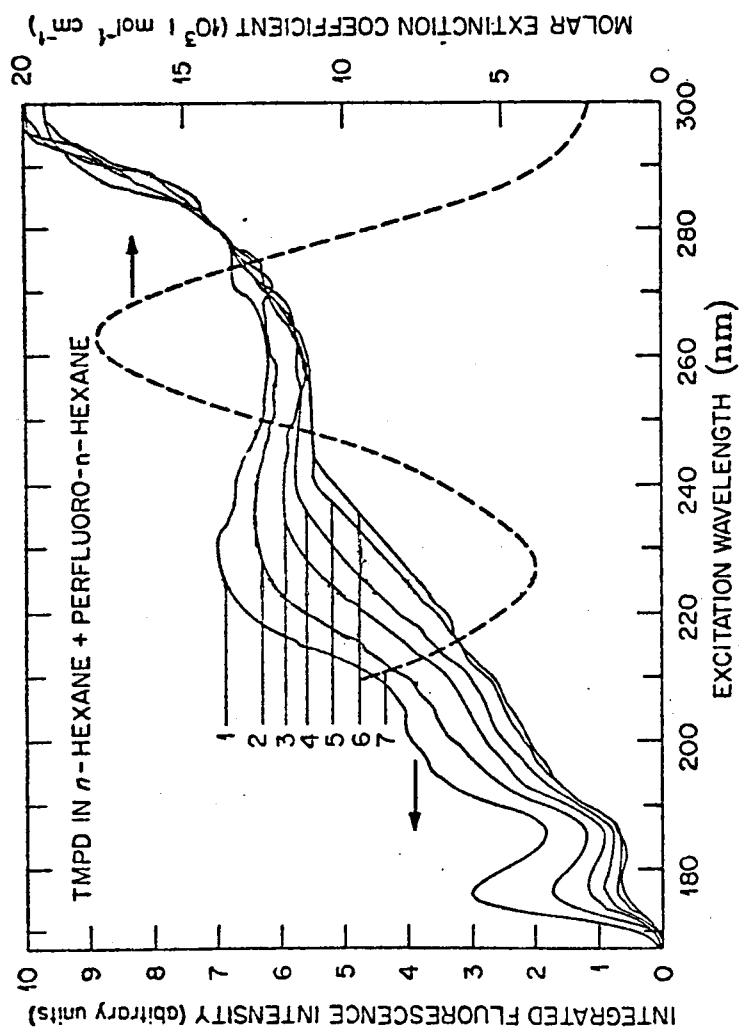


Fig. 3.9. Integrated fluorescence intensity (solid lines) as a function of the excitation wavelength for a 10^{-5} mol l^{-1} TMPD solution in n-hexane (1) and various concentrations of perfluoro-normal-hexane: 0.06 mol l^{-1} (2), 0.25 mol l^{-1} (3), 0.42 mol l^{-1} (4), 1.25 mol l^{-1} (5), and 1.45 mol l^{-1} (6). The spectra were normalized at 280 nm. The dashed curve (7) is the TMPD absorption spectrum in n-hexane.

however, exhibit a rather pronounced such effect below ~ 250 nm. The large decrease in $I_F(\lambda_{\text{exc}})$ around 235 nm is very interesting. The shift of the onset of this large quenching effect to longer values of λ_{exc} with increasing PFn-H concentration is taken to be indicative of the first ionization threshold. The data in Fig. 3.9 for the highest ($1.45 \text{ mol } \ell^{-1}$) concentration of PFn-H were plotted in Fig. 3.10 as $R_{1.45}(\lambda_{\text{exc}})$. The break at $248 \pm 1.5 \text{ nm}$ ($5.00 \pm 0.03 \text{ eV}$) is ascribed to the first ionization threshold, I_L^1 .

Although the data in Figs. 3.8 and 3.10 are difficult to analyze accurately below ~ 220 nm, there is rather strong evidence for the existence of a second break located around $190 \pm 5 \text{ nm}$ ($6.52 \pm 0.15 \text{ eV}$), which may be associated with the second ionization threshold, I_L^2 , of TMPD in n-H. This would imply an energy difference $I_L^2 - I_L^1 = 1.44 \pm 0.15 \text{ eV}$ which agrees well with the corresponding energy difference $I_G^2 - I_G^1 = 1.52 \text{ eV}$ between the second, I_G^2 , and the first, I_G^1 , ionization potentials on TMPD in the gas phase (Egdell and coworkers, 1975). The values of I_L^1 , I_L^2 and $I_L^2 - I_L^1$ determined from Figs. 3.8 and 3.10 are given in Table 3.3. The drop in fluorescence intensity in Figs. 3.6, 3.7 and 3.9 at $\lambda_{\text{exc}} > 175 \text{ nm}$ is due to solvent absorption.

This value of I_L^1 is higher than that determined with the photoconductivity technique (3.88 eV for TMPD in n-P; see CHAPTER 4), and somewhat higher than that (4.91 eV) of Kam-chu-Wu and Lipsky (1977) determined in a manner similar to the present one, but using CHCl_3 as

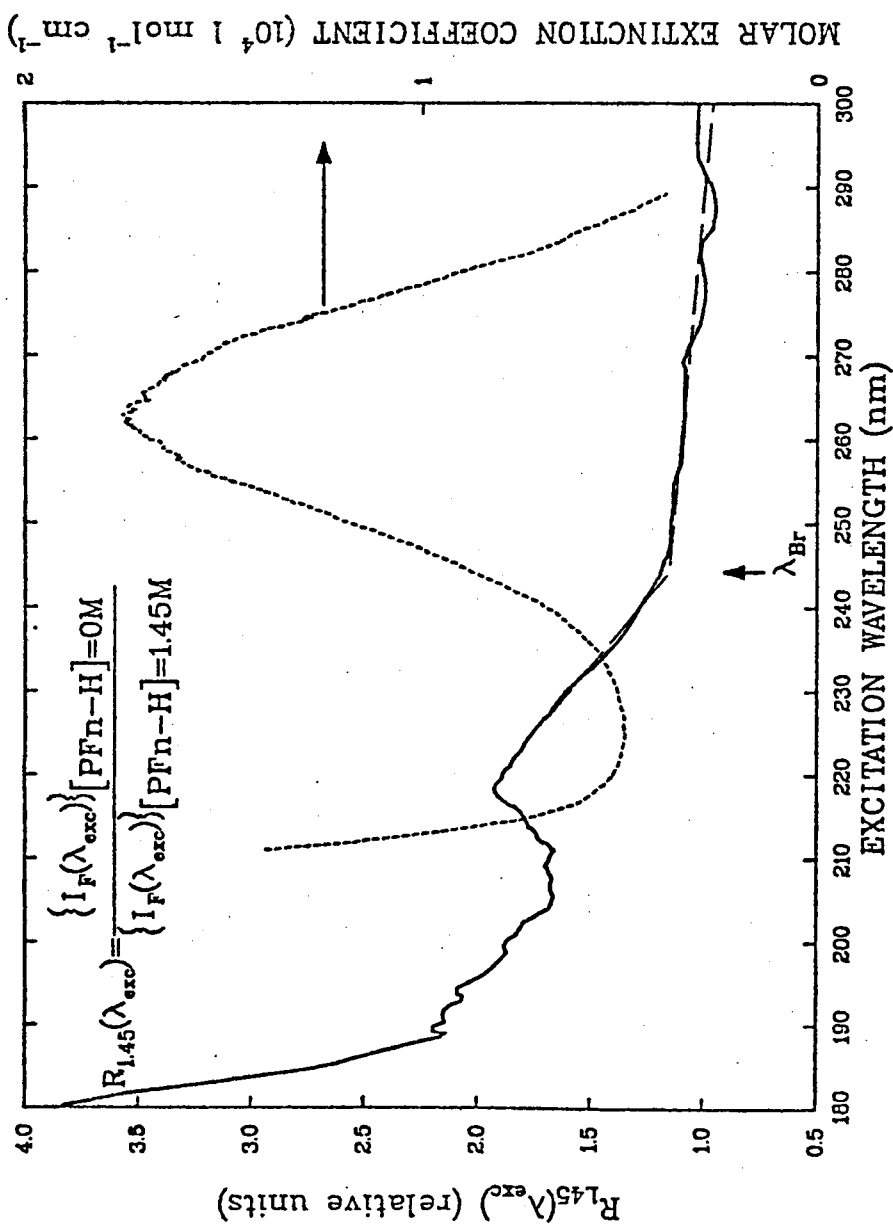


Fig. 3.10. Ratio of TMPD integrated fluorescence intensity (10^{-3} mol l^{-1} of TMPD in n-hexane) in the absence of perfluoro-normal-hexane to that in the presence of 1.45 mol l^{-1} of perfluoro-normal-hexane plotted versus the excitation wavelength. The symbol M = mol l^{-1} .

the electron attaching molecule. We measured $I_F(\lambda_{exc})$ for various concentrations of $CHCl_3$ up to 10^{-1} mol ℓ^{-1} in a number of TMPD solutions but were unable to establish accurately the breaks in $I_F(\lambda_{exc})$ or $R(\lambda_{exc})$ ascribed to I_L^1 or I_L^2 . The same authors reported that the value of I_L^1 is independent of the electron scavenger A. It is noted that the ratio of the values of I_F below (at ~ 260 nm) and above (~ 200 nm) I_L^1 from Fig 3.9 are large (larger than those reported by Kam-chu-Wu and Lipsky, 1977) and depend on the concentration of the electron attaching molecule. For 1.45 mol ℓ^{-1} PFn-H this ratio is ~ 2.60 and indicates substantial reduction in the geminate recombination of the electron-ion pair.

Table 3.3. Values of I_L^1 , I_L^2 and $I_L^2 - I_L^1$ for TMPD in n-Hexane^a

I_L^1 (eV)	I_L^2 (eV)	$I_L^2 - I_L^1$ (eV)	
5.03 ± 0.05			Fig. 3.8
5.00 ± 0.03	5.52 ± 0.15	1.44 ± 0.15	Fig. 3.10
<5.02>			Mean value

^aRoom Temperature Results.

3.4 Photoionization of Fluoranthene in Dielectric Liquids

The photoionization threshold of fluoranthene was determined for five hydrocarbon liquids (n-P, n-H, n-Hp, neo-H, i-P) using three electron attaching compounds (PFn-H, c-C₇F₁₄, c-C₆F₁₂). Figure 3.11

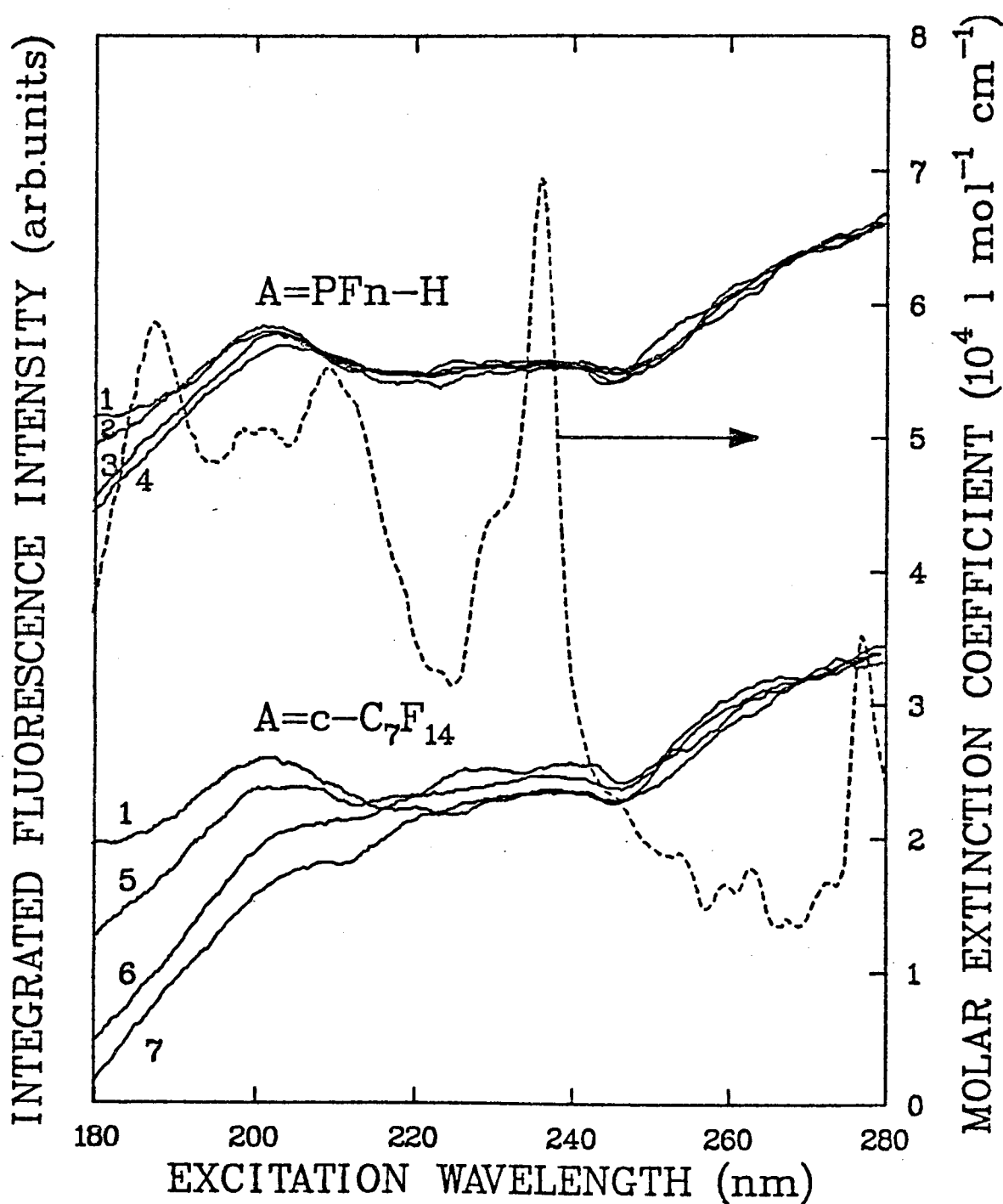


Fig. 3.11. Integrated fluorescence intensity vs excitation wavelength for a $10^{-2} \text{ mol l}^{-1}$ solution of fluoranthene in n-pentane at room temperature [A] (PFn-H): 0.0 mol l^{-1} (curve 1), 0.25 mol l^{-1} (curve 2), 1.01 mol l^{-1} (curve 3), 1.48 mol l^{-1} (curve 4), and [A] (c-C₇F₁₄): 0.26 mol l^{-1} (curve 5), 1.04 mol l^{-1} (curve 6), and 1.51 mol l^{-1} (curve 7). The spectra were normalized at 270 nm. The dashed curve represents the absorption spectrum of fluoranthene in n-pentane.

shows typical integrated fluorescence intensity spectra of fluoranthene in n-P. The integrated fluorescence intensity, $I_F(\lambda_{exc})$, is plotted vs. the excitation wavelength for a 10^{-2} mol ℓ^{-1} solution of fluoranthene in the absence of the electron attaching additive (curve 1), in the presence of PFn-H (curves 2-4) and in the presence of c-C₇F₁₄ (curves 5-7). All spectra were normalized at 270 nm. Any other normalization point in the wavelength region ~230-280 nm would have been equally appropriate. The absorption spectrum of fluoranthene in n-P (see CHAPTER 5) is shown also in the same picture (dashed curve). The $I_F(\lambda_{exc})$ for 10^{-2} mol ℓ^{-1} fluoranthene solution is independent of the molar extinction coefficient variations and no correction for the fraction of the absorbed photons as a function of λ_{exc} is necessary. For the PFn-H-containing solutions, $I_F(\lambda_{exc})$ decreases considerably for $\lambda_{exc} < 205$ nm while for the c-C₇F₁₄-containing solutions this decrease starts around 220 nm. Similar results were obtained for the solvents n-H, n-Hp, neo-H, i-P using PFn-H, c-C₇F₁₄ and c-C₆F₁₂ as electron attaching additives.

The ratio $R[A](\lambda_{exc})$ of the $I_F(\lambda_{exc})$ in the absence of A to that in the presence of A has been determined. Figures 3.12 and 3.13 show (solid lines) two typical examples for a 10^{-2} mol ℓ^{-1} solution of fluoranthene in n-P at a PFn-H-concentration of 1.01 mol ℓ^{-1} (Fig. 3.12) and at a c-C₇F₁₄ concentration of 1.51 mol ℓ^{-1} (Fig. 3.13). The data were analyzed as it was described in the case of pyrene (section 3.2). From such analyses the first ionization threshold I_L^1 , identified with $\lambda_{Br}^{(4)}$ in Figs. 3.12 and 3.13, in the five hydrocarbon liquids were determined and are listed in Table 3.4.

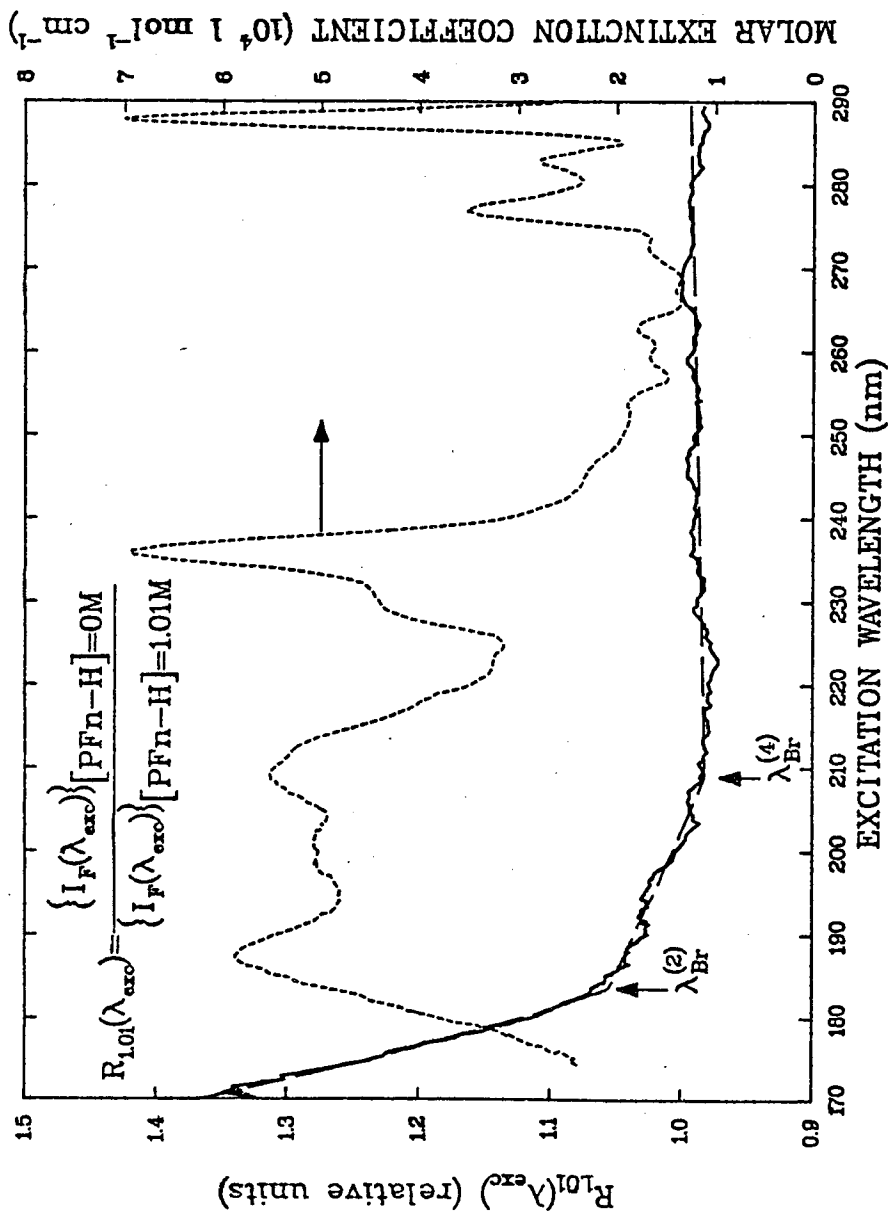


Fig. 3.12. The ratio of fluoranthene integrated fluorescence intensity ($10^{-2} \text{ mol l}^{-1}$ solution in n-pentane) in the absence of PFn-H (the electron attaching compound) to that in the presence of 1.01 mol l^{-1} of PFn-H as a function of the excitation wavelength. The long dashed lines (---) through the experimental data (solid line) are obtained by a least squares fitting procedure (see text). The fluoranthene absorption spectrum in n-pentane is shown by the dashed line (---). The symbol M = mol l^{-1} .

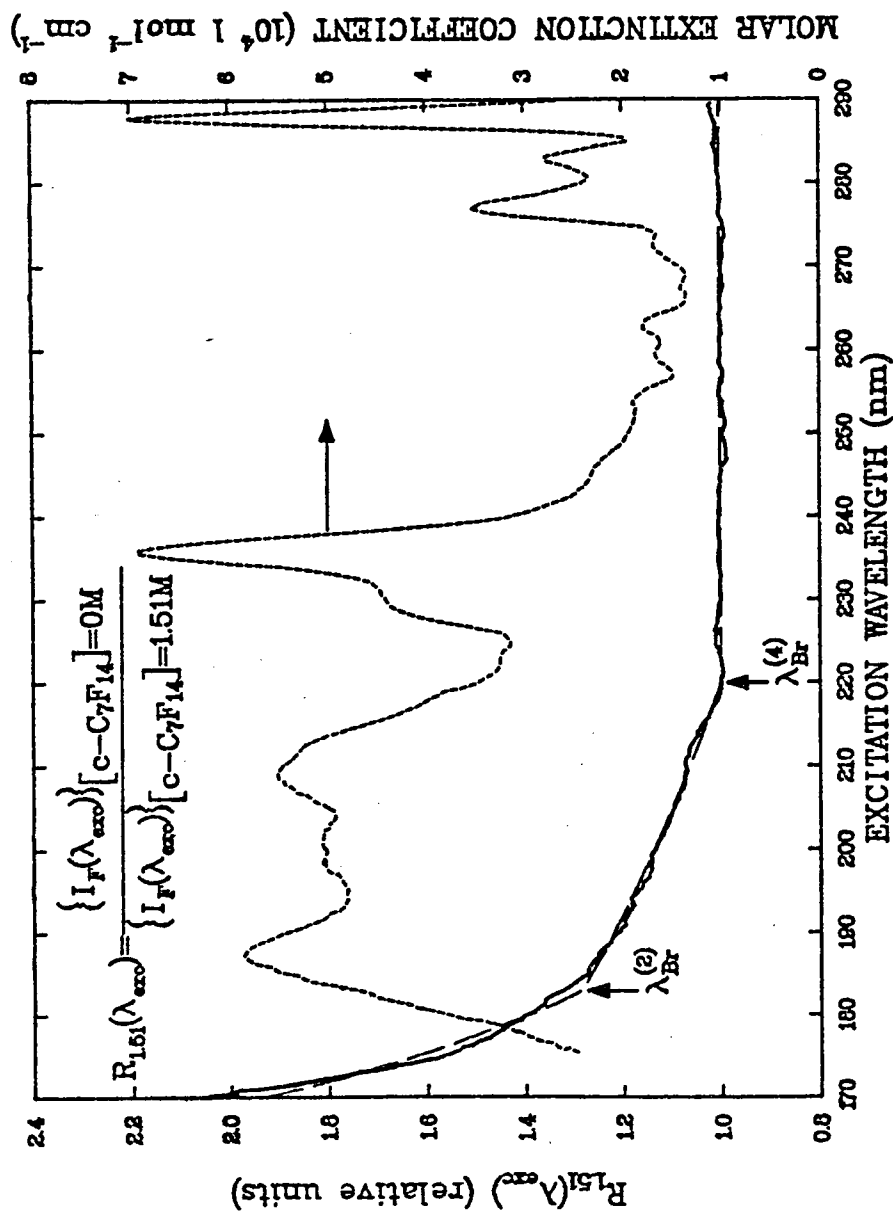


Fig. 3.13. The ratio of fluoranthene integrated fluorescence intensity (10^{-2} mol ℓ^{-1} solution in n-pentane) in the absence of c-C₇F₁₄ (the electron attaching compound) to that in the presence of 1.51 mol ℓ^{-1} of c-C₇F₁₄ as a function of the excitation wavelength. The long dashed lines (---) through the experimental data (solid line) are obtained by a least squares fitting procedure (see text). The fluoranthene absorption spectrum in n-pentane is shown by the dashed line (- - -). The symbol M = mol ℓ^{-1} .

TABLE 3.4. Values of the Photoionization Threshold I_L^1 for Fluoranthene in Dielectric Liquids

Liquid	Ionization Threshold ^a I_L^1 (eV)					
	PFn-H		c-C ₇ F ₁₄		c-C ₆ F ₁₂	
	X	Y	X	Y	X	Y
n-Pentane	5.93±0.10	5.90±0.03	5.66±0.03	5.64±0.03	5.64±0.04	5.64±0.03
n-Hexane			5.56±0.03	5.58±0.03	5.56±0.04	5.56±0.03
n-Heptane			5.49±0.06	5.57±0.03	5.57±0.09	5.56±0.03
Neohexane	6.01±0.09	5.94±0.03	5.59±0.04	5.53±0.03		
Isopentane			5.50±0.10	5.53±0.03		

^aAll data on I_L^1 are for fluoranthene concentration of 10^{-2} mol ℓ^{-1}

X Mean values of I_L^1 for an A concentration range of 0.25 - 1.50 mol ℓ^{-1}

Y values of I_L^1 for the highest concentration (1.50 mol ℓ^{-1}) of A used.

The I_L^1 data (Table 3.4) exhibit the same features as in the case of pyrene. (i) The I_L^1 values of fluoranthene in the dielectric liquids determined with this technique are higher than the I_L^1 of fluoranthene in n-P (4.50 ± 0.05 eV) determined with the TPI technique (see CHAPTER 4). (ii) The I_L^1 values of fluoranthene in the dielectric hydrocarbon liquids determined with PFn-H as the additive are higher by $\sim 0.35 \pm 0.13$ eV than the I_L^1 values using c-C₇F₁₄ or c-C₆F₁₂ as As. This difference [I_L^1 (PFn-H) - I_L^1 (c-C₇F₁₄)] is in agreement with the corresponding difference in the case of pyrene (~ 0.4 eV). (iii) For All electron attaching additives the I_L^1 values are independent of the nature of the liquid medium in which the fluoranthene is embedded, and (iv) The determined I_L^1 values are apparently independent of the concentration of A for concentrations ≥ 0.25 mol l⁻¹.

Finally we note a difference in the shape of the $R_{[A]}(\lambda_{exc})$ curve obtained from c-C₇F₁₄ (Fig. 3.13) with that corresponding to pyrene for the same electron attaching additive (Fig. 3.4). The break at (3) λ_{Br} appearing in $R_{[A]}(\lambda_{exc})$ for pyrene using the electron attaching molecules c-C₇F₁₄ (Fig. 3.4), c-C₆F₁₂ and c-C₈F₁₆ does not appear in the $R_{[A]}(\lambda_{exc})$ of fluoranthene using c-C₇F₁₄ (Fig. 3.13) and c-C₆F₁₂.

3.5 Rationale of the Experimental Results

In Table 3.5 a summary of the present results is presented along with the ionization potentials of the studied molecules in the gas-phase (column 2) and their thresholds in n-P solutions obtained from the photoconductivity technique (column 3). We have seen in

Table 3.5. Photoionization Thresholds I_G^1 and I_L^1 of Pyrene, TMPD and Fluoranthene in the Gas Phase and in Dielectric Liquids

MOLECULE	1 I _G eV	1 ^a I _L eV	1 ^b I _L eV					ELECTRON ATTACHING MOLECULE		
			n-P	n-H	n-Hp	i-P	c-P		neo-H	TMSi
PYRENE	7.41 ^c	4.80±0.02	6.06±0.04	5.97±0.12	5.80±0.03		5.80±0.01	5.76±0.21	PFn-H	
			5.44±0.05	5.43±0.11	5.46±0.02	5.54±0.05	5.51±0.01	5.46±0.04	5.51±0.01	c-C ₇ F ₁₄
								5.45±0.08		c-C ₆ F ₁₂
								5.39±0.08		c-C ₈ F ₁₆
TMPD	6.20±0.02 ^d	3.88±0.05		5.02±0.05					PFn-H	
FLUORANTHENE	7.72 ^e	4.50±0.05	5.93±0.10					6.01±0.09	PFn-H	
			5.66±0.03	5.56±0.03	5.49±0.10	5.50±0.10		5.59±0.04		c-C ₇ F ₁₄
			5.64±0.04	5.56±0.04	5.57±0.09					c-C ₆ F ₁₂

^aValues obtained from the laser two-photon ionization technique in n-P solution (see CHAPTER 4)^bAll values are mean values obtained from solutions 10⁻² mol l⁻¹ and for concentration of the electron attaching additive in the range 0.25 - 1.50 mol l⁻¹^cG. Clar and W. Schmidt, Tetrahedron, **35**, 1027 (1979)^dY. Nakato, M. Ozaki, A. Egawa and H. Tsobomura, Chem. Phys. Letts **9**, 615 (1971)^eW. F. Frey, R. N. Compton, W. T. Naff and H. C. Schweinler, Intern. J. Mass. Spectrom. Ion Phys. **12**, 19 (1973)

CHAPTER 1 that the first ionization threshold, I_L^1 , of a molecule M in a liquid medium is related to its gaseous value by (Raz and Jortner, 1969)

$$I_L^1 = I_G^1 + P^+ + V_0 \quad (3.7)$$

where I_G^1 is the first ionization potential of M in the gas phase, P^+ is the polarization energy of the liquid medium due to M^+ and V_0 is the ground state energy of the electron in the medium. Equation (3.7) assumes that both M^+ and e^- are solvated. Assuming that P^+ can be calculated from the Born equation (Born, 1920)

$$P^+ = - \frac{(ze)^2}{2r_i} \left(1 - \frac{1}{\epsilon}\right) \quad (3.8)$$

with r_i and ϵ the ionic radius and the dielectric constant of the liquid medium respectively, and that the value of P^+ does not vary among the liquid hydrocarbons used in the present study, the values of I_L^1 of a solute M in various liquids should correlate with the variations of V_0 in a straightforward manner. As can be seen from the data in Table 3.1 the V_0 values vary from ~ 0.00 eV for n-hexane to ~ -0.60 eV for TMSi.

This expected (Eq. 3.7) dependence of I_L^1 on V_0 seems not to be exhibited by the results of the present study obtained from photoluminescence measurements and the effect of electron attaching additives on the integrated fluorescence intensity as a function of λ_{exc} . As can be seen from Table 3.5, the I_L^1 values of pyrene and fluoranthene in the solvents used with PFn-II as the A are higher ($\sim 0.40 \pm 0.12$ eV) than the I_L^1 values using the cyclic perfluorocarbons A (c-C₇F₁₄, c-C₆F₁₂, c-C₈F₁₆). For all A's the values I_L^1 of pyrene and

fluoranthene are independent of the nature and "sphericity" of the molecules of the dielectric liquid in which they are embedded and the I_L^1 values are independent of the concentration of A used ($> 0.25 \text{ mol l}^{-1}$).

In our effort to rationalize these experimental findings, we considered the electron capturing characteristics of the A's used in the present study and also the time evolution of the photoionization and the electron attachment processes. The electron attachment rates $k_{\text{cap}}(\langle \epsilon \rangle)$ for PFn-H (Ghemati and coworkers, 1979) and c-C₇F₁₄, c-C₈F₁₆ and c-C₆F₁₂ (Christodoulides and Christophorou, 1979; Pai and coworkers, 1979) as a function of the mean electron energy $\langle \epsilon \rangle$ in the gaseous phase are shown in Fig. 3.14. The magnitude of the electron attachment rates of all the cyclic perfluorocarbons we used attain their largest values between 0.05 and 0.2 eV and decrease with increasing $\langle \epsilon \rangle$. However, the PFn-H additive shows a rather different behavior; its electron attachment rate maximizes at a higher $\langle \epsilon \rangle$, namely at $\sim 1 \text{ eV}$, and its magnitude at the peak is ~ 48 times smaller than that of the cyclic compounds.

Consequently the cyclic perfluorocarbons attach electrons having thermal energies much more efficiently than PFn-H does; the latter compound will attach more efficiently electrons with higher energies ("hot" electrons (e^-)*). This statement of course implies that although in going from the gaseous to the liquid phase the attachment rate vs $\langle \epsilon \rangle$ functions in Fig. 3.14 shift to lower energies, this shift, on the basis of the discussion by Christophorou (1976) for the case of PFn-H is expected to be less than 1 eV and the peak in the

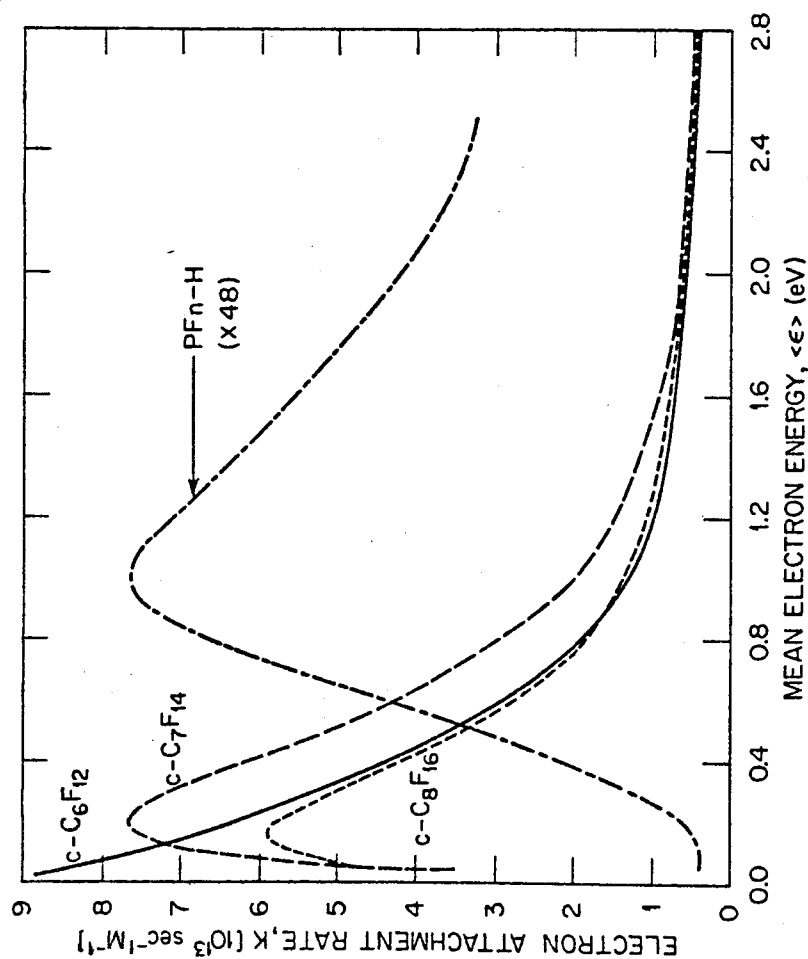


Fig. 3.14. Electron attachment rates k vs $\langle \epsilon \rangle$ for PFn-H (Chemati and coworkers, 1979), $\text{c-C}_7\text{F}_{14}$ (Christodoulides and Christophorou, 1979), $\text{c-C}_6\text{F}_{12}$ and $\text{c-C}_8\text{F}_{16}$ (Pai and coworkers, 1979). Note that the data for the PFn-H were multiplied by a factor of 48 for convenience of display. The symbol $\text{M} = \text{mol l}^{-1}$.

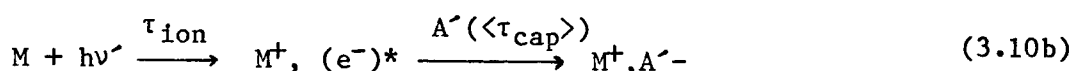
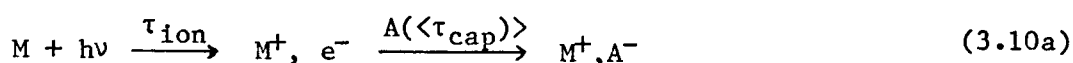
$k_{\text{cap}}(\langle \epsilon \rangle)$ function is still above thermal energy. Knowing the electron attachment rates from the gaseous phase - the attachment rates are taken from the data in Fig. 3.14 and correspond to the peak values in the $k_{\text{cap}}(\langle \epsilon \rangle)$ functions - and the concentration of A in the solutions studied, we estimated the mean time $\langle \tau_{\text{cap}} \rangle$ required for an electron to be captured by A at a given concentration of A through

$$\langle \tau_{\text{cap}} \rangle = \frac{1}{\langle k_{\text{cap}} \rangle \cdot [A]} \quad (3.9)$$

For $[A] = 1.50 \text{ mol l}^{-1}$ and $\langle k_{\text{cap}} \rangle = 7.7 \times 10^{13} \text{ s}^{-1} \text{ mol}^{-1}$ (Fig. 3.14) which is typical for the cyclic A's $\langle \tau_{\text{cap}} \rangle$ is $\sim 10^{-14} \text{ s}$. This time is longer than the time required for the photoionization process, $\tau_{\text{ion}} \sim 10^{-16} \text{ s}$, but is shorter than the solvation time, $\langle \tau_{\text{solv}} \rangle$, of the photoejected electron, e^- , i.e. the time required for the photoelectron to reach its final solvated state, e_{solv} .

Solvation times for dielectric hydrocarbon liquids have been found experimentally to be $\sim 10^{-12} \text{ s}$ (Kenney-Wallace, 1981). The difference of about two orders of magnitude between $\langle \tau_{\text{cap}} \rangle$ and $\langle \tau_{\text{solv}} \rangle$ leads us to conclude that the photoejected electron, e^- , in our experiments with high concentration of an efficient A is captured by A before it had the time to reach its solvated state which is associated with the V_0 value of the particular liquid. Although the A concentrations are high and the medium (solvent + A) properties would be probably different from those of the pure solvent ($[A] = 0$), still we assume that the properties of the medium are characteristic of those of the dielectric liquid. This seems to be supported by the fact that $\frac{1}{I_L}$ is independent of the concentration of A.

In the light of the preceding discussion we propose an interaction mechanism shown by reactions (3.10 a, b) and represented schematically in Fig 3.15 which accounts for the photoionization behaviour of a molecule M in a liquid medium in the presence of an efficient A at high concentration viz.



where $h\nu' > h\nu > I_L^1(M)$. According to reactions (3.10a, b) the e^- , M^+ pair is formed at times characteristic of the photoionization process and the e^- can then be removed via attachment to an A, when it escapes the geminate recombination with thermal energy or via attachment to an A' when the e^- escapes the geminate recombination as a hot electron, $(e^-)^*$, i.e. an electron with kinetic energy in excess of thermal. Thus the first gives a lower I_L^1 value than the latter. In the latter case the I_L^1 value should be dependent on the position of the maximum of the $k_{cap}(\langle\epsilon\rangle)$ function of A' i.e., the photoionization threshold is moved to an apparent higher value depending on the position of the maximum of the attachment cross section of the electron attaching additive. That the electron can be captured by A' as a "hot" electron before it is thermalized by the medium can be shown by the following. The mean scattering cross sections for thermal and near thermal energy electrons for the alkanes have been measured both in the gaseous (Christophorou and coworkers, 1976) and in the liquid phase (Sowada and coworkers, 1977). These studies have shown that the scattering cross sections for liquid alkanes are very

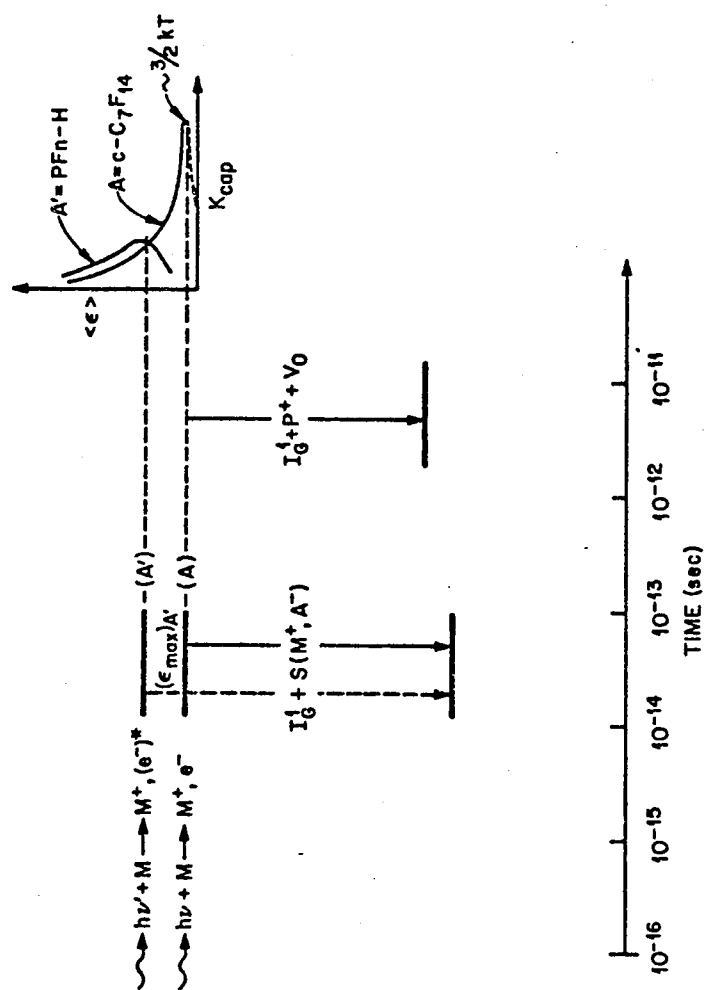


Fig. 3.15. A schematic illustration of the photionization and electron attachment processes in the present solutions with efficient electron attaching additives possessing different capture cross section functions (see text for discussion).

close (slightly larger) to the corresponding gaseous values. On the basis of this knowledge then we estimated a mean time between collisions for electrons of 0.5 eV energy in the liquid of $\sim 10^{-14}$ s. Since moreover it has been shown (Christophorou and coworkers, 1975) that for alkanes the mean fractional energy loss per collision is <0.5 , the time required for thermalization of the "hot" electron is $>10^{-14}$ s. In both processes 3.10a and 3.10b the e^- is captured in a state different from its solvated state. This implies that the expected I_L^1 dependence on V_0 should not be observed in the presence of an efficient electron attaching additive at high concentration. Only when $\langle \tau_{cap} \rangle > \langle \tau_{solv} \rangle$ should I_L^1 , determined by the present technique, be related to photoconductivity values of I_L^1 .

With the above in mind, equation (3.7) is now written

$$I_L^1 = I_G^1 + S(M^+, A^-) \quad (3.11)$$

In equation (3.11) I_L^1 and I_G^1 have the same meaning as in equation (3.7) and $S(M^+, A^-)$ now represents the solvation energy of the created positive-negative ion pair M^+, A^- . In this rationale the difference ΔI_L^1 in the first ionization threshold of the pyrene and fluoranthene molecules in n-P as determined in the photoconductivity technique and in the integrated fluorescence technique with highly efficient electron attaching additives can be expressed as

$$\Delta I_L^1 = S(M^+, A^-) - (P^+ + V_0) \quad (3.12)$$

and since V_0 for n-P at room temperature is ~ 0.00 eV (see Table 3.1), knowing P^+ an estimate of $S(M^+, A^-)$ can be made. Alternatively Eq. (3.11) could be used to calculate the difference $I_L^1 - I_G^1$ once an

estimation of $S(M^+, A^-)$ is made. This quantity can be written as a sum of three terms (Klopman, 1967)

$$S(M^+, A^-) = P^+ + P^- + \frac{e^2\Gamma}{\epsilon} \quad (3.13)$$

where P^+ , P^- are the polarization energies of the medium due to the positive and negative ion respectively, ϵ is the dielectric constant of the medium and Γ is the intermolecular coulomb interaction. For our purpose P^+ and P^- can be calculated from the Born formula [Eq. (3.8)]; then (3.13) becomes:

$$S(M^+, A^-) = -\frac{e^2}{2r_+} \left(1 - \frac{1}{\epsilon}\right) - \frac{e^2}{2r_-} \left(1 - \frac{1}{\epsilon}\right) - \frac{e^2\Gamma}{\epsilon} \quad (3.14)$$

For the case of pyrene in n-P with c-C₇F₁₄ as electron attaching molecule, taking $r_+ \sim 4\text{\AA}$, $r_- \sim 3\text{\AA}$ (Tables of interatomic distances, 1958), $\epsilon = 1.845$ (Table 3.1) and ignoring the mutual interaction term which is small compared to the polarization energies, the value of $S(M^+, A^-)$ is:

$$S(M^+, A^-) \sim (-0.82 - 1.10) \text{ eV} = -1.92 \text{ eV}$$

Equation (3.11) gives $I_L^1 - I_G^1 = S(M^+, A^-) \sim -1.92 \text{ eV}$. From Table 3.5 the experimental value of $I_L^1 - I_G^1$ for pyrene in n-P with electron attaching molecule c-C₇F₁₄ is -1.97 eV in very good agreement with the above estimated value from Eq. (3.11).

Turning now to electron attaching additives with small electron attachment rate constants for thermal and near thermal energies and $k_{\text{cap}}(\langle\epsilon\rangle)$ functions peaking at energies higher than thermal we note that in such cases it might be possible to determine a value of I_L^1 which would agree with the photoconductivity result and be

consistent with equation (3.7) when $\langle \tau_{\text{cap}} \rangle > \langle \tau_{\text{solv}} \rangle$. This, however, is rather difficult in view of the small effect on the $I_F(\lambda_{\text{exc}})$ functions of an inefficient A. Furthermore, we may invoke the difference in the energy, ϵ_{max} , where the maximum of the attachment rate occurs, to explain (Fig. 3.14) the difference between the I_L^1 values observed for PFn-H and c-C₇F₁₄, although the data in Fig. 3.14 will be different in the liquid phase. There will be a shift of the $k_{\text{cap}}(\langle \epsilon \rangle)$ function to lower energies; this shift may be <1 eV. Actually, if this interpretation is correct, the $\Delta I_L^1 = I_L^1(\text{c-C}_7\text{F}_{14}) - I_L^1(\text{PFn-H}) \approx 0.40$ eV for both pyrene and fluoranthene may indicate the value of $\langle \epsilon \rangle_{\text{max}}$ of the mean electron energy at which the $k_{\text{cap}}(\langle \epsilon \rangle)$ for PFn-H peaks in these liquids.

In Table 3.6 we list the energies (in eV) which correspond to the breaks ($\text{Br}^{(n)}$ ($n = 2, 3, 4$)), identified in Figs. 3.2, 3.3, 3.11 and 3.12 with $\lambda_{\text{Br}}^{(n)}$ ($n = 2, 3, 4$) for the different dielectric liquids studied and for the A's PFn-H and c-C₇F₁₄. The values of $\text{Br}^{(4)}$ we identified, as discussed earlier, with I_L^1 . The values of $\text{Br}^{(2)}$ are independent of A. From optical absorption measurements we performed on the solvent-A systems under consideration, it has been found that $\text{Br}^{(2)}$ is due to the sharp onset of the absorption of the solvent-A medium and not due to any higher ionization onset of M. The differences $\Delta \text{Br}^{(2,4)}$ are independent of the liquid solvent but differ from the two electron attaching additives PFn-H and c-C₇F₁₄. As has been discussed earlier, the difference in $\Delta \text{Br}^{(2,4)}$ is attributed to the difference in the position of the maximum values in the $k_{\text{cap}}(\langle \epsilon \rangle)$ functions of the A's. As can be seen, all cyclic A's whose $\langle \epsilon \rangle_{\text{max}}$ is

Table 3.6. Values of $\text{Br}(n)$ ($n=2, 3, 4$) in the $I_P(\lambda_{\text{exc}})$ Functions and $\Delta\text{Br}(2,4)$

Molecule	Liquid medium	A = PFn-H			A = c-C ₇ F ₁₄			
		Br(2)(eV)	Br(4)(eV)	ΔBr(2,4)eV	Br(2)(eV)	Br(3)(eV)	Br(4)(eV)	ΔBr(2,4)(eV)
Pyrene	n-Pentane	6.48 ± 0.11 ^a	6.06 ± 0.04	0.42 ± 0.15	6.44 ± 0.04	5.83 ± 0.01	5.44 ± 0.05	1.00 ± 0.10
	n-Hexane	6.43 ± 0.02	5.97 ± 0.12	0.46 ± 0.14	6.38 ± 0.04	5.75 ± 0.12	5.43 ± 0.11	0.95 ± 0.15
	n-Heptane	6.44 ± 0.03	5.80 ± 0.03	0.64 ± 0.06	6.46 ± 0.01	5.79 ± 0.02	5.46 ± 0.02	1.00 ± 0.03
	c-Pentane	6.32 ± 0.01	5.81 ± 0.01	0.52 ± 0.02	6.50 ± 0.01	5.78 ± 0.01	5.51 ± 0.01	0.96 ± 0.02
	Neohexane	6.35 ± 0.05	5.76 ± 0.21	0.60 ± 0.26	6.45 ± 0.02	5.82 ± 0.02	5.46 ± 0.04	1.00 ± 0.06
	Isopentane ^b	-	-	-	6.50 ± 0.02	5.81 ± 0.03	5.54 ± 0.05	0.96 ± 0.07
	TMS ^c	-	-	-	-	5.83 ± 0.01	5.51 ± 0.01	-
Average ^a	6.40 ± 0.06	5.88 ± 0.12	0.53 ± 0.08	6.45 ± 0.04	5.80 ± 0.03	5.48 ± 0.04	0.98 ± 0.06	
Fluoranthene	n-Pentane	6.73 ± 0.02	5.93 ± 0.12	0.80 ± 0.14	6.82 ± 0.07	-	5.66 ± 0.03	1.16 ± 0.10
	Neohexane	6.67 ± 0.15	6.01 ± 0.07	0.66 ± 0.22	6.79 ± 0.07	-	5.59 ± 0.04	1.20 ± 0.11

^aThe errors given are standard deviations.^bThe breaks for liquid isopentane were not measured in the case of PFn-H, because PFn-H was found not to dissolve in this liquid in the concentration range studied (see text).^cThe breaks for liquid TMS were not measured in the case of PFn-H, because PFn-H was found not to dissolve in this liquid in the concentration range studied (see text) and because TMS absorbs below 210 nm.

$\sim 3/2 kT$, $\Delta Br(2,4)$ are roughly the same and different from that of PFn-H (Table 3.7).

As is shown in Fig. 3.3 for the cyclic highly attaching A's whose $\langle \epsilon \rangle_{\max} \approx 3/2 kT$ an additional break, $Br(3)$ is observed (Tables 3.6 and 3.7) at ~ 5.80 eV only in the case of pyrene. This could be due to a superexcited state of the pyrene at this energy.

Table 3.7. Values of $\text{Br}(n)$ ($n=2, 3, 4$) in the $I_F(\lambda_{\text{exc}})$ Function for Pyrene in Neohexane and for Cyclic A's^a.

A	$\text{Br}(2)\text{eV}$	$\text{Br}(3)\text{eV}$	$\text{Br}(4)\text{eV}$	$\Delta\text{Br}(2,4)\text{eV}$
PFn-H	6.35 ± 0.05^b		5.76 ± 0.21	0.59 ± 0.26
c-C ₇ F ₁₄	6.45 ± 0.02	5.82 ± 0.02	5.46 ± 0.04	1.00 ± 0.06
c-C ₇ F ₁₄ ^c	6.35 ± 0.11	5.80 ± 0.01	5.49 ± 0.01	0.86 ± 0.12
c-C ₆ F ₁₂	6.53 ± 0.04	5.99 ± 0.31	5.45 ± 0.08	1.08 ± 0.12
c-C ₈ F ₁₆	6.52 ± 0.05	6.18 ± 0.11	5.39 ± 0.03	1.13 ± 0.08

^aAll data are for 10^{-2} mol ℓ^{-1} of pyrene in neohexane unless as otherwise indicated.

^bAll errors are standard deviations.

^cData for 10^{-3} mol ℓ^{-1} solution of pyrene in neohexane.

CHAPTER 4

LASER ~~TWO~~-PHOTON IONIZATION OF MOLECULES IN LIQUIDS

4.1 Introduction

The minimum photon energy required to induce conductivity in a solution of a molecule in a dielectric liquid is assigned as the first ionization threshold (I_L^1), of the molecule in this liquid assuming that $(I_L^1)_{\text{solute}} < (I_L^1)_{\text{solvent}}$. In this technique the observed final products are the positive ion and the electron in their final states into the bulk of the medium (solvent). Most of the aromatic molecules possess gas phase ionization onsets in the range of 7-9 eV (Blaunstein and Christophorou, 1971) and their expected ionization thresholds in solution may be in an energy range where the solvents start absorbing (saturated alkanes start absorbing at ~7.2 eV; Raymonda and Simpson, 1967). The solvent absorption may interfere with the photoionization of the solute resulting in complications and difficulties in the interpretation of the data. This limitation in the one-photon induced conductivity measurements can be avoided by utilizing a two-photon excitation using an intense laser beam.

The theoretical model of the two-photon absorption (Geoppert-Mayer, 1931) is that two photons of an intense exciting light beam are simultaneously absorbed in the same quantum act raising the molecule to an excited state of energy equivalent to that of two photons. This state may decay like any other excited state, either radiatively or not radiatively to the ground state. Alternatively it

may autoionize, if this state is embedded in the ionization continuum, or undergo a photochemical change. The problem could theoretically be dealt with the time dependent perturbation theory and consists of solving the Schrodinger equation for the molecular system interacting with the radiation field. (McClain and Harris, 1977; Bakos, 1974; Peticolas, 1967) The hamiltonian, H_i of a single electron in the radiation field A is:

$$H_i = \frac{1}{2m} [\bar{p}_i - e\bar{A}(\bar{r}_i, t)][\bar{p}_i - e\bar{A}(\bar{r}_i, t)] + V_i \quad (4.1)$$

where e and m are the charge and the mass of the electron respectively, $\bar{r}_i$ its position vector, $\bar{p}_i$ its momentum vector and V_i the effective potential. Expanding (4.1) and keeping terms up to the first power of the electronic charge e , we have:

$$H_i = H_0 + H' = \frac{\bar{p}_i^2}{2m} + V_i - \frac{e}{m} \bar{A}(\bar{r}_i, t) \cdot \bar{p}_i \quad (4.2)$$

where the term

$$H' = - \frac{e}{m} \bar{A}(\bar{r}_i, t) \cdot \bar{p}_i \quad (4.3)$$

is the perturbation to the first approximation in e . This perturbation approach is valid for the laser intensities used in the present experiments (Lambropoulos, 1980). The solution of the Schrodinger equation for the hamiltonian (4.2) can be written as:

$$\Psi = \sum_k a_k(t) \cdot u_k^0(\bar{r}) \cdot \exp(-i\omega_k t) \quad (4.4)$$

where $a_k(t)$ are time dependent parameters and $u_k^0(\bar{r}) \cdot \exp(-i\omega_k t)$ are the solutions of the Schrodinger equation for the unperturbed system (H_0). The coefficients $a_k(t)$ must be found by an iterative approach

$a_k(t) = a_k^{(0)}(t) + a_k^{(1)}(t) + a_k^{(2)}(t) + \dots$, from the recurrence relation:

$$\frac{d}{dt} a_k^{(\ell+1)}(t) = (i\hbar)^{-1} \cdot \sum_n H'_{kn}(t) \cdot a_n^{(\ell)}(t) \cdot \exp(-i\omega_{kn}t) \quad (4.5)$$

where H'_{kn} is the matrix element of the perturbation. In the electron dipole approximation:

$$H'_{kn} = eA_0\omega_{kn} \int u_k^0(\vec{r}) \cdot (\vec{d} \cdot \vec{r}) \cdot u_n^0(\vec{r}) d\vec{r} \equiv eA_0\omega_{kn} \langle k | \vec{d} \cdot \vec{r} | n \rangle \quad (4.6)$$

where A_0 is the amplitude of the radiation field and $\vec{d}$ is the complex polarization vector of unit length ($\vec{d} \cdot \vec{d}^* = 1$). The first and the second iterative solutions of (4.5) give the first and second-order perturbed wave functions:

$$\psi_n^{(1)}(\vec{r}, t) = \psi_n^{(0)}(\vec{r}, t) + \sum_k \frac{eA_0}{i\hbar} \omega_{kn} [\vec{d} \langle n | \vec{r} | k \rangle] u_k^0(\vec{r}) \cdot$$

$$\left[\frac{\exp[i(\omega_{kn} - \omega)t]}{\omega_{kn} - \omega} \right] \quad (4.7)$$

$$\psi_n^{(2)}(\vec{r}, t) = \psi_n^{(1)}(\vec{r}, t) + \frac{e^2 A_0^2 \omega^2}{\hbar^2} \cdot \sum_{\ell} S_{n\ell} u_{\ell}^0(\vec{r}) \cdot$$

$$\left[\frac{1 - \exp[-it(\omega_{\ell n} - 2\omega)]}{\omega_{\ell n} - 2\omega} \right] \quad (4.8)$$

where $\omega_{kn} = \omega_k - \omega_n$ and $S_{n\ell} = \sum_k \frac{\omega_{\ell k} \omega_{kn}}{\omega^2} \cdot \left[\frac{\vec{d} \langle n | \vec{r} | k \rangle \langle k | \vec{r} | \ell \rangle \vec{d}}{\omega_{kn} - \omega} \right]$

In the first order wave function (4.7) resonance occurs at a frequency

$\omega_{kn} = \omega$ at which the coefficient $u_k^0(\vec{r})$ grows monotonically in time

and the transition $n \rightarrow k$ takes place with one photon $\hbar\omega = \hbar\omega_{kn}$

absorbed. In the second order wavefunction (4.8) resonance occurs

at a frequency $\omega_{2n} = 2\omega$ and a transition in which two photons of energy $\hbar\omega$ are absorbed and an excitation of energy $\hbar\omega_{2n} = 2\hbar\omega$ appears, all in the same quantum act. The rate constant $W_{nl}^{(2)}$ for a two photon transition may be calculated from:

$$W_{nl}^{(2)} = 8\pi \frac{e^4 A_0^4}{\hbar^4} \iint |S_{nl}|^2 \cdot \omega^4 \cdot g_M(2\omega) \cdot g_L(\omega) d\omega \quad (4.9)$$

where $g_M(2\omega)$, $g_L(\omega)$ are the spectral distributions of the molecular transition and of the incident light respectively. For nearly monochromatic light ($g_L(\omega)$ much sharper than $g_M(2\omega)$) and using the relation of the flux, F , to the A_0^2 ($\hbar\omega F = \omega^2 A_0^2 / 2\mu_0 c; \mu_0$ magnetic permeability) (4.9) takes the form:

$$W_{nl}^{(2)} = 128\pi^3 \alpha^2 \omega^2 F^2 \cdot |S_{nl}|^2 \cdot g_M(2\omega) \quad (4.10)$$

or for the measurable molecular quantity:

$$\sigma_{nl} = \frac{W_{nl}^{(2)}}{F^2} = 128\pi^3 \alpha^2 \omega^2 \cdot |S_{nl}|^2 \cdot g_M(\omega) \quad (4.11)$$

where α is the fine structure constant.

The two-photon absorptivity σ_{nl} has dimensions of cm^4s per photon per molecule and typical values for allowed two-photon transitions in the liquid phase are of the order of $10^{-50} \text{ cm}^4\text{s}$ per photon per molecule.

From the above analysis several interesting conclusions can be drawn about the two-photon absorption:

1. The selection rules for the two-photon absorption, in the electric-dipole approximation employed, are different than the one photon rules. One-photon absorption can excite transitions in which the transition density $\Psi_i^*(\vec{r}) \cdot \Psi_f(\vec{r})$ ($\Psi_i(\vec{r})$ initial, $\Psi_f(\vec{r})$ final states) transforms under symmetry operations like x , y or z ;

the two-photon excite transitions in which the density transforms like x^2 , y^2 , z^2 , xy , xz , or zy . In molecules with center-of-inversion this leads to the reversal of the usual parity rules. Two-photon transitions are allowed among states with the same parity.

2. Two-photon excited states lie at twice the energy of the individual photons, so VUV molecular states can be reached with existing laser systems.
3. The symmetry of given transitions in the condensed phase can be studied using laser polarization spectroscopical techniques.
4. Spectroscopical studies of molecules in the liquid phase are limited by the absorption of the host medium. In a two photon technique photoionization studies can be carried out, as a function of the laser photon energy, $h\nu_{\text{laser}}$, from the photoionization threshold, I_L^1 , up to energies $E = 2 h\nu_{\text{laser}}$ for $h\nu_{\text{laser}} < E_1$, where E_1 is the energy of the first absorption band of the solvent. Thus ionization thresholds of molecules in dielectric liquids as high as ~ 10 eV can be studied with frequency-tunable dye lasers (ionization thresholds of n-alkanes are > 10 eV).

The TPI technique is not only suitable for the accurate determination of I_L^1 but also for obtaining information on molecular states embedded in the ionization continuum and lying between $(I_L^1)_{\text{solute}}$ and the onset of the solvent absorption. The I_L^1 is lower than the corresponding ionization potential I_G^1 of a molecule in the gas phase, thus bound molecular states in the energy range from I_L^1 to I_G^1 become autoionizing in solution.

In addition, the TPI technique can be employed to probe photophysical processes resulting from two-photon transitions which do not lead to ionization (Robin, 1980). In this chapter, results are reported and discussed on the photoionization of TMPD and fluoranthene in liquid n-pentane.

4.2 The Two-Photon Ionization Spectrum of TMPD in n-Pentane

The TPI spectrum of $\sim 5 \times 10^{-6}$ mol ℓ^{-1} solution of TMPD in n-P in the laser-wavelength range from 360 to ~ 650 nm, corresponding to two-photon transitions from 180 to ~ 325 nm, is shown in Fig. 4.1. This spectrum comprises 15 individual spectra corrected for I_{laser}^2 (see section 2.3) and combined by normalization in the respective regions of overlap. The TPI current shows a monotonic slow increase with decreasing λ_{laser} until $\lambda_{\text{laser}} \approx 425$ nm ($\sim 47000 \text{ cm}^{-1}$), where it rises very steeply. Distinct structure is exhibited for the whole energy region investigated. The positions of the peaks in the TPI spectrum are given in Table 4.1. The photocurrent approaches a "zero level"[†], established as the minimum detectable signal, at $\lambda_{\text{laser}} = 639.1 \pm 4.1$ nm (see Fig. 4.1). This corresponds to a two-photon energy of 3.88 ± 0.05 eV which we identify as the first ionization threshold (I_L^1) of TMPD in liquid n-P.

[†]The background conductivity signal was measured under the same conditions as the TPI spectrum and found to be of the same magnitude as the "zero level" of the TPI signal and independent of the excitation laser wavelength in the spectral region covered. Using extensively purified n-pentane we estimated a background photocurrent of $< 10^{-13} \text{ A}$.

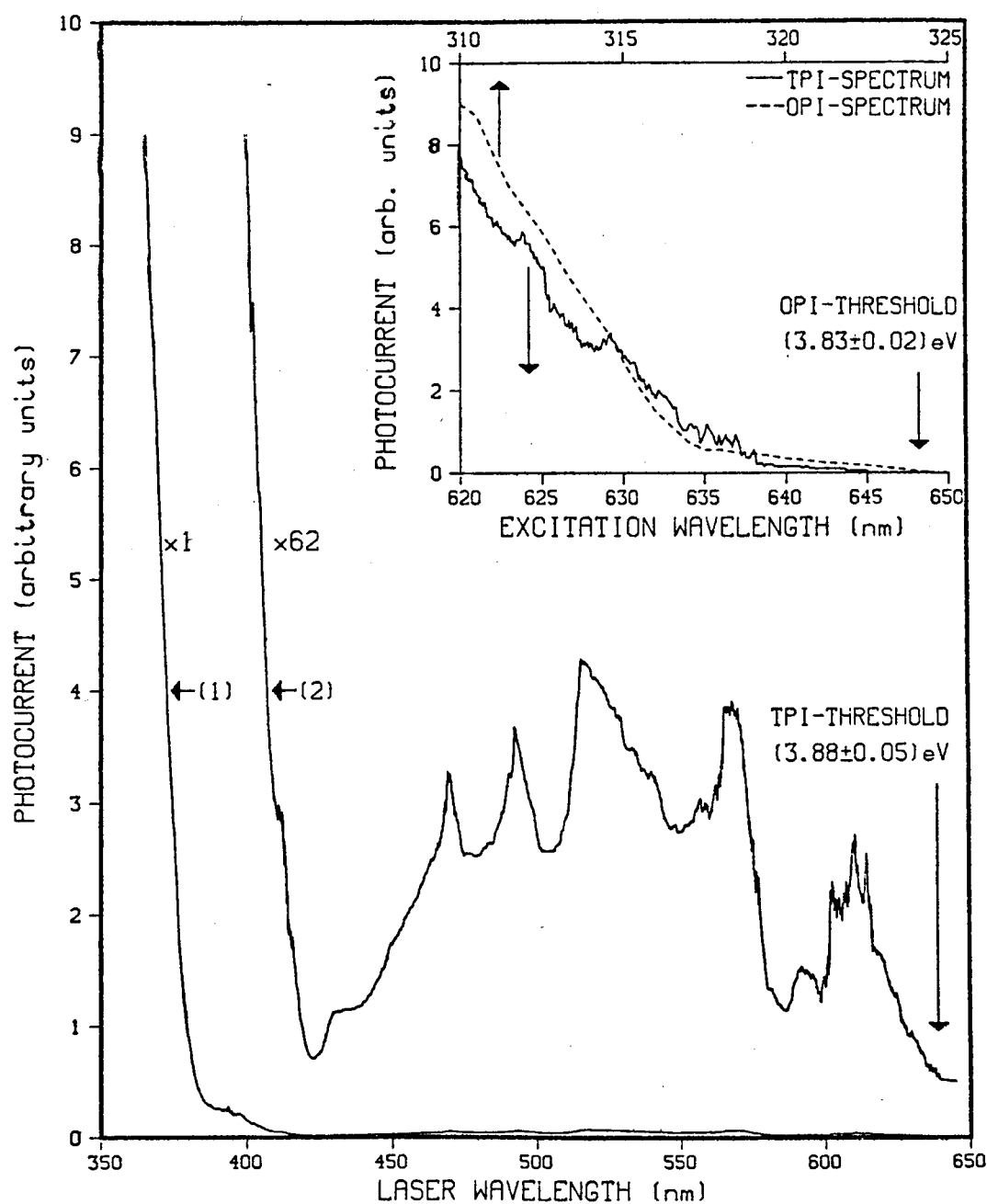


Fig. 4.1. Two-photon ionization (TPI) current of TMPD in n-pentane as a function of the laser wavelength (curve 1). The section of this spectrum above 400 nm (curve 2) is magnified by a factor of 62. The arrow indicates the position of the photoionization threshold. The literature value of 4.89 eV (Holroyd and Russell, 1974) would have corresponded to $\lambda_{\text{laser}} = 507$ nm. *Insert:* The one-photon ionization (OPI) current (dashed line) as a function of the laser wavelength (upper scale). The arrow indicates the OPI threshold. For comparison the TPI spectrum (solid line) is also presented.

Table 4.1. Positions (in cm^{-1}) of the Observed Maxima in the TPI Spectrum of TMPD in n-Pentane (Two-Photon Resonant Transitions).

31451 $\pm$ 100	38039 $\pm$ 200
31778 $\pm$ 30	38804 $\pm$ 130
32353 $\pm$ 100	40621 $\pm$ 260
32745 $\pm$ 320	42582 $\pm$ 160
33791 $\pm$ 180	44444 $\pm$ 160
34673 $\pm$ 100	46373 $\pm$ 200
35229 $\pm$ 160	48183 $\pm$ 100
35948 $\pm$ 160	48598 $\pm$ 80
37026 $\pm$ 100	49466 $\pm$ 100
37487 $\pm$ 100	49771 $\pm$ 80

In Fig. 4.2 the two-photon excitation scheme of TMPD in liquid n-P is illustrated. The one-photon absorption spectrum (Fig. 6.2) of TMPD in n-P shows three wide bands with maxima at 38010 cm^{-1} , 49530 cm^{-1} and 58400 cm^{-1} and half-widths of $\sim 4600 \text{ cm}^{-1}$, their positions are indicated in Fig. 4.2. The TMPD molecule, whose structural formula is also shown in Fig. 4.2, belongs to the D_{2h} symmetry-group (Goeppert-Meyer and McCallan, 1942) and the molecular states are represented by wavefunctions with well defined parity. Transitions from the totally symmetric (even parity) ground state to upper even parity states are one-photon forbidden, but two-photon allowed. Therefore we ascribe the observed resonances in the TPI spectrum to two-photon excitation of one-photon forbidden autoionizing states at

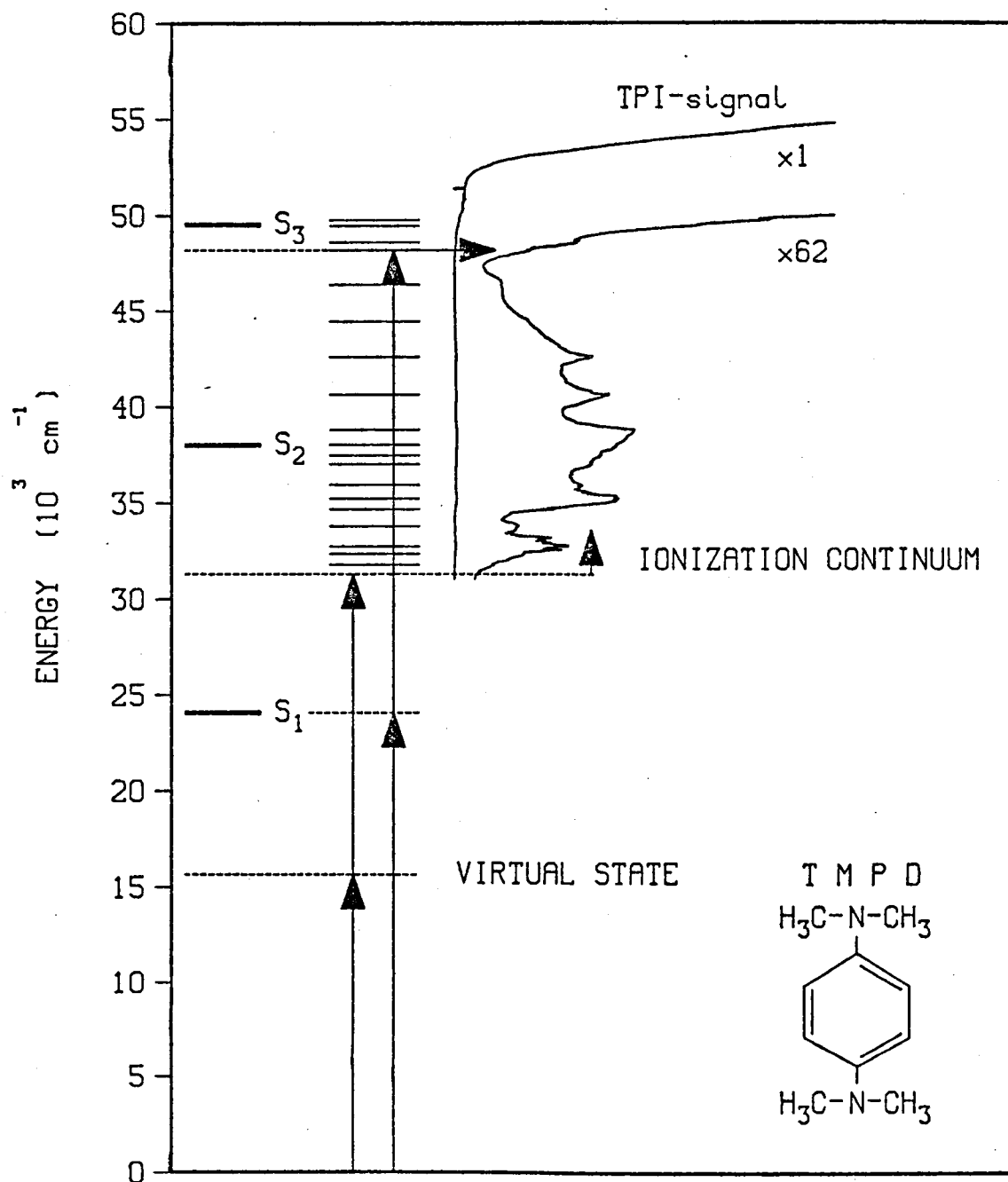


Fig. 4.2. Energy diagram of TMPD in n-pentane. The TPI-spectrum of TMPD in n-P and the positions of the TPI resonances are also shown.

energies $> 31294 \text{ cm}^{-1}$. The portion of the TPI spectrum from the threshold (31294 cm^{-1}) up to $\sim 48300 \text{ cm}^{-1}$ (Fig. 4.2) is due to autoionizing states which are reached via two-photon excitation through a virtual intermediate state. The "cross section" for such a process is very small of the order of $10^{-50} \text{ cm}^4\text{s}$ per photon per molecule (McClain and Harris, 1977) explaining the small photocurrent intensity in this region. When the one-photon energy becomes equal to the energy corresponding to the first singlet state, the two-photon resonance proceeds through a real intermediate state (S_1) and the cross section for such process is large, of the order of 10^{-16} cm^2 per molecule, and the TPI signal increases sharply.

To ensure that the 3.88 eV value for the I_L^1 of TMPD in n-P, obtained from the TPI spectrum, is not influenced by any higher-order multiphoton process, we measured (using the modified experimental set up described in section 2.3) the one-photon ionization (OPI) spectrum of TMPD in n-P from 310 to 325 nm. This spectrum is shown by the dashed line in the insert of Fig. 4.1, for comparison, the TPI spectrum is also plotted. The OPI current decreases smoothly with increasing λ_{laser} and reaches asymptotically a "zero-level" at $324 \pm 3 \text{ nm}$. This onset corresponds to an I_L^1 value for TMPD in n-P of $3.83 \pm 0.02 \text{ eV}$, in agreement with the $3.88 \pm 0.05 \text{ eV}$ value determined from the TPI spectrum.

The present value of I_L^1 for TMPD in n-P is $\sim 1 \text{ eV}$ lower than the literature value of 4.89 eV reported by Halroyd and Russell (1974) for TMPD in n-hexane. The latter value would have corresponded to $\lambda_{\text{laser}} = 507 \text{ nm}$ in the TPI spectrum.

4.3 The Two-Photon Ionization Spectrum of Fluoranthene in n-Pentane

The TPI spectrum of $\approx 5 \times 10^{-6}$ mol ℓ^{-1} solution of fluoranthene in n-pentane is shown in Fig. 4.3. The photocurrent is plotted as a function of λ_{laser} in the spectral region 366 to 560 nm which corresponds to two-photon transitions in the range 188 to 280 nm. The spectrum presented comprises ten individual corrected spectra which were combined by normalization in the respective region of overlap. The TPI spectrum shows three important features: (1) The photocurrent declines sharply for $\lambda_{\text{laser}} > 420$ nm and then reaches asymptotically a "zero level" as the wavelength increases. (2) Distinct structure is observed over the entire energy range investigated. (3) The photocurrent declines for $\lambda_{\text{laser}} < 414$ nm.

Feature (1) was utilized to determine the I_L^1 of fluoranthene in n-pentane. The photocurrent reaches asymptotically a "zero level" at 551.0 ± 6.2 nm. This corresponds to an energy for a two-photon transition of 4.50 ± 0.05 eV, which we identify with the I_L^1 of fluoranthene in n-pentane.

The structure of the TPI spectrum is attributed to autoionization of discrete states embedded in the ionization continuum and excited by two-photon absorption. The fluoranthene molecule, whose structural formula is shown in Fig. 4.4, belongs to the C_{2v} symmetry group (Thulstrup and Eggers, 1968). Members of this group do not possess center of symmetry and thus all excited states are both one and two-photon allowed (Peticolas, 1967). In Fig. 4.4 the two-photon excitation scheme of fluoranthene in n-P is illustrated. For the two-photon excitations in the energy range $36300\text{--}48280$ cm^{-1} , in which the one-

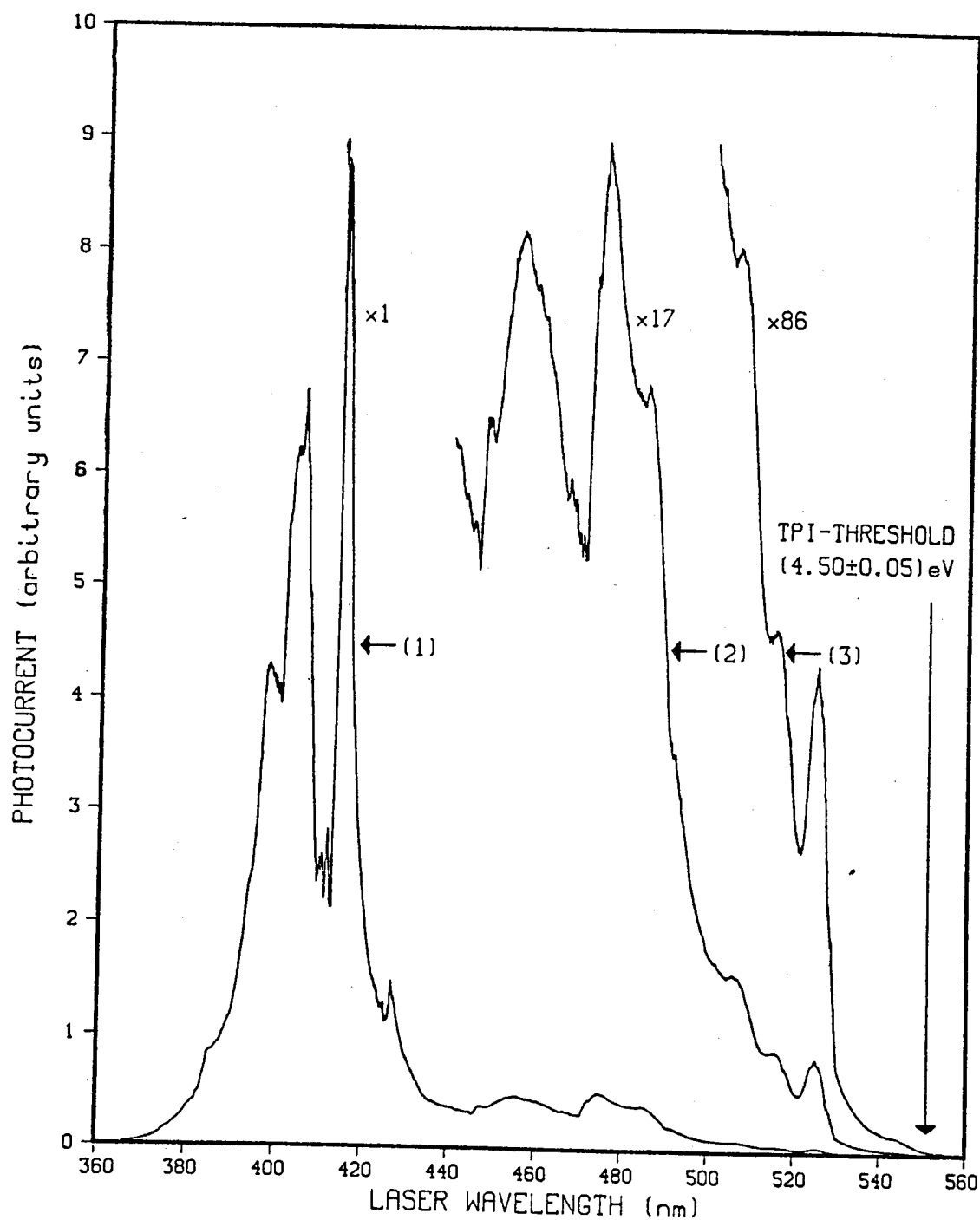


Fig. 4.3. Two photon ionization (TPI) current of fluoranthene in n-pentane as a function of the laser wavelength (curve 1). The sections of this spectrum above 440 nm (curve 2) and 500 nm (curve 3) are magnified by factors of 17 and 86, respectively. The arrow indicates the position of the photoionization threshold.

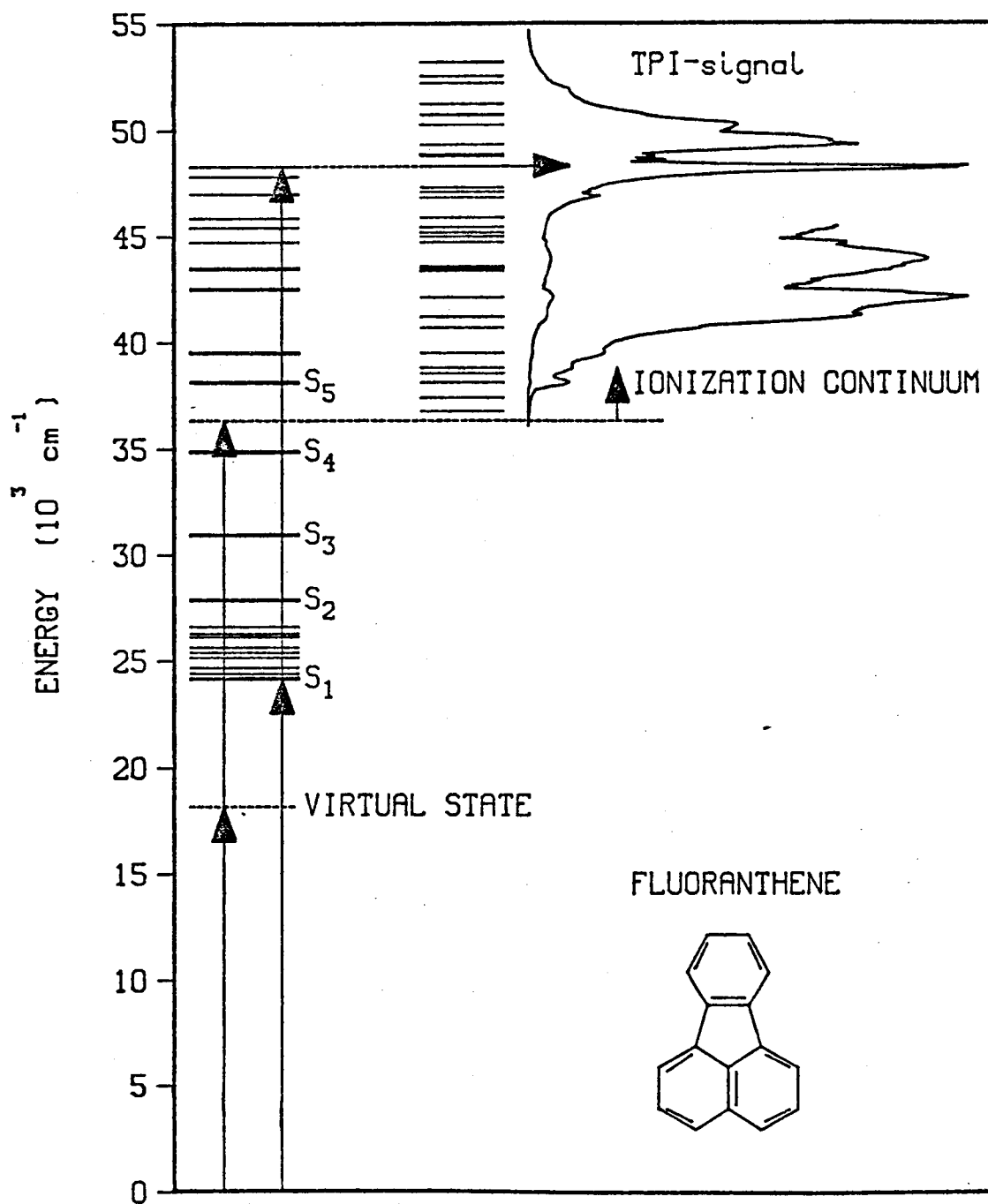


Fig. 4.4. Energy diagram of fluoranthene in n-pentane. The TPI-spectrum and the positions of the TPI resonances are also shown.

photon energy is below the first singlet state ($S_{1,0}$ lies at 24140 cm^{-1}), the intermediate state is a virtual one. The TPI resonances in this energy interval come from the autoionization of molecular states excited via a two-photon absorption. Indeed, superimposing the TPI-spectrum on the optical absorption spectrum (Fig. 4.5), the positions of the absorption and the TPI bands coincide with only exception of the TPI bands at 42474 cm^{-1} and 43450 cm^{-1} . These bands are shifted by $\sim 300\text{ cm}^{-1}$ with respect to the corresponding absorption bands. This shift may be an indication of a strong symmetric character of these states revealed by the two-photon transition. For energies above 48280 cm^{-1} the two-photon excitation proceeds through a real intermediate state, in this case a vibrational level of the first singlet state, and the structure of the TPI spectrum reflects the positions of the intermediate states. The TPI spectrum in this energy range is more clearly resolved than the one-photon absorption spectrum enabling us to accurately locate the positions of the first electronic state S_1 and its vibrational sublevels. This was impossible from the absorption spectrum due to its diffuse character in this region (Berlman and coworkers, 1968, Michl, 1969; Kolc and coworkers, 1974). It should, however, be kept in mind that in the photoabsorption spectrum one observes the disappearance of photons from the excitation beam independently of the ensuing processes, while in TPI we probe only the two-photon absorption as monitored by the ionization channel. The positions of the TPI bands as well as the positions of the absorption bands are given in the Table 4.2. The positions of the

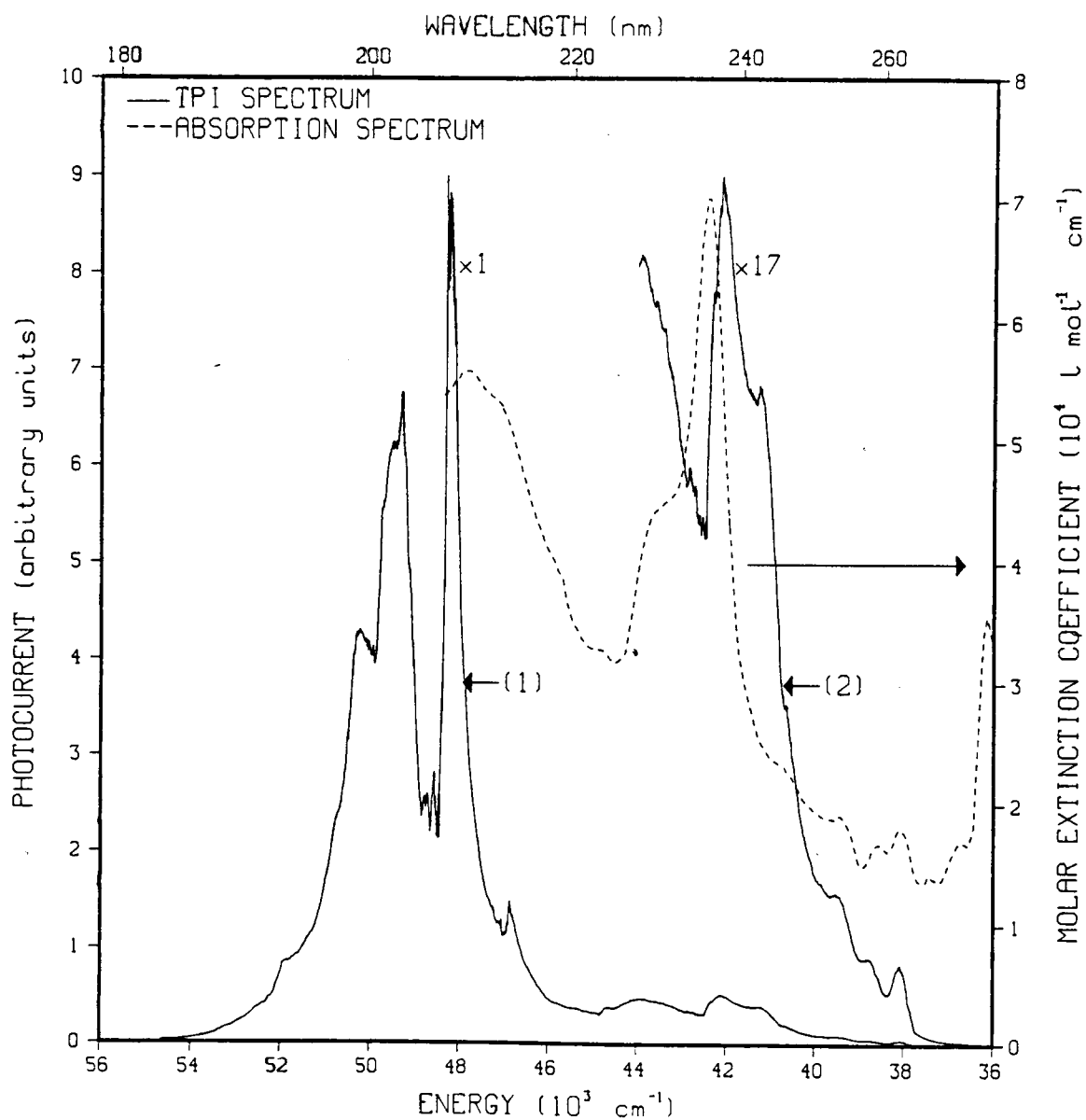


Fig. 4.5. The TPI spectrum of fluoranthene in n-pentane (solid line), the section of the spectrum below 44000 cm^{-1} (curve 2) is magnified by a factor of 17. The absorption spectrum (dashed line) is shown for energies up to 48280 cm^{-1} , twice as much as the energy of the $S_{1,0}$.

Table 4.2. Positions (in cm^{-1}) of the Maxima in the One-Photon Absorption and TPI Spectra of Fluoranthene in n-Pentane.

One-photon ^{a)} absorption	TPI		TPI	
	Two-photon resonant transitions	One-photon absorption	One-photon resonant transitions	
36742 $\pm$ 80	36742 $\pm$ 80	—		
37390 $\pm$ 80	37390 $\pm$ 80	—	24140 $\pm$ 30	(48280) ^b
38105 $\pm$ 80	38105 $\pm$ 80	—		
38531 $\pm$ 80	38531 $\pm$ 130	—	24384 $\pm$ 100	(48768) ^b
	38789 $\pm$ 130			
39500 $\pm$ 100	39500 $\pm$ 100	—	24655 $\pm$ 80	(49311) ^b
40684 $\pm$ 130	40684 $\pm$ 180			
41205 $\pm$ 100	41205 $\pm$ 80	—	25129 $\pm$ 80	(50258) ^b
42474 $\pm$ 50	42105 $\pm$ 100			
	42842 $\pm$ 50	—	25368 $\pm$ 150	(50737) ^b
	43474 $\pm$ 80			
43450 $\pm$ 400	43579 $\pm$ 50	—	25618 $\pm$ 150	(51237) ^b
	43942 $\pm$ 100			
44705 $\pm$ 80	44705 $\pm$ 80	—	26105 $\pm$ 150	(52211) ^b
	44974 $\pm$ 50			
	45168 $\pm$ 80	—	26265 $\pm$ 150	(52531) ^b
45400 $\pm$ 130	45421 $\pm$ 100			
45842 $\pm$ 130	45868 $\pm$ 130	—	26592 $\pm$ 150	(53184) ^b
46980 $\pm$ 200				
	46816 $\pm$ 50			
	47079 $\pm$ 80			
	47289 $\pm$ 130			

^aSee CHAPTER 6.

^bThese are the positions of the maxima in the TPI spectrum due to one-photon resonant two-photon ionization.

possible electronic states of fluoranthene as found from different methods are compared in Table 4.3.

The decline of the TPI current at energies above 48300 cm^{-1} is a very interesting feature of the TPI spectrum. It is seen from Fig. 4.3 that at $\lambda_{\text{laser}} \sim 421\text{ nm}$ ($\sim 23750\text{ cm}^{-1}$) corresponding to the onset of the first absorption band of fluoranthene, the TPI signal increases sharply as expected for one-photon resonant two-photon transitions. The TPI signal, however, unexpectedly decreases for $\lambda_{\text{laser}} < 414\text{ nm}$. This decline in the TPI spectrum (Fig. 4.3) was not observed for the other molecules - pyrene (Siomos and Christophorou, 1980) and TMPD (see Fig. 4.1) studied by us using the same technique.

It is known (Robin, 1980; Jackson and Lin, 1978; Freedman, 1977) that the long ($>10^{-9}\text{ s}$) lifetimes of intermediate states, as opposed to the short ($\sim 10^{-15}\text{ s}$) lifetimes of virtual states, not only contribute to the probability of upward transitions but also allow for other processes which under favorable time and energy conditions compete effectively with multiphoton ionization. Since the decline in the TPI current sets in when TPI occurs via the one-photon resonant S_1 manifold and since autoionization usually is faster than dissociation, it seems reasonable to attribute the decrease in the TPI signal above 48300 cm^{-1} to molecular dissociation from the $S_{1,n}$ state, a process competing with two-photon ionization via this state. The molecule probably starts to predissociate at energies just higher than the energy (24140 cm^{-1}) of $S_{1,0}$, where two-photon ionization still competes effectively with dissociation. As the photon energy increases, direct dissociation seems to predominate, so that the TPI

Table 4.3. Positions (in cm^{-1}) of the 0-0 Transitions of the Possible Electronic States of Fluoranthene

Possible excited electronic state	Positions of 0-0 transitions		
	One-photon absorption		TPI ^b
	Theory	Experiment	
1	26778 ^c	~26000 ^c	24140 $\pm$ 30 ($\nu' = 0$) ^d
	26600 ^f	24670 ^e	24645 $\pm$ 50 ($\nu' = 1$) ^d
	28311 ^{c,g}	27800 ^{c,g}	
2	28400 ^{f,g}	27840 ^{e,g}	
	31698 ^{c,g}	30800 ^{c,g}	
3	31800 ^{f,g}	30910 ^{e,g}	
	36135 ^{c,g}	34800 ^{c,g}	
4	36000 ^{f,g}	34840 ^{e,g}	
	40974 ^{c,g}	38200 ^{c,g}	
5	43200 ^f	38170 ^c	38105 $\pm$ 80
	41377 ^c	40000 ^c	
6	40400 ^f	39530 ^e	39500 $\pm$ 100
	43474 ^c	42400 ^c	
7	45200 ^f	42460 ^e	42105 $\pm$ 100
	43474 ^c		
8	46100 ^f	43450 ^f	43940 $\pm$ 100

^aAlthough for the 1st, 5th, and 6th electronic states the energy position assigned to the respective 0-0 transitions are in agreement with the corresponding resonances in the TPI spectrum, a small shift is observed in the 0-0 transitions of the 7th and 8th states which may indicate that the symmetric character of these states is quite significant.

^bPresent work.

^cE. Heilbronner, J. P. Weber, J. Michl and R. Zahradnik, *Theoret. Chim. Acta* **6**, 141 (1966).

^dOur analysis suggests that the $S_{1,0}$, $S_{0,0}$ transition energy should be 24140 cm^{-1} . The energy 24670 cm^{-1} associated with this transition by Michl (see below) should correspond rather to the $S_{1,1}$, $S_{0,0}$ transition.

^eJ. Michl, *J. Mol. Spectrosc.* **30**, 66 (1969).

^fT. Kolc, E. W. Thulstrup and T. Michl, *T. Am. Chem. Soc.* **96**, 7188 (1974).

^gThese states cannot be seen in the TPI spectrum because they lie outside the energy range of observation (see Fig. 4.3).

current goes virtually to "zero" at energies of the one-photon resonant transition of $\sim 27320 \text{ cm}^{-1}$ ($\sim 3.39 \text{ eV}$) which corresponds to a position above $S_{1,8}$. In support of this explanation for the decline of the TPI signal the following two points can be made:

- 1) Fluoranthene although planar in the ground state, S_0 , is considered nonplanar in the first excited singlet State S_1 , (Berlman and coworkers, 1968). Also, the fluorescence spectrum of fluoranthene is diffuse (Berlman and coworkers, 1968; Michl, 1969; Kolc and coworkers, 1974; Siomos and Christophourou, 1981) due perhaps to the nonplanarity of S_1 and the associated change of the bond lengths which calculations suggest must be considerable, particularly for the single C-C bonds of the five-member ring of fluoranthene. Both factors would lower the energy required for molecular dissociation from $S_{1,n}$.
- 2) Dissociation energies of $\sim 3.6 \text{ eV}$ have been reported (Eisenthal and coworkers, 1966) for the single bonds of benzyl-benzyl type of molecules. Further studies using tunable pulsed lasers in the picosecond range would undoubtedly elucidate the competitive processes of multiphoton ionization and molecular dissociation.

CHAPTER 5

THE PHOTOIONIZATION THRESHOLD OF MOLECULES IN LIQUID MEDIA

5.1 The Value of the Photoionization Threshold of a Molecule in a Liquid Medium.

The accurate determination of the ionization threshold of molecules in liquid media is extremely important in efforts to link the properties of isolated molecules with those in the liquid phase and in efforts to assess the effect of the medium on charge-separated states. For this reason it has been the subject of many studies over the last two decades (see, e.g. CHAPTER 1 and references therein). Despite these efforts, basic questions remain concerning both the accurate measurement of I_L^1 and the effect of the medium on it.

It is obvious from the data presented in Table 5.1 that the photoionization-threshold value of a molecule in a liquid medium depends on the technique employed for its determination. The integrated fluorescence technique gave consistently higher photoionization-threshold values for all the molecules studied than the TPI technique. This could be attributed to the fact that the final state of the photoejected electron in the liquid, i.e. the state which is revealed in the experimental observation, is different in the two techniques. In the integrated fluorescence technique the photoejected electron is captured by the electron attaching molecule at times $\sim 10^{-14}$ (see CHAPTER 3) whereas in the TPI technique is observed as quasi-free electron. Recently, in subpicosecond spectroscopical studies

Table 5.1. Values of the Photoionization Threshold (in eV) of TMPD, Fluoranthene and Pyrene.

Molecule	$I_L^1(\text{IFT})^a$	$I_L^1(\text{TPI})^b$	I_G^1	$\Delta I = I_G^1 - I_L^1(\text{TPI})$
TMPD	5.02 ± 0.05^c	3.88 ± 0.05 4.89^e	6.20 ± 0.02^g	2.32 ± 0.07
Fluoranthene	5.66 ± 0.03^d	4.50 ± 0.05	7.72^h	3.22
Pyrene	5.44 ± 0.05^d	4.80 ± 0.02^f	7.42^i	2.61

^a $I_L^1(\text{IFT})$ represent values obtained with the integrated fluorescence technique.

^b $I_L^1(\text{TPI})$ represent values obtained with the two-photon ionization technique.

^cIn n-hexane with PFn-H as electron attaching compound.

^dIn n-pentane with c-C₇F₁₄ as electron attaching compound.

^eLiterature value (R. A. Holroyd, J. Chem. Phys. 57, 3007 (1972)).

^fK. Siomos and L. G. Christophorou, Chem. Phys. Lett. 72, 43 (1980).

^gY. Nakato, M. Ozaki, A. Egawa, and Tsubomura, Chem. Phys. Lett. 6, 615 (1971).

^hW. F. Frey, R. N. Compton, W. T. Naff and H. C. Schweinler, Intern. J. Mass. Spectrum. Ion. Phys. 12, 19 (1973).

ⁱE. Clar and W. Schmidt, Tetrahedron 35, 1027 (1979).

Wiesenfeld and Ippen (1980) have shown that the photoejected electron in liquid water is captured by electron-attaching additives at times faster than the solvation time. The present results in connection with these findings seem to indicate a different time evolution of the photoionization process, as probed in our experiments. This may influence differently the energetics of the photoionization and thus the determined threshold values as they are revealed by the integrated fluorescence and the laser two-photon ionization techniques.

With respect to the measurement of I_L^1 , attention should be drawn to the much lower values of I_L^{1+} obtained by us, using the laser two-photon ionization technique, compared with those obtained by others (Kevan and Webster, 1976; Holroyd and Russell, 1974; Bullo and Gauthier, 1977) using a photoconductivity technique. As in any measurement of a threshold quantity, the value determined is a function of the sensitivity of the method employed. We believe that our ability to detect very small signals (see section 2.3 and Figs. 4.1 and 4.3 also Siomos and Christophorou, 1980) enables us to locate I_L^1 more accurately. This advantage of our method removed the need of fitting assumed "threshold-law" functions to the data "close" to the threshold to infer I_L^1 , as has been practiced by others (Holroyd and Russell, 1974; Bernas and coworkers, 1980; Schmidt and Döldissen,

[†]It is important to note that the values of I_L^1 thus determined could be an upper limit. It is possible that improvement of the signal-to-noise ratio could give a slightly lower value of I_L^1 .

1978; Sowada and Holroyd, 1979). Analyses based on threshold laws are beset with serious problems: lack of knowledge of the energy region over which the assumed threshold law is valid (usually this region is of the order of a few meV), lack of accurate knowledge of the angular momentum of the electron prior to ejection, which determines the threshold behavior itself (Hotop and Lineberger, 1973); and the serious assumption that the ionization is direct. Clearly the present work shows that photoionization is strongly influenced by autoionization.

5.2 The Effect of the Medium on the Threshold

Concerning the effect of the medium on the photoionization threshold value, attention is drawn to the following findings:

1. The I_L^1 of TMPD, fluoranthene and pyrene (Siomos and Christophorou, 1980) as measured with the present technique are given in the Table 5.1 along with their onsets, I_G^1 , in the gas-phase. The differences $\Delta I = I_G^1 - I_L^1$, also listed in this table, are much larger than those inferred from other data on a number of molecules in nonpolar liquids (Kevan and Webster, 1976; Holroyd and Russell, 1974; Bernas and coworkers, 1980)
2. The results of chapter 3 show that the value of I_L^1 depends on the time evolution of the photoionization and electron attachment processes. It was inferred from those studies that the photoejected electron is captured by the electron-attaching additive at times of the order of $\sim 10^{-14}$ s.
3. Dynamical studies of electron solvation, following photoionization in liquid water using laser picosecond techniques

(Wiesenfeld and Ippen, 1980) indicated that the visible absorption spectrum of solvated electrons appears at times $< 3 \times 10^{-13} \text{s}$.

The aforementioned findings seem to suggest that the photoionization process for a solute molecule in a liquid medium is completed at times $< 10^{-13} \text{s}$ independently of the nature of the medium. They also suggest that sub-picosecond dynamical effects of the medium on the photoionization process are probably responsible for the lowering of I_L^1 compared to the I_G^1 .

CHAPTER 6

VUV ABSORPTION SPECTRA OF AROMATIC MOLECULES IN SOLUTION

6.1 Introduction

Knowledge of the photoabsorption properties of organic molecules, especially aromatics, in solution and in the VUV region, is of great importance. The VUV region for most aromatic molecules is the ionization and the Rydberg transition region and for this reason the absorption spectrum will give information on the effect of the medium (solvent) on these transitions. In addition, the knowledge of the absorption spectra of molecules in solution and in the VUV has been necessary in the previous chapters for the understanding of the photoionization data. In the integrated fluorescence technique the fluorescence intensity of molecules in dilute solutions must be corrected for the fraction of the photons absorbed as a function of the excitation wavelength. In the TPI technique the interpretation of the structure in the TPI-spectrum and the understanding of the mechanisms involved in the two-photon induced ionization required knowledge of the absorption spectra of the molecules under study in solution.

Although absorption spectra of organic molecules in solution are readily available (UV-atlas of Organic Compounds, 1971; Lang, 1966; Berlman, 1971) for the ultraviolet (UV) spectral region ($<50000\text{ cm}^{-1}$), they are scarce in the VUV region ($>50000\text{ cm}^{-1}$). This is mainly due to the lack of solvents transmitting in the VUV and to the experimental difficulties associated with this spectral region. To overcome these difficulties one has to use solvents of better optical quality

and fabricate very thin cells. Still one cannot have both of these at the same time. Solvents transmitting deeper in the VUV are less polarizable. This in turn will make them poor solvents.

Additionally, a thinner cell requires a higher concentration for detectable absorption as it is shown by Beer's law,

$$I = I_0 10^{-\epsilon cd} \quad (6.1)$$

where for a given value of the extinction coefficient ϵ the smaller the d (light path) the larger the c (concentration) for the ratio I/I_0 to remain in the sensitivity region of the instrumentation used.

In this chapter the absorption spectra of benzene, naphthalene, azulene, TMPD, pyrene, and fluoranthene in PFn-H for photon energies $< 65\,000\text{ cm}^{-1}$ and n-P for photon energies $< 59\,000\text{ cm}^{-1}$, taken with a newly developed technique (see Section 2.4), are presented and discussed. The transmission spectra of perfluoro-normal-nexane, n-pentane, n-hexane, n-heptane, isopentane, neoheptane, and cyclohexane are also presented.

6.2 Results

In Figs. 6.1 - 6.3 the absorption spectra of benzene naphthalene, azulene, TMPD, pyrene and fluoranthene in liquid PFn-H and n-P are presented. The extinction coefficient scale was established by normalizing the present spectra to literature values at energies as indicated in Table 6.1. To our knowledge the absorption spectra of these organic molecules in PFn-H in the energy region $35000\text{--}65000\text{ cm}^{-1}$ are reported for the first time and so are the absorption spectra in n-P for energies $> 50000\text{ cm}^{-1}$. The positions of the observed absorption bands of the above molecules in PFn-H solution are listed in

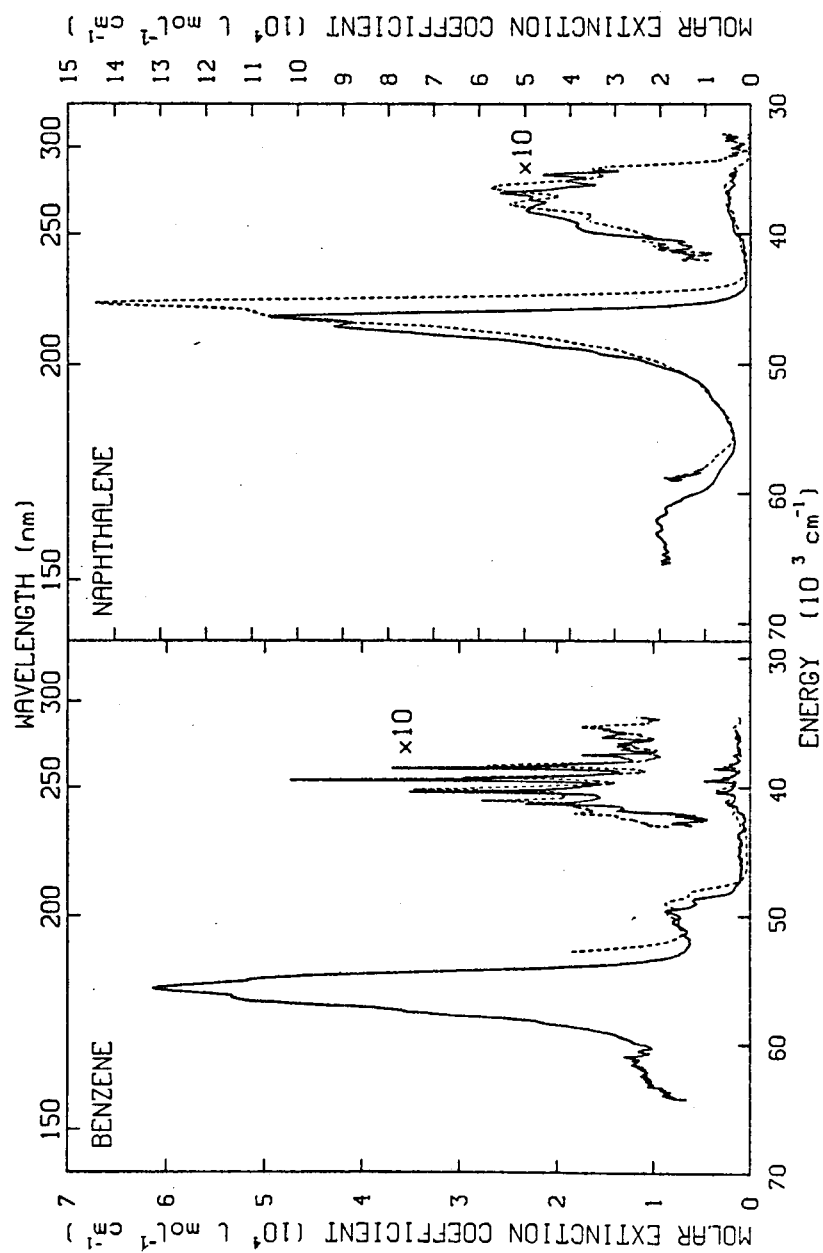


Fig. 6.1. Absorption spectra of benzene and naphthalene in PFn-H (solid lines) and n-P (dashed lines) solutions. The portions of the spectra corresponding to ${}^1B_{2u}$ state of benzene and ${}^1B_{1u}$ state of naphthalene are magnified by a factor of 10 for the convenience of the display. The spectra were normalized as indicated in Table 6.1.

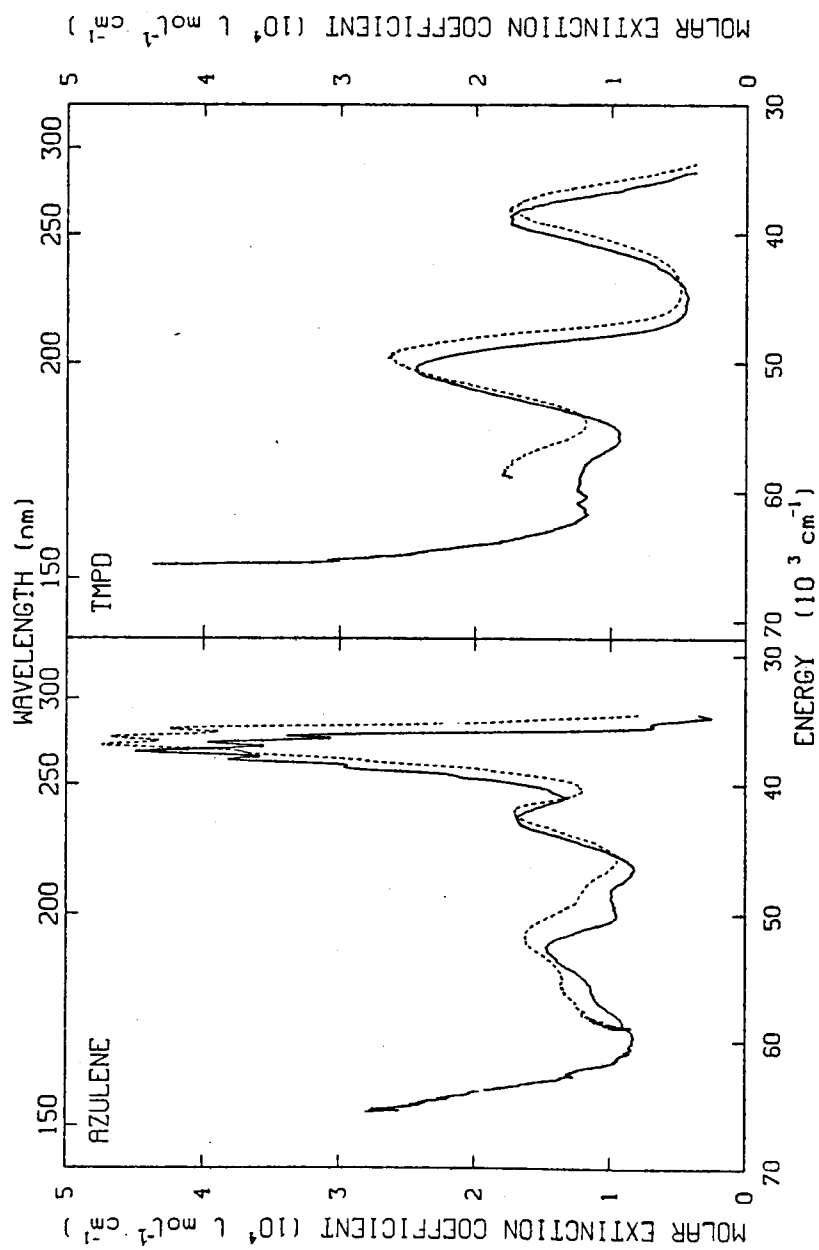


Fig. 6.2. Absorption spectra of azulene and N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD) in PFn-H (solid lines) and *n*-P (dashed lines) solutions. The spectra were normalized as indicated in Table 6.1.

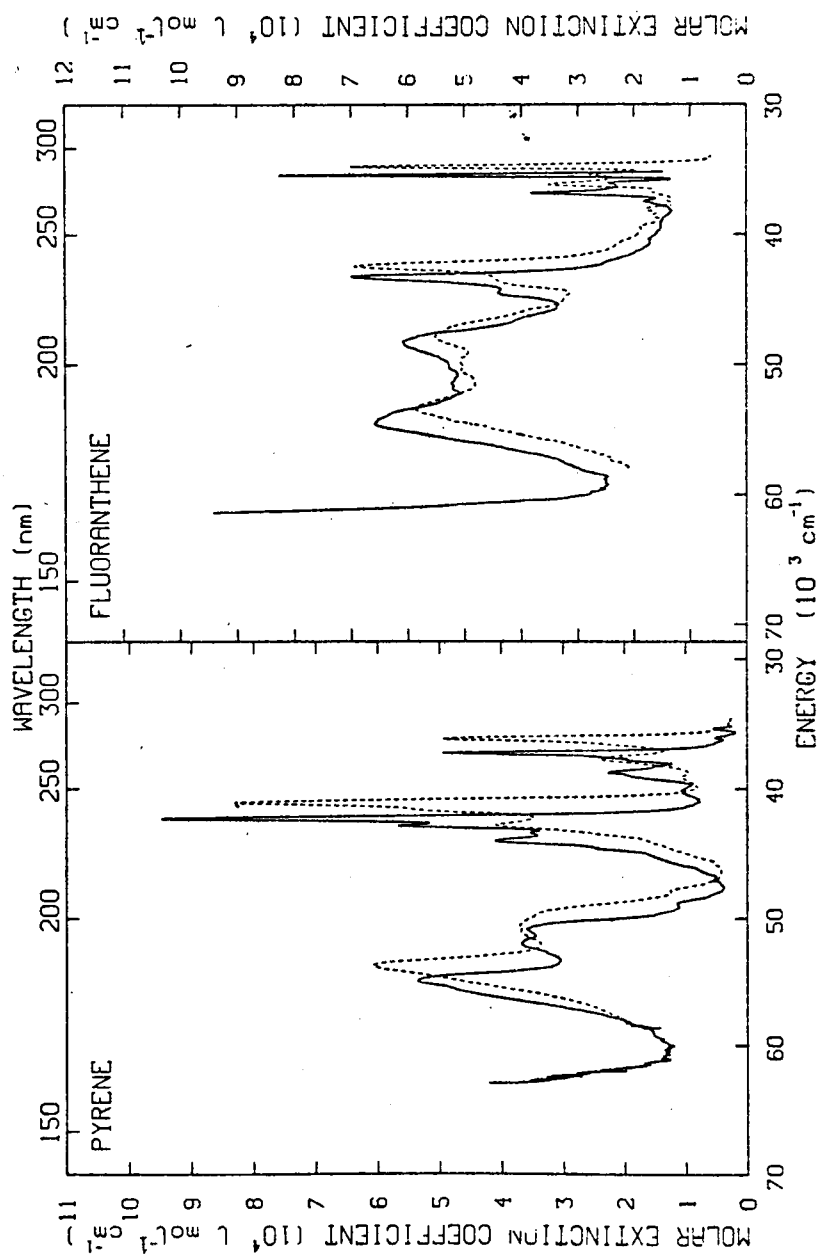


Fig. 6.3. Absorption spectra of pyrene and fluoroanthene in PFn-H (solid lines) and n-P (dashed lines) solutions. The spectra were normalized as indicated in Table 6.1.

Table 6.1. Energy and Respective Extinction Coefficient Values to Which the Present Absorption Spectra Were Normalized^a

Molecule	Normalization Energy (cm ⁻¹)	Extinction Coefficient (l mol cm ⁻¹)
Benzene	49000	8800 ^b
Naphthalene	36400	5600 ^b
Azulene	42100	17000 ^b
TMPD	37700	17600 ^c
Pyrene	36700	54000 ^b
Fluoranthene	42460	70000 ^d

^aThe spectra in PFn-H were normalized to the band maxima corresponding to the energies given in column 2.

^bUV-atlas of Organic Compounds, Vols. 1-5, Butterworths, London (1967-1971).

^cI. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, 2nd ed., Academic Press (1971).

^dJ. Michl, J. Mol. Spectrosc. 30, 66 (1969).

Table 6.2. Table 6.3 lists the observed absorption bands of the same molecules in n-P solution.

Figure 6.4 gives the transmission spectra of several commonly used hydrocarbon solvents and PFn-H. The measurements were performed with a cell of 150- μ m thickness for two cases: (1) The samples used were as supplied by the manufacturer (Fig. 6.4a). (2) The samples used were further purified as described in the experimental section (Fig. 6.4b). The improvement in the transmission properties after purification is evident. The PFn-H has excellent transmission properties (Dickinson and Johnson, 1971). The transmission spectrum of the sample used in the present measurements has a cut-off at ~ 152 nm and is 100% transparent at ~ 168 nm. The purified n-P has a cut-off at 170 nm and is 100% transparent at ~ 178 nm.

6.3 Discussion

In addition to the intrinsic value and practical utility (see Section 6.1) of the present results we wish to draw attention to the following general features of the spectra obtained: (1) The red shift of the solution spectra with respect to the gas phase spectra is larger for n-P than PFn-H. This can be understood from the fact that spectral shifts of nonpolar solutes in nonpolar solvents are related to the solvent refractive index, n , through the formula (Nicol, 1974)

$$\Delta\nu = A \frac{n^2 - 1}{2n^2 + 1} = Af(n), \quad (6.2)$$

where A is a quantity dependent to a first approximation on the properties of the solute molecule. The function $f(n)$ is always

Table 6.2. Positions of the Absorption Bands (in cm^{-1}) of Benzene, Naphthalene, Azulene, TMPD, Pyrene and Fluoranthene in PFn-H Solution.

Benzene	Naphthalene	Azulene	TMPD	Pyrene	Fluoranthene
37500 $\pm$ 50	35450 $\pm$ 50	35320 $\pm$ 80	38820 $\pm$ 400	37286 $\pm$ 42	35410 $\pm$ 50
38550 $\pm$ 50	35900 $\pm$ 50	36250 $\pm$ 50		37594 $\pm$ 142	36000 $\pm$ 50
39480 $\pm$ 50	36550 $\pm$ 100	36800 $\pm$ 50	50480 $\pm$ 400	37807 $\pm$ 144	36780 $\pm$ 50
40380 $\pm$ 50	36820 $\pm$ 50	37470 $\pm$ 50		38300 $\pm$ 140	37420 $\pm$ 80
41300 $\pm$ 50	37350 $\pm$ 100	38100 $\pm$ 50	59400 $\pm$ 600	38790 $\pm$ 45	
42250 $\pm$ 50	38200 $\pm$ 100	38680 $\pm$ 50		38900 $\pm$ 140	39000 $\pm$ 100
	39700 $\pm$ 150	39400 $\pm$ 100		40209 $\pm$ 49	
		40500 $\pm$ 150			40320 $\pm$ 200
48750 $\pm$ 80	46330 $\pm$ 50			42283 $\pm$ 54	42180 $\pm$ 200
49580 $\pm$ 50	47080 $\pm$ 50	42600 $\pm$ 150		42882 $\pm$ 55	
50400 $\pm$ 80	47320 $\pm$ 100	48200 $\pm$ 200		43384 $\pm$ 57	43220 $\pm$ 100
51400 $\pm$ 100	47585 $\pm$ 100			44014 $\pm$ 58	44430 $\pm$ 180
		52500 $\pm$ 150		44603 $\pm$ 100	45520 $\pm$ 200
55050 $\pm$ 100	48600 $\pm$ 150	56300 $\pm$ 200		45455 $\pm$ 207	
55650 $\pm$ 50	49200 $\pm$ 150	58800 $\pm$ 200		46296 $\pm$ 108	46620 $\pm$ 300
56380 $\pm$ 80	19800 $\pm$ 200	62600 $\pm$ 150		47059 $\pm$ 67	47850 $\pm$ 300
57400 $\pm$ 100				48123 $\pm$ 116	
58220 $\pm$ 150	52500 $\pm$ 200				48200 $\pm$ 200
59800 $\pm$ 150	54200 $\pm$ 300			48780 $\pm$ 72	50200 $\pm$ 300
	58300 $\pm$ 300			50761 $\pm$ 78	51600 $\pm$ 300
				51876 $\pm$ 81	54480 $\pm$ 200
	60420 $\pm$ 200			54855 $\pm$ 90	57380 $\pm$ 400
	61100 $\pm$ 200			55380 $\pm$ 150	
	62040 $\pm$ 200			58000 $\pm$ 200	
				59100 $\pm$ 200	
	64120 $\pm$ 200				
	64680 $\pm$ 200				
	65200 $\pm$ 200				

Table 6.3. Positions of the Absorption Bands (in cm^{-1}) of Benzene, Naphthalene, Azulene, TMPD, Pyrene and Fluoranthene in n-Pentane Solution.

Benzene	Naphthalene	Azulene	TMPD	Pyrene	Fluoranthene
37300 $\pm$ 100	34980 $\pm$ 50	35720 $\pm$ 50	38010 $\pm$ 400	36697 $\pm$ 40	34720 $\pm$ 50
38300 $\pm$ 50	35250 $\pm$ 50	36390 $\pm$ 50			35350 $\pm$ 50
39210 $\pm$ 50		36990 $\pm$ 50	49530 $\pm$ 400	38241 $\pm$ 45	36120 $\pm$ 50
40200 $\pm$ 50	36400 $\pm$ 100	37500 $\pm$ 100			36742 $\pm$ 80
41080 $\pm$ 50		38180 $\pm$ 100	58400 $\pm$ 600	39700 $\pm$ 48	37390 $\pm$ 80
42050 $\pm$ 50	37700 $\pm$ 100	38870 $\pm$ 100			38105 $\pm$ 80
	38950 $\pm$ 150			41580 $\pm$ 52	38531 $\pm$ 80
		42000 $\pm$ 150		42070 $\pm$ 180	39500 $\pm$ 100
48230 $\pm$ 80	45290 $\pm$ 50	48200 $\pm$ 200		42500 $\pm$ 180	40684 $\pm$ 130
49000 $\pm$ 50	46100 $\pm$ 200			43197 $\pm$ 50	41205 $\pm$ 100
49800 $\pm$ 80		51700 $\pm$ 200		43769 $\pm$ 190	42474 $\pm$ 50
50700 $\pm$ 100	48400 $\pm$ 200	55400 $\pm$ 200		44635 $\pm$ 200	43450 $\pm$ 400
	49200 $\pm$ 300	57100 $\pm$ 200			44705 $\pm$ 80
	52700 $\pm$ 300			47619 $\pm$ 220	45400 $\pm$ 130
	57300 $\pm$ 300			47619 $\pm$ 220	45842 $\pm$ 130
					46980 $\pm$ 200
					47300 $\pm$ 400
				48309 $\pm$ 70	47800 $\pm$ 200
				50505 $\pm$ 225	49600 $\pm$ 400
				53850 $\pm$ 87	50400 $\pm$ 400
					53400 $\pm$ 200

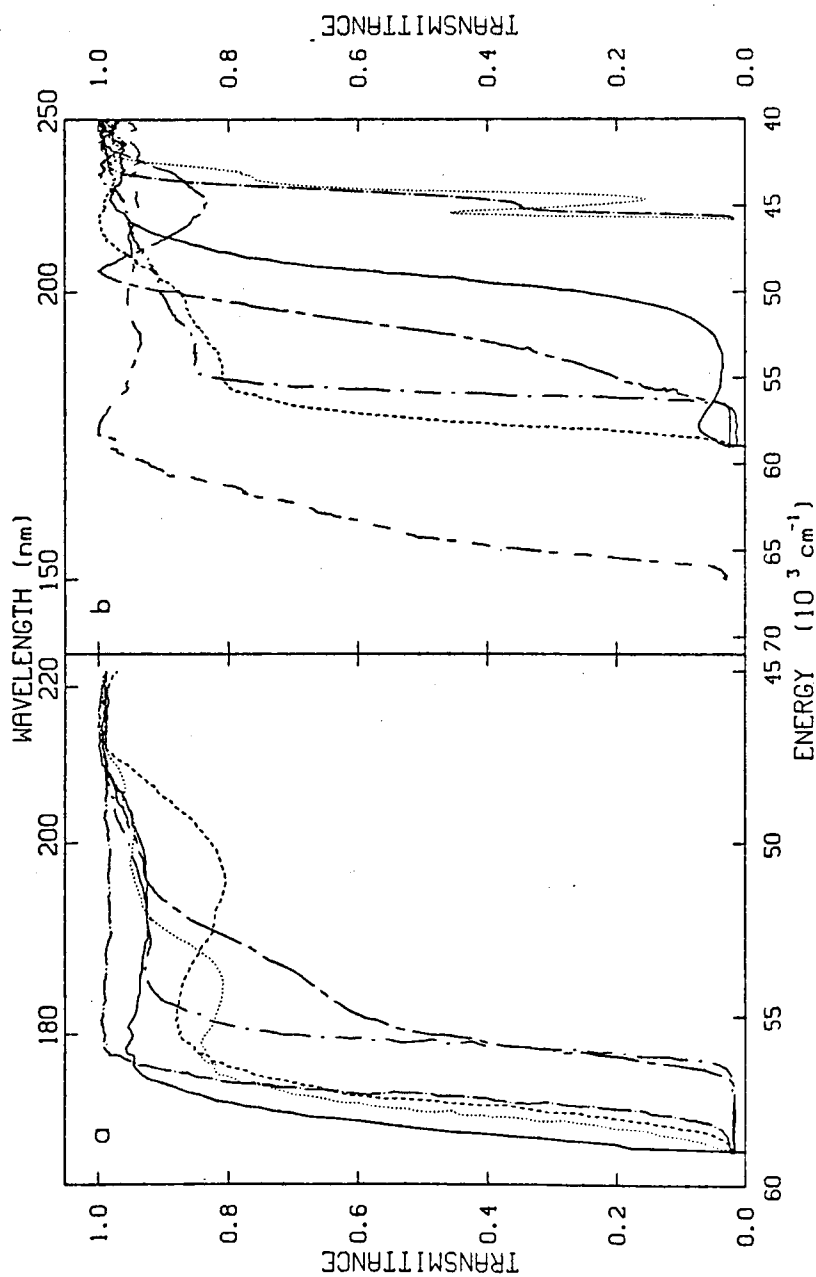


Fig. 6.4. (a) Transmission spectra of n-pentane (—), n-hexane (···), n-heptane (---), isopentane (-·-·-), neohexane (— — —), and cyclohexane (- - -) purified as described in the experimental section. (b) The transmission spectra of the above solvents and of PFn-hexane (— — —) as supplied. In both cases the transmittance was measured using the cell of $150 \mu\text{m}$ thickness.

increasing with n , and since the refractive index of n -P is larger than that of PFn-H (see Table 6.4), the value of $f(n)$ is larger for n -P than for PFn-H. In Table 6.4 the spectral shifts of the B_{1u} and B_{2u} states of naphthalene in solution relative to the gas phase are listed and the quantity A for each state is determined. In Table 6.5 the spectral shifts of the B_{1u} state of benzene are compared with the shifts calculated from the empirical relation

$$\Delta\nu = 500-3500 \frac{n^2 - 1}{2n^2 + 1} \text{ (cm}^{-1}\text{)}, \quad (6.3)$$

suggested by Sverdlova (1963) for the spectral shifts of this state of benzene. The experimental and the calculated shifts are in good agreement. For the rest of the molecules similar studies are not possible because, to the best of our knowledge, no optical gaseous-phase absorption spectra exist in this region.

(2) The absorption spectra of the molecules studied exhibit more structure in PFn-H than in n -P, for the whole energy region investigated. There is an overall trend in the PFn-H spectra indicating that the sharpness of the solute spectra in PFn-H decreases as the energy increases. At lower energies, the spectra in PFn-H appear more resolved than in n -P and are similar in structure with the corresponding gas-phase spectra as could be verified by comparison [e.g. benzene (Pantos and coworkers, 1978), naphthalene (Koch and coworkers, 1972) and azulene (Weigang, 1960)]. At higher energies, spectral characteristics such as structure and bandwidth become increasingly closer to the corresponding ones in n -P. This spectral

Table 6.4. Experimental Values of the Spectral Shifts, $\Delta\nu$ (in cm^{-1}), of the ${}^1\text{B}_{1u}$ and ${}^1\text{B}_{2u}$ States of Naphthalene in PFn-H and n-P

State	Gas Phase ^a		PFn-H		n-P		
	ν	ν	$\Delta\nu$	A^b cm^{-1}	ν	$\Delta\nu$	AC cm^{-1}
${}^1\text{B}_{1u}$	35910	35450 ± 50	460	3171 ± 344	34980 ± 50	930	4885 ± 262
	35440	35900 ± 50	540	3723 ± 344	35250 ± 50	1190	6245 ± 262
	37311	36820 ± 100	491	3385 ± 689	36400 ± 100	911	4759 ± 522
	38867	38200 ± 50	667	4598 ± 344	37700 ± 100	1167	6064 ± 572
	40240	39700 ± 150	540	3723 ± 1034	38950 ± 150	1290	6667 ± 775
${}^1\text{B}_{2u}$	47507	46330 ± 50	1177	8115 ± 394	45290 ± 50	2217	11116 ± 262

^a E. E. Koch, A. Otto and K. Radler, Chem. Phys. Letts. 16, 131 (1972).

^b A was calculated using for PFn-H $n_{250} = 1.27$ [it has been assumed that $n_{250}(\text{PFn-H}) \sim n_{250}(\text{PFn} - \text{heptane}) = 1.27$ (O. V. Sverdlova, Opt. Spectry 6, 223 (1959)) since both compounds have similar optical properties.

^c A was calculated using different values of $n(\text{n-P})$ obtained from the extrapolation procedure according to T. L. Lauer, J. Chem. Phys. 16, 612, (1948).

Table 6.5. Spectral Shifts, $\Delta\nu$, and A Values (in cm^{-1}) of the ${}^1\text{B}_{2u}$ State of Benzene in PFn-H and n-P.

Solution					
PFn-H			n-P		
$\Delta\nu^b$		A	$\Delta\nu^c$	A	
Experimental	Theoretical ^d	Theoretical	Experimental	Theoretical ^d	Theoretical
38580	30 ± 50	(-) 8	250 ± 50	(-) 175	1296
39546	84 ± 50	(-) 8	354 ± 50	(-) 178	1228
40437	57 ± 50	(-) 8	237 ± 50	(-) 181	1218
41350	50 ± 50	(-) 8	270 ± 50	(-) 184	1382
42298	48 ± 50	(-) 8	248 ± 50	(-) 187	1264

^aE. Paatos, J. Phillis and A. Bolovinos, J. Mol. Spectrosc. 72, 36 (1978)

^b $\Delta\nu$ was calculated according to Eq. (6.3) with refractive index n obtained in footnote b, Table 6.8.

^c $\Delta\nu$ was calculated according to Eq. (6.3). The refractive index, n, of n-Pt was obtained according to J. L. Lauer, J. Chem. Phys. 16, 612 (1948).

^dNegative calculated values indicate red shifts.

behaviour in PF_n-H might be explained by the fact that PF_n-H is a non-polar low-polarizability⁺ molecule and thus introduces a small perturbation, especially on the lower excited states of the solute. The effectiveness of this perturbation on the solute states is also reflected in the efficiency of the internal conversion processes. Thus, it was found (Lawson and coworkers, 1969) that the internal S₃ → S₁ conversion efficiency of benzene in PF_n-H is much smaller (~0.04) than in n-hexane[#] (~0.25). For higher energies, other than dispersive interactions may come into play.

(3) It has been always a problem to distinguish core from Rydberg excitations in gaseous molecular spectra frequently encountered in the VUV spectral region. Rydberg transitions are much more sensitive to external perturbation than core transitions (Robin, 1974) thus providing a way of distinguishing them. By putting the absorber in a condensed phase of low electronic mobility, the core bands will be slightly broadened and shifted to the red, whereas Rydberg bands will be strongly shifted to the blue and so broadened as to become unobservable (Vaida and coworkers, 1978 and references therein). Thus, the "disappearance" of a prominent gas-phase band in a solution spectrum is sufficient evidence for assigning it as a Rydberg transition. The PF_n-H, having low electronic mobility, because of its strong electron

⁺The polarizability α is related to the index of refraction n and the molecular radius r according to $\alpha = r^3 \frac{n^2 - 1}{n^2 + 2}$ (Bakhshiev, 1961); for

$r_{n-P} \sim r_{PF_n-H}$, $\alpha_{n-P}/\alpha_{PF_n-H} \sim 1.4$

[#]One expects similar results for n-P.

attaching properties and transmitting in the VUV region up to 66000 cm^{-1} (in a 150- μm thick cell, see Fig. 6.4b) which is the Rydberg transition region of the molecules under study, is well suited as solvent to study the Rydberg transition region. In this regard the present absorption spectra in PFn-H can be helpful for the classification of the molecular states in this region. Thus, the first Rydberg transition of benzene in the gas phase appears at 57000 cm^{-1} (Robin, 1974) and the corresponding state in PFn-H is absent.

For naphthalene the situation is more complex; there is still a controversy concerning the assignment of the states in the 54000-66000 cm^{-1} region (Koch and coworkers, 1972; Angus and coworkers, 1968), for this molecule. The difficulty lies in separating the Rydberg from the underlying core transitions. The states appearing in the naphthalene spectrum in PFn-H in this region may all be ascribed to core excitations. In Table 6.6 the bands appearing in PFn-H solution are compared with the gas-phase bands assigned to $\pi-\pi^*$ transitions (Angus and coworkers, 1968). Considering the red shifts of the transitions in solution with respect to the gas phase we see that there is a one-to-one correspondence between the solution and gas-phase $\pi-\pi^*$ excitations except for the state at 63230 cm^{-1} which is probably not resolved in the solution spectrum. This confirms the assignment of the $\pi - \pi^*$ excitations in the Rydberg region of the naphthalene spectrum as given by Angus and coworkers (1968). Also in Table 6.6 the bands of azulene appearing in PFn-H solution and in the gas-phase spectrum (Bouler and coworkers, 1979) in the energy region 45000 - 64000 cm^{-1} are listed. In the energy range 48000 to ~56000

Table 6.6. Positions of the Gas-Phase and PFn-H Solution Bands (in cm^{-1}) of Naphthalene and Azulene in Their Rydberg Region.

Naphthalene		Azulene	
Gas-phase ^a	in PFn-H solution ^b	Gas-phase ^c	In PFn-H solution ^b
61890 $\pm$ 40	60420 $\pm$ 200	46664 ^d	
62350 $\pm$ 10	61100 $\pm$ 200	48355 ^d	
63060 $\pm$ 20	62040 $\pm$ 200	49180	
63230 $\pm$ 30		49586	48200 $\pm$ 200
66450 $\pm$ 40	64120 $\pm$ 200	51483	
66870 $\pm$ 50	64680 $\pm$ 200	52174	
67250 $\pm$ 50	65200 $\pm$ 200		
		52356 ^d	52500 $\pm$ 150
		53260 ^d	
		54054	
		54830	
		55249 ^d	
		55555 ^d	
		56657 ^d	56300 $\pm$ 200
		57555 ^d	
		57554 ^d	
		58015 ^d	
		58395 ^d	
		63276	58800 $\pm$ 200

^a π - π^* transitions according to J. G. Angus, B. J. Christ, and G. C. Morris, Aust. J. Chem. 21, 2153, (1968).

^bPresent work.

^cD. Boulter, W. S. Felps, J. Lewis, R. V. Namman and S. P. McGlynn, Chem. Phys. Lett. 67, 420 (1979).

¹Rydberg transitions according to reference given at c above.

cm^{-1} theoretical calculation predict five $\pi-\pi^*$ transitions (Pariser, 1956). However, on degeneracy and intensity grounds, probably only three at energies 49930, 55387 and 56605 cm^{-1} can be resolvable. These bands may correspond to the three observed bands in PFn-H solution in this energy range. The first of them at 48200 cm^{-1} corresponds to the gas-phase band starting at 49180 cm^{-1} confirming its assignment as of intravalence character (Bouler and coworkers, 1979). The second at 52500 cm^{-1} corresponds to a $\pi-\pi^*$ transition which in the gas-phase spectrum extends from ~ 52000 to $\sim 55000 \text{ cm}^{-1}$ and includes several bands assigned to core transitions (Bouler and coworkers, 1979). The gas-phase band at 51483 cm^{-1} , assigned to a $\pi-\pi^*$ (Bouler and coworkers, 1979; Clark, 1966) or to a Rydberg (Kitagawa and coworkers, 1966) transition, does not appear in the solution spectrum suggesting that it is of Rydberg character. Finally, the solution band at 58800 cm^{-1} corresponds to the broad gas-phase band starting at $\sim 60000 \text{ cm}^{-1}$.

CHAPTER 7

SUMMARY AND CONCLUSIONS

The photoionization of molecules in dielectric liquids has been studied with two methods, the integrated fluorescence technique and the two-photon ionization technique. The photoionization thresholds of a number of molecules in a number of dielectric liquids have been determined with the integrated fluorescence technique, from the decline in the fluorescence intensity of the solute molecule for energies $>I_L^1$ in the presence of an electron-attaching additive, and with the two-photon ionization technique, from the onset of conductivity in solution for energies higher than the solute ionization threshold I_L^1 . The two methods gave complementary results which have been rationalized in terms of the time evolution and the different mechanisms involved in the photoionization process.

Integrated fluorescence excitation spectra of pyrene, TMPD, and fluoranthene in dielectric liquid solutions in the presence of an efficient electron-attaching additive, A, of concentration in the range of 0.25 - 1.50 mol ℓ^{-1} were used to determine the photoionization thresholds of the above molecules. The I_L^1 were found to be 5.48 eV for pyrene and 5.57 eV for fluoranthene for all cyclic A's (c-C₇F₁₄, c-C₆F₁₂, c-C₈F₁₈) and 5.88 eV for pyrene and 5.97 eV for fluoranthene for the non-cyclic A(PFn-H). The so obtained I_L^1 were independent both of the concentration of A and the solvent used. The threshold of TMPD ionization was determined with the same technique in n-hexane using PFn-H as electron attaching additive and was found to be 5.02 eV. On

the basis of these data it was concluded that in the presence of an efficient electron attaching additive at high concentration, the photoejected electron is captured by A at times $\langle\tau_{\text{cap}}\rangle(\sim 10^{-14}\text{s})$ shorter than the time $\langle\tau_{\text{solv}}\rangle(\sim 10^{-12}\text{s})$ required for it to reach its solvated state, which is associated with the V_0 value of the particular liquid and I_L^1 should then be independent of V_0 .

It was also concluded that in these cases I_L^1 is related to I_G^1 by $I_L^1 = I_G^1 + S(M^+, A^-)$ where $S(M^+, A^-)$ represents the solvation energy of the created positive-negative ion pair (M^+ , A^-).

The value of I_L^1 of pyrene and fluoranthene for PFn-H was higher by ~ 0.40 eV compared to its value for the c-C₇F₁₄, c-C₆F₁₂ and c-C₈F₁₆. This was attributed to the fact that the cyclic perfluorocarbons attach electrons having thermal and near thermal energies much more efficiently than does PFn-H which attaches more efficiently electrons with higher energies.

This study shows that the photoionization threshold for a given molecule, M, is both a function of the electron attaching properties of A and the time evolution of the photoionization and electron capture processes.

In the TPI technique the photo-ejected electron is relaxed in the liquid and the energetics of the photoionization is influenced from this relaxation. The I_L^1 values for TMPD and fluoranthene were found to be 3.88 ± 0.05 and 4.50 ± 0.05 eV respectively (i.e. 2.32 and 3.22 eV lower than the corresponding gas-phase ionization potentials). These differences are much larger than those inferred from other data on photoionization of molecules in non-polar liquids (Holroyd, 1972;

Bulot and Guathier, 1977; Bernas and coworkers, 1975). These differences are difficult to rationalize by the P^+ and V_0 values in Eq. (3.7)

$$I_L^1 = I_G^1 + P^+ + V_0$$

as these quantities used to be calculated or estimated (Grand and Bernas, 1977; Bernas and coworkers, 1980). The TPI spectra obtained with this technique apart from providing the I_L^1 values contained important information concerning other molecular properties in liquids. In the case of TMPD the positions of two-photon allowed transitions were revealed (Table 4.1). For fluoranthene the positions of the transitions were determined (Tables 4.2, 4.3) and also a dissociation process was revealed taking place from the vibrational progression of the first excited electronic state, $S_{1,n}$ for energies > 3.39 eV.

Basic questions relating to the understanding of the energetics of the photoionization in liquids remain unanswered. Time resolved studies in the subpicosecond region may answer some of the questions on the dynamics of the photoionization, solvation and electron capture processes. These processes are crucial in the understanding of the energetics of the photoionization process in liquids. In this respect work is needed to evaluate P^+ and elucidate the meaning of V_0 in both non-polar and polar liquids. Finally the threshold behavior of the photoionization yield could provide threshold laws important for the understanding of the dynamics of the photoionization process in liquids.

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