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MULTIPHOTON IONIZATION AND TWO-PHOTON EXCITATION
OF AROMATIC MOLECULES IN LIQUIDS

A Dissertation
Presented for the
Doctor of Philosophy
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ABSTRACT

The two-photon excitation of benzene and toluene in a number of different nonpolar liquids (n-pentane, tetramethylsilane, perfluoro-n-hexane, perfluoromethylcyclohexane, and perfluorodimethylcyclobutane) was studied over the 360-560 nm laser excitation wavelength range. The effect of the solvent on the upper excited states was investigated and a peak, observed in the two-photon excitation spectra of benzene, was assigned to the $(3s)^1E_{1g}$ Rydberg state based on the unusual solvent dependence of its relative intensity and spectral shift. Polarization studies and signal vs. laser intensity measurements were also carried out.

Vibrational analyses of the entire range of the $^1B_{2u}$ state of benzene and of the 1B_2 state of toluene, including the hot bands, were performed based on the spectra measured in perfluoro-n-hexane. The 0-0 transitions of these states in perfluoro-n-hexane and n-pentane were observed at 38050 cm^{-1} and 37853 cm^{-1} for benzene and at 37411 cm^{-1} and 37220 cm^{-1} for toluene, respectively.

The two-photon excitation spectrum of fluoranthene in a solution of n-pentane over the 420-860 nm laser excitation range was also measured. The 0-0 transition of the first singlet state was observed at 24800 cm^{-1} , resolving thus the ambiguity about the exact position of that state.

The multiphoton ionization of benzene in dilute solutions of n-pentane and tetramethylsilane was also studied, over the 360-570 nm laser excitation range. Polarization studies and signal vs. laser

intensity measurements were performed and the dependence of the spectral features and of the polarization ratio on the laser intensity was studied.

The multiphoton ionization mechanism, the location of the ionization threshold of benzene in n-pentane and in tetramethylsilane and the effect of the medium on the ionization threshold are discussed. A particular ionization behavior was observed in a wavelength region corresponding to the channel 3 relaxation which resulted in a dependence of the apparent order of the ionization process on the laser intensity.

The ionization threshold of benzene in n-pentane and tetramethylsilane, based on the results of the signal vs. intensity measurements, was estimated to lie between 7.35 and 6.8 eV and 6.6 and 5.9 eV, respectively.

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CHAPTER I

INTRODUCTION

1.1. General Considerations

Optical spectroscopy provides some of the most fundamental ways of probing the structure of atoms and molecules. Using frequency tunable sources of monochromatic light, physical quantities such as the oscillator strengths and the lifetimes of excited states, and other properties, as for example, the symmetry selection rules and the polarization dependence of the transition probabilities were measured in the past by optical techniques. These optical techniques are now called "linear optics" or "one-photon" spectroscopy because one photon at a time is interacting with the system under study.

It is possible, however, to have two (or more) photons interacting simultaneously with an atom or a molecule. Thus the simultaneous absorption of two photons (TPA) is a special case in a large class of events, called multiphoton processes, which among others includes stimulated two-photon emission and the well-known Raman scattering.

The first detailed theoretical analysis of TPA, based on time-dependent perturbation theory, was given by Maria Goeppert-Mayer in 1931. The probability of TPA is so low that such an event is practically beyond observation with the light intensities attainable by the usual thermal sources. Since, however, the transition rate is

proportional to the fourth power of the electric field amplitude, TPA will be significant and observable at extremely high photon fluxes. The experimental demonstration of such a process therefore had to await for almost 30 years (Kaiser and Garret, 1961) until the invention of the laser.

By the mid 1970s high intensity, narrow bandwidth, frequency tunable dye lasers were already commercially available and two-photon or generally multiphoton spectroscopy was becoming increasingly popular. It was not, however, just the availability of the lasers, but also certain inherent advantages and characteristics of the multiphoton spectroscopy, that facilitated its rapid growth. The most fundamental of these are:

(a) Selection Rules

Dipole transition selection rules allow one-photon excitation to reach only a limited subset of the possible eigenstates of a system. The different selection rules for multiphoton excitation make a much larger set of states accessible, including most of the states that were "hidden" to one-photon methods (Mahr, 1975). For example, the parity selection rules are reversed in the two-photon case, as compared to the one-photon case, for molecules that possess a center of inversion such as benzene (McClain and Harris, 1977); i.e., for centrosymmetric molecules, one-photon allowed transitions are two-photon forbidden and vice versa. For molecules without a center of symmetry both one- and two-photon transitions can in principle reach the same states, although the intensity distributions for the two kinds of transitions may be different.

(b) Transmission Cut-Off

It is well known that molecular absorption coefficients for the higher excited states are usually large (UV-Atlas, 1966). It is also known that most hydrocarbon solvents exhibit a transmission cut-off at wavelengths below ~ 200 nm (Kourouklis et al., 1982; Scott and Albrecht, 1982). A major difficulty, therefore, when studying the condensed matter (solids, liquids) is the strong absorption in the UV spectral region at energies above the first excited singlet state (S_1) of either the molecule under study or the host medium. Absorption cross sections at energies exceeding S_1 are generally a significant fraction ($\sim 1/10$) of the cross sectional area of the molecule. As a result, light penetrates only a few molecular layers and only the "skin" of the bulk matter is probed. Since, however, the two-photon absorption cross sections are extremely small ($\sigma \approx 10^{-50}$ cm⁴·s) (Ito and Mikami, 1980), the material is transparent at half the energy (provided that the photon energy is below S_1) and therefore this limitation is circumvented in two-photon techniques.

(c) Polarization Studies

One-photon polarization studies for randomly tumbling molecules (gases, liquids) are impossible, since the transition cross section is proportional to the average over all possible directions of the polarization vector, and any polarization dependence averages out to zero. On the contrary, a two-photon process is described by an absorption tensor whose elements depend on the symmetry of the molecule and the symmetry of the initial and the final state of the transition

(Monson and McClain, 1970; McClain, 1971). The orientation average of this tensor is generally nonzero and depends on the relative polarization of the two photons. According to McClain and Harris (1977) a set of any three independent polarization experiments allows the determination of all molecular polarization parameters and a unique identification of the symmetry of the states involved in the transition.

These characteristic properties of multiphoton spectroscopy have attracted a great deal of attention over the last ten years, so that today multiphoton spectroscopy is approaching a level of relative maturity. The numerous review articles and books (Mahr, 1975; McClain and Harris, 1977; Letockov and Chebotayev, 1977; Braünlich, 1978; Mainfray and Manus, 1978; Friedrich and McClain, 1980; Ito and Mikami, 1980; Lin et al., 1984), which contain detailed discussions of the principles and the experimental techniques of multiphoton spectroscopy, attest to that.

The object of the present work is multiphoton spectroscopy of aromatic molecules in dilute solutions of nonpolar liquids. More specifically the properties of multiphoton ionization (MPI) of benzene in n-pentane (n-Pt) and tetramethylsilane (TMSi) were studied and the two-photon resonant multiphoton ionization spectra were measured for laser excitation wavelengths (λ_{exc}) lying in the 360-570 nm spectral range. The two-photon excitation (TPE) spectra of benzene and toluene in n-Pt, TMSi and a number of perfluorocarbons [perfluoro-n-hexane ($\text{n-C}_6\text{F}_{14}$), perfluoromethylcyclohexane ($\text{c-C}_7\text{F}_{14}$) and

perfluorodimethylcyclobutane (C_6F_{12}) were also measured over the same wavelength regions. Finally, the TPE spectrum of fluoranthene in n-Pt for $420 \text{ nm} \leq \lambda_{\text{exc}} \leq 860 \text{ nm}$ was measured as well.

In the following sections we shall briefly discuss the basic experimental techniques of multiphoton absorption and present a summary of the available knowledge relevant to this work, as well as similar studies performed using multiphoton absorption techniques. The emphasis will be on room temperature, liquid phase, multiphoton investigations.

1.2. Experimental Methods

1.2.1. Introduction

Generally, one detects experimentally the creation of an excited species (molecule) by monitoring either the final products of the excitation process or the way the molecule reverts back to the ground state. One can classify, therefore, broadly the multiphoton techniques according to the major (deexcitation) pathway that they monitor into:

- a. Ionization techniques, if charged species (electrons, ions) are created and measured.
- b. Fluorescence techniques, if the molecule returns radiatively back to the ground state and the emitted photons are measured.
- c. Nonradiative techniques, if the dissipation of photon energy into heat or shock waves is monitored.

1.2.2. Multiphoton Ionization (MPI)

The charges that are created, following the absorption of a number (n) of photons by the molecule, are swept by an applied electric field, and the current vs. photon energy represents the ionization spectrum. Briefly, the process can be described by one of the mechanisms shown schematically in Figure 1.1. Case (a) represents the direct n -photon nonresonant ionization. Case (b) is the m -photon resonant, n -photon ionization process ($m < n$), while (c) represents a particular case when $m = n$ and the resonant state lies in the ionization continuum (autoionizing state). Case (d) is also m -photon resonant but unlike case b the ionization proceeds via a lower lying, usually long-lived, state S' (i.e., triplet, excimeric or first excited singlet state). In this context, long-lived is any state that has a longer lifetime than the originally prepared state and the laser pulse duration (~ 10 ns). Of course, an efficient and fast (within the laser pulse duration) relaxation mechanism is assumed to couple the two states together.

Multiphoton ionization (Bakos, 1974; Johnson, 1980; Scott and Albrecht, 1982; Parker, 1983; Chin and Lambropoulos, 1984) has proven to be a sensitive technique both in the gas (Boesl et al., 1981) and the liquid phase (Christophorou and Siomos, 1984), which in addition to allowing a direct estimate of the ionization threshold, provides valuable spectroscopical data, especially for non- or weakly-fluorescing molecules.

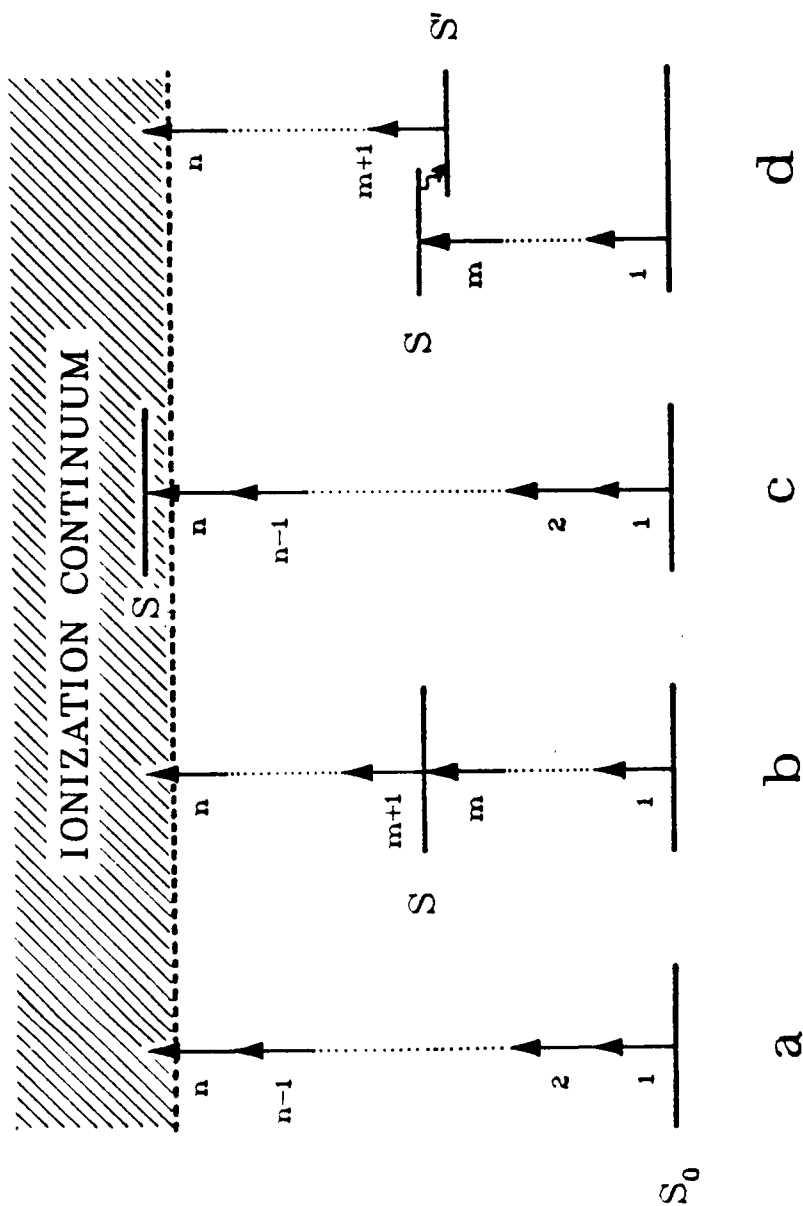


Figure 1.1. Different ionization pathways. (a) Direct n-photon ionization, (b) m-photon resonant, n-photon ionization, (c) n-photon ionization via a resonant autoionizing state, (d) m-photon resonant, n-photon ionization via a lower lying state S' . Only cases (a) and (c) represent real coherent n-photon events.

A critical and not always straightforward task, especially in the liquid phase, is the determination of the mechanism and the establishment of the order of the ionization process (number n of photons absorbed). Also important is the assignment of the observed structure in the spectrum to specific energy levels, which is complicated by the fact that any of the sequentially absorbed photons might be in resonance. In other words (see Figure 1.1), it is important to determine n , m and distinguish between cases (b) and (d). The difference between cases (a) and (c) on one hand and (b) and (d) on the other should also be stressed. The former are coherent n -photon processes entailing simultaneous absorption of these photons, while the latter are m -photon resonant ($m < n$) and can be considered as two-step processes. They will be therefore characterized by different multiphotonic transition rules.

The n -photon transition probability ($\sigma^{(n)}$) is expressed in units of $\text{cm}^{2n} \cdot \text{s}^{-n-1}$, so that the product $\sigma^{(n)} \cdot I^n$ (where I is the laser intensity in $\text{photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) is the n -photon transition rate constant per molecule. Then the ionization signal (S_I), defined as the number of charge carriers produced and measured per pulse, will be given by:

$$S_I = A \int_t N_0 \cdot \sigma^{(n)} \cdot I^n(t) dt \quad (1.2.1)$$

where A is a constant including the yield for charge carrier (ion-electron pairs) production following ionization and other instrumental

constants, and N_0 is the number of ground state molecules in the interaction volume. Assuming a square laser pulse of duration τ and that N_0 does not change significantly during the laser pulse, Equation 1.2.1 becomes:

$$S_I = (A N_0 \tau) \cdot \sigma^{(n)} \cdot I^n \quad (1.2.2a)$$

or

$$S_I = C \cdot I^n \quad (1.2.2b)$$

1.2.3. Two-Photon Excitation (TPE)

In this technique, two photons are used to excite the molecule and the total fluorescence intensity emitted is monitored as a function of the excitation energy. The fluorescence signal (S_F) by analogy to Equation 1.2.2a will be:

$$S_F = (A N_0 \tau) \cdot \beta \cdot \delta \cdot I^2 \quad (1.2.3a)$$

or as a function of the excitation wavelength λ_{exc}

$$S_F = (A N_0 \tau) \cdot \beta(\lambda_{exc}) \cdot \delta(\lambda_{exc}) \cdot I^2(\lambda_{exc}) \quad (1.2.3b)$$

where A is an instrumental constant including the efficiency of the collecting optics, the filters and the photomultiplier, $\beta(\lambda_{exc})$ and $\delta(\lambda_{exc})$ are the fluorescence quantum yield and the two-photon transition probability ($\sigma^{(2)} \equiv \delta$), respectively, as a function of wavelength and all other symbols are as defined in Equation 1.2.1. Assuming a constant or a slowly varying fluorescence quantum yield

($\beta(\lambda_{\text{exc}})$) with excitation wavelength, and for relatively low concentrations ($<10^{-2}$ M), the TPE spectrum will correspond to the relative TPA cross section ($\delta(\lambda_{\text{exc}})$), after correcting for variations of the laser intensity.

Two-photon excitation can be a very sensitive technique for strongly fluorescing molecules, that allows complete polarization studies (Lombardi et al., 1976). In addition to this, TPE offers a double discrimination against impurity molecules; not only in terms of the excitation energy, but also through the emission wavelength (fluorescence). It has the advantage, therefore, over other methods (i.e., MPI) that it is less prone to impurity interference. It is limited, however, by the fact that for higher-lying vibronic levels and electronic states, nonradiative relaxation becomes increasingly important and the fluorescence yield declines significantly. Moreover, TPE cannot reach states lying close to (or exceeding) twice the energy of the fluorescence emission because of strong interference in the signal, from laser scattered light and/or one-photon fluorescence. A review of one- and two-photon laser excitation spectroscopy with emphasis on the experimental aspects of the technique is given by Birge (1983).

1.2.4. Optoacoustic (OA) and Thermal Lensing (TL) Spectroscopy

These techniques monitor the effects of the heat produced by the nonradiative transitions following excitation of the molecules.

Sensitive microphones embedded in the medium under study or coupled to the walls of the cell containing the sample, measure the pressure

waves generated in the medium by the absorption of a pulsed light beam in OA spectroscopy (Tam and Patel, 1979; Tam, 1983). The thermal lensing technique utilizes the fact that the index of refraction depends on temperature. As a result of this, the medium at the focus of a Gaussian beam behaves like a, usually diverging, lens and the divergence induced on a second weak colinearly propagating probing beam, provides the thermal lensing signal (Twarowski and Kliger, 1977; Fang and Swofford, 1983).

1.3. Benzene—Previous Work

1.3.1. Introduction

The benzene molecule has a planar hexagonal geometry and belongs to the D_{6h} symmetry point group. It is composed of 12 atoms and has 30 vibrational degrees of freedom. It is therefore a relatively large polyatomic system with properties typical of large and complex molecular systems. Its extremely high symmetry, however, and the not prohibitively large size, render benzene accessible to theoretical calculations. It is not surprising therefore that benzene is one of the most well-studied theoretically molecules. On the other hand, as the testing ground of many theories, it has been the subject of extensive and repeated experimental investigations under a variety of conditions and with numerous techniques.

One of the earliest theoretical calculations of the lower excited states of benzene is that of Goeppert-Mayer and Sklar (1938). Later refinements of these calculations include those of Parr et al.

(1950). More recent ab initio calculations were done by Buenker et al., (1968). There are many detailed reviews on benzene spectroscopy. Robin (1975) discusses extensively the upper excited states of benzene, both Rydberg and valence, lying at energies above $\sim 50,000 \text{ cm}^{-1}$. Cundall and Ogilvie (1975) and Cundall et al. (1977) review the one-photon spectroscopy and the photochemistry in the liquid phase. Parmenter (1972) studied the spectroscopy and relaxation of the first singlet state using single vibronic level fluorescence (one-photon excitation). Ziegler and Hudson (1982) present the most recent and systematic review of benzene spectroscopy, with emphasis on multiphoton studies and discussions on the symmetry assignments of the states and the transition selection rules.

There seems to be a general agreement among different theoretical calculations and experimental results on the energies and the symmetry assignments of the lower singlet and all of the triplet states. Theoretical calculations of the energies of the upper singlet states (lying above $\sim 50,000 \text{ cm}^{-1}$), however, differ greatly depending on the values of the parameters chosen. These theoretical uncertainties coupled with ambiguous experimental results have led to very different, if not conflicting, interpretations of the photo-physics of benzene in the corresponding energy region (Ziegler and Hudson, 1982).

Figure 1.2 shows the relative position and symmetry assignment of some of the theoretically expected singlet and triplet states of benzene, as well as the lowest of the Rydberg states. Table 1.1 gives

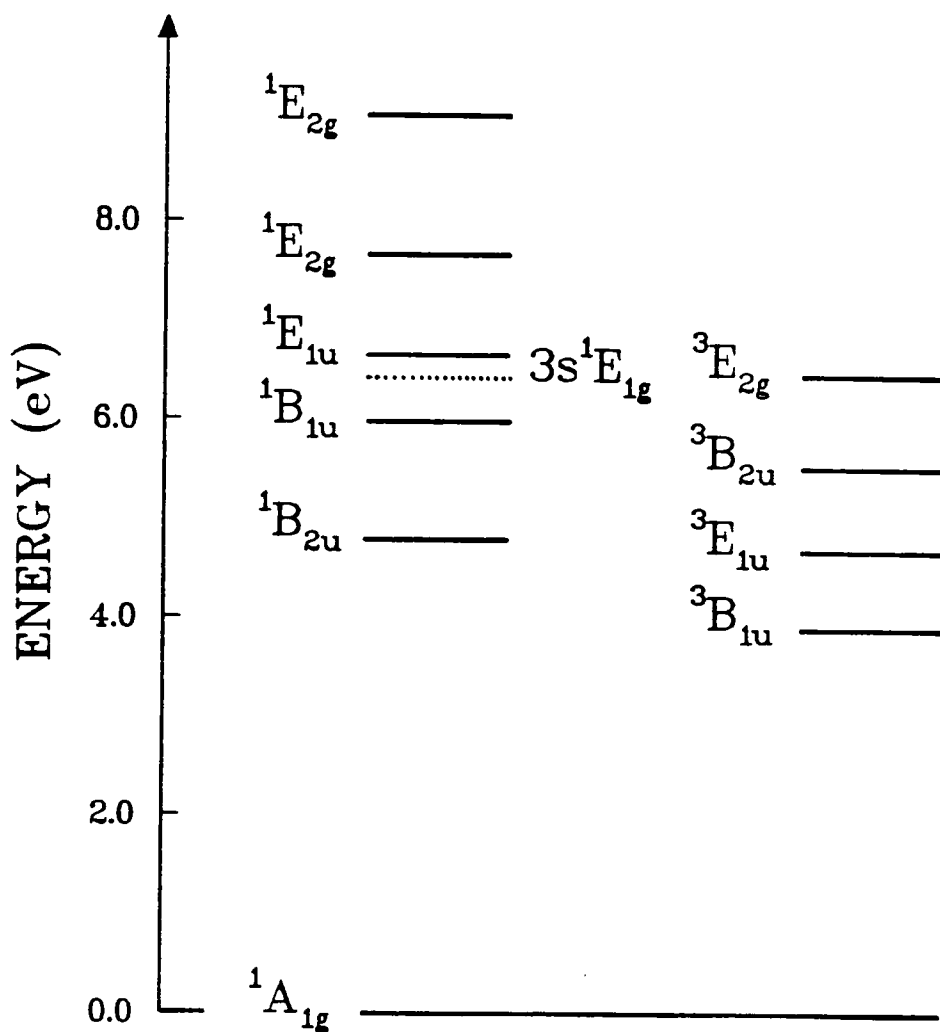


Figure 1.2. The singlet and triplet valence states of benzene. With dotted line the lowest lying Rydberg state ($3s^1E_{1g}$) is indicated. The positions and the ordering of the states are those of Table 1.1.

Table 1.1. Energies and Symmetry Assignments of the States of Benzene

	Singlet States			Triplet States			
	Symmetry	Energy ^a eV	Wavelength ^b nm	Selection ^c Rules	Symmetry	Energy ^a eV	Wavelength ^b nm
S ₃	¹ E _{2g}	9.2 ^d	270	+			
	¹ E _{2g}	7.8 ^d	318	+			
	¹ E _{1u}	6.75	367	*	³ E _{2g}	6.55	379
	(3s) ¹ E _{1g}	6.52 ^e	380	+	³ B _{2u}	5.60	443
S ₂	¹ B _{1u}	6.08	408		³ E _{1u}	4.75	522
S ₁	¹ B _{2u}	4.88	508		³ B _{1u}	3.95	628
S ₀	¹ A _{1g}	0.0					

^aAll energies unless otherwise noted are from Cundall et al. (1977).

^bThe wavelength corresponding to a two-photon resonant process.

^cThe + indicates a two-photon allowed and the * a one-photon allowed transition from the ground state.

^dFrom Nakashima et al. (1980).

^eFrom Scott and Albrecht (1981).

the energies of these states and the corresponding laser excitation wavelength for a two-photon process. All the energies are experimentally determined in the liquid phase for the singlet and in the gas phase (by electron impact methods) for the triplet states (Cundall et al., 1977).

It has already been mentioned that for benzene the one-photon parity allowed transitions are two-photon parity forbidden and vice versa. It is, however, possible that a transition is both one-photon and two-photon forbidden due to violation of different selection rules. For example, the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition is one-photon symmetry and two-photon parity forbidden. It is also possible that a transition is two-photon allowed but "two-photon identity forbidden"; that is, allowed for two different photons but forbidden for two identical photons (McClain and Harris, 1977).

It turns out that according to dipole selection rules (Ziegler and Hudson, 1982) all transitions from the ground (${}^1A_{1g}$) to the singlet states of benzene, with the exception of the ${}^1E_{1u}$ state, are either one-photon symmetry or one-photon parity forbidden; on the other hand, the transitions to the ${}^1E_{1u}$, ${}^1B_{1u}$ and ${}^1B_{2u}$ states are two-photon parity forbidden. It should be noted, however, that since all these selection rules are based on symmetry considerations, any vibrational mode which will break the molecular symmetry will also break the corresponding selection rule. For example, mixing of the "forbidden" ${}^1B_{2u}$ state with the allowed ${}^1E_{1u}$ state via vibrations of e_{2g} symmetry makes the former "weakly allowed" and thus observable in one-photon spectroscopy (Callomon et al., 1966).

The early spectroscopical data on benzene were supplied by one-photon gas-phase absorption techniques (Wilkinson, 1956; Callomon et al., 1966; Koch and Otto, 1972). Inagaki (1972) measured the one-photon absorption spectrum of neat liquid benzene, while Pantos et al. (1974) studied the low temperature thin film absorption. More recent one-photon gas-phase absorption studies were reported by Fischer and Jacobson (1979), Pantos et al. (1978) and Philis et al. (1981). Atkinson and Parmenter (1978) gave the most recent and complete vibronic analysis of the $^1B_{2u}$ state using one-photon absorption (OPA) in the vapor. Stephenson et al. (1984a, 1984b, 1984c) studied the one-photon excitation and relaxation of jet cooled benzene and benzene rare gas complexes.

1.3.2. Multiphoton Studies of Benzene in the Gaseous Phase

Hochstrasser et al. (1973, 1974a) were the first to study the TPE of benzene, by measuring the TPE spectra of the $^1B_{2u}$ state in the gaseous phase and the low temperature (2 °K) crystal. More detailed gas phase studies followed with higher resolution (Hochstrasser et al., 1974b; Wunsch et al., 1975a,b; Bray et al., 1975; Lombardi et al., 1976a,b; Hampf et al., 1977). Wunsch et al. (1977) have given the most detailed two-photon study of the $^1B_{2u}$ state of benzene in the gas phase to date. They measured the TPE spectra for $465 \text{ nm} < \lambda_{\text{exc}} < 550 \text{ nm}$ and studied the polarization behavior and the rotational structure of different vibronic bands. The same authors assigned most of the observed structure to transitions to specific vibronic bands, originating either from the vibrationless ground state (cold band

spectrum), or from thermally excited vibrational levels of the ground state (hot band spectrum) and they identified the $14_0^1 1_0^n$, as the dominant progression in the spectrum.

It should be noted that customarily the individual vibronic levels of benzene are specified by a symbol of the form N_g^e , where N is an integer ($1 \leq N \leq 20$) indicating one of the 20 normal vibrational modes, following Wilson's numbering (Wilson, 1934) and g and e are integers ($0 \leq g, e$) indicating the number of the ground and the excited state quanta of the vibration, respectively.

All of the TPE studies mentioned above were limited on the high energy side of the $1B_{2u}$ transition by the fluorescence cut-off due to the onset of the "channel 3." The channel 3 is a very fast non-radiative relaxation route from the first excited singlet state (S_1) to the ground state (S_0), which is activated about 3000 cm^{-1} above the origin (38086 cm^{-1}) of the S_1 and which increases the nonradiative rate by three orders of magnitude. There has been a great deal of speculation in the past about the possible mechanism and nature of this sudden increase of the nonradiative relaxation rate. Photoisomerization or coupling to an unknown singlet state have been proposed among other mechanisms (Parmenter, 1972; Callomon et al., 1972; Wunsch et al., 1981). Recent evidence, however, suggests that the $S_1 \rightarrow S_0$ relaxation proceeds via the very dense vibrational "ladder" of the ground state (Nakashima and Yoshihara, 1982).

The MPI of benzene in a supersonic beam expansion over the $1B_{2u} \leftarrow 1A_{1g}$ transition was studied by Aron et al. (1980) and Sur et al.

(1982). The former authors reached in their studies energies well into the channel 3 region and measured the natural linewidth of successive members of the $14_0^1 1_0^n$ progression for $n \leq 5$. They observed that the broadening of the linewidth with respect to energy, levels off for the upper members of the progression or at about 6000 cm^{-1} above the origin of the $1B_{2u}$ state. These results could imply that at some energy level (6000 cm^{-1} above the origin of the $1B_{2u}$ state or higher) the channel 3 relaxation might cease to be the dominant relaxation mode. A similar behavior is observed also in the liquid phase where, for energies above $\sim 6.5 \text{ eV}$, a recovery of the fluorescence is observed due to ionization and geminate recombination (Miyasaka et al., 1985).

Gas phase rotational contours of the 14_0^1 band were studied with MPI by Thakur and Goodman (1983). The MPI spectrum of benzene, for $360 \text{ nm} < \lambda_{\text{exc}} < 450 \text{ nm}$, was measured by Johnson (1976). A strong two-photon resonant peak at $\lambda_{\text{exc}} = 391 \text{ nm}$, originally thought to be the "elusive" $1E_{2g}$ state (Johnson, 1975) was finally assigned to the $(2p\pi \rightarrow 3s) 1E_{1g}$ Rydberg transition (Ziegler and Hudson, 1982).

The two-photon resonant MPI spectrum of jet-cooled benzene, for $365 \text{ nm} > \lambda_{\text{exc}} > 265 \text{ nm}$, reaching up to the gas phase ionization threshold (9.24 eV) was reported by Whetten et al. (1983).

1.3.3. Multiphoton Studies of Benzene in the Liquid Phase

The first MPI spectrum of neat liquid benzene was measured by Vaida et al. (1978) and covered the $360 \text{ nm} < \lambda_{\text{exc}} < 450 \text{ nm}$ region. Comparing the MPI with a thermal lensing spectrum which was

qualitatively similar, these authors attributed the broad monotonically rising band below $\sim 400 \text{ nm } \lambda_{\text{exc}}$ to direct two-photon ionization. This interpretation was supported by indirect estimations of the ionization threshold of liquid benzene, which placed it somewhere around 7 eV (Fuchs and Voltz, 1973). The same structure observed in thermal lensing spectra has been assigned by Twarowski and Kliger (1977) to the $^1E_{2g}$ state, while by Ziegler and Hudson (1980) to the $^1E_{1u}$ state.

The multiphoton ionization of neat liquid benzene with circularly and linearly polarized light at $\lambda_{\text{exc}} = 355 \text{ nm}$ was studied by Scott et al. (1979). Their measurements showed a cubic dependence of the signal on the laser intensity. They interpreted this as indicating a two-photon excitation of benzene, electronic relaxation to a relatively long-lived state, and subsequent ionization by the absorption of one additional photon (case (d) of Figure 1.1, p. 7). Later Scott et al. (1982) reported a three-photon ionization spectrum of neat liquid benzene for $360 \text{ nm} < \lambda_{\text{exc}} < 440 \text{ nm}$. At $\lambda_{\text{exc}} = 337 \text{ nm}$, however, they observed along with the three-photon, a competing two-photon ionization process as well. They proposed also that the long-lived intermediate state, mentioned previously, is the lowest singlet excimeric state. Scott and Albrecht (1982) proposed a somewhat different ionization mechanism for dilute solutions of benzene, whereby the first excited singlet state (S_1) serves as the intermediate state from which the third photon is absorbed (although they do not report any ionization studies in dilute solutions). They do not exclude also

the possibility that direct two-photon ionization might be occurring to a lesser degree in the $360 \text{ nm} < \lambda_{\text{exc}} < 440 \text{ nm}$ region.

Miyasaka et al. (1985) conducted transient absorption measurements in neat liquid benzene, following biphotonic picosecond excitation at $\lambda_{\text{exc}} = 355 \text{ nm}$. The absorption they observed originated from a transient excimeric species whose formation time (risetime of absorbance from 10% to 90% of plateau value) was $\sim 57 \text{ ps}$. They identified, however, as the precursor of the excimeric species the geminate electron-ion pair whose formation time was 10-20 ps. These results suggest that two-photon ionization is possible at $\lambda_{\text{exc}} = 355 \text{ nm}$ (6.98 eV) and that ionization precedes excimer formation.

The TPE spectra and the polarization ratio Ω (ratio of the signal obtained with circularly, to that obtained with linearly polarized light), for $360 \text{ nm} < \lambda_{\text{exc}} < 440 \text{ nm}$, of both the neat liquid benzene and a 3% solution of benzene in n-hexane, were measured by Scott and Albrecht (1981).

It should be noted at this point that all the spectroscopical studies of neat liquid benzene, reported in the literature, were in qualitative agreement regardless of the experimental method that was used (MPI, TPE or TL). All the spectra measured consisted of a weak structureless band at $\lambda_{\text{exc}} \approx 420 \text{ nm}$ which was unanimously assigned to the two-photon resonant $^1B_{1u}$ state, and a monotonically rising band below 400 nm whose assignments varied greatly (direct two-photon ionization, $^1E_{2g}$ or $^1E_{1u}$ state). The spectrum of the 3% solution in n-hexane, however, was qualitatively different and exhibited a distinct

strong peak at $\lambda_{\text{exc}} = 380$ nm. This peak was assigned (Scott and Albrecht, 1981) to the $(3S) {}^1E_{1g}$ Rydberg state. The same Rydberg state had been observed by Johnson (1976) at $\lambda_{\text{exc}} = 391$ nm in the gaseous phase, and the blue shift observed in the liquid was considered as, among other pieces of evidence, demonstrating the Rydberg character of the state. Rydberg states in the gas phase are known to be shifting to the blue with increasing pressure of the gas and the liquid phase sometimes is thought of as a very dense gas.

Two-photon excitation spectra of neat liquid benzene covering the entire ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition ($410 \text{ nm} < \lambda_{\text{exc}} < 540 \text{ nm}$) were reported by Razumova and Starobogotov (1980), while the TPE spectrum of a 10^{-2} M solution of benzene in n-hexane was measured by Scott et al. (1982) for $390 \text{ nm} < \lambda_{\text{exc}} < 540 \text{ nm}$. Friedrich et al. (1980) also measured the TPE spectra of pure liquid benzene and solutions of benzene in perfluoro-n-hexane and cyclohexane, using both circularly and linearly polarized light. They studied the low energy side of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition, close to the origin, and they estimated the polarization ratios for the forbidden 0-0 (or alternatively 0_0^0) transition and the 18_0^1 and 14_0^1 progressions.

One general observation that can be made concerning similar spectra measured at different concentrations of benzene in a solvent is that the lower the concentration, the higher the spectral resolution of the spectrum obtained. For example, the 10^{-2} M spectrum of Scott et al. (1982) offers a much higher spectral resolution than the neat liquid or the high concentration spectra in the corresponding

wavelength regions. It is well known also that spectra measured in perfluoro-n-hexane offer a superior spectral resolution compared to spectra measured in hydrocarbon solvents (Kourouklis et al., 1982) and exhibit a minimum red shift with respect to the gas phase spectra.

1.4. Toluene—Previous Work

Toluene is a methyl-substituted benzene and belongs to the C_{2v} symmetry group. In spite of its lower symmetry it is expected to exhibit a pattern of electronic transitions similar to that of benzene (Petruska, 1961a,b). This expectation is indeed verified by comparison of their corresponding spectra (Bolovinos et al., 1981, 1982). This similarity is indicative of the fact that the electronic wavefunctions of the π molecular orbitals are not drastically affected upon methyl substitution. The methyl group, however, causes a significant red shift in the spectrum of toluene with respect to that of benzene, which is approximately 620 cm^{-1} for the neat liquids (Razumova and Starobogatov, 1980). The symmetry of the states and the selection rules are also different between benzene and toluene. For example, the one-photon symmetry forbidden ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition corresponds to the one-photon allowed ${}^1B_2 \leftarrow {}^1A_1$ transition of toluene. Moreover, since toluene is not centrosymmetric and therefore does not have parity, both one- and two-photon transitions may in theory reach the same states.

One of the oldest and most systematic high resolution, one-photon absorption studies of gaseous toluene covering the ${}^1B_2 \leftarrow {}^1A_1$

transition is given by Ginsburg et al. (1946). The one-photon spectroscopy of gaseous toluene in both the valence- and Rydberg-state regions was studied more recently by Bolovinos et al. (1981) and Bolovinos et al. (1982). One-photon excitation spectra of jet-cooled toluene corresponding to the low energy side of the ${}^1B_2 \leftarrow {}^1A_1$ transition were studied by Hopkins et al. (1979) and Seliskar et al. (1983).

Vasudev and Brand (1979a) measured the two-photon excitation spectrum of gaseous toluene and studied the vibrational assignment in the region of the ${}^1B_2 \leftarrow {}^1A_1$ transition. The multiphoton ionization spectra of jet-cooled toluene corresponding to the ${}^1B_2 \leftarrow {}^1A_1$ transitions were studied by Murakami et al. (1981), while the higher Rydberg states of toluene, using a two-photon ionization technique, were studied by Whetten et al. (1984). Uneberg et al. (1980) observed two sharp peaks at $\lambda_{\text{exc}} = 365 \text{ nm}$ and $\lambda_{\text{exc}} = 379 \text{ nm}$, in the two-photon resonant, three-photon ionization spectra of gaseous toluene, which they assigned to 3p Rydberg transitions. It should be noted that the 3s Rydberg transition is also observed in benzene in the corresponding energy region.

The TPE spectrum of neat liquid toluene for $410 \text{ nm} < \lambda_{\text{exc}} < 550 \text{ nm}$ was measured by Razumova and Starobogatov (1980), while the low energy side of the ${}^1B_2 \leftarrow {}^1A_1$ transition in the neat liquid was studied by Friedrich et al. (1980) using both linearly and circularly polarized light.

1.5. Fluoranthene—Previous Work

Fluoranthene is one of the most common nonalterant aromatic hydrocarbons which present considerable environmental interest (they are present, for example, in car exhaust fumes and in the by-products of oil refineries), in relation to the carcinogenicity of the polycyclic aromatic hydrocarbons (Morgan et al., 1977).

Pestel et al. (1964) made one of the first vibrational analyses of the absorption and fluorescence spectra of fluoranthene by considering fluoranthene as a combination of a naphthalene and a benzene molecule. Originally fluoranthene was thought to possess three electronic transitions in the 200-450 nm region. Semiempirical calculations together with anomalous fluorescence characteristics, such as a long fluorescence lifetime and a large Stokes shift, however, suggested the existence of a lower lying first excited singlet state (S_1), hidden by a much stronger second singlet state (S_2) (Berlman et al., 1968). Indeed, extremely weak shoulders (indicating forbidden one-photon transitions) at ~ 390 nm were observed by Heilbronner et al. (1966) and by Michl (1969) in room and low temperature absorption spectra.

In fact, Michl (1969) and Kolc et al. (1974) identified eight and possibly nine different electronic transitions in the 200-450 nm region, in agreement with theoretical calculations. Still, however, questions regarding the lack of structure in the fluorescence spectrum as opposed to the richness of structure in absorption spectra, the long fluorescence lifetime and the relative immunity to oxygen and

concentration quenching (Berlman et al., 1968; Gusten and Heinrich, 1982), remain basically unanswered. Fluoranthene is also known to exhibit dual fluorescence as a result of the close energy spacing between the S_1 and S_2 excited states. Philen and Hedges (1976) studied the fluorescence from these two states in rigid glass at 77 °K. They found that the fluorescence originating from the S_2 state has a longer lifetime than that originating from the S_1 (143 ns and 58 ns, respectively) and that both lifetimes are much longer than the theoretically predicted ones. All these observations point towards the fact that the photophysics of the lower excited states of fluoranthene are still poorly understood.

Chan and Dantus (1985) studied the one-photon excitation and emission spectra of jet-cooled fluoranthene. They made a vibrational analysis of the first excited singlet state and they located the 0-0 transition at 396.56 nm (one-photon wavelength).

Time resolved fluorescence spectra of pure fluoranthene crystals using both one- and two-photon excitation were measured by Kobayashi and Nagakura (1972). Siomos et al. (1981) reported the two-photon ionization spectrum of fluoranthene in n-pentane at room temperature. They observed a decline in their ionization signal when the ionization was proceeding via the one-photon resonant S_1 state, which was interpreted as indicating dissociation of the fluoranthene molecule. The same authors located the ionization threshold, as indicated by the onset of the two-photon ionization signal, at $4.5 \pm .05$ eV. No other multiphoton study on fluoranthene appears to exist.

1.6. Present Work

It is clear from the preceding exposition that multiphoton studies of the molecules under consideration in the liquid phase are rare. For fluoranthene no TPE studies have been reported, while for toluene only the TPE spectra of the first singlet state of the neat liquid have been measured. Benzene has been studied more extensively, but again most studies have concentrated on the neat liquid, or on solutions of relatively high concentrations. Moreover, no ionization spectra and studies of the $^1B_{2u}$ state of benzene have been reported, no complete TPE measurements over the entire 360-550 nm λ_{exc} range exist and no hot band study has been undertaken up to now.

In addition to the apparent need of such studies and possibly because of their lack, a number of outstanding questions regarding the photophysics of benzene still remain:

- a. The exact location of the ionization threshold and the multiphoton ionization mechanism of benzene in the liquid phase have not yet been determined.
- b. The two degenerate $^1E_{2g}$ states of benzene continue to elude experimentalists and theoreticians alike.
- c. The possible existence and observability of Rydberg states of benzene (or other molecules) in the liquid phase is still an open question.
- d. The nature of the channel 3 nonradiative process and its role in the liquid phase are still open to speculation.

The present study attempts to provide additional information on the photophysics of molecules in the liquid phase, both in controversial areas (such as the channel 3 and the Rydberg states), and in areas where such information is lacking (ionization threshold and mechanism).

For this reason the two-photon resonant MPI spectra of benzene in n-pentane and tetramethylsilane (TMSi) were measured for $360 \text{ nm} < \lambda_{\text{exc}} < 570 \text{ nm}$. Extensive signal vs. laser intensity measurements were carried out in this spectral range in order to locate the ionization threshold and determine the ionization mechanism. Multiphoton ionization polarization studies were also performed in the $465 < \lambda_{\text{exc}} < 540 \text{ nm}$ range. The TPE spectra of benzene and toluene in a number of nonpolar solvents [n-pentane, TMSi, perfluoro-n-hexane ($\text{n-C}_6\text{F}_{14}$), perfluoromethylcyclohexane ($\text{c-C}_7\text{F}_{14}$) and perfluorodimethylcyclobutane ($\text{c-C}_6\text{F}_{12}$)] which differ in various physicochemical properties (see Section 3.2), were measured for $360 \text{ nm} < \lambda_{\text{exc}} < 550 \text{ nm}$ with light of either circular or linear polarization. Comparison of the relative intensities and positions of the observed structure for $\lambda_{\text{exc}} < 440 \text{ nm}$ in the spectra of benzene and toluene in different solvents will help elucidate the nature of the charge-transfer states in this region, as well as the interaction of the valence states with them.

The relatively high resolution of the spectra obtained in the $\text{n-C}_6\text{F}_{14}$ solutions—which is comparable to that of low resolution gas phase spectra—allowed the identification of the observed vibronic

structure of the $^1B_{2u}$ state of benzene well into the channel 3 region (up to excess energy of 9000 cm^{-1} above the origin), as well as the observation of hot bands lying below the origin of the transition.

Finally, the TPE spectrum of fluoranthene in n-pentane was measured for $420\text{ nm} < \lambda_{\text{exc}} < 860\text{ nm}$, and signal vs. laser intensity measurements were carried out. The wavelength range under study varied continuously from the one-photon resonant ($\sim 420\text{ nm}$) up to the two-photon resonant, with the S_1 state, wavelengths.

CHAPTER II

EXPERIMENTAL TECHNIQUES AND PROCEDURES

2.1. Introduction

Two very different but complementary experimental techniques, which provide information on different aspects of the excitation and deexcitation processes of a molecule in a liquid medium, were used in the present experiments, the multiphoton ionization (MPI) and the two-photon excitation (TPE) techniques. The MPI technique is valuable in helping elucidate the mechanism of the ionization process and the effect of the medium on the ionization threshold. Experimental constraints, however, limit its use to highly purified nonpolar liquids when detailed and high resolution studies are desired. The TPE technique, on the other hand, although relatively immune to impurity interference, is restricted to fluorescing molecules and to excitation energies less than twice the energy of the observed fluorescence emission. It can provide, however, detailed spectroscopical data, especially when a perfluorocarbon is used as a solvent. Moreover, a comparison of the spectra of the same molecule in different solvents provides information on the effect of specific medium properties (i.e., electron mobility, electron affinity) on the upper excited states of the embedded molecule.

The experimental system can be subdivided into four distinct and independent parts, which will be described separately in the

following sections: (a) the circularly or linearly polarized light generating system, which includes the lasers and the polarization optics; (b) the liquid photoconductivity cell with the accompanying signal-processing instruments; (c) the fluorescence cell with the accompanying instruments; and (d) the vacuum purification system. Finally, the method for data analysis will be discussed.

2.2. Light-Generating Systems

2.2.1. Lasers

Three different types of frequency tunable dye lasers were used as light sources to cover the entire wavelength range from the near UV (340 nm) up to the near IR (900 nm). A nitrogen-laser pumped dye laser (nitrogen-dye laser)—Molelectron UV1000/DL 300—was used in the 360-650 nm region. An excimer-pumped dye laser (excimer-dye laser)—Lambda Physik EMG101MSC/FL2002—was used in the 340-600 nm region; the excimer laser was operating with XeCl (pumping wavelength 308 nm). Finally a Nd:Yag (second harmonic)-pumped dye laser (Yag-laser)—Quanta Ray DCR2A(10)/PDL-1—was used for the measurements in the 600-900 nm region.

The spectral bandwidth of the light produced by all the dye lasers was of the order of ~ 0.02 nm and the wavelength accuracy better than 0.1 nm. The pulse duration of the nitrogen-dye laser was ~ 5 ns (FWHM) and the energy per pulse reaching the interaction volume in the liquid ranged from 50 to 150 μ J depending on the wavelength and the efficiency of the dye being used. The excimer-dye laser had a

pulse duration of ~ 10 ns and was capable of producing pulses of much higher energy. Pulse energies varied from ~ 50 μ J up to ~ 6 mJ depending on the experimental constraints and the need to produce adequate or even measurable signal. Generally, high pulse energies were avoided, because of the high possibility of burning black spots on the inside surface of the cell windows, and because photochemical reactions might be induced in the liquid sample under study. Relatively high energies per pulse were required to produce adequate fluorescence signal for wavelengths above ~ 600 nm in the TPE of fluoranthene.

To cover the entire wavelength region under study (340-900 nm) a number of different dyes and dye mixtures were used. Table 2.1 contains a list of the dyes used in the present studies, together with their respective wavelength ranges.

The light which was generated by the lasers was polarized circularly or linearly before it was focused into the cell that contained the solution of the molecule under study. Two different polarization techniques were used, one for the nitrogen-dye laser and one for the excimer-dye laser.

2.2.2. Polarization Technique for the Nitrogen-Dye Laser

Figure 2.1 shows the spatial filtering and polarization optics used with the nitrogen-dye laser. The laser beam was first spatially filtered by passing through a telescope. Special care was taken to maintain a symmetric Gaussian profile of the beam (Siomos et al., 1983). In this way "hot" spots in the beam profile, which could

Table 2.1. Dyes and Dye-Mixtures

Dye Name	Supplier*	Wavelength Range (nm)		
		Pumping Laser		
		Nitrogen	Excimer	Nd:Yag
PTP	L		332-350	
PTP/DMQ (2/1)			340-365	
DMQ	L		346-377	
PBD	E	360-386		
BBQ	E	373-399		
QUI	L	372-412	368-402	
QUI/DPS (3/4)		381-415		
DPS	E	396-416		
DPS/Bis-MSB (2/3)		396-430		
Bis-MSB	E	411-430		
Bis-MSB/Coumarin 440 (2/1)		415-440		
Coumarin 440	E	420-457		
Coumarin 460	E	440-478		
Coumarin 481	E	460-517		
Coumarin 102	L		460-510	
Coumarin 500	E	473-547		
Coumarin 307	L		479-553	
C 485	M	490-562		
Coumarin 540A	E	515-583		
Rhodamin 590	E	568-605	569-608	
Rhodamin 610	E	594-643		
Sulforhodamin B	L		594-642	
DCM	E	601-716		610-685
LDS 698	E			660-738
LDS 751	E			720-798
LDS 820	E			770-860

*L = Lambda Physik; E = Exciton; M = Molelectron.

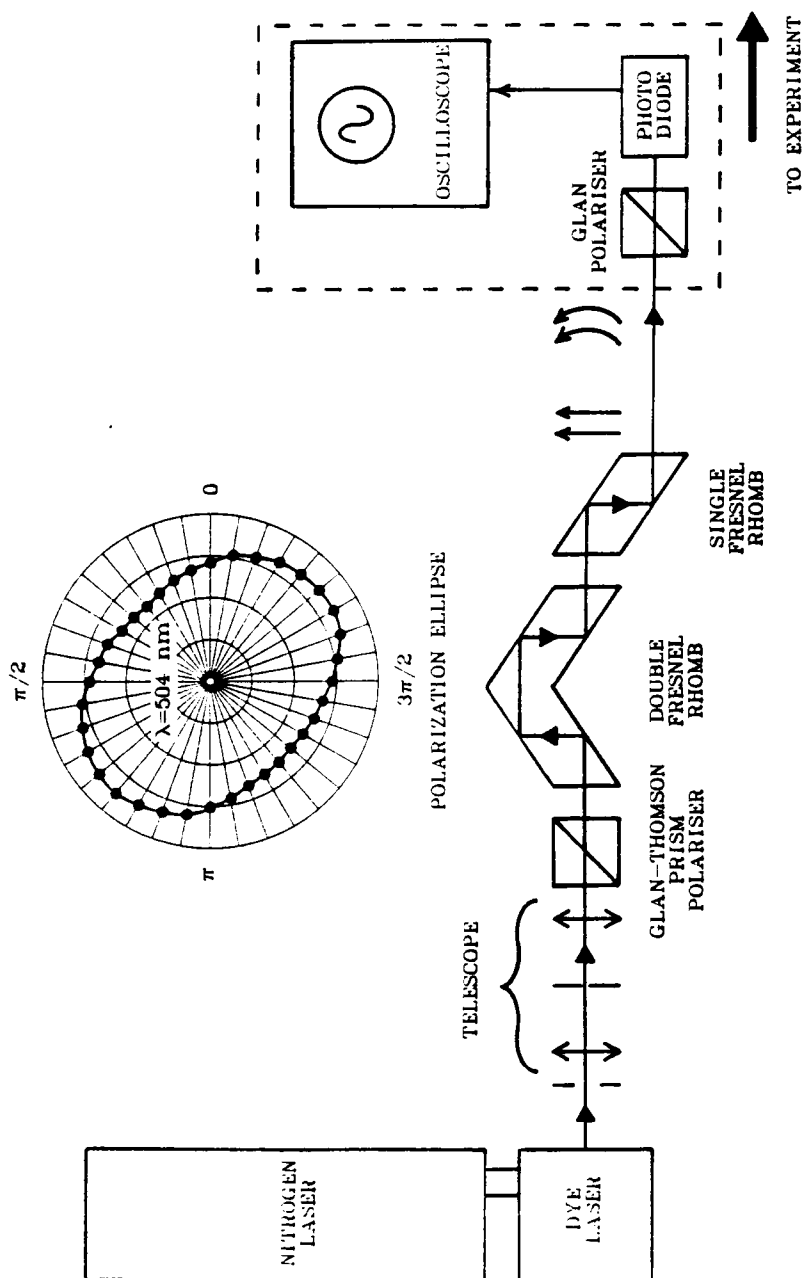


Figure 2.1. Spatial filtering and polarization optics for the nitrogen pumped dye laser. The polarization ellipse is the transmitted light intensity through the second polarizer (inside the dashed line frame) as a function of its angle of rotation. The eccentricity of the ellipse is $e = 1.4$.

complicate the observed signal vs. laser intensity, were avoided. Then the beam was linearly polarized by a Glan-Thomson prism polarizer (PL) and sent through a polarizing assembly comprised of a double (DFR) and a single (SFR) Fresnel rhomb.

The plane of polarization of the laser radiation was oriented with respect to the fast axis of the SFR by rotating the DFR, so that the light leaving the single Fresnel rhomb was either circularly or linearly polarized. The quality of the generated circularly polarized light was determined by placing a second polarizer (inside the dashed line frame in Figure 2.1) after the polarizing assembly and monitoring the intensity of the transmitted light as a function of the rotation angle (0° - 360°) of the polarizer.

For perfectly circularly polarized light the intensity of the transmitted light should remain constant and a plot of the intensity vs. angle of rotation in polar coordinates (polarization ellipse) should be a perfect circle. If, however, an ellipse is measured, then there is a linearly polarized component still present in the circularly polarized light. The eccentricity, e , of the ellipse gives a measure of the quality (or purity) of the circularly polarized light obtained.

The inset in Figure 2.1 shows the polarization ellipse of the circularly polarized light obtained with the above-discussed technique at $\lambda = 504$ nm laser wavelength. The eccentricity in this case is $e' = 1.4$ and generally ranged from 1.3 to 1.4 at different laser wavelengths.

According to Malus' law (Klein, 1970) the transmitted intensity (I_t) through a polarizer is given by:

$$I_t = I_i \cos^2 \theta \quad (2.2.1)$$

where I_i is the incident light intensity and θ is the angle between polarization plane of the incident light and the polarizer. For circularly polarized light averaging over 2π gives:

$$\overline{I_t} = I_i \overline{\cos^2 \theta}$$

or

$$\overline{I_t} = \frac{I_i}{2\pi} \int_0^{2\pi} \cos^2 \theta \, d\theta$$

or

$$\overline{I_t} = \frac{I_i}{2} \quad (2.2.2)$$

Consider now a mixture of circularly and linearly polarized light with corresponding intensities I_C and I_L . The polarizer will transmit a maximum intensity $I_L + (I_C/2)$, which corresponds to the major axis of the polarization ellipse, and a minimum intensity $I_C/2$ corresponding to the minor axis. The eccentricity, therefore, of the ellipse is:

$$e = 1 + 2I_L/I_C \quad (2.2.3)$$

and the fraction of the linearly polarized light is:

$$\frac{I_L}{I_C + I_L} = \frac{e - 1}{e + 1} \quad (2.2.4)$$

An eccentricity of $e = 1.4$ therefore corresponds to a linearly polarized fraction of the total intensity equal to 0.166 or $\sim 17\%$.

2.2.3. Polarization Technique for the Excimer-Dye Laser

A different optical arrangement which can produce circularly polarized light of much higher quality was used with the excimer-dye laser (see Figure 2.2). This method uses essentially only a single Fresnel rhomb, oriented in such a way that it produces circularly polarized light and a prism polarizer (PL4 in Figure 2.2) to convert that to linearly polarized light when it is needed. It requires relatively high laser output light intensities (for this reason it was not used with the nitrogen-dye laser) because of large optical losses; it can generate, however, circularly polarized light of 99% purity ($e = 1.02$).

The light exiting the laser is passed through a Glan-Thomson prism polarizer (PL1) to improve its linear polarization, through a beam-splitter and through a second Glan-Thomson polarizer (PL2) before it enters the single Fresnel rhomb (SFR) which is oriented in such a way as to convert it into circularly polarized light. In order to optimize the alignment of the SFR so that circularly polarized light of the highest possible quality is produced, a mirror is placed after the SFR at normal incidence. The light is back-reflected onto the beam-splitter and is monitored by a sensitive photodiode. Generally, the light leaving the SFR after its first passage will contain both a circularly and a linearly polarized component. The circularly polarized component, after reflection on the mirror, will have

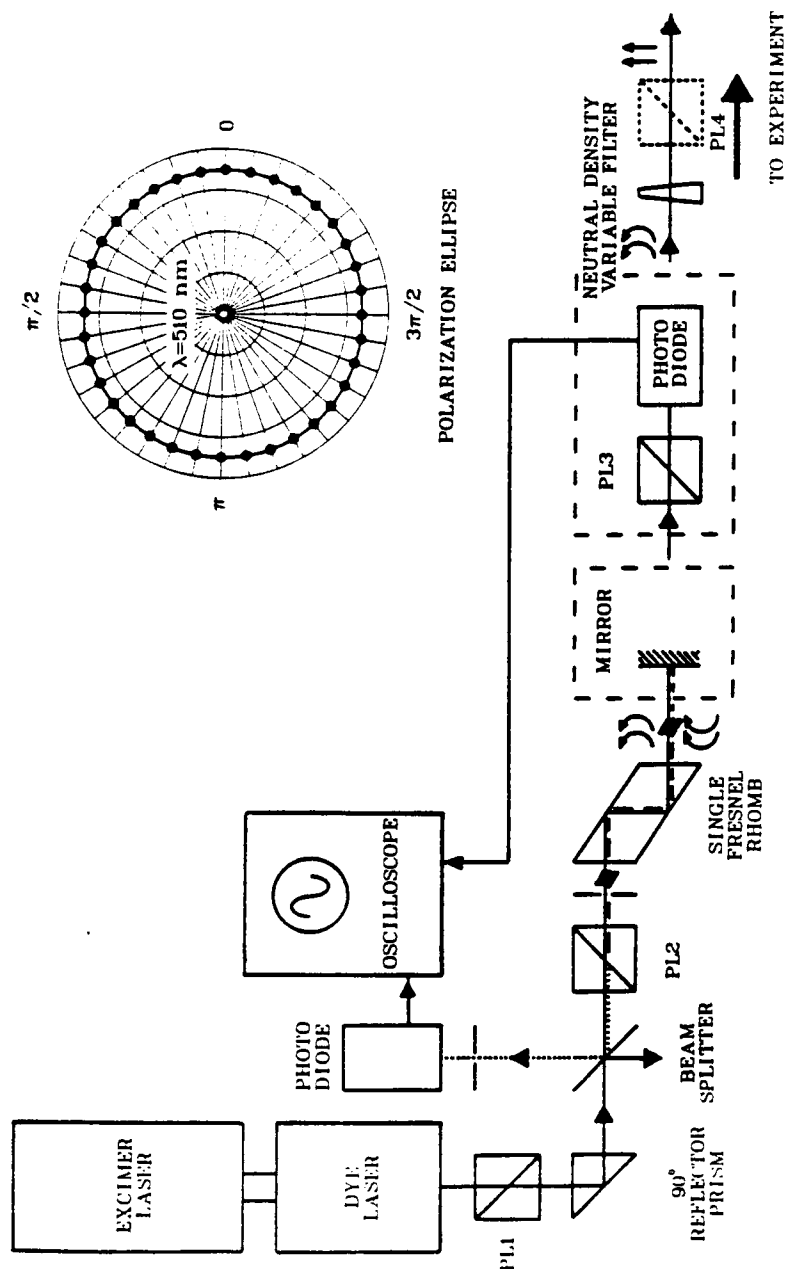


Figure 2.2. Polarization optics for the excimer pumped dye laser. The optical elements inside the dashed line frames are used temporarily for alignment or for checking purposes and they are removed during the experiment. The eccentricity of the polarization ellipse is $e = 1.02$.

opposite helicity (the polarization vector will be rotating in the opposite sense; from clockwise to counterclockwise and vice versa), so that after the second passage through the SFR it will again become linearly polarized but with its plane of polarization rotated 90° with respect to the original direction (plane). It will be therefore completely blocked by the polarizer (PL2) and it will not reach the sensitive photodiode. The linearly polarized component, however, will be unaffected by the reflection and will become circularly polarized after the second passage through the SFR; half of it will pass the polarizer (PL2) and a fraction of it will be reflected by the beam-splitter onto the photodiode. By means of rotation and translation of the SFR it is possible to minimize the back-reflected light detected by the photodiode, which is proportional to the fraction of the linearly polarized light in the original beam.

The inset in Figure 2.2 shows the polarization ellipse of light obtained with this method at $\lambda = 510$ nm. The eccentricity is $e = 1.02$ corresponding to less than 1% linearly polarized component. The purity of the circularly polarized light was checked also after passage through the TPE cell (filled with the solution) and was found to be better than 98%. A variable neutral density filter was used to maintain equal intensities for both polarizations while recording the corresponding spectra.

2.3. Multiphoton Ionization Technique

The technique used in the multiphoton ionization studies has been described by Siomos and Christophorou (1980). Figure 2.3 shows schematically the photoconductivity cell and the accompanying electronics. The circularly or linearly polarized light of the laser enters the ionization cell and is focused in the area between the electrodes by a lens of typically 15 cm focal length, down to a waist of ~ 0.2 mm. The interaction volume is therefore a cylindrical filament of ~ 1 cm length and $\sim 10^{-4}$ cm² cross section, containing $\sim 6 \times 10^{13}$ solute molecules (for a typical concentration $c = 10^{-3}$ M or 6×10^{17} molecules $\cdot$ cm⁻³). The laser flux (or intensity) for a 5 ns, 100 μ J/pulse at $\lambda = 500$ nm is $\sim 2.5 \times 10^{14}$ photons/pulse or $\sim 5 \times 10^{27}$ photons $\cdot$ cm⁻² $\cdot$ s⁻¹ at the focal point.

The photoconductivity cell consisted of two chambers that could be evacuated independently down to a residual pressure of $\sim 1 \times 10^{-7}$ Torr. The high voltage chamber (designated by A in Figure 2.3) allowed for the connection of the high voltage feed through to the high voltage electrode and was maintained at high vacuum ($\sim 1 \times 10^{-7}$ Torr). The second chamber (designated by B in Figure 2.3) contained the solution under study. The electrodes were two parallel gold-plated disks 2 cm in diameter. The first electrode (high voltage or cathode) was fixed on the wall that separated the two chambers, while the second electrode (anode) was mounted on a micrometer and was movable, so that the electrode distance could be varied (0-1 cm); this distance during the course of these experiments was 1 mm, while the voltages applied

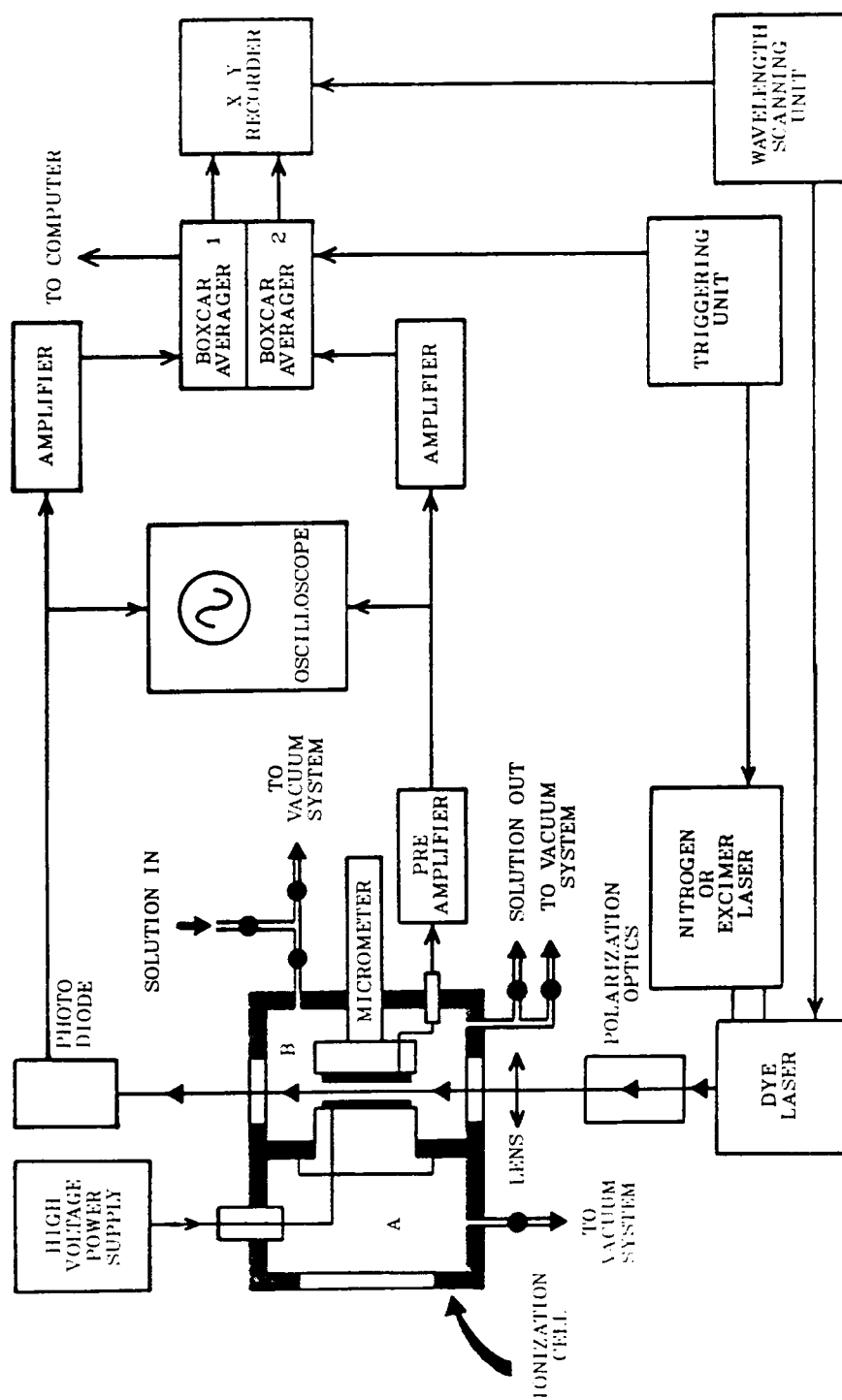


Figure 2.3. Layout of the multiphoton ionization technique. (A) High voltage chamber, (B) liquid chamber.

on the electrodes ranged from 1 to 2 kV, corresponding to fields of 10 to 20 kV $\cdot$ cm⁻¹. The electrode pair was coupled to a high impedance (10^{11} Ω) charge sensitive preamplifier with a gain of 10. The two electrodes formed a charge sensitive conductivity detector; the characteristics of the output signal of this detector will be discussed in the next section.

Two pairs of quartz windows at crossed geometry allowed for the entrance and exit of the laser beam. The laser beam intensity was monitored after the cell by a photodiode (Molelectron J3) of known spectral responsivity. The signal outputs of the preamplifier and the photodiode were amplified by linear amplifiers (Tennelec TC200) and then they were sampled by boxcar integrators (EG & G 162). Finally, both signals were plotted on a two-channel X-Y recorder as a function of wavelength, before they were transferred to a computer for analysis.

2.4. The Photoconductivity Detector Signal

The laser beam entering the photoconductivity cell creates in the interaction volume between the electrodes a number, N_0 , of geminate electron-ion pairs. Of these geminate pairs most recombine and only a small fraction, N , are separated, move under the influence of the external applied field and induce a current in the external circuit. Moreover, if electron attachment occurs (by the host or the solute molecules), negative ions will also contribute to the current.

Figure 2.4a shows schematically the electrode pair-preamplifier conductivity detector. The electrode pair forms a capacitor of capacitance C_0 and together with the external circuit they have a total capacitance C . Let us assume that a number N of a given singly charged species have been created at a distance x from the electrode towards which they will drift (say the anode), with an average drift velocity w . The induced current in the external circuit due to the movement of one species of charge carriers (see Appendix) is:

$$i = N \cdot e \cdot w/d \quad (2.4.1)$$

where e is the electron charge and d is the electrode separation.

Let us define as collection time the quantity $\tau = x/w$ and let us assume that:

- a. τ is much smaller than the time constant of the external circuit;
- b. the lateral dimensions of the interaction volume are much smaller than the electrode distance d ;
- c. there are no "sinks" or "sources" during the drifting time for this species (i.e., all attachment processes occur at much earlier times).

All the assumptions above are met under the experimental conditions of the present photoconductivity system, and the discussion that follows applies to any type of charge carriers.

The rate of change of the anode potential due to the movement of this species is: $\frac{dV}{dt} = \frac{d}{dt} \left(\frac{Q}{C} \right)$ or

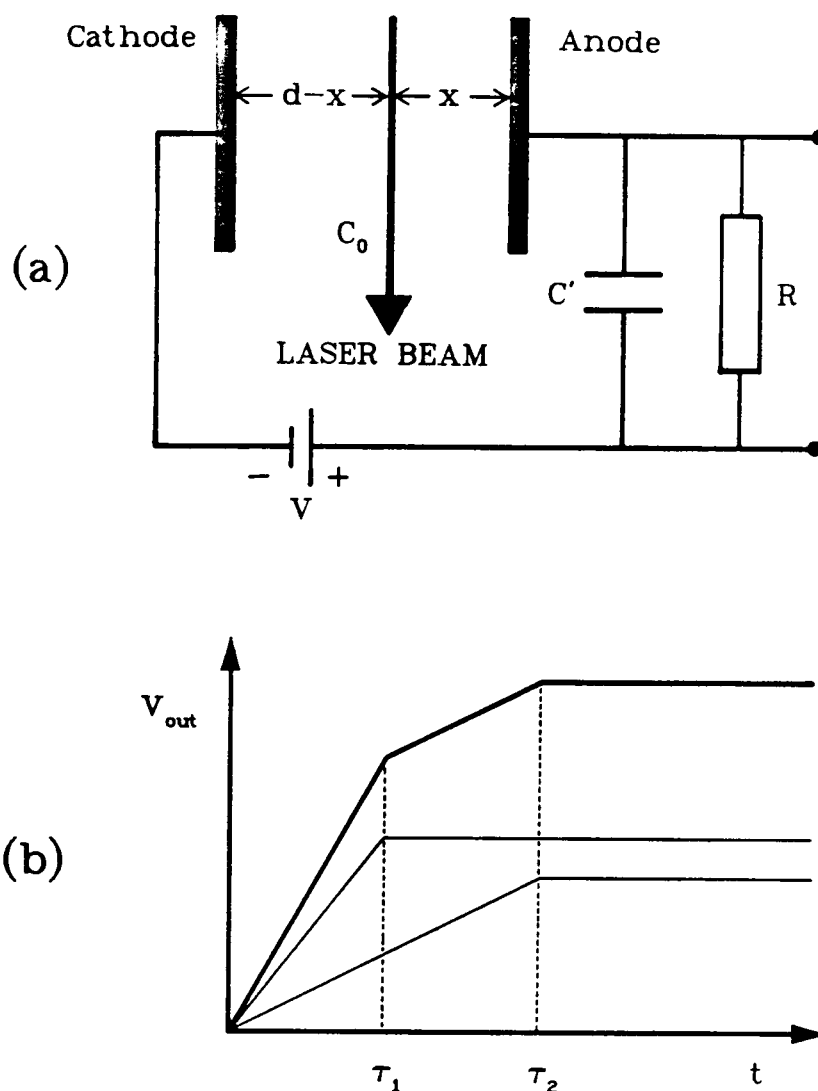


Figure 2.4. (a) Schematic diagram of the charge-sensitive parallel-plate photoconductivity detector. (b) The output voltage signal of the photoconductivity detector as a function of time. The thin lines represent the output voltage due to the movement of each of two species of charge carriers having different mobilities and collection times. The thick line represents the total voltage output due to both species (see text).

$$\frac{dV}{dt} = - \frac{1}{C} \left(\frac{N e w}{d} \right) \quad (2.4.2)$$

After integration the voltage as a function of time will be:

$$\begin{aligned} V(t) &= V(0) - \frac{N e w t}{C d} & \text{for } t < \tau \\ \text{and} & & \\ V(t) &= V(0) - \frac{N e w \tau}{C d} & \text{for } t \geq \tau \end{aligned} \quad (2.4.3)$$

When two oppositely charged species contribute to the signal (i.e., electrons and positive ions or negative and positive ions), the output voltage pulse defined as $V_{out} = V(0) - V(t)$ will be:

$$\begin{aligned} V_{out} &= \frac{N_1 e w_1 t}{C d} + \frac{N_2 e w_2 t}{C d} & \text{for } t < \tau_1 \\ &= \frac{N_1 e w_1 \tau_1}{C d} + \frac{N_2 e w_2 t}{C d} & \text{for } \tau_1 < t < \tau_2 \\ &= \frac{N_1 e w_1 \tau_1}{C d} + \frac{N_2 e w_2 \tau_2}{C d} & \text{for } t > \tau_2 \end{aligned} \quad (2.4.4)$$

where the two species are indicated with indices 1 and 2 and where it is assumed that $\tau_1 < \tau_2$. Figure 2.4b shows graphically V_{out} as a function of time for the case when two species are contributing to the signal. During the first time-interval ($t < \tau_1$) both species are drifting and contributing to the current. The slope of the signal vs. time is $(N_1 w_1 + N_2 w_2) e / C d$. If electrons are one of the two species, because of their high mobility and drift velocity (compared to ions),

they dominate this portion of the signal. The collection time τ_1 depends on x and is in the order of microseconds for electrons and milliseconds for ions. During the second time-interval ($\tau_1 < t < \tau_2$) one of the species has already been collected and the slope is determined only by the ionic drift velocity of the remaining species, $N_2 w_2 e / Cd$. Time τ_2 is always in the order of milliseconds. After all charges have been collected ($t > \tau_2$), the voltage should remain constant; at very long times, however, exceeding the time constant (RC) of the external circuit, the signal starts decaying.

Figure 2.5 shows the oscilloscope traces of the photoconductivity signal outputs produced by the ionization of benzene in n-pentane and TMSi for different laser beam positions between the electrodes. In photographs (b) the laser beam passes through the middle of the electrode distance ($x = d/2$), while (a) and (c) correspond to points lying symmetrically about the middle; (a) towards the cathode and (b) towards the anode. Both signals obey the general equation 2.4.4 although the signal in TMSi is composed of an electronic and an ionic component, while the signal in n-pentane consists of two ionic components. The fast-rising electronic signal in TMSi has a collection time in the range of microseconds, while the ions in both liquids are collected within a few milliseconds.

Since $\tau_1 w_1 = x$ and $\tau_2 w_2 = d - x$, dividing we have:

$$\frac{d}{x} = \frac{w_2}{w_1} \left(\frac{\tau_2}{\tau_1} \right) + 1 \quad (2.4.5)$$

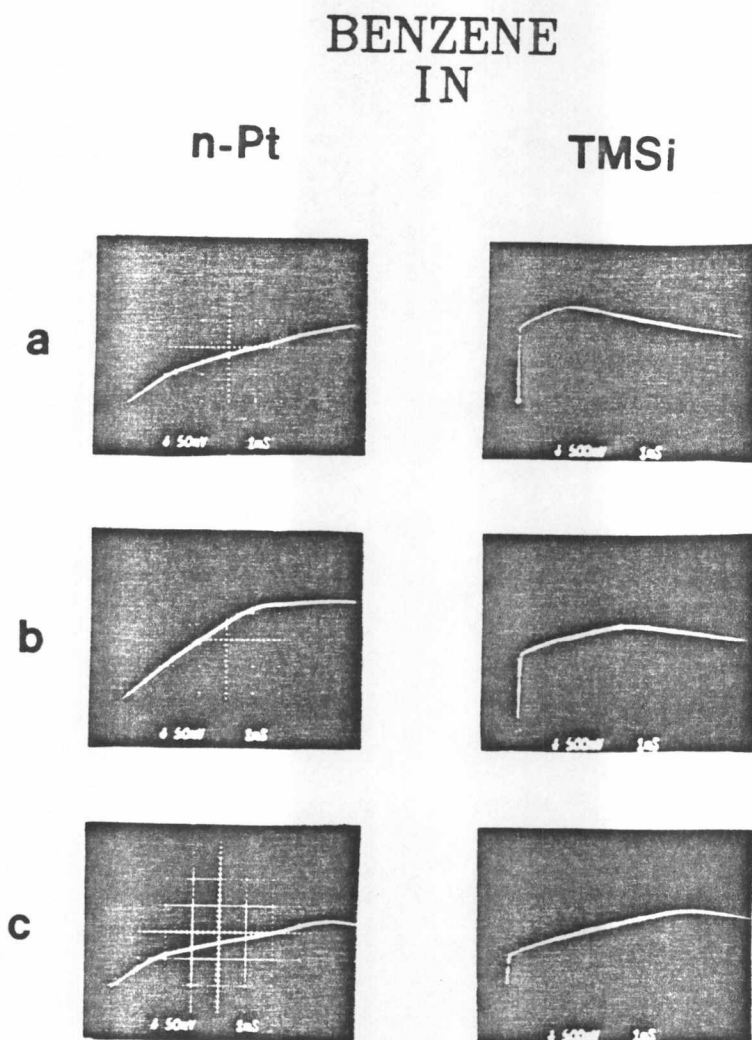


Figure 2.5. Oscilloscope voltage traces following the photoionization of benzene in n-pentane (n-pt) and tetramethylsilane (TMSi), for different laser beam positions between the electrode plates. (a) Beam close to the cathode, (b) beam at the middle, (c) beam close to the anode. Note the absence of an electronic signal component in n-pentane. The field between the plates was 10 kV/cm and the scales of the photographs are: 1 ms/div, 50 mV/div (for n-pentane) and 1 ms/div, 500 mV/div (for tetramethylsilane).

Indeed an analysis of a series of photographs of the voltage pulse shape in n-pentane corresponding to different laser beam position revealed that $1/x$ is linearly correlated to τ_2/τ_1 and that $w_2/w_1 = 1.00 \pm 0.01$. For this reason in picture (b), for n-pentane, only one slope is seen; because if $x = d-x$ and $w_1 = w_2$ then $\tau_1 = \tau_2$.

According to Huang and Freeman (1979) the low ionic mobilities in the liquid phase are mainly due to the obstruction of translational motion by the closely spaced repulsive cores. The mobility (μ) therefore obeys a form of Stokes law, $\mu = e/6n\pi r$, where e is the charge of the ion and r is the effective radius of the moving ion. If a cluster of molecules forms around the ion then r is the radius of the cluster. Actually there is strong evidence suggesting that a cluster does form around benzene ions because their collection times are significantly longer than those of larger molecules, such as TMPD, fluoranthene, and pyrene (Christophorou and Siomos, 1984). The size of the cluster is determined by the number of the immediate neighbors of the ionic core, which is strictly related to the size of the ion. Therefore, within the error of our measurements, equal drift velocities under the same applied electric field imply equal mobilities and consequently ions of the same size. Moreover, if different ions and different size clusters were formed one would observe a gradual variation of the slopes of the oscilloscope traces and not just two distinct slopes. Since only benzene is present in the liquid at appreciable concentration, it is

reasonable to conclude that the ions in n-pentane are positive and negative benzene ions. This assertion is supported by the results of Winokur et al. (1975) who find equal drift velocities for positive and negative ions of the same molecule.

The question therefore arises as to why benzene attaches electrons in n-pentane, as apparently it does, but does not do so in TMSi. Benzene is known to capture electrons in alcohol solutions (Ogura and Hamill, 1974; Marketos et al., 1974). It is also known that benzene captures low energy ($\lesssim 0.2$ eV) electrons in the gas phase (Christophorou and Goans, 1974). Although more complete studies are needed to explain the behavior of benzene in TMSi and n-pentane, the following suggestions can be put forward:

- a. Because TMSi has a negative V_0 value (Christophorou and Siomos, 1984), it is possible that the electron energy distribution in this liquid depends not only on the temperature, but also on the applied electric field. At the field intensities (10 kV cm^{-1}) that were used, it is possible that the mean electron energy in TMSi is high enough for the electrons to escape capture, while this is not the case in n-pentane.
- b. The electrons are captured by benzene in both liquids, but the negative ion solvation energy is much higher in n-pentane than in TMSi. As a result, the lifetime of the negative benzene ion in TMSi is so short as to render it

unobservable, while the lifetime in n-pentane is long enough for it to be observed.

As a result of the electronic component in the signal of benzene in TMSi, the voltage output is also much higher in this liquid. The ratio of the pulse output voltages in TMSi and n-pentane is approximately 10. The fact that the signal in n-pentane is much weaker, and that higher laser intensities are required to produce adequate signal, has important implications which will be discussed in Chapter IV.

2.5. Two-Photon Excitation Technique

The fluorescence cell (see Figure 2.6) was made out of pyrex glass with three quartz windows for the entrance and exit of the laser beam and the observation of the emitted fluorescence. A Wood's horn opposite to the observation window prevented any scattered light from being reflected back onto it, while two light baffles blocked the light scattered on the entrance and exit windows, from reaching the collection optics. The collection optics consisted of a system of quartz lenses inserted in a light tight tube, which focused the emitted fluorescence light onto the entrance slit of a double monochromator (Jarrell Ash model 82/410). When the fluorescence was relatively weak the monochromator was replaced by a set of filters and the light was focused directly on the photomultiplier. The studies on fluoranthene, which exhibits strong fluorescence, were

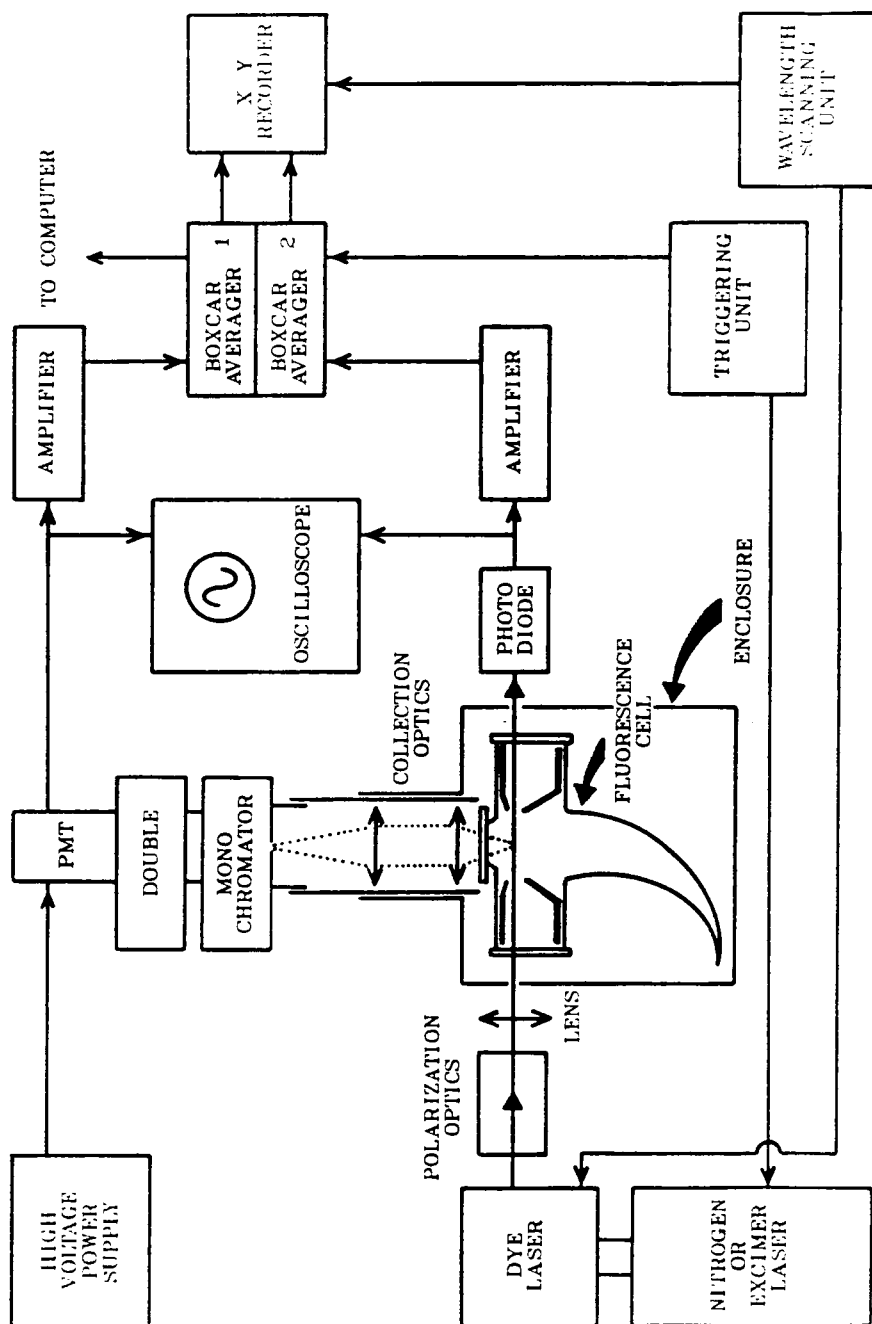


Figure 2.6. Layout of the two-photon excitation technique. The double monochromator was replaced by a set of filters for certain measurements (see text).

performed using the monochromator set at an observation wavelength $\lambda_{\text{obs}} = 460 \text{ nm}$ (or even lower depending on the excitation wavelength) for the laser excitation (λ_{exc}) region below $\sim 650 \text{ nm}$. The wavelength difference between λ_{obs} and λ_{exc} was always maintained sufficiently large so that not only the scattered light, but also certain Raman lines that were present in the emission, were avoided. An interference filter (maximum transmittance at $\lambda = 435 \text{ nm}$, 5 nm bandwidth) was used for the region above 650 nm due to the weak fluorescence signal in this wavelength range.

Most of the measurements on benzene in n-pentane were made using an interference filter (maximum transmittance 27.8% at $\lambda = 285 \text{ nm}$, 14 nm bandwidth) and a colored filter (Inrad #3). All other measurements on benzene and toluene in various liquids and especially the measurements below 420 nm were done using a combination of an inorganic solution filter and the colored filter (Inrad #3). The liquid filter consisted of a solution of $\text{NiSO}_4 \cdot 7 \text{ H}_2\text{O}$ ($250 \text{ g} \cdot \text{dm}^{-1}$) and $\text{CoSO}_4 \cdot 6 \text{ H}_2\text{O}$ ($50 \text{ g} \cdot \text{dm}^{-1}$) in distilled water having an optical path of 4 cm . Discussions of UV transmitting filters can be found in Kasha (1948), Pellicori (1964), Pellicori et al. (1966), Wladimiroff (1966), Childs (1961) and Laporta and Zagara (1981). Figure 2.7 shows the transmission spectra of the liquid filter alone and the liquid filter plus the colored filter. The colored filter was completely eliminating a small transmission window at $\sim 570 \text{ nm}$, so that the transmittance over the $360\text{-}650 \text{ nm}$ region was less than 0.1% . The transmittance was actually less than the

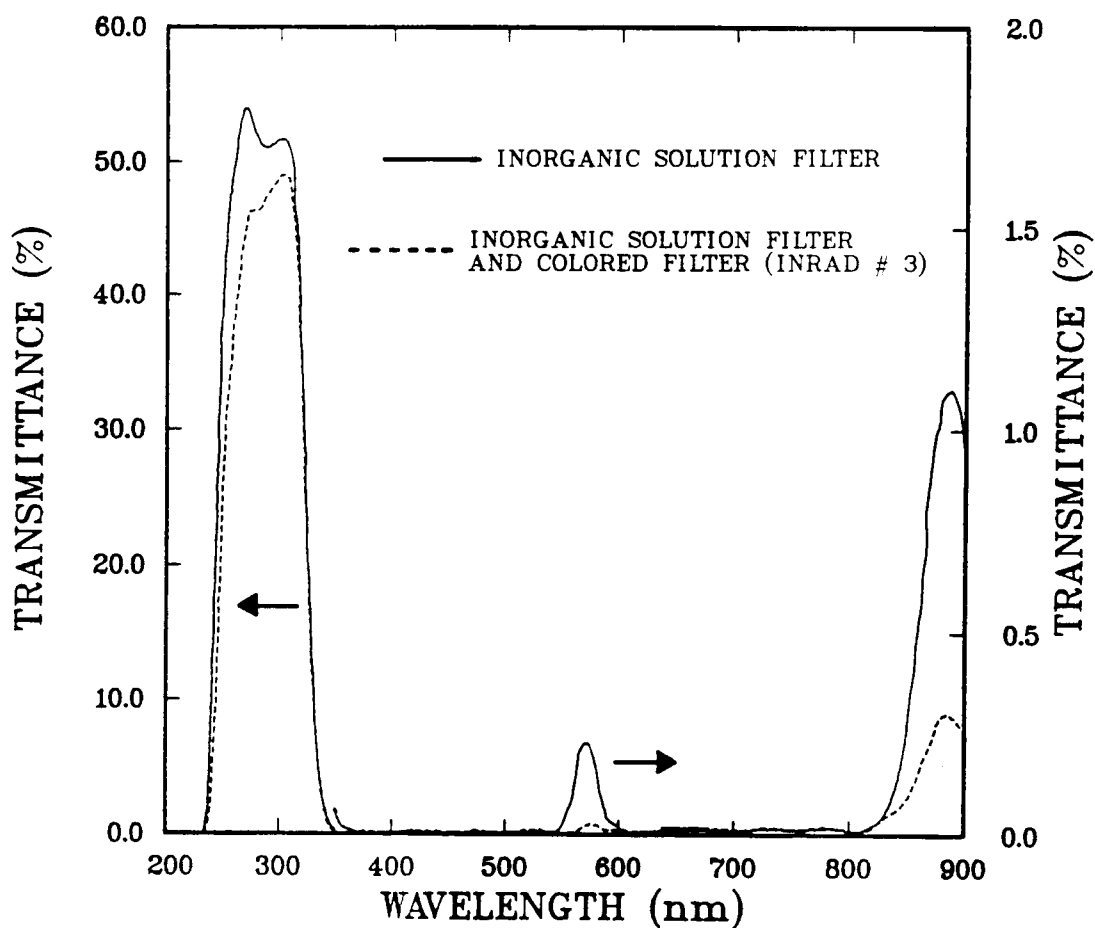


Figure 2.7. Transmission curves of the inorganic solution filter (—), and the solution filter with the colored filter (---). The curves above 350 nm refer to the right hand scale. The inorganic filter consisted of a 4 cm thick, distilled water, solution of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ ($250 \text{ g} \cdot \text{dm}^{-3}$) and $\text{CoSO}_4 \cdot 6 \text{H}_2\text{O}$ ($50 \text{ g} \cdot \text{dm}^{-3}$).

sensitivity of the photometer used to record the spectra (IBM 9240 UV-Vis spectrophotometer). It should be noted that there were no differences in the spectra of the same solution obtained with either the interference or the liquid filter for wavelengths above 420 nm λ_{exc} . Below 420 nm the liquid filter was better in reducing the scattered light and in transmitting the fluorescence light. The liquid filter-colored filter combination started transmitting below ~ 360 nm and for this reason the double monochromator was used in this wavelength range. The λ_{obs} was set at 280 nm, there was no entrance slit and the exit slit of the monochromator was 500 μ m. Because benzene and toluene emit fluorescence at relatively short wavelengths (~ 280 nm), a solar-blind photomultiplier (EMI Cesium Telluride, G26H315) was used to further reduce the contribution of scattered light to the fluorescence signal.

The laser intensity was monitored after the cell by a photodiode (Molelectron J3), and the two signals, the photomultiplier signal for the fluorescence and the photodiode for the laser intensity, were amplified and sampled by a boxcar before they were recorded.

Relatively long focal length lenses ($f = 38$ cm or $f = 100$ cm) were used to focus the laser inside the cell depending on the intensity of the fluorescence signal. Care was taken to ensure that no saturation occurred in the interaction volume (see Sections 2.7 and 3.5), and that the response of the photomultiplier to incident light was linear. Finally, the fluorescence cell could be attached

to the vacuum purification system and pumped down to a residual pressure of 1×10^{-6} Torr. The purified solutions were then transferred into the fluorescence cell under vacuum.

2.6. The Vacuum Purification System and the Materials

All the liquids used in the present experiments were purified and/or deoxygenated. Figure 2.8 shows schematically the entire vacuum purification system. The hydrocarbons used (e.g., n-pentane, TMSi) were first chemically purified. They were repeatedly treated with sulfuric acid to remove olefinic compounds (compounds containing double bonds). The reaction of olefins with sulfuric acid gives a yellowish color to the acid and the hydrocarbon liquids were stirred repeatedly for many hours at a time with a fresh acid solution until no coloration was observed. After separation from the H_2SO_4 they were stirred with BaCO_3 to remove any remaining traces of the acid.

After chemical purification the liquid was introduced into the vacuum system (position 1 in Figure 2.8) where it underwent successive purification steps. After an initial deaeration with successive freeze-pump-thaw (FPT) cycles it was passed over a column containing NaOH pellets (2) to remove acids, H_2O and CO_2 . Then it was collected in a glass bottle (3) where it underwent FPT cycles to remove dissolved air. Following that it was passed over a column of silica gel which had been activated at 240°C (4) and a column of charcoal activated at 500°C (5), which trapped any water traces and was collected in the metal bottle (6), where it underwent further FPT

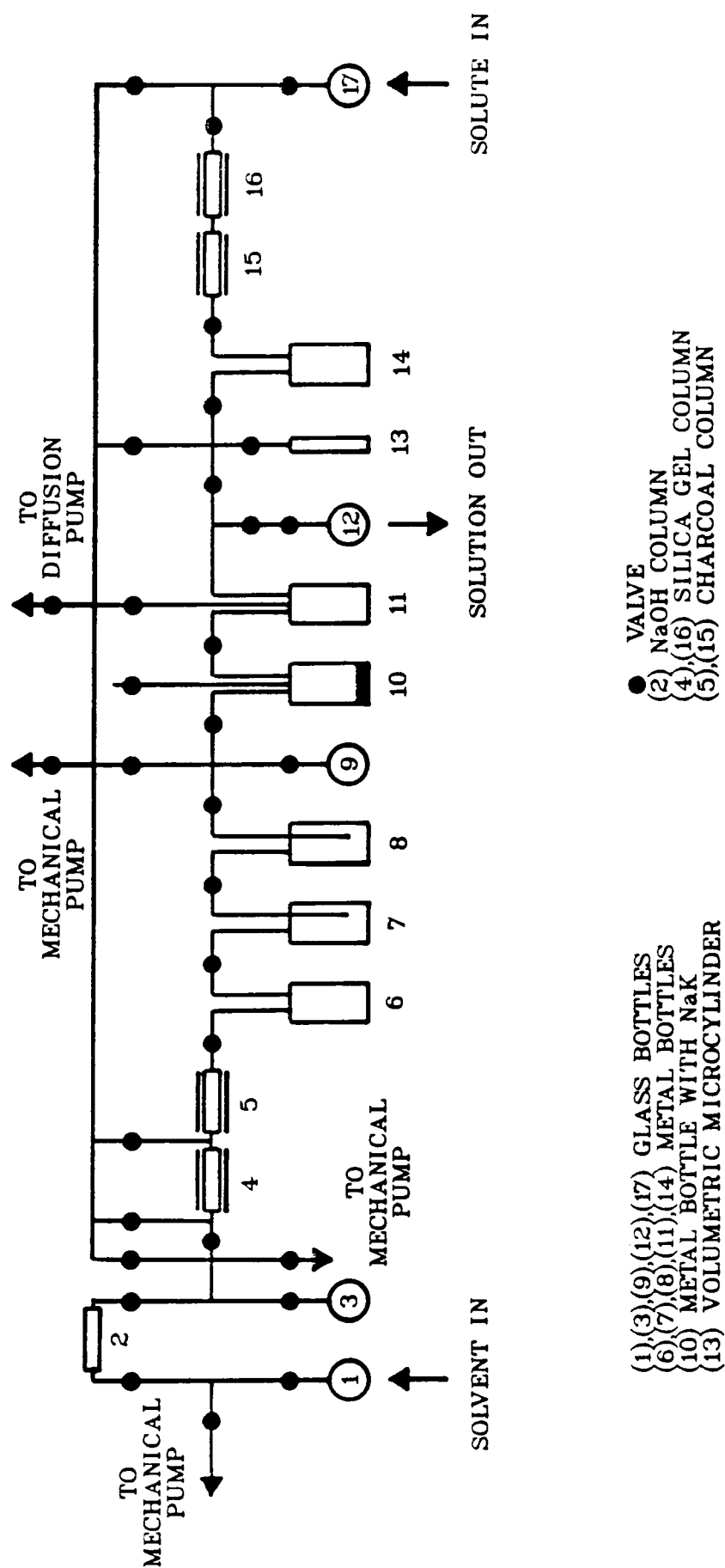


Figure 2.8. The vacuum purification system. The silica gel columns (4, 16) were activated at 240°C and the charcoal columns (5, 15) at 500°C.

cycles and was stored. The quantity that was needed for the experiment was transferred while pumping through bottles (7) and (8) removing thus all dissolved air into bottle (9) and finally into the metal bottle containing liquid NaK (10). The liquid was stirred in the NaK for 24 h, or more, reducing even further any remaining traces of O_2 and H_2O . It was then transferred to an evacuated volumetric bottle (12) containing a measured quantity of the molecule under study, and from there to the liquid cell.

Benzene was also chemically treated, first with H_2SO_4 and then with $LiAlH_4$. After fractional distillation it was introduced into the vacuum purification system (17). It was passed over traps of silica gel (16) and charcoal (15) and underwent FPT cycles before it was transferred into the graduated microcylinder (13). Quantities as small as 0.01 ml could be measured and transferred under vacuum from the microcylinder into bottle 12. The liquids used in the TPE studies only (toluene and the perfluorocarbons) were deaerated with successive FPT cycles.

Fluoranthene of quoted purity 99.99% was used as supplied; n-pentane and benzene were Phillips Research Grade (purity better than 99.98%). Toluene was Eastman Spectro ACS and the TMSi was Aldrich 99.9+% NMR grade. The electron attaching solvents were perfluoro-n-hexane ($n-C_6F_{14}$) (Pierce 99% pure), perfluoromethylcyclohexane ($c-C_7F_{14}$) (PCR Research Chemicals, 97%) and perfluorodimethylcyclobutane ($c-C_6F_{12}$) (Columbia Organic Chemicals, 97%).

2.7. Analysis of Data

The ionization (or fluorescence) signal and the laser intensity signal after digitalization were transferred to a computer for further analysis. The signals were processed by the computer as double arrays of numbers, one array expressing the value of the signal itself, the other the value of the corresponding wavelength.

The signal was first corrected for variations of the dye laser intensity by dividing its value with the appropriate power of the corresponding laser intensity. Equation 1.2.2a ($S_I = C \cdot I^n$) was used to analyze the measurements of the signal dependence on the laser intensity (to be referred to as signal vs. intensity measurements) and obtain the appropriate exponent n . Theoretically n should be a positive integer ($n = 2$ for TPE) expressing the number of photons absorbed. Various processes, however (i.e., saturation, coexistence of different order processes), can lead to noninteger exponents. For this reason the empirical equation:

$$S_I = C \cdot I^S \quad (2.7.1)$$

is introduced to express the signal, where C is a constant and S is a real number. Then $\log S_I = \log C + S \log I$ and

$$S = \frac{d \log S_I}{d \log I} \quad (2.7.2)$$

The quantity S , to be referred to as the slope of the signal vs. intensity measurements (or slope), expresses the number of photons absorbed, as determined experimentally and is the apparent order of the process.

Following this correction the individual spectra (arrays) were combined in their areas of mutual overlap. Effort was taken during the experiment (by using many dyes and dye mixtures) to ensure that the laser intensity profiles overlapped sufficiently well, so that only the spectral segments corresponding to the central and more or less flat portions of the laser intensity profiles were used for the combined spectrum. Additional effort was taken to combine them at points such that the derivatives of the spectra on both sides of the combination point were equal. In this way no false structures were introduced. The reason for using only the portion of the spectrum that corresponds to a flat laser intensity is a less than proportionate (according to the observed intensity dependence) reduction of the signal at the wings of the laser-dye gain profile with respect to the center. This leads to an apparent (and artificial) enhancement of the signal at the wings after correction and therefore to a distortion of the spectrum. This behavior is probably due to an increase in the two-photon transition rate associated with changes in the laser pulse characteristics at the edges of the dye gain profile curve (Birge, 1983). In spectral areas where weak and broad features are present, this phenomenon can be very troublesome and can lead to distortion of the structure beyond recognition.

Figure 2.9 shows the corrected TPE spectra of benzene in n-pentane over the $^1B_{1u}$ state obtained with different laser intensity profiles (upper plot). The effect of the shape of the intensity profile on the spectrum can clearly be seen. As the laser intensity drops, the corrected signal appears to be relatively stronger. It should be noted that these intensity profiles were obtained using dye mixtures (varying amounts of the dyes DPS and Bis-MSB). Single dye intensity profiles failed to yield discernible structure in the same wavelength region.

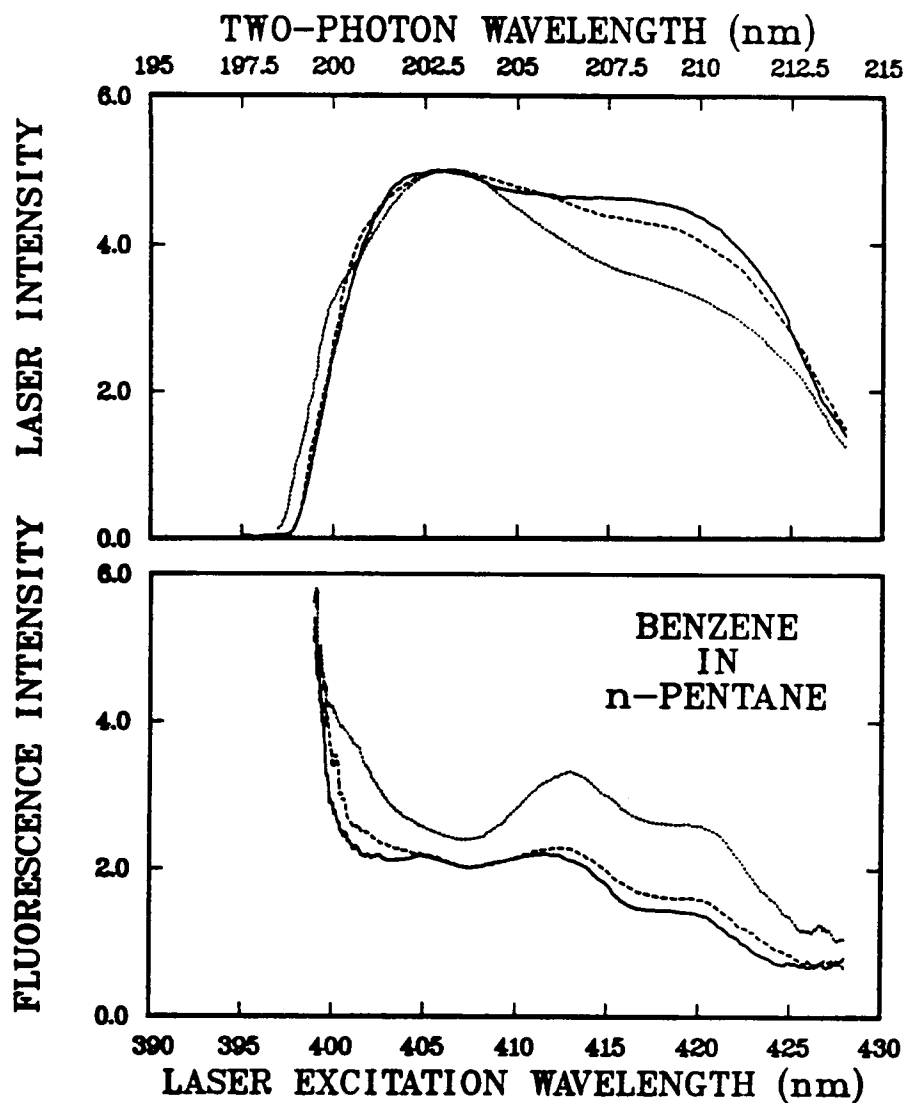


Figure 2.9. Two-photon excitation spectra, corrected for laser intensity variations, by dividing with the square of the intensity (lower plot) and the corresponding laser intensity profiles (upper plot). Note the increase in the relative intensity of the corrected fluorescence signal as the laser intensity drops.

CHAPTER III

TWO-PHOTON EXCITATION OF BENZENE, TOLUENE AND FLUORANTHENE IN NONPOLAR SOLVENTS

3.1. Introduction

Benzene exhibits three different electronic transitions in the energy range below 7 eV. The highest, energetically, of these transitions is the ${}^1E_{1u} \leftarrow {}^1A_{1g}$ which is one-photon allowed, two-photon forbidden, and appears as a very strong peak at ~ 180 nm in the one-photon absorption spectrum, with practically no vibrational structure resolved in the liquid phase. The ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition lies at ~ 210 nm ($\lambda_{\text{exc}} = 420$ nm). Although this transition is one- and two-photon forbidden, it still appears weakly on top of a high background in both the one- and the two-photon spectra, and exhibits a weak but distinct vibrational structure. The reason for its appearance is that it becomes vibrationally allowed via mixing with either the ${}^1E_{1u}$ valence (for the one-photon case) or the ${}^1E_{1g}$ Rydberg state (for the two-photon case).

The ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition is by far the richest vibrationally and most extensively studied benzene transition. Figure 3.1 displays the thirty vibrational modes of benzene, following Wilson's numbering (Wilson, 1934), along with their symmetry designation. Modes 6 through 10 and 16 through 20 are doubly degenerate, so that there are only 20 energetically different normal modes. Of these twenty normal modes,

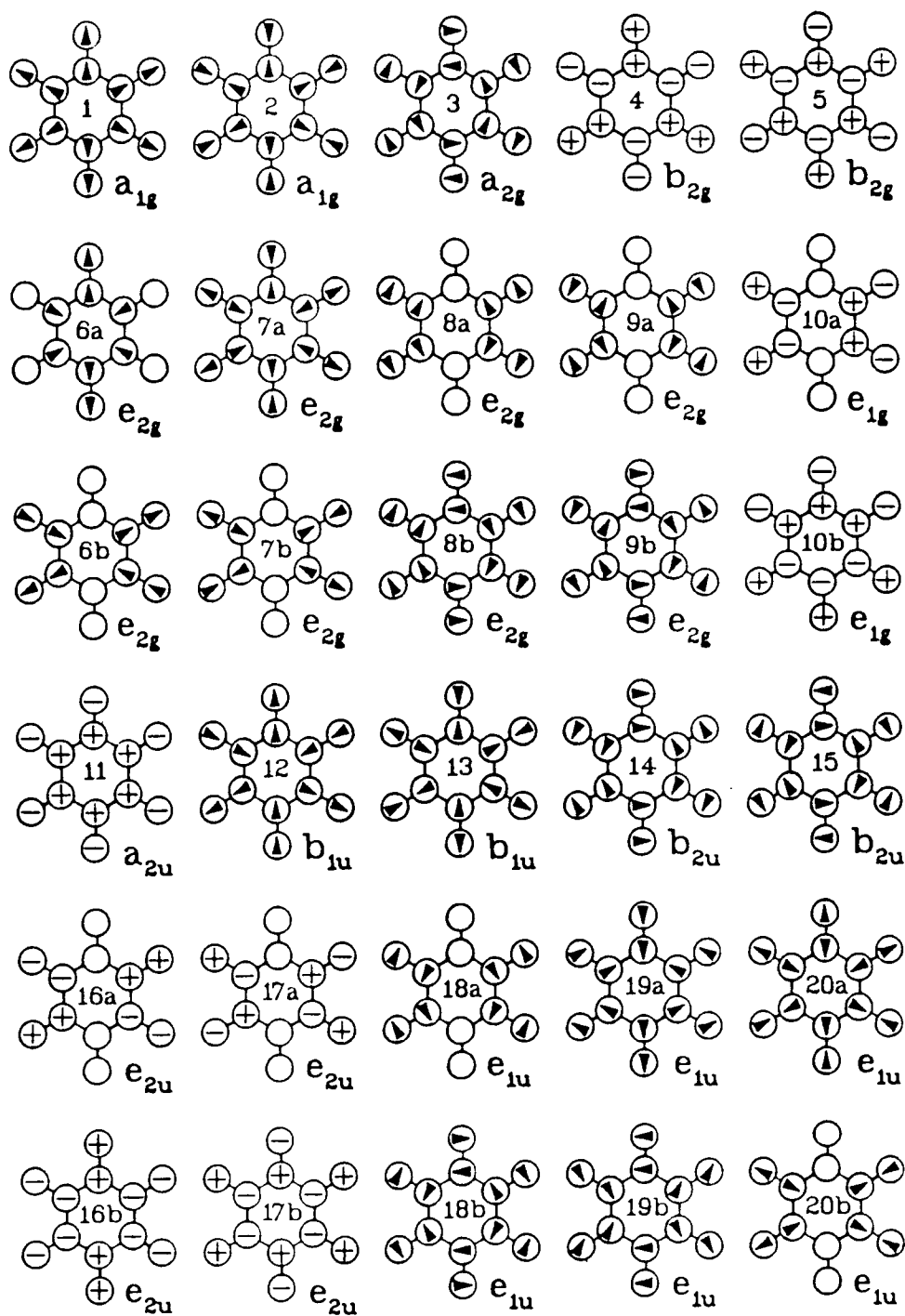


Figure 3.1. The normal modes of benzene following the numbering of Wilson (1934).

only the ones with g-parity (1 through 10 in Figure 3.1) will appear as electric dipole allowed vibrations (i.e., one-photon allowed) and of these the 6 (e_{2g}) gives rise to the major progression observed in the one-photon spectra. The u-parity modes, on the other hand, break the centrosymmetry of the benzene molecule and thus the corresponding vibrations become two-photon allowed. Still, however, the 11 (a_{2u}) mode remains symmetry forbidden and the 12 (b_{1u}) and 13 (b_{1u}) modes are identity forbidden (Goodman and Rava, 1982). In the two-photon case the 14 (b_{2u}), 15 (b_{2u}) and the 18 (e_{1u}) modes are the major active vibrations on which different progressions are built. In both the one- and the two-photon cases, however, quantum 1 (a_{1g}) is the promoting mode which generates the successive members of the different progressions.

The symbol e in the symmetry designation indicates degenerate modes, while the symbols a and b stand for nondegenerate totally symmetric (symmetric with respect to rotation about the 6th order axis), and nondegenerate nontotally symmetric (antisymmetric) modes, respectively. The vibrational modes of benzene are further classified into C-H stretching modes (9, 7, 13, 20), which are highly energetic, C-C breathing modes (1) and out of plane modes (4, 5, 10, 11, 16, 17).

Table 3.1 contains the energies in the gas and the liquid phases and the symmetries of the normal modes of benzene for both the ground ($^1A_{1g}$) and the first excited singlet ($^1B_{2u}$) states. The liquid phase energy values were determined in this work from the TPE studies of benzene in $n\text{-C}_6\text{F}_{14}$. Table 3.2 gives the corresponding values for

Table 3.1. Fundamental Vibrational Frequencies of Benzene

Mode ^a	Symmetry	¹ A _{1g} State		¹ B _{2u} State	
		$\bar{\nu}$ [cm ⁻¹]		$\bar{\nu}$ [cm ⁻¹]	
		Gas ^b	Solution ^c	Gas ^b	Solution ^c
1	a _{1g}	993.1	995	923	920
2	a _{1g}	3,073		3,130.1	
3	a _{2g}	1,350		1,210 ^d	
4	b _{2g}	707		365	
5	b _{2g}	990		744.6	745
6	e _{2g}	608.3		521.4	
7	e _{2g}	3,056		3,077.2	
8	e _{2g}	1,599		1,516 ^e	
9	e _{2g}	1,178		1,147.7	
10	e _{1g}	846	840	580.7	580
11	a _{2u}	674		~516	
12	b _{1u}	1,010		985 ^d	
13	b _{1u}	3,057		3,130 ^d	
14	b _{2u}	1,309	1,320	1,570 ^f	1,570
15	b _{2u}	1,146	1,155	1,148 ^f	1,150
16	e _{2u}	398.8	400	237.5	240
17	e _{2u}	967	985	715 ^f	
18	e _{1u}	1,037	1,050	919 ^f	920
19	e _{1u}	1,482		~1,330 ^g	
20	e _{1u}	3,064		3,130 ^d	

^aNumbering after Wilson (1934).

^bUnless otherwise indicated, the energies are taken from Atkinson and Parmenter (1978).

^cPresent work (~10⁻² M of benzene in perfluoro-n-hexane).

^dFrom Spears and Rice (1971). ^eFrom Stephenson et al. (1984).

^fFrom Wunsch et al. (1977). ^gFrom Aron et al. (1980).

Table 3.2. Fundamental Vibrational Frequencies of Toluene

Mode	Symmetry	¹ A ₁ State		¹ B ₂ State	
		$\bar{\nu}$ [cm ⁻¹]		$\bar{\nu}$ [cm ⁻¹]	
		Gas ^a	Solution ^b	Gas ^a	Solution ^b
1	A ₁	1,002		932	932
6a	A ₁	521		456	
7a	A ₁	1,210		1,193 ^c	1,197
8					
9a	A ₁	1,175		1,035 ^c	
10a	A ₂	842			
11	B ₂	216			
12	A ₁	785	788	753 ^c	760
13					
14	A ₁	(1,299) ^d	1,251	1,562 ^c	1,560
15					
16a	A ₂	405	411		
17a	A ₂	985	981	966 ^c	
18a	A ₁	1,030			

^aUnless otherwise indicated, the energies are taken from Ginsburg et al. (1946).

^bPresent work ($\sim 10^{-2}$ M of toluene in perfluoro-n-hexane).

^cFrom Vasudev and Brand (1979a)

^dFrom Vasudev and Brand (1979b). The energy is for the 14₁⁰ quantum of fluorobenzene.

toluene both in the gas and the liquid phases. The normal modes of toluene are indicated, in correspondence with benzene, following Wilson's numbering. The only difference is that the degenerate modes of benzene are nondegenerate for toluene and therefore they are differentiated with an a and a b.

The differences between one- and two-photon transitions are illustrated in Figure 3.2, which shows the one-photon absorption (OPA) and the TPE spectra of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene in $n\text{-C}_6\text{F}_{14}$. Although, in both cases, the $1(a_{1g})$ vibration is the major promoting mode which produces the successive members of each progression, different progressions are active in each case ($6_0^1 1_0^n$ for the one-photon and $14_0^1 1_0^n$ for the two-photon case). Note also the absence in the OPA spectrum of the 0-0 transition, which can be clearly observed in the TPE spectrum at $\lambda_{\text{exc}} = 525.6 \text{ nm}$. The two-photon spectrum is from this work, while the OPA spectrum is from Kourouklis (1982).

The different vibronic bands (vibrational levels) observed in the spectrum are composed of varying contributions of rotational branches—namely the O, P, Q, R and S branches—which are partially overlapping and which have different polarization behavior, that is, different intensity with light of circular or linear polarization (Wunsch et al., 1977). Theoretically, the maximum polarization ratio ($\Omega = \text{Signal}_{\text{circ.}} / \text{Signal}_{\text{lin.}}$) that can be observed in a two-photon process is $\Omega = 3/2$. This maximum value will appear for transitions to states having less than the full molecular symmetry, while it will be

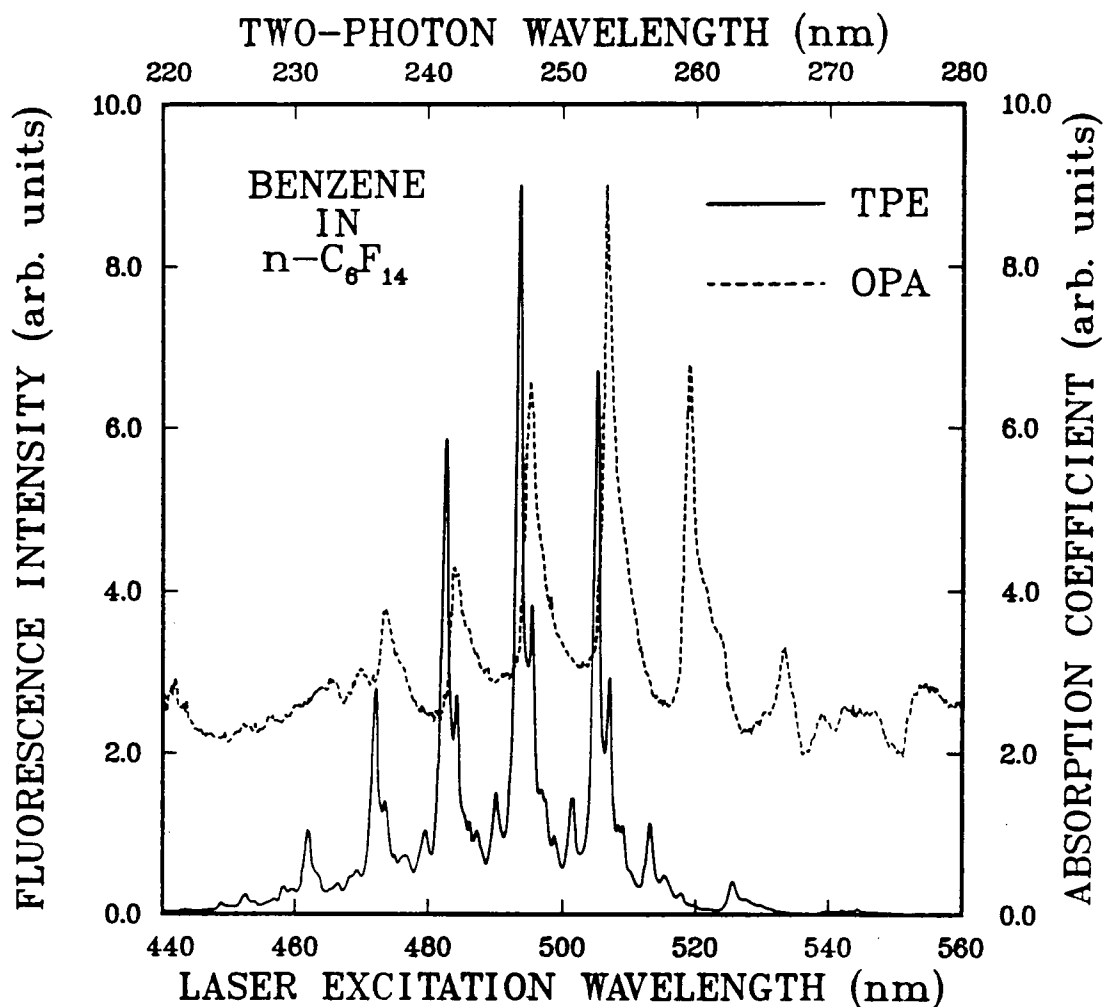


Figure 3.2. Two-photon excitation (TPE) and one-photon absorption (OPA) spectra of the ${}^1B_{2u}$ state of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$). The major progression in the TPE spectrum is the $14_0^1 1_0^n$, while in the OPA is the $6_0^1 1_0^n$. Note the absence of the 0-0 transition ($\lambda_{\text{exc}} = 525.6 \text{ nm}$) from the OPA spectrum. The TPE spectrum is from the present work and the OPA is from Kourouklis (1982).

$\Omega < 3/2$ for transitions to totally symmetric states (Berg et al., 1978; Friedrich and McClain, 1975). It turns out that the anisotropic contributions to the vibronic bands (the O, P, R and S branches) have a polarization ratio of $3/2$, while the mostly isotropic Q branch has a theoretically estimated ratio of $1/14.4$ (Wunsch et al., 1977). The polarization ratio of the overall vibronic band is therefore a weighted average of the individual ratios depending on their contribution to the intensity of the band.

The experimental determination of Ω for a given vibrational band is complicated by the fact that many bands are partially overlapping (especially in the liquid phase). In addition to this, the circularly polarized light always contains a small linearly polarized component (1%-20%) which contributes to the signal. The effect of this linearly polarized component on the signal and the transition probability involving one circularly and one linearly polarized photon are not exactly known. On the other hand, theoretical calculations of the ratio require knowledge of the relative intensities of the individual rotational branches in the vibrational band which is derived from the fitting of the theoretical to the experimental band contours (Wunsch et al., 1977). One can clearly differentiate, however, between totally symmetric vibrational bands, such as the 14 (b_{2u}) and the 15 (b_{2u}), whose strength is derived mostly from isotropic (Q branch) contribution and whose intensity drops dramatically with circularly polarized light (experimental ratio 0.2) and the 18 (e_{1u}) band whose intensity increases or stays the same with circular polarization (experimental ratio ≈ 1.0) (Wunsch et al., 1977; Friedrich and McClain, 1975).

Toluene also exhibits the same pattern of electronic states as benzene ($^1B_2 \leftarrow ^1B_1 \leftarrow ^1E_1$); especially the energetically lowest transition ($^1B_2 \leftarrow ^1A_1$) appears very similar with that of benzene. It is red-shifted, however, by $\sim 600 \text{ cm}^{-1}$. The most active progression building vibrational mode is again the 14 (A_1), while the 12 (A_1) and 1 (A_1) modes, which are forbidden in benzene, appear in toluene weakly. In toluene, however, due to the different symmetry both the 1 (A_1) and the 12 (A_1) are promoting modes, while the $14_0^1 7_0^1$ combination mode serves as the origin of a long progression.

In addition to the valence states discussed above, the lowest Rydberg states of both benzene and toluene lie in the wavelength region under study ($\lambda_{\text{exc}} \gtrsim 360 \text{ nm}$). Multiphoton ionization studies in the gas phase have located the two-photon resonant, two-photon allowed $(3s)^1E_{1g}$ Rydberg transition of benzene at $\lambda_{\text{exc}} = 391.5 \text{ nm}$ (Johnson, 1976; Krogh-Jespersen et al., 1979) and the two 3p Rydberg transitions of toluene at $\lambda_{\text{exc}} = 365 \text{ nm}$ and $\lambda_{\text{exc}} = 379 \text{ nm}$, respectively (Uneberg et al., 1980). There is some evidence suggesting that the two-photon allowed $(3s)^1E_{1g}$ transition can be observed even in the liquid phase at $\lambda_{\text{exc}} \approx 380 \text{ nm}$ (Scott and Albrecht, 1981).

In the following sections the TPE studies of benzene, toluene and fluoranthene will be presented. For benzene there will be a separate discussion of the spectral features of the first singlet state ($^1B_{2u}$) on the one hand, and of the higher excited states ($^1B_{2u}$, 380 nm peak) on the other. First, however, some of the physicochemical properties of the perfluorocarbons vis-a-vis those of the hydrocarbons

will be discussed together with their peculiar behavior as spectroscopical solvents.

3.2. Physicochemical Properties of Perfluorocarbon Solvents

Fluorine is the first member of the halogen atom series and having an atomic number 9 is one electron short of acquiring the electronic structure and resulting inertness of neon. It has, therefore, an extremely high ionization potential (IP = 17.5 eV)—it is the second highest after that of He (24.4 eV)—and an electron affinity of 3.65 eV (Reed, 1964). It is the most electronegative of all elements.

Because of its small size and the fact that the length of the C-F bond is shorter than the length of the C-C bond (1.36 vs. 1.54 Å), fluorine can substitute hydrogen in essentially all the hydrocarbon structures without distorting or straining them significantly, as the other halogens, for example, do. As a result, perfluorocarbons are of the most stable and least reactive compounds (CF_4 decomposes at temperatures over 2000°C).

Theoretically, the physicochemical properties of dense matter can be deduced by calculating the interaction energy between neighboring molecules as a function of the distance between centers of interaction and the relative orientation of the molecules. This interaction potential contains both attractive and repulsive terms, the former being dominant, so that the molecules are held together by Van der Waals forces. In hydrocarbons, because of the very small size of the hydrogen atom, not only H,H but also C,H and C,C interactions between

adjacent molecules contribute to the interaction potential which is strongly attractive. In fluorocarbons, however, because the fluorine atom is larger than the hydrogen, adjacent molecules are kept more apart so that the F,F interactions contribute predominantly to the interaction potential, and since they contain strong repulsive terms, they lead to very weak attractive forces between molecules. In many respects perfluorocarbons exhibit a rare gas-like behavior. For example, there is a very good correlation between perfluorocarbons and rare gases when comparing boiling points as a function of atomic or molecular weight (Bryce, 1964).

Perfluorocarbons, therefore, are very interesting as nonpolar solvents although their solubility, for the reasons outlined above, is rather low. They possess ionization potentials that are significantly higher than the corresponding ones for the hydrocarbons. This difference gives rise to an unusual and nonideal behavior (in the sense that it deviates from Raoult's law) of hydrocarbon-fluorocarbon binary mixtures (Reed, 1964). More specifically, the volume change upon mixing of perfluorocarbons with hydrocarbons is positive and unusually large, while it is negligible in perfluorocarbon-perfluorocarbon mixtures and very small in hydrocarbon-hydrocarbon mixtures.

Table 3.3 gives the corresponding values of some of the physical properties of n-fluorocarbons and n-hydrocarbons. Perfluorocarbons, as a group, have very low indices of refraction; in fact, $n\text{-C}_5\text{F}_{12}$ ($n = 1.2437$ at $\lambda = 435$ nm) has the lowest refractive index ever measured for a material in the condensed phase (Reed, 1964). They have, compared to

hydrocarbons, higher liquid compressibility, higher vapor pressure, higher free volume, lower polarizability and lower velocity of sound. These properties suggest that molecules dissolved in such liquids find themselves in a "gas-like" environment.

Table 3.3. Values of Selected Physicochemical Properties of n-Perfluorocarbons and n-Hydrocarbons^a

	n-Fluorocarbon	n-Hydrocarbon	Number of C Atoms
Isothermal compressibility	2.7 atm ⁻¹	1.68 atm ⁻¹	6
Velocity of sound	614 m · s ⁻¹	1238 m · s ⁻¹	7
Index of refraction	1.2545	1.3748	6
Ionization potential	~ 17 eV	10.48 eV	6
Surface tension	13.7 dyn · cm ⁻¹	21.8 dyn · cm ⁻¹	8
Molar volume	202 cm ³	130 cm ³	6

^aCompiled from values in Reed (1964).

A very interesting effect associated with the perfluorocarbon properties and especially their low polarizability is the anomalous behavior of the spectral shifts of benzene in perfluoro-n-hexane. It is well known that the spectra of aromatic molecules shift to the red when the molecule is transferred from the vapor to a solvent. This shift is understood to arise from the action of dispersion forces which lower the energy of the excited state more than that of the ground state. McRae (1957) using second order perturbation theory and considering dipole interactions derived a formula for the spectral red-shift with respect to the gas phase, which for nonpolar solutes and in a simplified form is given by:

$$\Delta\bar{\nu} = (A L_0 + B) \left(\frac{n^2 - 1}{2n^2 + 1} \right) \quad (3.2.1)$$

where A and B are constants characteristic of the solute, n is the index of refraction of the solvent and L_0 is the so-called "weighted mean wavelength" which is a function of the wavelengths of the excited states of the solvent. For saturated hydrocarbons and for solute transitions well below the first singlet state of the solvent, L_0 can be considered constant with a value $\sim 1000 \text{ \AA}$. The redshift generally increases with the index of refraction and the oscillator strength of the transition.

Since pressure increases the density and therefore the refractive index, it is expected that higher pressures will cause shifts of the spectrum to the red. Zipp and Kauzmann (1973) studied the pressure dependence of the spectral shifts of the S_1 state of a number of aromatic molecules (benzene, chlorobenzene, naphthalene, phenanthrene) in various solvents (water, $n\text{-C}_6\text{F}_{14}$, alcohols, hydrocarbons). They found that only for benzene in $n\text{-C}_6\text{F}_{14}$ a blue-shift is observed with increasing pressure. Similarly a blue-shift is observed, with increasing pressure, in the spectrum of benzene in helium as a carrier gas (Robertson and King, 1959). A blue-shift is also observed between the position of the $^1E_{1u}$ state of benzene in $n\text{-C}_6\text{F}_{14}$ (179.9 nm; Kourouklis, 1982), and the corresponding position in the gas phase (180.412 nm; Wilkinson, 1956).

Equation 3.2.1 accounts for the spectral shift which is due to dipole interactions only. According to McRae (1957) other types of

interactions can make important or even dominant contributions to the frequency shift of the spectrum, such as charge-transfer complex formation, intermolecular repulsive forces and changes in the size and shape of the solute upon excitation. All these observations point towards the fact that the interpretation of the spectral shifts of benzene in perfluorocarbons, especially for the higher excited states, might not be a straightforward task.

Another difference between perfluorocarbons and hydrocarbons is that chain branching in the former is expected to have a much smaller effect on their physicochemical properties than in the latter and in the opposite direction. Branching in hydrocarbons reduces the number of C,C interactions by "burying" C atoms in the molecular core thus reducing the attractive van der Waals forces and making the medium more gas-like (higher vapor pressure, lower density, lower index of refraction, etc.). For perfluorocarbons the C,C interactions are negligible any way, while the branching brings closer together the fluoromethyl groups, so that F,F interactions are slightly increased, leading to stronger attraction.

3.3. Two-Photon Excitation of Benzene. The ${}^1B_{2u} \leftarrow {}^1A_{1g}$ Transition

The TPE spectra of $\sim 10^{-2}$ M solutions of benzene in TMSi, n-pentane, n-C₆F₁₄, c-C₇F₁₄, c-C₆F₁₂ are shown in Figures 3.3 through 3.7. The spectra shown were measured with linearly polarized light over the $360 \text{ nm} < \lambda_{\text{exc}} < 560 \text{ nm}$ region and have been corrected for the laser light intensity variations. The polarization ratio corresponding

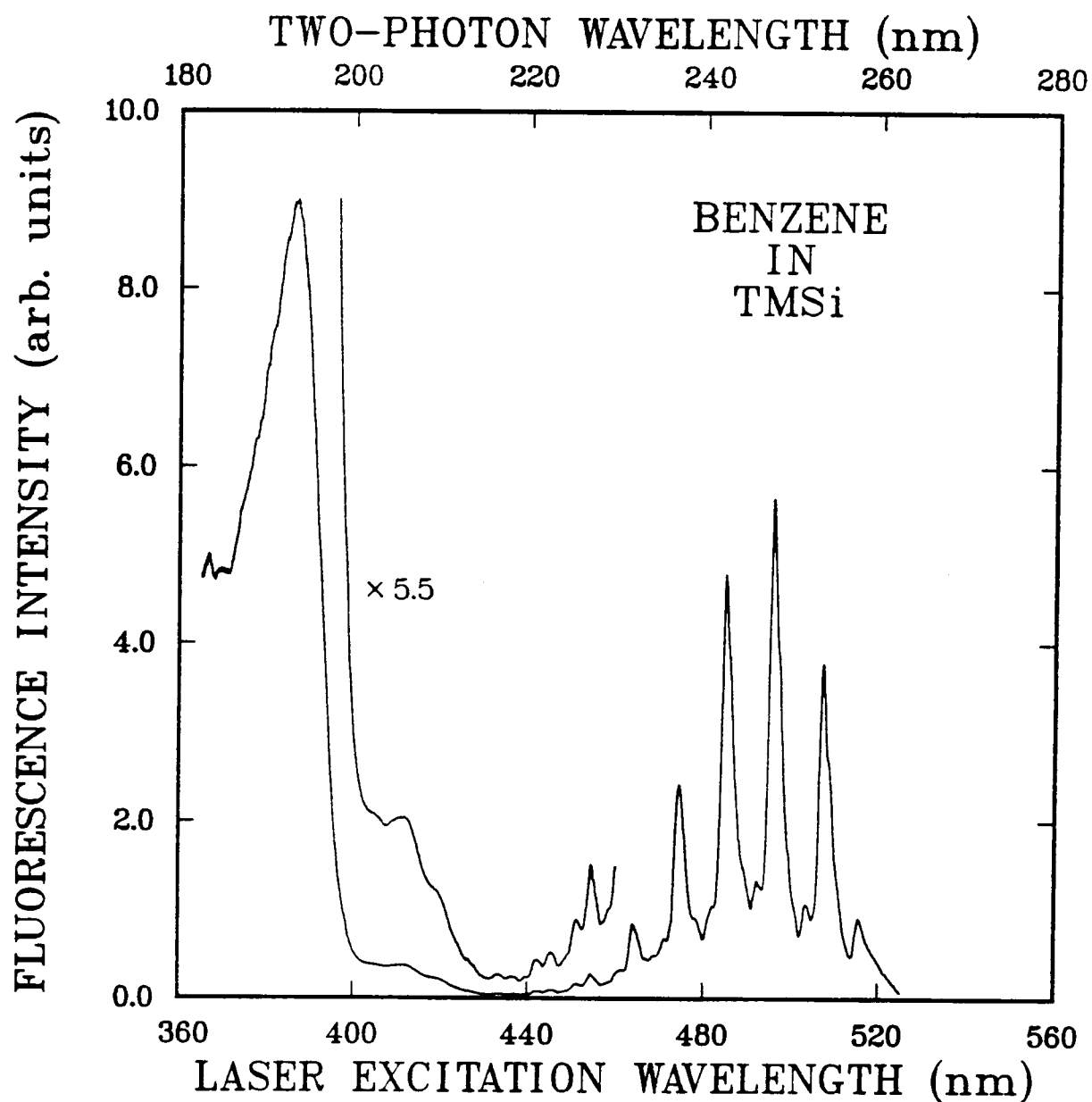


Figure 3.3. Two-photon excitation spectrum of benzene in tetramethylsilane (TMSi).

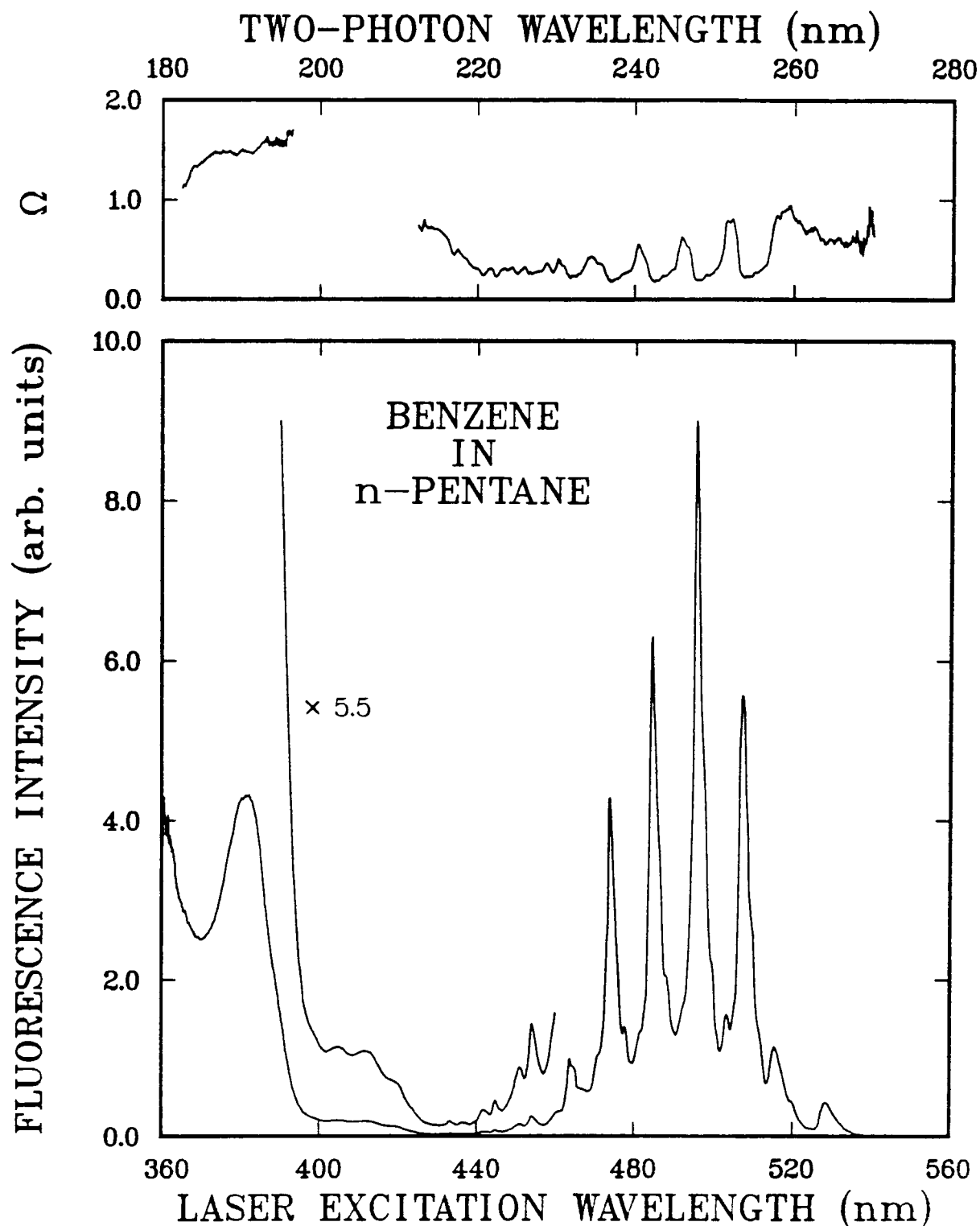


Figure 3.4. Two-photon excitation spectrum of benzene in n-pentane. The corresponding polarization ratio Ω is shown in the graph exactly above.

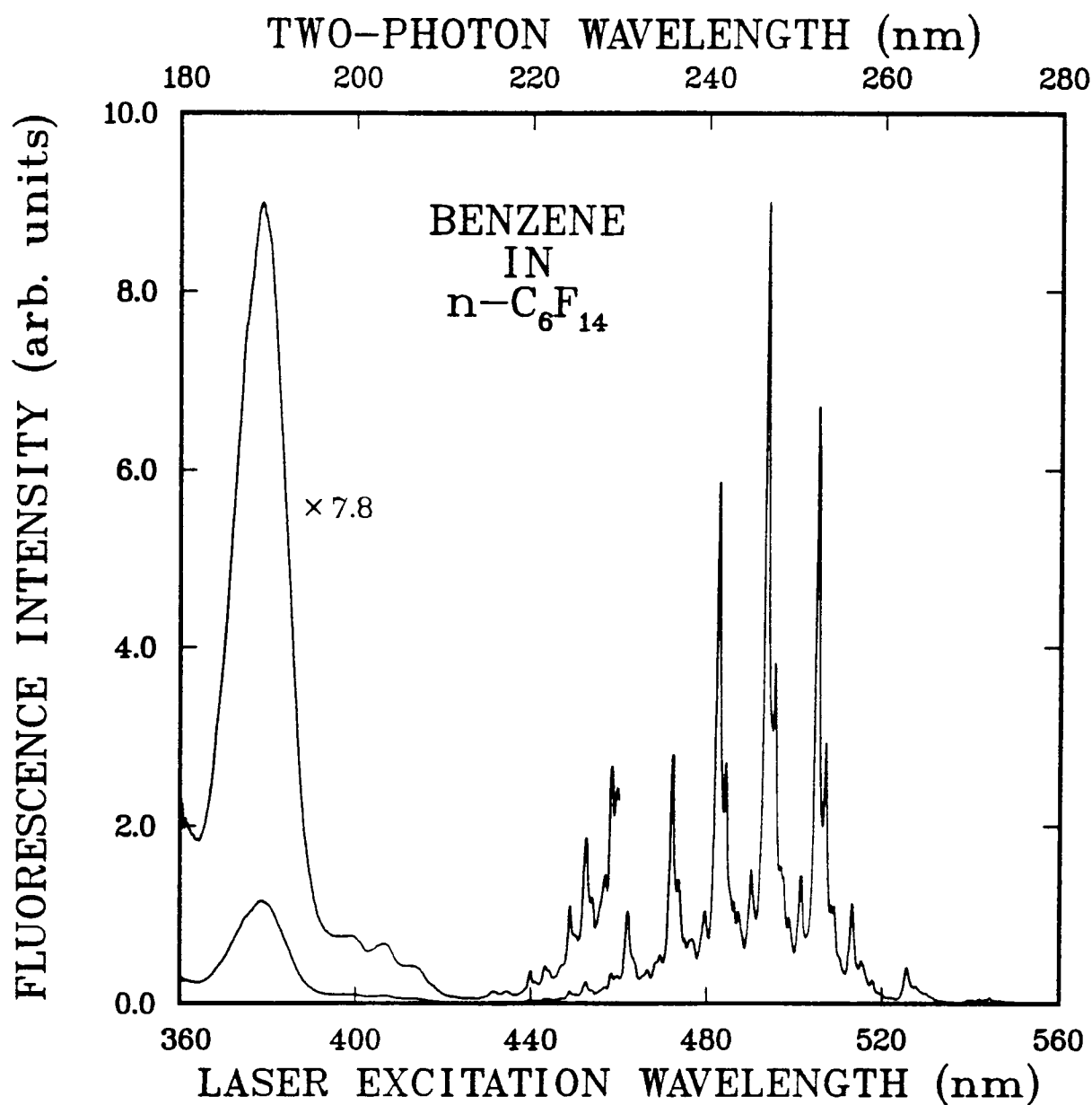


Figure 3.5. Two-photon excitation spectrum of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$).

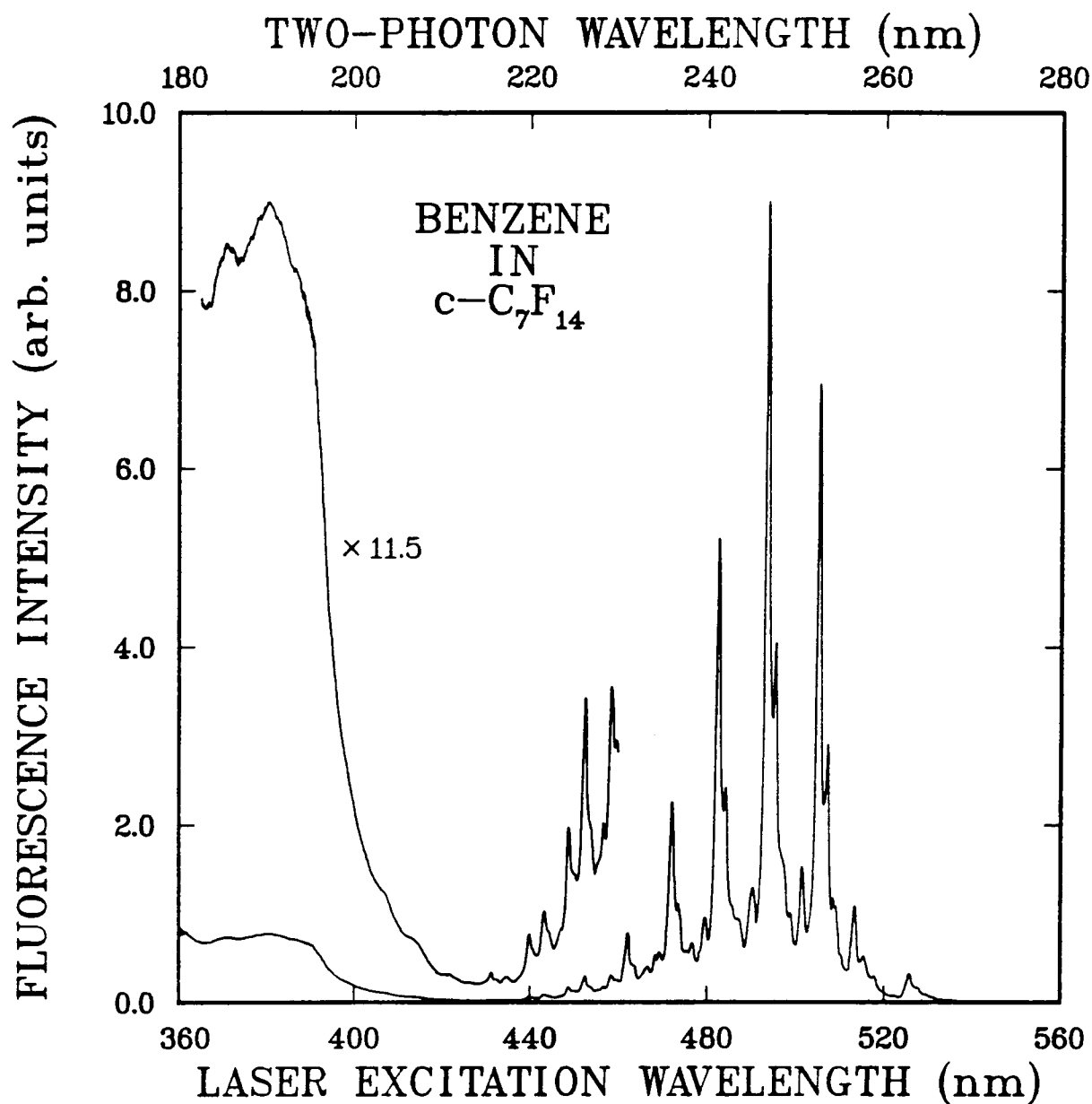


Figure 3.6. Two-photon excitation spectrum of benzene in perfluoromethylcyclohexane (c-C₇F₁₄).

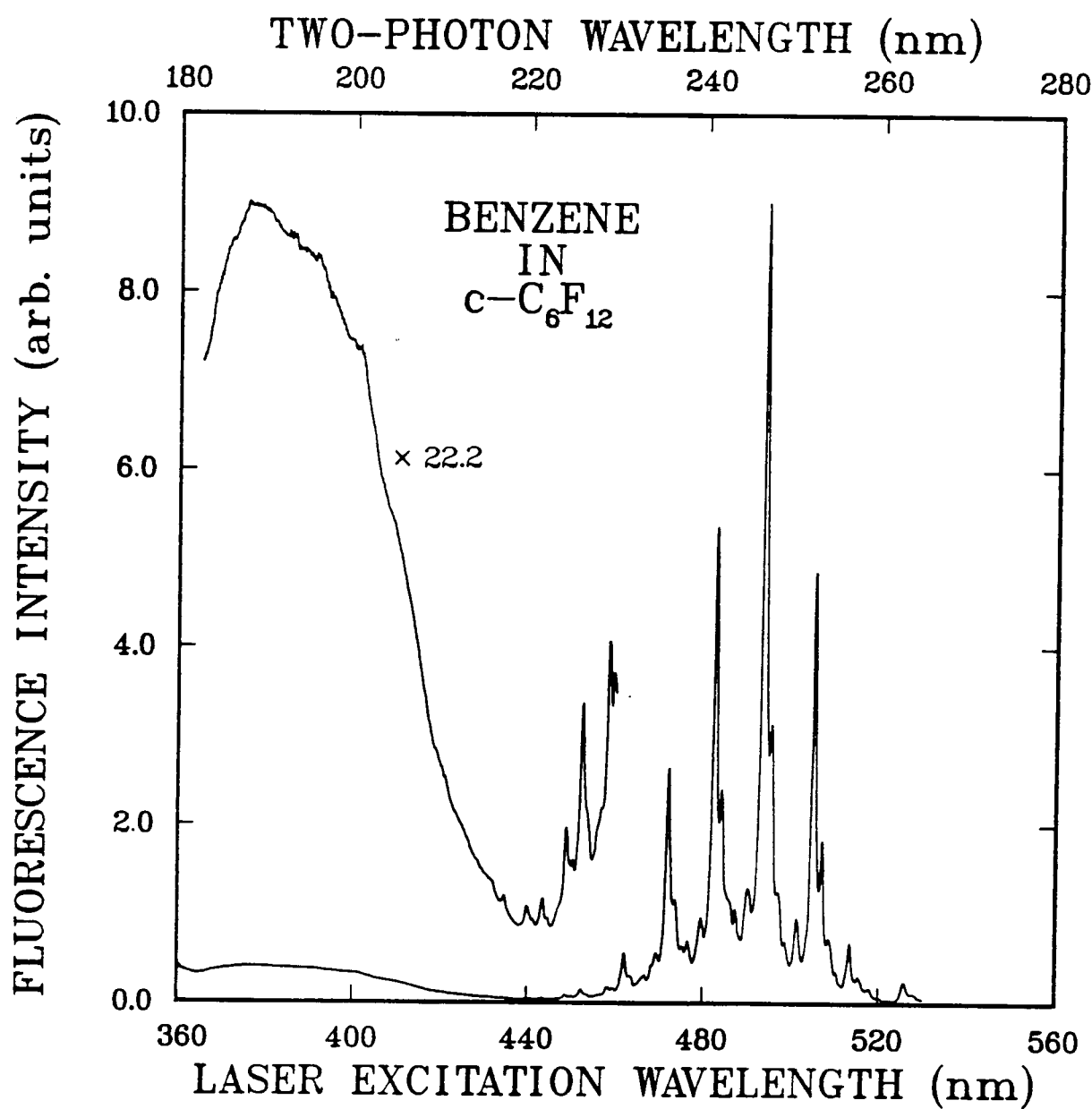


Figure 3.7. Two-photon excitation spectrum of benzene in perfluoro-dimethylcyclobutane (c-C₆F₁₂).

to the n-pentane solution is also shown above the spectrum in Figure 3.4. Three different transition bands can be distinguished in all these spectra; the ${}^1B_{2u}$ manifold, extending from ~ 560 nm up to ~ 420 nm laser excitation wavelength; the ${}^1B_{1u}$ manifold, extending from ~ 420 nm up to 395 nm and the strong peak at $\lambda_{exc} \approx 380$ nm. In this section the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition manifold will be discussed.

As far as the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition is concerned, the different solvents can be grouped into two categories considering the resolution and the relative red-shifts of their corresponding spectra. TMSi and n-pentane, causing a spectral red-shift with respect to the gas phase of ~ 230 cm^{-1} and having indices of refraction $n = 1.3585$ and $n = 1.3579$, respectively, form the one group; the perfluorocarbons causing a red-shift of ~ 30 cm^{-1} and with $n \approx 1.26$ ($n = 1.2509$ for n- C_6F_{14} and $n = 1.2781$ for c- C_7F_{14}), form the other. Each solvent group gave practically identical spectra over the ${}^1B_{2u}$ state, which is, of course, expected theoretically, considering McRae's formula and their indices of refraction. The spectrum in n- C_6F_{14} , because of its superior resolution, was used for the assignment of the observed structure.

Figure 3.8 shows the spectrum of benzene in n- C_6F_{14} and directly above the diagram indicates the various vibrational progressions and the assignment of each peak. Table 3.4 contains the energies from the ground state, the energy from the transition origin ($\Delta\bar{\nu} = \bar{\nu} - 38050$ cm^{-1}) and the assignment of the structure. For comparison the gas phase energies from Wunsch et al. (1977) are also given.

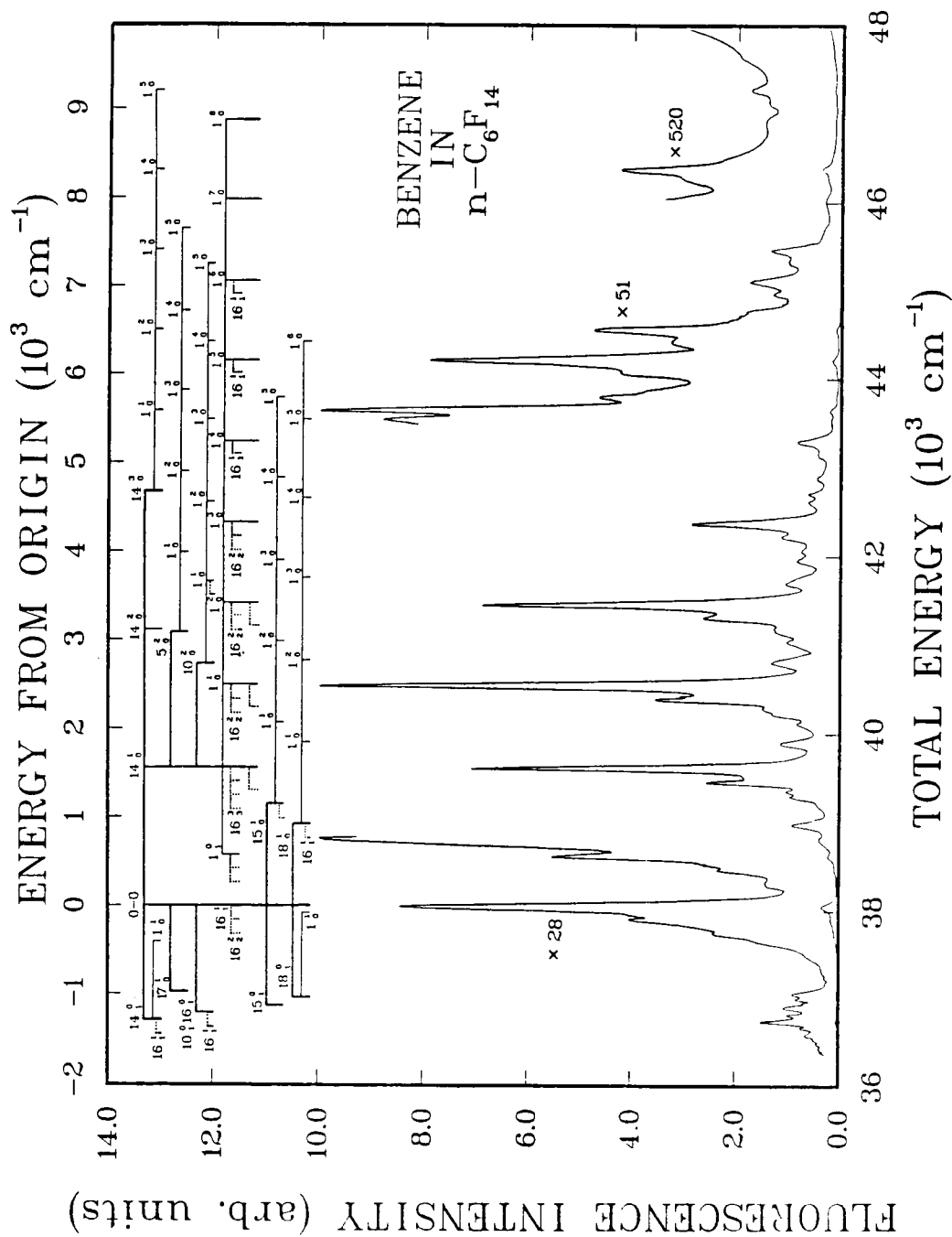


Figure 3.8. The two-photon excitation spectrum of the ${}^1\text{B}_{2u}$ state of benzene in perfluoro- n -hexane ($n\text{-C}_6\text{F}_{14}$). See text.

Table 3.4. Vibrational Energy Levels of the ${}^1B_{2u}$ State of Benzene in Perfluoro-n-Hexane

Solution $\bar{\nu}$ [cm^{-1}]	Solution $\Delta\bar{\nu}$ [cm^{-1}] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm^{-1}]
36,570	-1,480	$14_1^0 16_1^1$	36,611
36,660	-1,390	$10_1^1 16_2^1$	36,686
36,730	-1,320	14_1^0	36,775
36,810	-1,240	$10_1^0 16_1^0$	36,853
36,895	-1,155	15_1^0	36,935
36,950	-1,100		
37,000	-1,050	18_1^0	37,052
37,065	-985	17_1^0	37,128
37,650	-400	$14_1^0 1_0^1$	37,689
37,745	-305	16_2^2	
37,905	-145	16_1^1	
37,960	-90	$18_1^0 1_0^1$ and $17_1^0 1_0^1$	
38,050	0	0-0	(38,086)
38,300	250	$14_0^1 1_1^0 16_2^2$	38,322
38,460	410	$14_0^1 1_1^0 16_1^1$	38,486
38,625	575	$14_0^1 1_1^0$	38,657
38,810	760	$18_0^1 16_1^1$	38,845
38,970	920	18_0^1	39,009
39,035	985	$15_0^1 16_1^1$	39,061
39,125	1,075	$14_0^1 16_3^3$	39,155

Table 3.4 (continued)

Solution $\bar{\nu}$ [cm ⁻¹]	Solution $\Delta\bar{\nu}$ [cm ⁻¹] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm ⁻¹]
39,200	1,150	15 ₀ ¹	39,228
39,285	1,235	14 ₀ ¹ 16 ₂ ²	39,319
39,350	1,300	14 ₀ ¹ 10 ₁ ¹	39,387
39,450	1,400	14 ₀ ¹ 16 ₁ ¹	39,485
39,620	1,570	14 ₀ ¹	39,650
39,890	1,840	18 ₀ ¹ 1 ₀ ¹	39,929
40,115	2,065	15 ₀ ¹ 1 ₀ ¹	40,160
40,220	2,170	14 ₀ ¹ 1 ₀ ¹ 16 ₂ ²	40,260
40,275	2,225	14 ₀ ¹ 1 ₀ ¹ 10 ₁ ¹	40,311
40,375	2,325	14 ₀ ¹ 1 ₀ ¹ 16 ₁ ¹	40,406
40,540	2,490	14 ₀ ¹ 1 ₀ ¹	40,574
40,780	2,730	14 ₀ ¹ 10 ₀ ²	40,817
40,810	2,760	18 ₀ ¹ 1 ₀ ²	40,856
41,030	2,980	15 ₀ ¹ 1 ₀ ²	41,081
41,140	3,090	14 ₀ ¹ 1 ₀ ² 16 ₂ ² and 14 ₀ ¹ 5 ₀ ²	41,177
41,160	3,110	14 ₀ ²	41,196
41,200	3,150	14 ₀ ¹ 1 ₀ ² 10 ₁ ¹	41,233
41,310	3,260	14 ₀ ¹ 1 ₀ ² 16 ₁ ¹	41,322
41,468	3,418	14 ₀ ¹ 1 ₀ ²	41,500
41,550	3,500	14 ₀ ¹ 10 ₀ ² 1 ₀ ¹ 16 ₁ ¹	41,586
41,590	3,540	18 ₀ ¹ 1 ₀ ³ 16 ₁ ¹	41,620
41,714	3,664	14 ₀ ¹ 10 ₀ ² 1 ₀ ¹	41,742

Table 3.4 (continued)

Solution $\bar{\nu}$ [cm ⁻¹]	Solution $\Delta\bar{\nu}$ [cm ⁻¹] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm ⁻¹]
41,751	3,701	18_0^{13}	41,782
41,950	3,900	15_0^{13}	41,991
42,038	3,988	$14_0^{13}16_2^2$ and $14_0^{12}5_0^11_0^1$	42,075
42,210	4,160	$14_0^{13}16_1^1$	42,244
42,377	4,327	14_0^{13}	42,409
42,610	4,560	$14_0^{12}10_0^21_0^2$	42,648
42,650	4,600	18_0^{14}	42,680
42,725	4,675	14_0^3	42,782
42,880	4,830	15_0^{14}	42,911
42,950	4,900	$14_0^{12}5_0^21_0^2$	42,976
43,140	5,090	$14_0^{14}16_1^1$	
43,290	5,240	14_0^{14}	
43,530	5,480	$14_0^{12}10_0^21_0^3$ and 18_0^{15}	
43,635	5,585	14_0^{31}	
43,790	5,740	15_0^{15}	
43,865	5,815	$14_0^{12}5_0^21_0^3$	
44,050	6,000	$14_0^{15}16_1^1$	
44,205	6,155	14_0^{15}	
44,420	6,370	$14_0^{12}10_0^21_0^4$ and 18_0^{16}	
44,560	6,510	14_0^{32}	
44,770	6,720	$14_0^{12}5_0^21_0^4$	
44,960	6,910	$14_0^{16}16_1^1$	

Table 3.4 (continued)

Solution $\bar{\nu}$ [cm^{-1}]	Solution $\Delta\bar{\nu}$ [cm^{-1}] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm^{-1}]
45,105	7,055	14_0^{16}	
45,310	7,260	$14_0^{10} 10_0^{25}$	
45,465	7,415	14_0^{33}	
45,700	7,650	$14_0^{15} 5_0^{25}$	
46,030	7,980	14_0^{17}	
46,216	8,166	$14_0^{34} 1_0^{16}$	
46,377	8,327	14_0^{34}	
46,948	8,898	14_0^{18}	
47,114	9,064	$14_0^{35} 1_0^{16}$	
47,281	9,231	14_0^{35}	

^aEnergy in cm^{-1} is measured from the origin of the 0-0 transition ($38,050 \text{ cm}^{-1}$).

^bFrom Wunsch et al. (1977). In the gas phase the origin of the 0-0 transition ($38,086 \text{ cm}^{-1}$) of benzene cannot be observed. The gas phase measurements stop at the high energy side at about $43,000 \text{ cm}^{-1}$.

The assignment in Figure 3.8 contains only the designation of the last quanta after the branching point of the progression, while in Table 3.4 the complete assignment is given, i.e., $16_2^2 \rightarrow 14_0^1 1_0^3 16_2^2$. The error in the determination of the positions of the strong well-resolved peaks is $\pm 10 \text{ cm}^{-1}$ while for the weak ones it is $\sim \pm 20 \text{ cm}^{-1}$. It should be noted that to a large extent this error is associated with the wavelength accuracy of the laser, which is 0.1 nm or 8 cm^{-1} at the two-photon energies at $\lambda = 500 \text{ nm}$. Although this is random from one spectrum scan to another, it is systematic within the same scan. It is possible therefore to determine energy differences (i.e., vibrational energies) within the same spectrum scan with an accuracy better than 5 cm^{-1} .

The 0-0 transition of the $^1B_{2u}$ state in $n\text{-C}_6\text{F}_{14}$ was observed at 38050 cm^{-1} (37853 cm^{-1} in $n\text{-pentane}$) while in the gas phase it is estimated to be at 38086 cm^{-1} . Because it is strictly forbidden by parity selection rules the 0-0 transition is not seen in two-photon gas phase studies; it becomes, however, solvent induced and is observed in the liquid phase. The "hot band" portion of the spectrum of the $^1B_{2u}$ state was observed from $\bar{\nu} = 36570 \text{ cm}^{-1}$ up to the 0-0 transition (38050 cm^{-1}) and the "cold band" portion was followed up to 47281 cm^{-1} , that is, up to and exceeding the eighth overtone of the $14_0^1 1_0^n$ progression. The assignment was based on that of Wunsch et al. (1977) in the gas phase for energies up to $\sim 43000 \text{ cm}^{-1}$ and was facilitated by the polarization measurements and the characteristic polarization behavior of the different vibrational bands. For example, the first

members of the $18_0^1 1_0^{n+2}$ and the $14_0^1 10_0^2 1_0^n$ progressions are practically overlapping, the former being the dominant. Higher overtones, however, become progressively more separated and the latter progression becomes relatively stronger. Spectra obtained with circularly and linearly polarized light (see Figure 3.9) demonstrate the admixing of the two progressions by exhibiting an apparent relative shift of the structure at ~ 479 nm, because with linearly polarized light the $14_0^1 10_0^2 1_0^1$ vibration ($\bar{\nu} = 41714 \text{ cm}^{-1}$) is relatively strong, while with circularly polarized light the $18_0^1 1_0^3$ vibration ($\bar{\nu} = 41751 \text{ cm}^{-1}$) dominates completely. For the same reason (the mixing of the two progressions), the peaks in the polarization ratio (see Figure 3.4, p. 76) due to the $18_0^1 1_0^n$ progression appear to be diminishing progressively in magnitude.

Although no rotational structure can be resolved in the liquid phase, one can discern indications of such structure in the apparent shift of the peaks of the $14_0^1 1_0^n$ progression by $\sim 4 \text{ cm}^{-1}$ towards higher energies in the spectrum obtained with circularly polarized light (see the expanded spectrum of the $14_0^1 1_0^2$ peak in Figure 3.9). The reason is, that the weighted average of the O, P, R and S branches, which provide most of the intensity with circularly polarized light, lies on the high energy side of the Q branch causing thus a shift in the peak positions between the two polarizations.

Spectra of the entire $^1B_{2u} \leftarrow ^1A_{1g}$ transition of benzene in n-pentane and n-C₆F₁₄ were measured with both circularly and linearly polarized light of equal intensity, so that the polarization ratios could be determined. A problem complicating the exact experimental

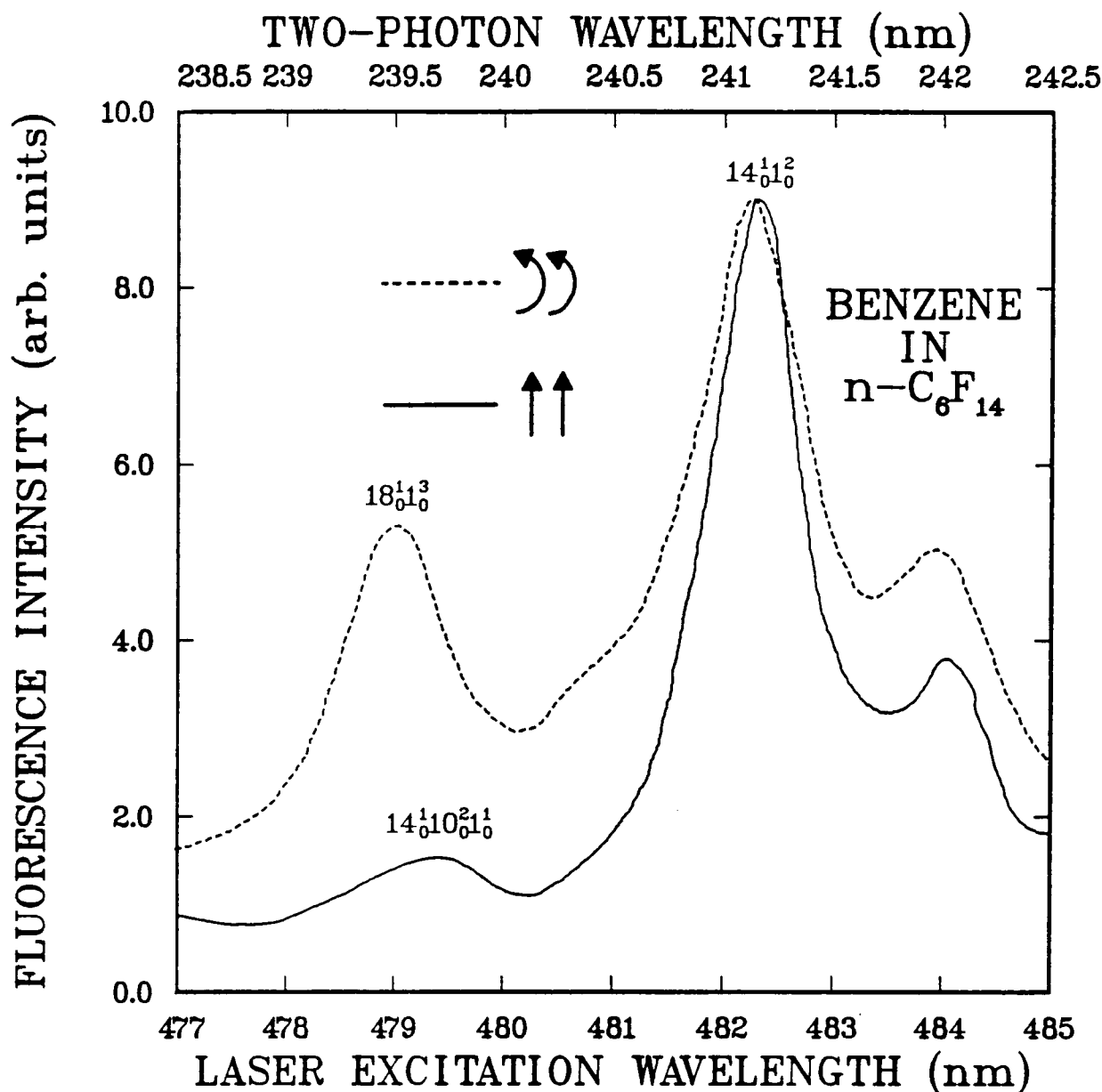


Figure 3.9. Portions of the two-photon excitation spectra of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$), measured using circularly (---) and linearly (—) polarized light. The two spectra are normalized on the major peak ($14_0^1 1_0^2$). Actually the circular polarization spectrum is ~ 5 times weaker. Note the prominence of the $18_0^1 1_0^3$ band with circular and of the $14_0^1 10_0^2 1_0^1$ with linear polarization. Note also the relative shift of the $14_0^1 1_0^2$ band with different polarizations.

determination of these ratios is the congestion background due to the overlap of neighboring bands (mostly originating from the strong 14_0^1 progression), on which the individual peaks are sitting. This background—especially prominent in the n-pentane spectra—has its own polarization behavior and tends to alter the polarization ratio of the individual peaks. Most seriously affected are the weaker peaks and especially the 18_{01}^{1n} progression; for example, the 18_0^1 peak theoretically is expected to have $\Omega = 3/2$, but instead it is found to have $\Omega \approx 1.0$. Figures 3.10 and 3.11 show the spectra obtained with circularly and linearly polarized light in n-pentane and n-C₆F₁₄, respectively, and directly above the corresponding polarization ratios. The ratio of the peak of the 18_0^1 band is 0.84 and 1.08 for n-pentane (Figure 3.10) and n-C₆F₁₄ (Figure 3.11), respectively.

One way of overcoming the difficulty in determining the exact ratio is the subtraction of the uniform background from the corresponding circular or linear spectra before dividing them to obtain the ratio. Figure 3.12 shows the direct (uncorrected) and the corresponding corrected (using the above method) polarization ratio over the $470 \text{ nm} < \lambda_{\text{exc}} < 530 \text{ nm}$ range of benzene in n-C₆F₁₄. The ratios thus obtained are exactly 1.5 for the 18_0^1 and less than 0.2 for the 14_0^1 . The former value coincides exactly with theoretical predictions (Wunsch et al., 1977). The polarization ratio of the 0-0 band is found to be ~ 0.7 . This implies that this band is composed of $\sim 40\%$ O, P, R and S contributions and $\sim 60\%$ Q branch contributions.

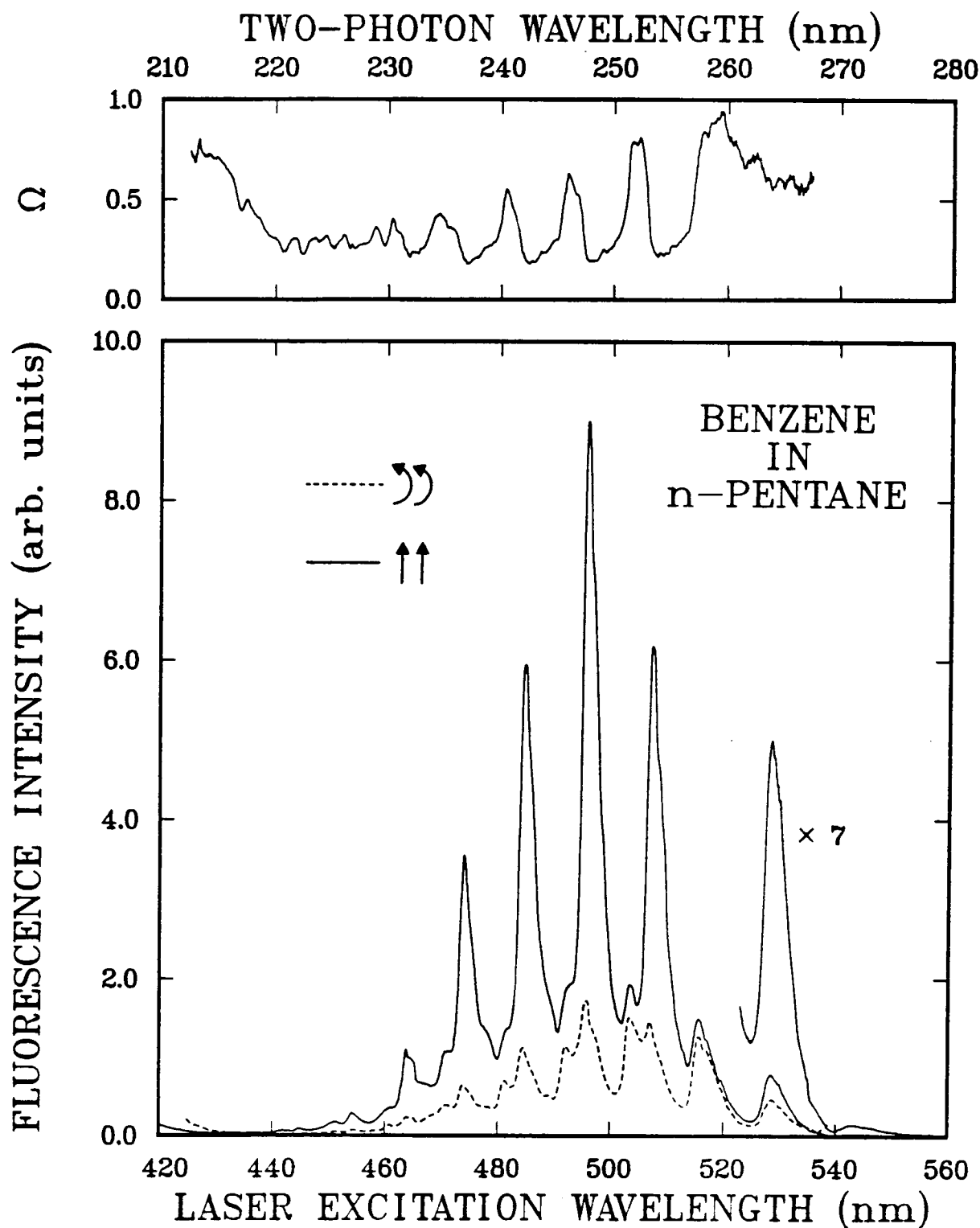


Figure 3.10. Two-photon excitation spectra of benzene in n-pentane measured with circularly (---) and linearly (—) polarized light and the corresponding polarization ratio, Ω , over the ${}^1B_{2u}$ state.

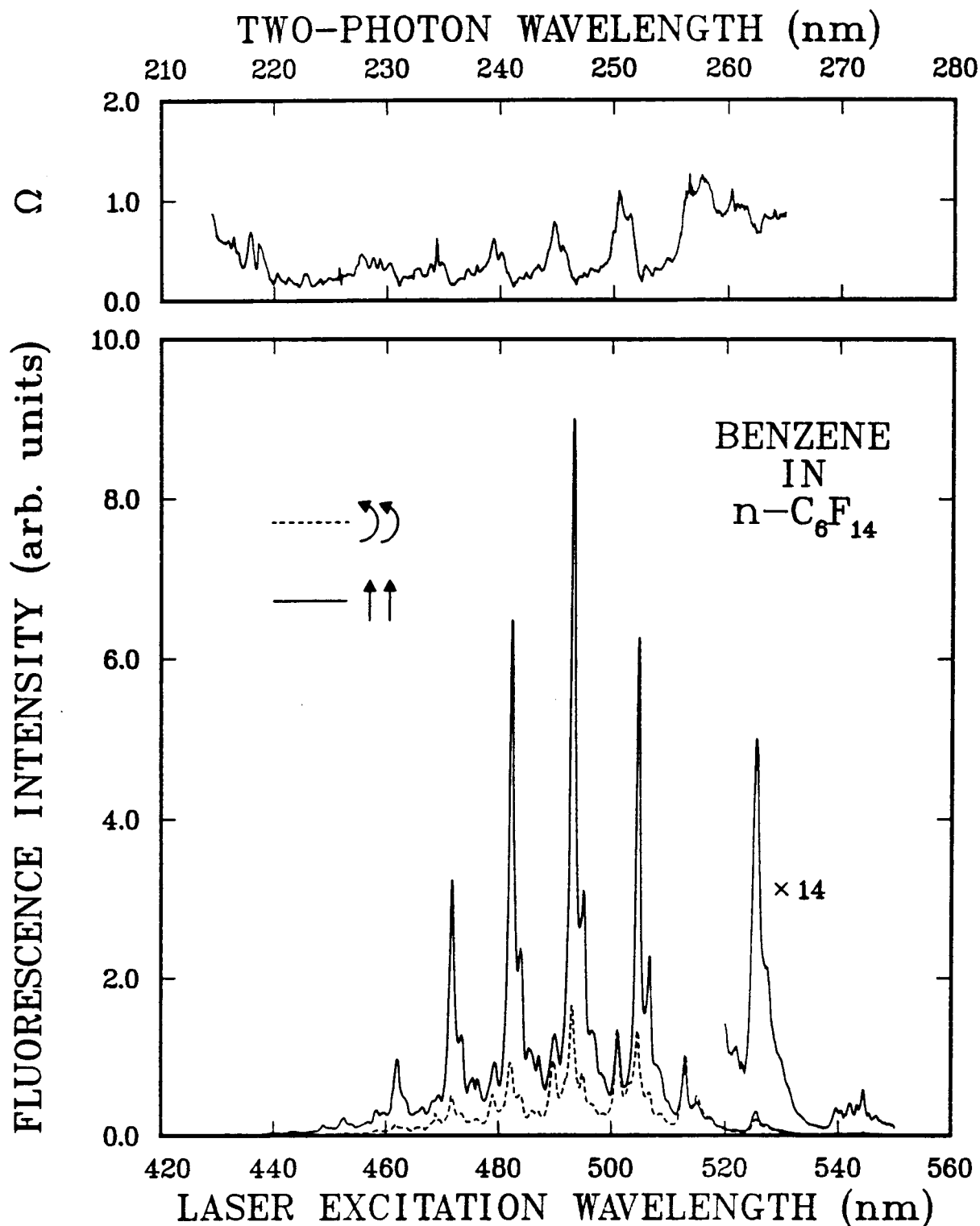


Figure 3.11. Two-photon excitation spectra of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$) measured with circularly (---) and linearly (—) polarized light and the corresponding polarization ratio, Ω , over the ${}^1\text{B}_{2u}$ state.

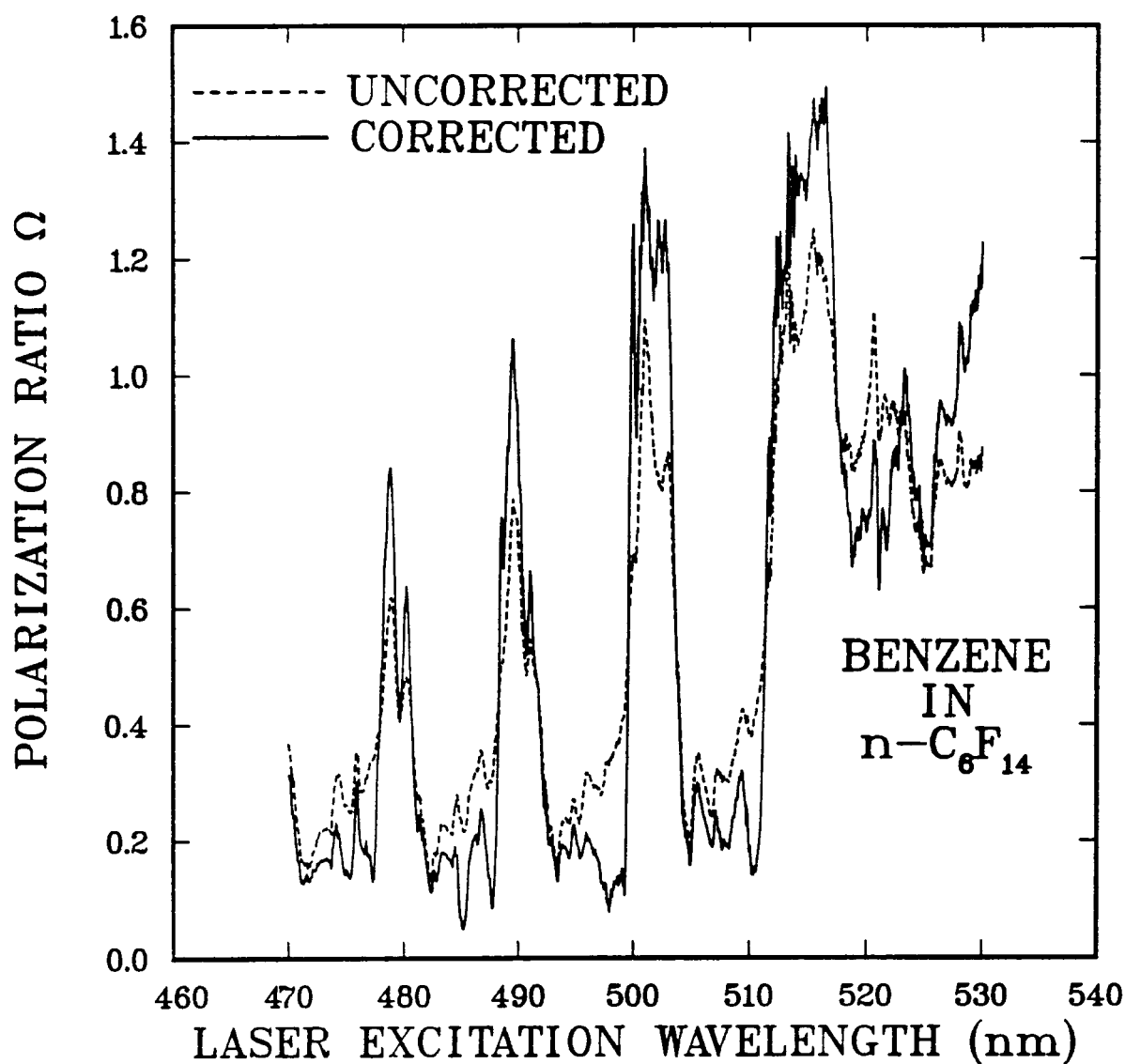


Figure 3.12. The corrected (see text) and uncorrected polarization ratios of the two-photon excitation spectra of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$). The corrected ratio for the 18_0^1 band ($\lambda_{\text{exc}} \approx 515$ nm) has exactly the theoretically expected value, $\Omega = 3/2$.

As has already been mentioned, the gradual decline of the polarization ratio of successive members of the $18_0^1 1_0^n$ progression in Figure 3.12 is due to the overlap with the gradually stronger $14_0^1 10_0^2 1_0^n$ progression which has a polarization ratio characteristic of the b_{2u} bands (e.g., the 14_0^1 band).

Finally, the following observations can be made concerning the relative intensity of different bands and progressions (see Figure 3.8, p. 81). First, the intensity of the peaks generally decreases with increasing energy and inside the same progression this trend is strictly monotonic, with the only exception of this rule being the second member of the $14_0^1 1_0^n$ progression which is the strongest peak of the spectrum. Second, the relative intensity of two progressions is affected by the number of vibrational quanta involved in the transitions. Generally the larger the number of quanta, the weaker the peak is, all other factors being the same. This is illustrated by comparison of the relative intensities of successive members of the $14_0^3 1_0^n$ and the $14_0^1 1_0^{3+n}$ progressions which reach the same energies approximately. Quantum 14 is more energetic than quantum 1 (1570 cm^{-1} vs. 923 cm^{-1}) and at gradually higher energies the members of the $14_0^3 1_0^n$ progression become relatively stronger because they involve fewer quanta. An analogous behavior is observed with the lifetimes of vibronic levels in the gas phase where there is a linear correlation of the lifetime with the number of quanta (Spears and Rice, 1971). Third, it appears that combination modes which distribute the excess vibrational energy to as many different modes as possible (i.e., $14_0^1 10_0^2 1_0^n$) tend to be

relatively stronger at higher energies. These observations can be explained assuming that the nonradiative relaxation rate, which is also a factor affecting the relative intensities, is an increasing function not only of the total energy, but also of the vibrational energy stored in a single vibrational mode.

3.4. The 380 nm Peak and the $^1B_{1u}$ Band of Benzene

The major feature in the $\lambda_{exc} < 430$ nm wavelength region is the strong peak at ~ 380 nm, on whose low energy side lies the weak $^1B_{1u}$ state. It has been proposed (Scott and Albrecht, 1981) that this peak is the two-photon allowed $(3s)^1E_{1g}$ Rydberg state and although the evidence is not conclusive, it does point toward a nonvalence state assignment.

The following observations can be made with respect to this strong peak. It is not the $^1E_{1u}$ transition which is one-photon allowed and should lie at $\lambda_{exc} \approx 360$ nm (see Figure 3.13). There are actually strong indications based on the following pieces of evidence that it belongs to a two-photon allowed transition: (a) it is much stronger than the forbidden $^1B_{1u}$ transition; (b) the $^1E_{1u}$ transition could not be observed anywhere around or below 360 nm given the experimental conditions (onset of transmission of the liquid filter below 360 nm and need to use the monochromator); (c) no indication of such a state exists in the one-photon spectrum (see Figure 3.13); (d) attempts to observe it, using a three photon excitation process ($\lambda_{exc} \approx 570$ nm) and employing high laser intensities and tight focusing (15 mJ pulse

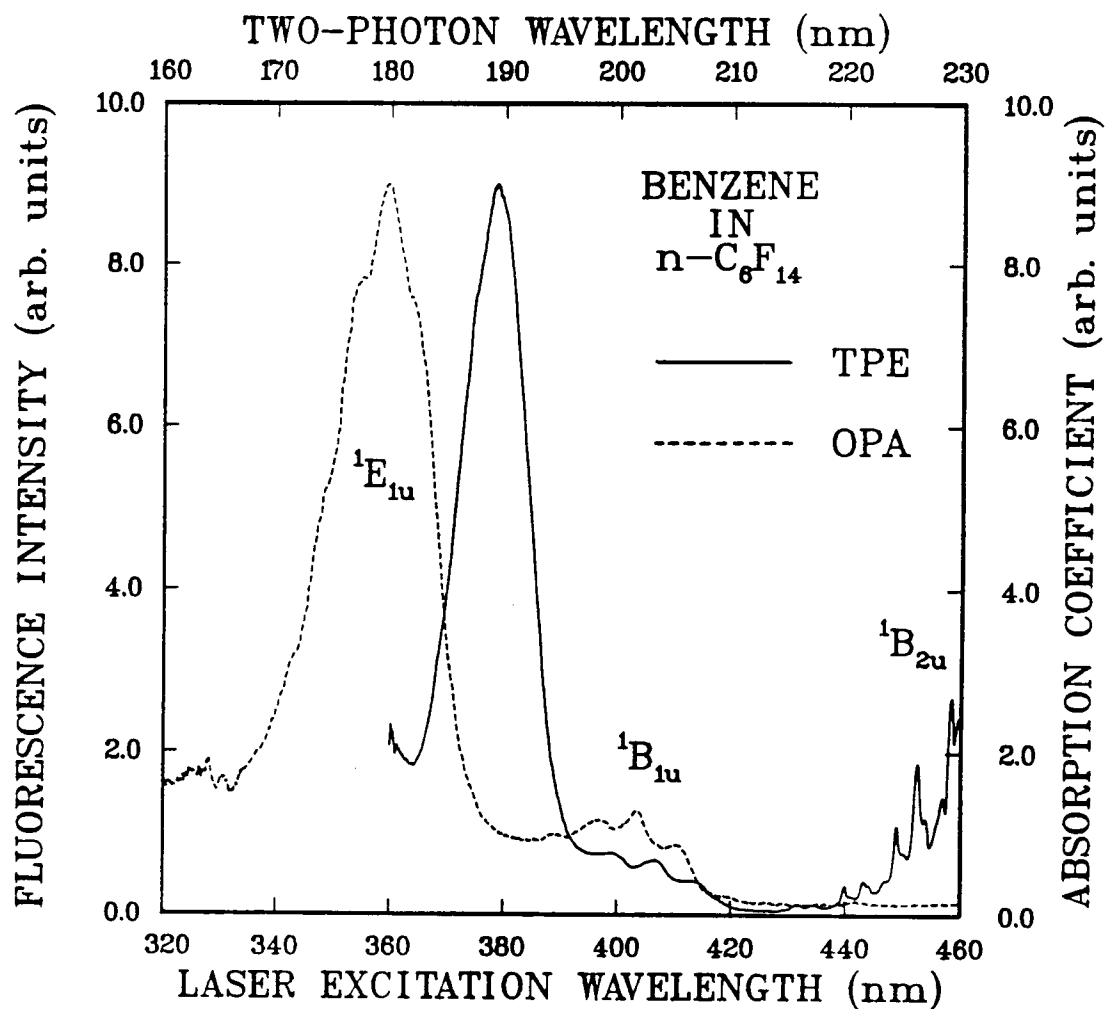


Figure 3.13. Two-photon excitation (TPE) and one-photon absorption (OPA) spectra of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$). The TPE spectrum is from the present work, the OPA is from Kourouklis (1982).

energy and 10 cm focal length), failed to yield any peak in the corresponding wavelength region (for benzene a two-photon allowed state is three-photon forbidden). The polarization ratio of this peak (see Figure 3.14) is ~ 1.5 which is consistent with an ${}^1E_{1g}$ or ${}^1E_{2g}$ assignment (Scott and Albrecht, 1981).

A peculiar characteristic of this peak is the solvent dependence of its relative intensity and spectral shifts. Figure 3.15 shows the TPE spectra in various solvents when they are normalized on the peak of the ${}^1B_{2u}$ state. The relative intensity of the 380 nm peak decreases monotonically in the various solvents and in the following order, TMSi, n-pentane, n-C₆F₁₄, c-C₇F₁₄, c-C₆F₁₂. At the same time, the peak is blue shifted from TMSi ($\lambda_{exc} = 386$ nm) to n-pentane ($\lambda_{exc} = 382$ nm) to n-C₆F₁₄ ($\lambda_{exc} = 378$ nm), while in the other two solvents it is almost nonexistent, being very broad and diffuse. In other words, there is a monotonic relationship between the spectral shifts and the relative intensity with respect to the ${}^1B_{2u}$ state. This portion of the spectrum as it appears in spectroscopically similar solvents (hydrocarbons, perfluorocarbons), normalized to the same peak intensity, is shown in Figures 3.16 and 3.17, respectively. It is important to note that the valence ${}^1B_{1u}$ state (like the ${}^1B_{2u}$) is not shifted at all in similar solvents. The intensity of the ${}^1B_{1u}$ state seems to be affected, but this is partly due to the fact that it is sitting on the rising slope of the 380 nm peak and partly because being forbidden gains strength from this allowed transition. Figure 3.17 shows very clearly how the ${}^1B_{1u}$ state progressively seems to disappear

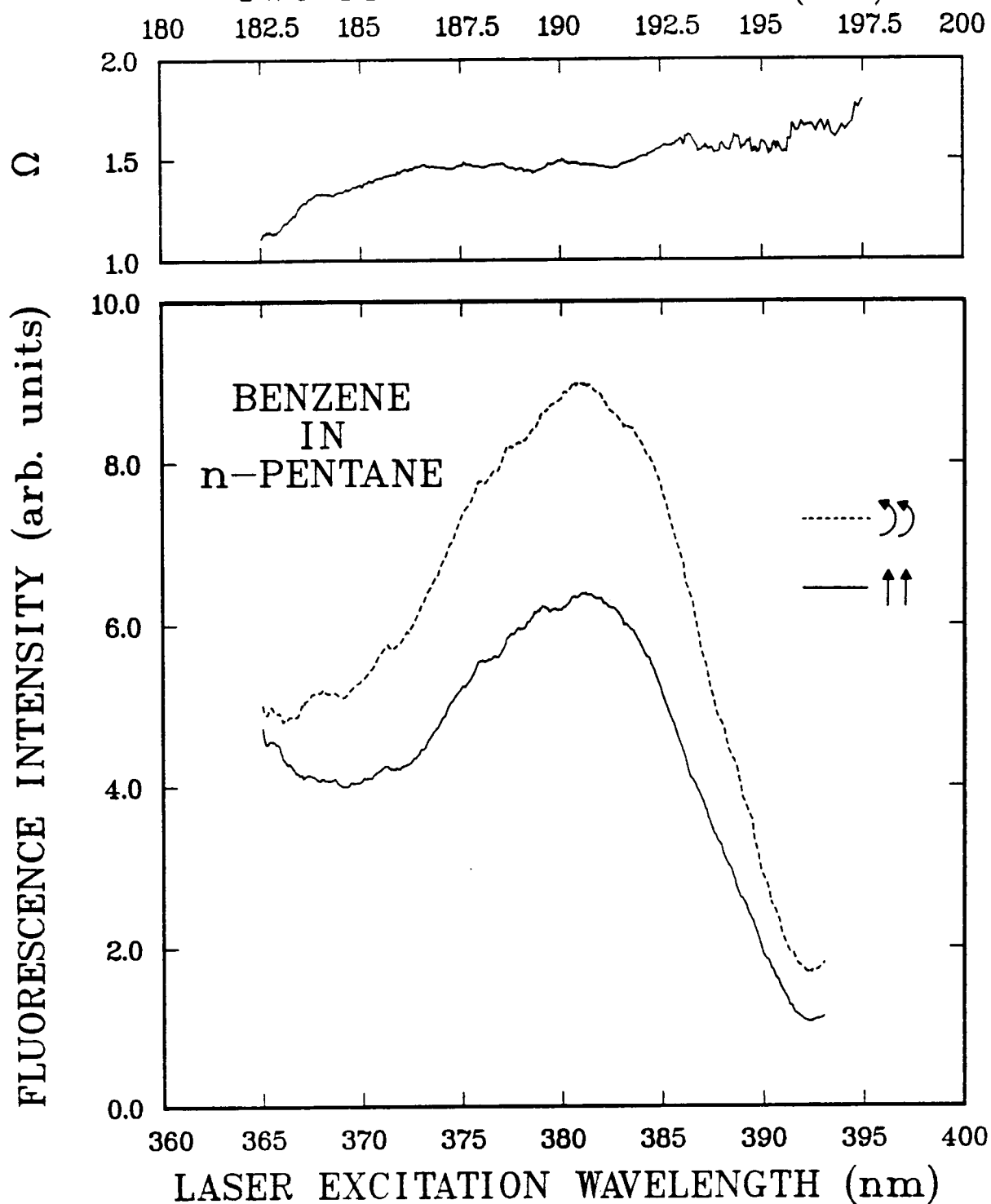


Figure 3.14. Two-photon excitation spectra of benzene in n-pentane measured with circularly (---) and linearly (—) polarized light and the polarization ratio, Ω , in the vicinity of the 380 nm peak. The ratio $\Omega = 3/2$ is compatible with an ${}^1E_{2g}$ or an ${}^1E_{1g}$ symmetry assignment.

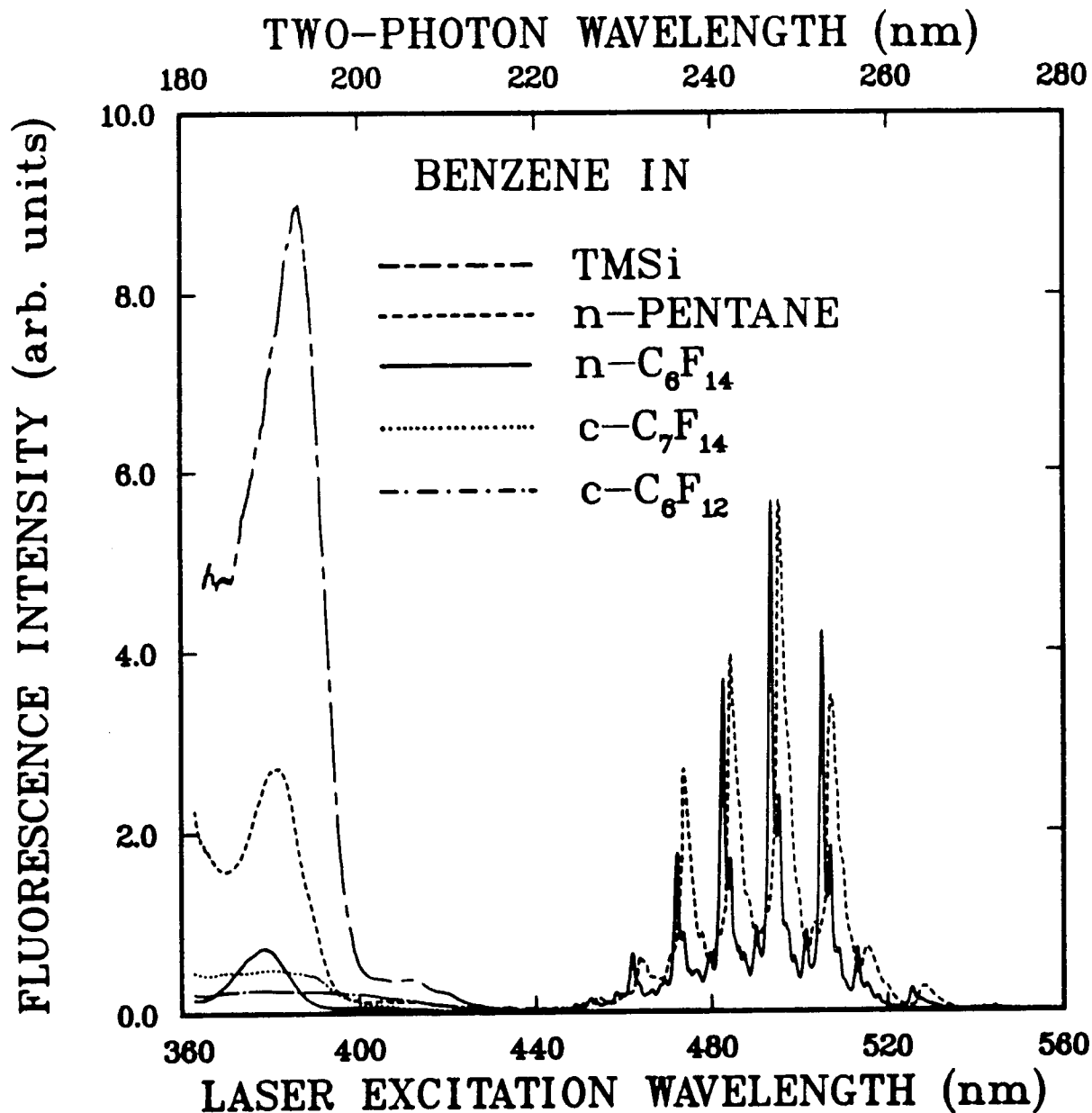


Figure 3.15. The two-photon excitation spectra of benzene in tetramethylsilane (TMSi), n-pentane (n-Pt), perfluoro-n-hexane (n-C₆F₁₄), perfluoromethylcyclohexane (c-C₇F₁₄), and perfluorodimethylcyclobutane (c-C₆F₁₂), normalized to the peak intensity of the ¹B_{2u} state. Note the solvent dependence of the relative intensities and spectral shifts of the 380 nm peak.

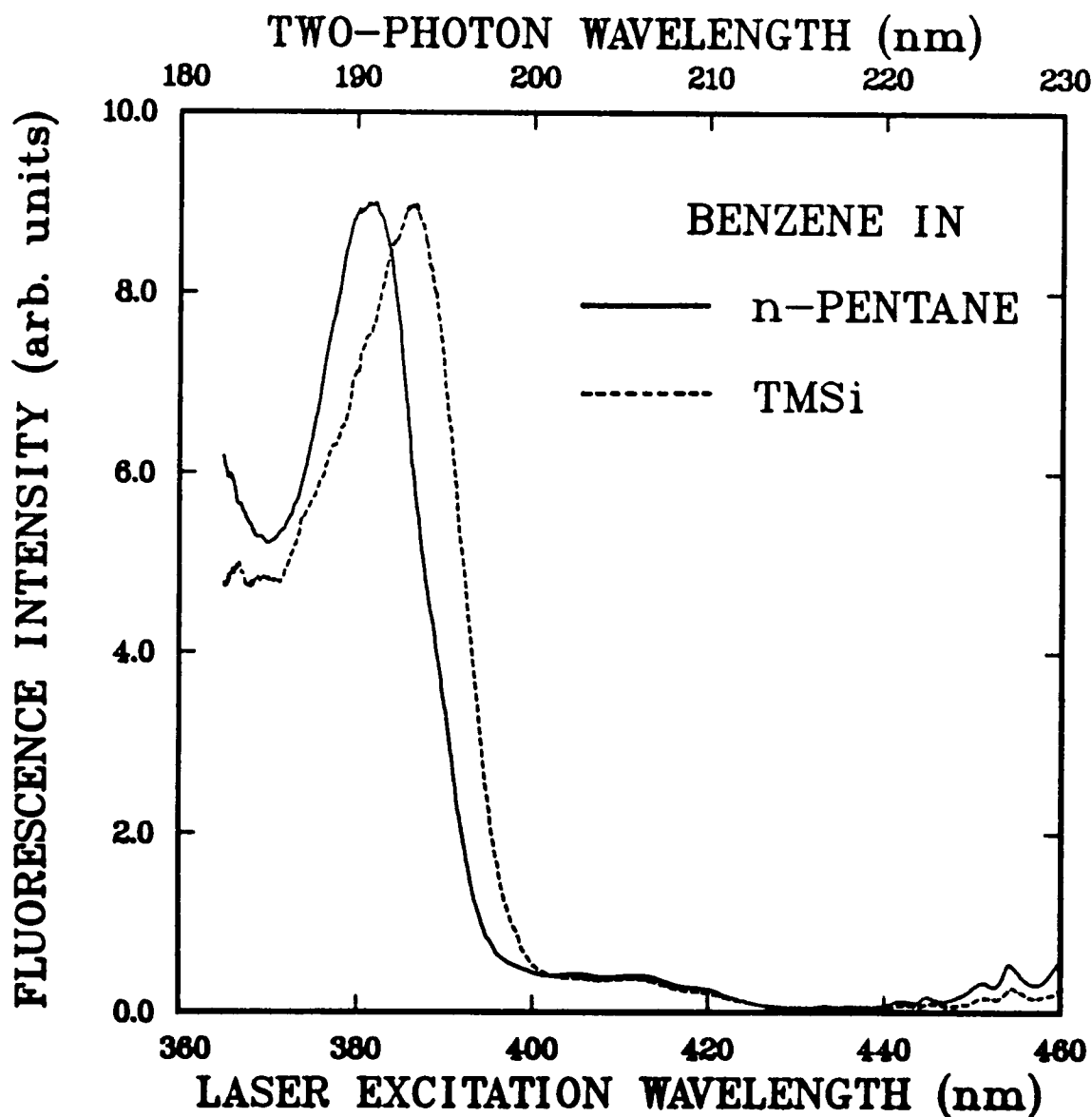


Figure 3.16. The two-photon excitation spectra of benzene in n-pentane and tetramethylsilane (TMSi) normalized to the same peak intensity. Note the spectral shift of the 380 nm peak and the coincidence of the ${}^1B_{1u}$ state ($400\text{ nm} < \lambda_{\text{exc}} < 420\text{ nm}$) in the two spectra.

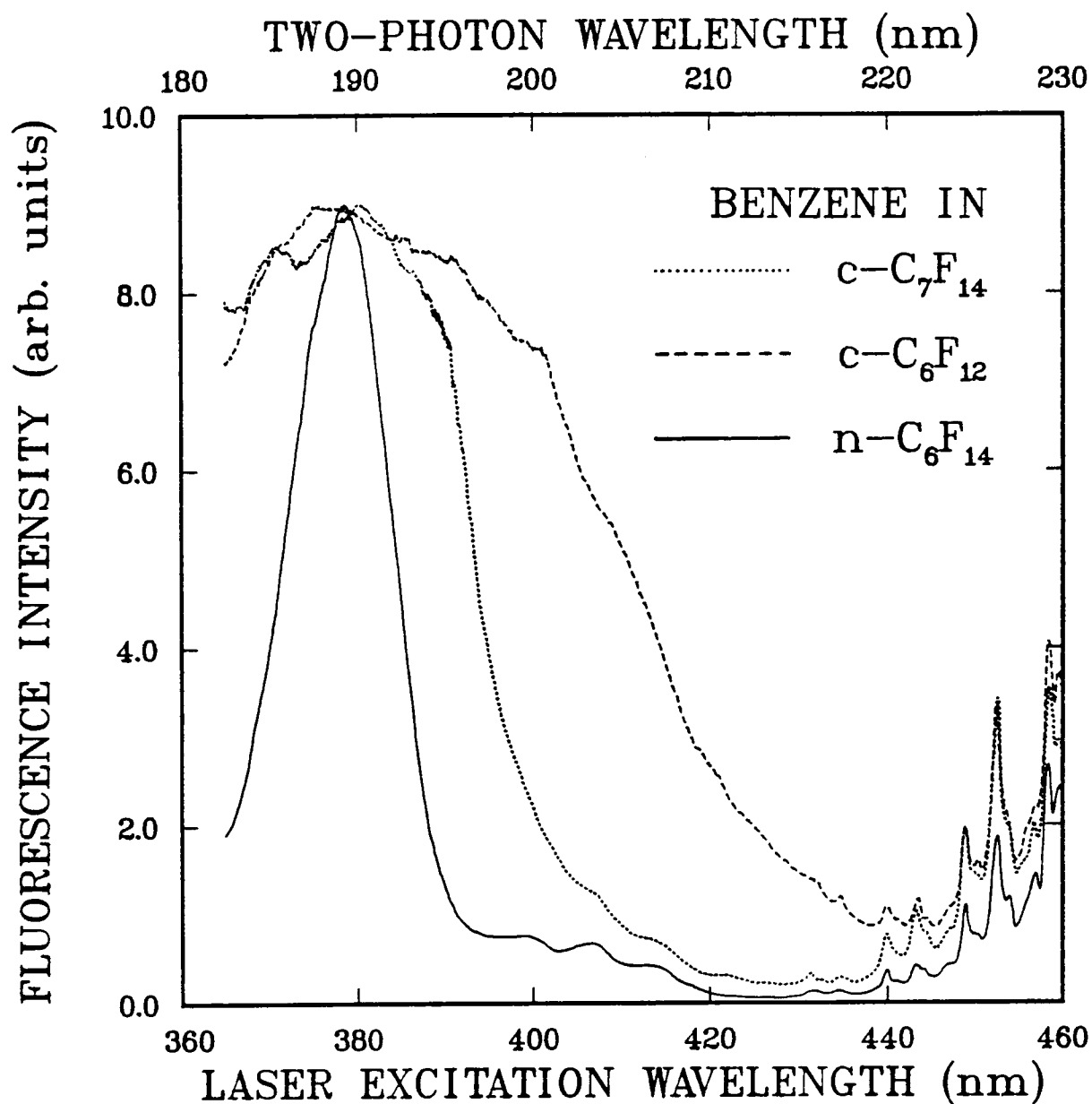


Figure 3.17. The two-photon excitation spectra of benzene in perfluoro-n-hexane ($n\text{-C}_6\text{F}_{14}$), perfluoromethylcyclohexane ($c\text{-C}_7\text{F}_{14}$) and perfluorodimethylcyclobutane ($c\text{-C}_6\text{F}_{12}$), normalized to the same peak intensity. Note the broadening of the 380 nm peak in different solvents and the gradual disappearance of the $^1\text{B}_{1u}$ state in the spreading background of the 380 nm peak.

into the spreading background of the 380 nm peak from one solvent to the other, although no spectral shift is apparent.

Three questions, therefore, arise with respect to the 380 nm peak. (a) What is different between these solvents that would leave unaffected the $^1B_{2u}$ transition (except for the known and expected spectral shift between hydrocarbons and perfluorocarbons), but would so drastically affect the 380 nm peak? (b) Would a Rydberg assignment explain this behavior? (c) Is it realistic to invoke the observation of Rydberg states in condensed matter and especially in the liquid phase? We will start answering these questions in reverse order by giving some background information on molecular Rydberg states in condensed phases.

As far as the solid phase is concerned, there has been a long-standing controversy (Gedanken et al., 1973; Chergui et al., 1985) regarding the observation or not of molecular Rydberg states in rare gas matrices. Rydberg states by their own nature (relatively large electron-core separation) are very sensitive to external perturbations. They are known to be blue-shifting and severely broadening with increasing pressure in the gas phase, while valence states are red-shifting and slightly broadening (Robin, 1975). It has been argued, therefore, that Rydberg states in the condensed phase should be blue-shifted and broadened beyond observation and actually it is considered as sufficient proof that a state is Rydberg in nature if it disappears in the liquid phase (Krogh-Jespersen et al., 1979). Rydberg states, however, of benzene (and other small molecules), have unquestionably

been observed not only in solid rare gases (Katz et al., 1969), but also in molecular solids such as N_2 and CF_4 (Gedanken et al., 1973). The higher Rydberg levels have been theoretically explained in terms of a Wannier model for impurity states in the solid matrix. In this case, because of strong dielectric screening, the electron-molecular core attraction is reduced and since the radius of the excited state exceeds the lattice spacing, the molecular and the crystal potentials are averaged out; then the state loses its molecular parentage and one talks about Wannier rather than Rydberg states.

For the lowest lying Rydberg states, however, this model is not adequate, because it overestimates greatly the blue-shifts and the relative intensities (Jortner, 1974; Resca and Resta, 1979), so that a modified tight binding Heitler-London approximation (or a modified Wannier model), is more appropriate. In this case the competition between the (blue-shifting) repulsive overlap exchange interactions and the (red-shifting) charge transfer and dispersion interactions is such that both the unique molecular parentage of the Rydberg state is maintained and a significant blue-shift is observed.

Resca and Resta (1979) have introduced a modified Rydberg formula based on an "unstructured" Hamiltonian to account for these states, which can be applied not only to solid matrices but to liquids as well. Although there are no extensive experimental data of these states in liquids (only two levels have been detected in liquid rare gases), the model predicts a density, rather than structure, dependence of the energy levels and a stronger Rydberg, rather than Wannier, character of these states in the liquid as compared to the solid phase.

In general, experience from solid matrix studies suggests that Rydberg states are more likely to be seen when the conduction band of the matrix is free electron-like with large bandwidth (2-3 eV) and weak electron-atom interactions, i.e., weak electron scattering and high electron mobility (Katz et al., 1969). For example, the lowest lying "extravalence" state of benzene in solid N_2 ($\mu = 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is much more blue-shifted extremely broadened and almost unobservable as compared to the same state in rare gas matrices ($\mu \gtrsim 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Gedanken et al., 1973).

Under these general considerations, a Rydberg state should be observable in the liquid, provided that the electron scattering by the host medium is not frequent enough so that an orbit cannot be closed. At the same time, a Rydberg-like nature of the 380 nm peak would explain qualitatively its observed (peculiar for a valence state) behavior and solvent dependence.

Figure 3.18 shows the electron attachment rate constants of the perfluorocarbons used in these experiments vs. the electron mean energy in the gas phase. The attachment rate constant for thermal electrons decreases from $c\text{-C}_6\text{F}_{12}$ to $c\text{-C}_7\text{F}_{14}$ to $n\text{-C}_6\text{F}_{14}$ and although these measurements (Hunter and Christophorou (1984) for $n\text{-C}_6\text{F}_{14}$, Pai et al. (1979) for $c\text{-C}_6\text{F}_{12}$ and Christodoulides and Christophorou (1979) for $c\text{-C}_7\text{F}_{14}$) refer to the gas phase, it is reasonable to assume that in the liquid phase also, the attachment rates will be decreasing in a corresponding fashion. Moreover, liquid phase studies suggest that the efficiency of electron capture depends on the structure of the

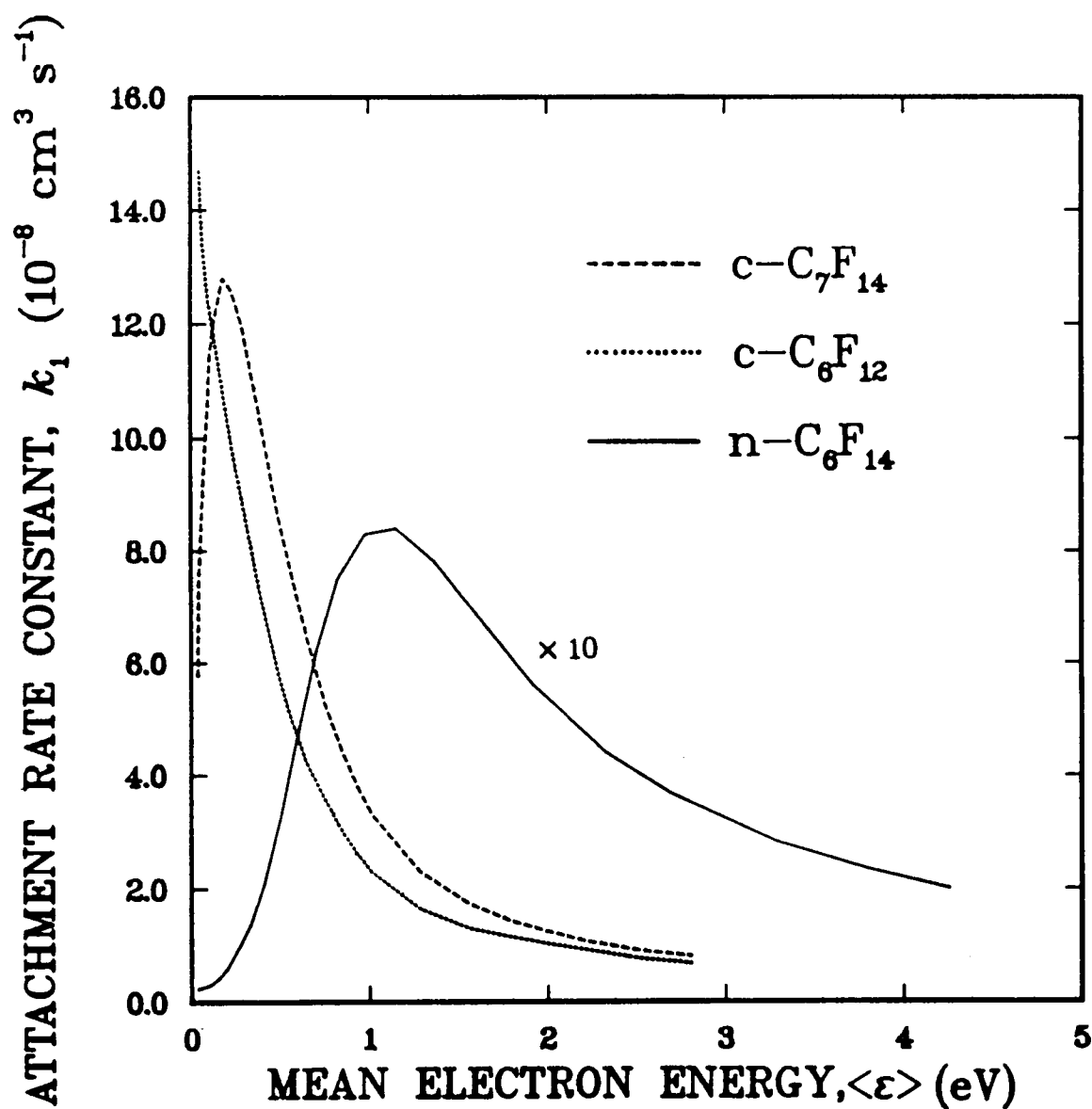


Figure 3.18. Electron attachment rate constants, as a function of mean electron energy, for perfluoro-n-hexane ($\text{n-C}_6\text{F}_{14}$), perfluoromethylcyclohexane ($\text{c-C}_7\text{F}_{14}$) and perfluorodimethylcyclobutane ($\text{c-C}_6\text{F}_{12}$), in the gas phase. The measurements are: for $\text{n-C}_6\text{F}_{14}$, from Hunter and Christophorou (1984), for $\text{c-C}_7\text{F}_{14}$, from Christodoulides and Christophorou (1979), and for $\text{c-C}_6\text{F}_{12}$, from Pai et al. (1979).

perfluorocarbon (i.e., cyclic, straight chain) and the degree of fluoromethyl substitution (Sutcliffe and McAlpine, 1973). On the other hand, it is known (Christophorou and Siomos, 1984) that TMSi has a much higher electron mobility than n-pentane ($\sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. $\sim 0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a negative V_0 value ($\sim -0.6 \text{ eV}$) as compared to the almost zero V_0 value of n-pentane (-0.01 eV). This means that the scattering length is much longer in TMSi than in n-pentane. A low lying Rydberg electron in the solvent can be visualized as moving on or very close to the imaginary surface separating the molecular core and the surrounding host molecules, so that it "feels" equally strong—both the parent molecular core underneath and the medium around it. Under these circumstances, in TMSi the orbit of a Rydberg electron would be perturbed to a minimum degree, compared to the perturbation in the other solvents, and therefore the energy level of the corresponding state would appear closer to the corresponding gas phase value. As a result, the Rydberg state would appear more stabilized (less blue-shifted) and more intense compared to other solvents of lower mobility. In the perfluorocarbons, on the other hand, which have a relatively high positive electron affinity, the Rydberg electron is captured very efficiently and this causes a reduction in the fluorescence—decrease in the intensity of the peak—shortening of the lifetime of the state and broadening of the peak. At the same time, the balance between attractive and repulsive forces strongly favors the latter so that a significant blue-shift is observed. In other words, once the electron is excited to this low lying "extravalence" state (extended state of a

nonvalence character), there is a competition between two processes; relaxation to lower lying states and particularly to the S_1 state which will yield fluorescence and charge transfer to the solvent. The second process becomes more efficient progressively in the various solvents in the following order: TMSi, n-pentane, n-C₆F₁₄, c-C₇F₁₄, c-C₆F₁₂.

The preceding arguments are purely qualitative and to a certain extent speculative, but they do point toward the fact that a Rydberg assignment for the 380 nm peak is not inconsistent with the experimental observations. Considering, also, that: (a) the polarization behavior ($\Omega = 3/2$) suggests an $^1E_{2g}$ or $^1E_{1g}$ assignment; (b) the $^1E_{2g}$ states, most likely, lie at much higher energies (Nakashima et al., 1982a,b); and (c) from gas phase studies, the only states known to lie in the vicinity of the 380 nm peak are the $^1E_{1u}$ and the $(3s)^1E_{1g}$, then, the $(3s)^1E_{1g}$ assignment for the 380 nm peak is the only viable hypothesis at the present time.

3.5. Two-Photon Excitation of Toluene

In view of the similarities between benzene and toluene and in order to verify the generality of the results obtained with benzene, a study of the TPE of toluene in the same solvents was undertaken. The concentrations used were the same as for benzene, $\sim 1 \times 10^{-2}$ M.

Figures 3.19 through 3.22 show the complete TPE spectra of toluene in TMSi, n-pentane, n-C₆F₁₄ and c-C₆F₁₂, while Figure 3.23 shows all these spectra plotted together and normalized on the peak of the 1B_2 state. A behavior similar to that of benzene can be observed

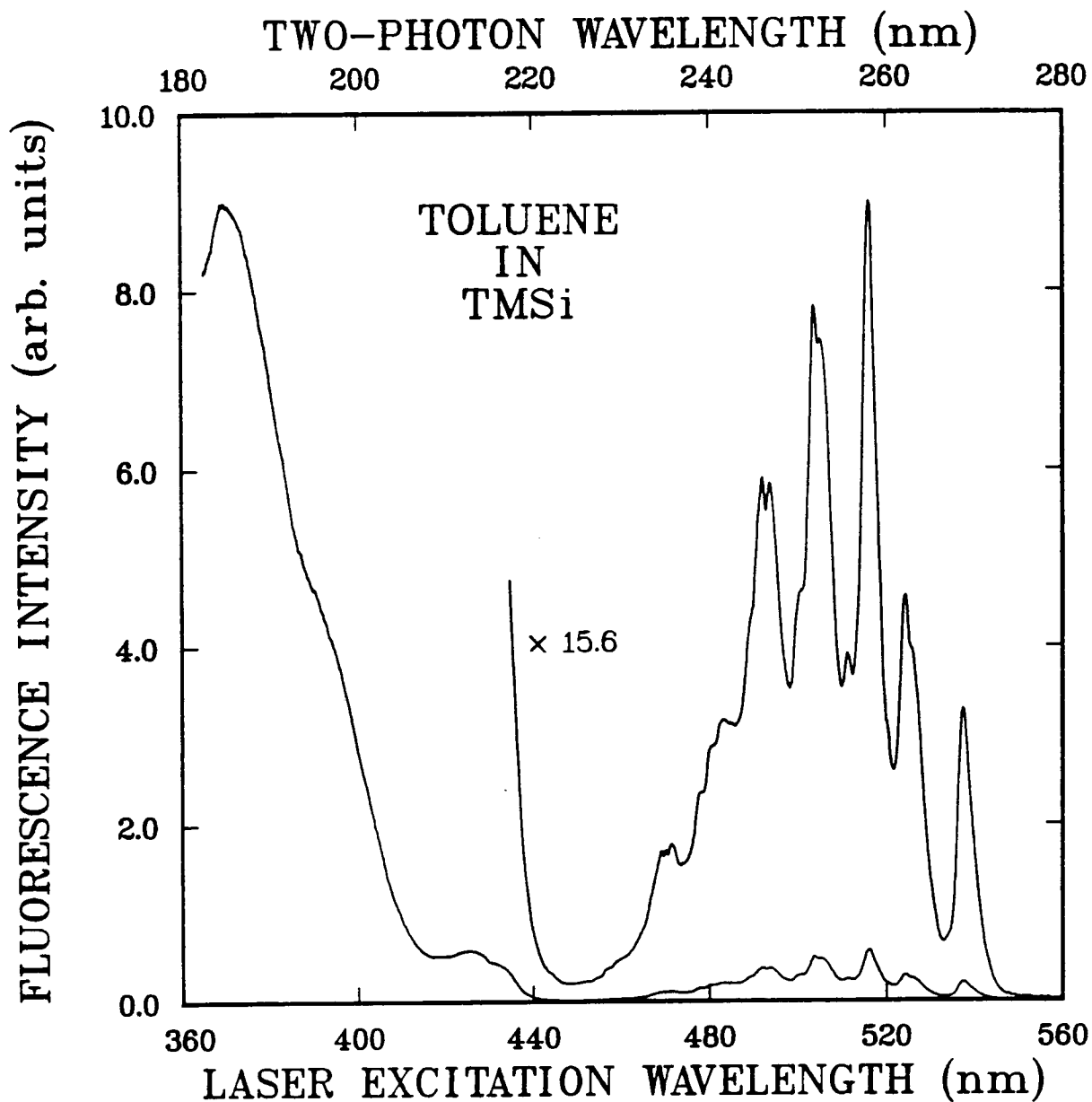


Figure 3.19. Two-photon excitation spectrum of toluene in tetramethylsilane (TMSi). The 1B_2 state extends from ~ 550 nm up to 460 nm λ_{exc} and the 1B_1 from ~ 440 nm up to 415 nm λ_{exc} .

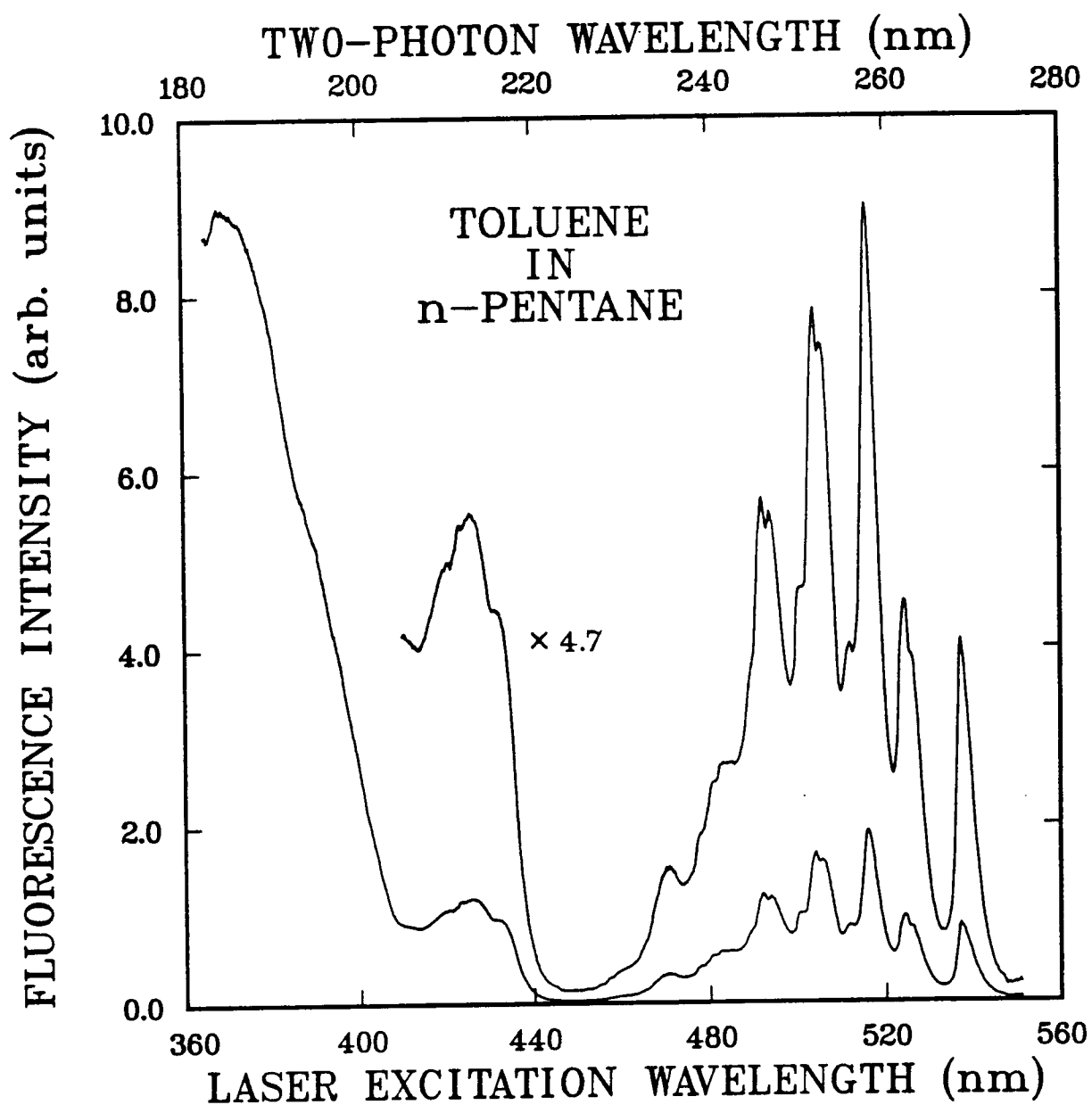


Figure 3.20. Two-photon excitation spectrum of toluene in n-pentane.

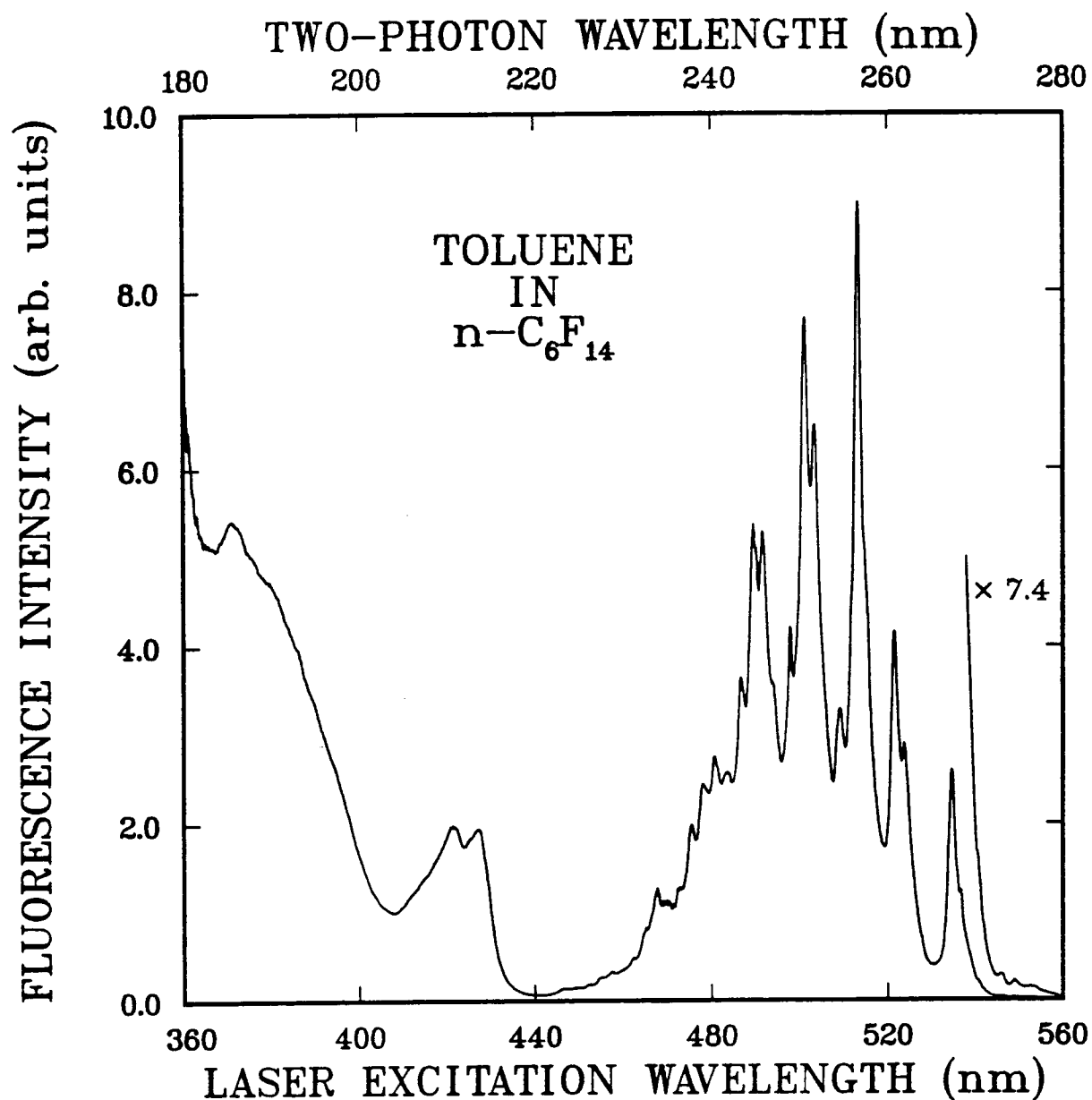


Figure 3.21. Two-photon excitation spectrum of toluene in perfluoro-n-hexane (n-C₆F₁₄).

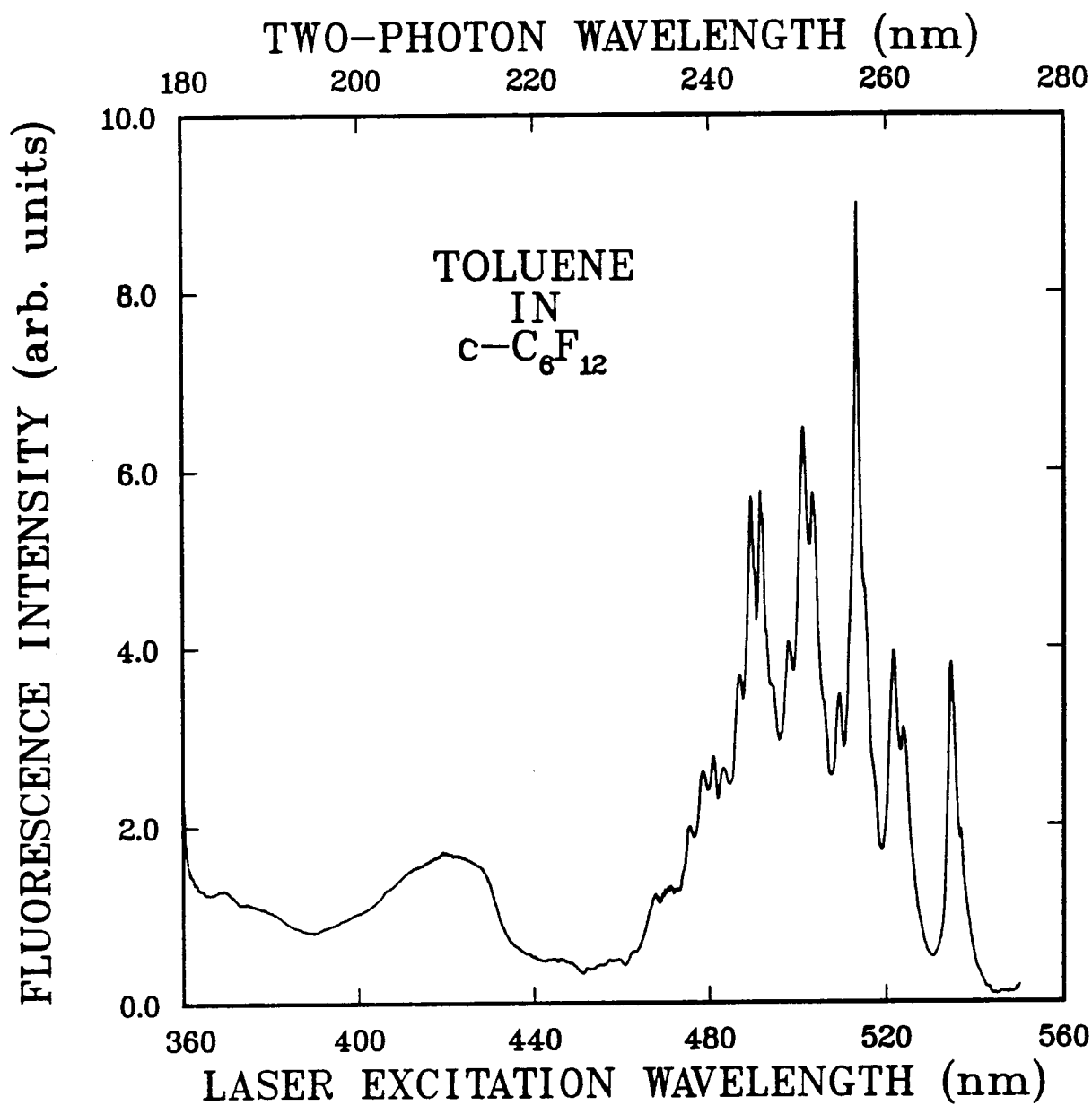


Figure 3.22. Two-photon excitation spectrum of toluene in perfluoro-dimethylcyclobutane (c-C₆F₁₂).

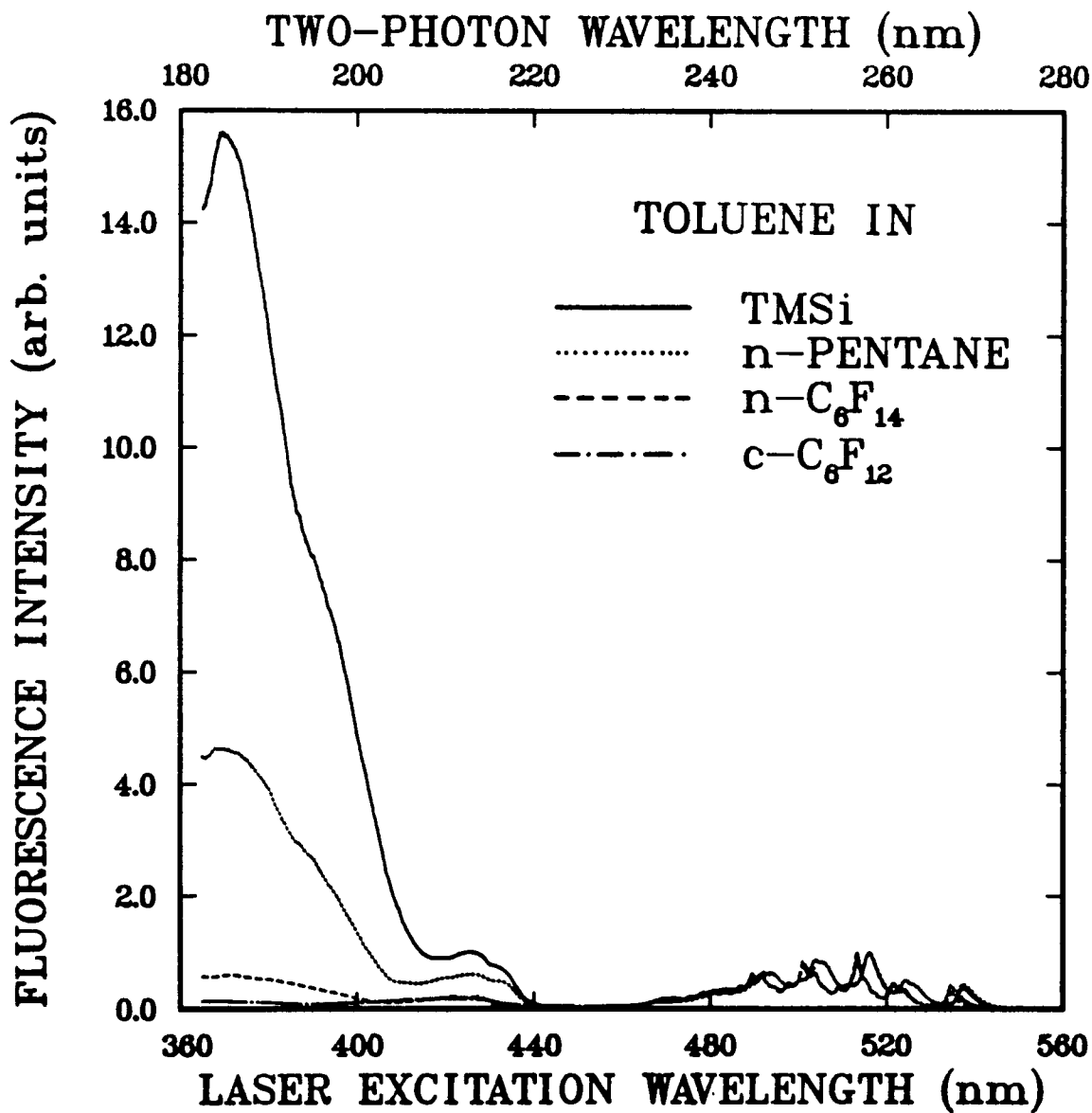


Figure 3.23. The two-photon excitation spectra of toluene in tetramethylsilane (TMSi), n-pentane, perfluoro-n-hexane (n-C₆F₁₄), and perfluorodimethylcyclobutane (c-C₆F₁₂) normalized to the same peak intensity of the ¹B₂ state.

by looking at Figure 3.23. The 1B_2 state is practically unaffected in spectroscopically similar solvents (TMSi, n-pentane on one hand, the perfluorocarbons on the other), while the structure below $\lambda_{exc} = 400$ nm is drastically reduced in intensity from one solvent to the other. From multiphoton ionization gas phase studies it is known (Uneberg et al., 1980) that toluene has two 3p Rydberg states in this wavelength region ($\lambda_{exc} = 365$ nm and 379 nm). It is also expected from OPA studies that the 1E_1 state lies at $\lambda_{exc} \approx 380$ nm. Indeed, there is a peak in the TPE spectra at $\lambda_{exc} \approx 370$ nm (corresponding probably to the 379 nm Rydberg state of the gas phase) and a shoulder at ~ 390 nm probably related to the 1E_1 state. The overlap of the two Rydberg states with the valence (1E_1) does not allow in the case of toluene the clear observation of spectral shifts in the different solvents. The reduction in the intensity of the 370 nm peak, however, is even more drastic from one solvent to the other, compared to that of benzene. A possible explanation is that the p Rydberg electron, having a more elliptical orbit than the s, enters deeper into the medium and is more affected by it. Similarly, as in benzene, the 1B_1 state seems to follow the intensity changes of the 370 nm peak but to a much lesser extent.

As far as the spectroscopy of the 1B_2 state is concerned, again the n- C_6F_{14} spectrum gave the highest resolution and was used for the assignment of the vibrational structure (see Figure 3.24). Table 3.5 contains the energies from the ground state and from the transition origin and the vibrational assignment of the observed

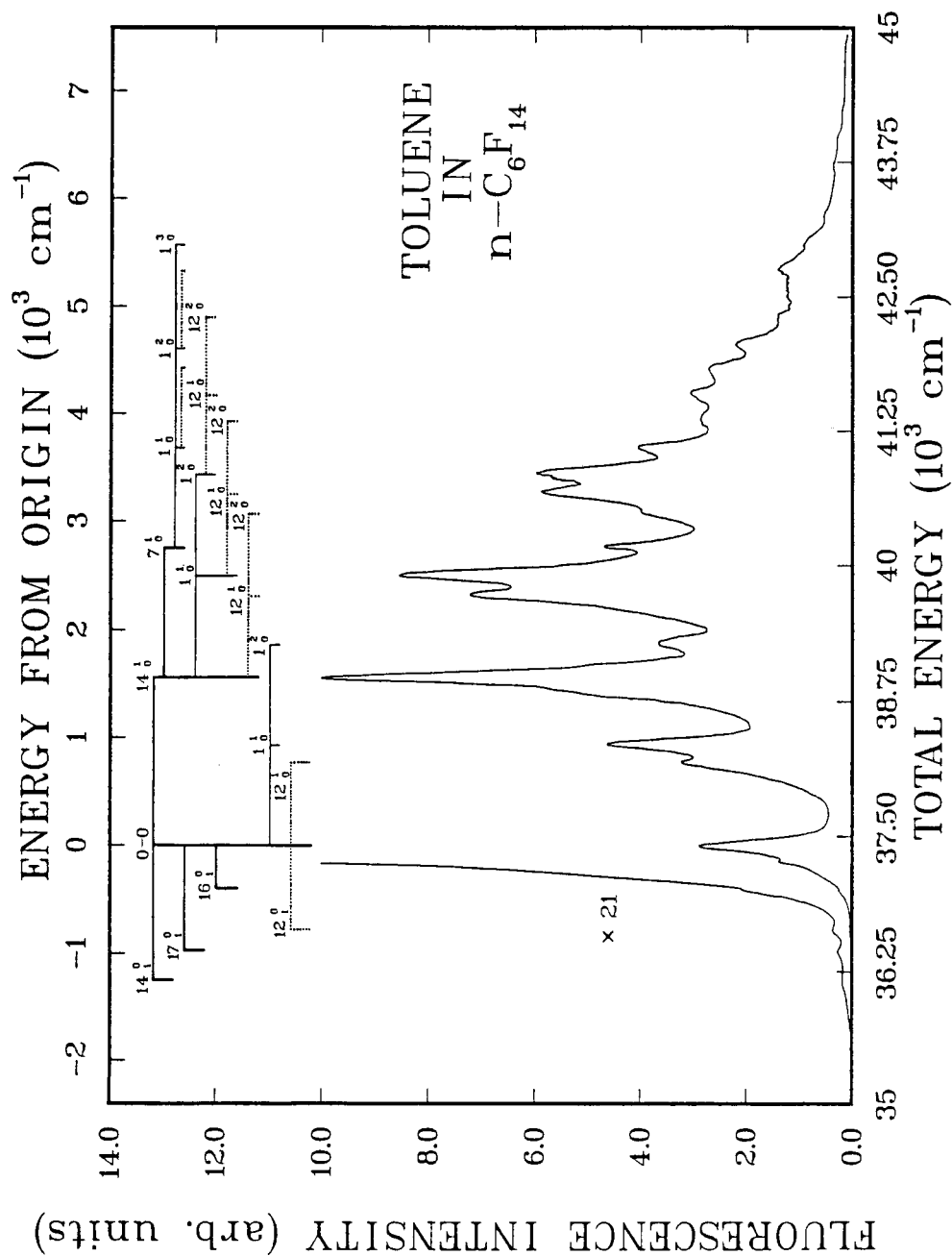


Figure 3.24. The two-photon excitation spectrum of the $^1\text{B}_2$ state of toluene in perfluoro- n -hexane ($n\text{-C}_6\text{F}_{14}$). See text.

Table 3.5. Vibrational Energy Levels of the 1B_2 State of Toluene in Perfluoro-n-Hexane

Solution $\bar{\nu}$ [cm^{-1}]	Solution $\Delta\bar{\nu}$ [cm^{-1}] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm^{-1}]
36,160	-1,251	14_1^0	
36,430	-981	17_1^0	
36,623	-788	12_1^0	
37,000	-411	16_1^0	
37,260	-151	sequence structure	
37,411	0	0-0	37,485
38,180	769	12_0^1	38,219
38,343	932	1_0^1	38,407 and 38,420
~38,800		sequence structure	
38,971	1,560	14_0^1	39,047
~39,090			
39,280	1,869	1_0^2	39,332 and 39,342
39,722	2,311	$14_0^1 12_0^1$	39,778 and 39,797
39,910	2,499	$14_0^1 1_0^1$	39,971 and 39,979
40,169	2,758	$14_0^1 7_0^1$	40,245
40,480	3,069	$14_0^1 12_0^2$	40,527 and 40,548
40,660	3,249	$14_0^1 1_0^1 12_0^1$	40,719
40,850	3,439	$14_0^1 1_0^2$	40,911
41,100	3,689	$14_0^1 7_0^1 1_0^1$	41,171
41,340	3,926	$14_0^1 1_0^1 12_0^2$	
41,600	4,189	$14_0^1 1_0^2 12_0^1$	
41,840	4,429	$14_0^1 7_0^1 1_0^1 12_0^1$	

Table 3.5 (continued)

Solution $\bar{\nu}$ [cm ⁻¹]	Solution $\Delta\bar{\nu}$ [cm ⁻¹] ^a	Vibrational Assignment	Gas ^b $\bar{\nu}$ [cm ⁻¹]
42,035	4,624	$14_0^{11}7_0^{11}1_0^{12}$	
42,320	4,909	$14_0^{11}1_0^{12}1_0^{12}2_0^{20}$	
42,750	5,339	$14_0^{11}7_0^{11}1_0^{12}1_0^{12}2_0^{10}$	
43,000	5,589	$14_0^{11}7_0^{11}1_0^{13}$	
43,262	5,851	$14_0^{11}1_0^{13}1_0^{12}2_0^{20}$	
44,693	7,282		

^aEnergy in cm⁻¹ is measured from the origin of the 0-0 transition (37,411 cm⁻¹).

^bFrom Vasudev and Brand (1979a).

structure; for comparison the gas phase energy values are also given up to the energy that they were available (from Vasudev and Brand, 1979a). To our knowledge, this is the first TPE study of toluene in solution and the first ever observation of the hot bands of the 1B_2 state.

The spectrum of toluene is very similar to that of benzene because the energies of corresponding vibrational modes are very close—within 20 cm^{-1} —in most cases (see Tables 3.1 and 3.2, pp. 64 and 65). A notable exception is the highly energetic in benzene C-H stretching quantum 7 whose energy is reduced by a factor of three in toluene because a C-C bond is stretched upon methyl substitution. The major differences between the benzene and toluene spectra stem from the fact that toluene has a lower symmetry (belongs to the C_{2v} group) and since it is not centrosymmetric it has no parity. With the relaxation of the parity rules more vibrational modes become allowed. For example, the 0-0 transition in toluene is allowed and very strong. The red-shift from gas to liquid is another difference between toluene and benzene. While for benzene the red-shifts are $\sim 30\text{ cm}^{-1}$ and $\sim 230\text{ cm}^{-1}$ in $n\text{-C}_6\text{F}_{14}$ and $n\text{-pentane}$, respectively, for toluene they are $\sim 75\text{ cm}^{-1}$ and $\sim 280\text{ cm}^{-1}$ correspondingly. This difference should be attributed to the methyl group which causes a greater stabilization in the liquid phase. In toluene also as in benzene indications of rotational structure can be observed. The shoulders on the red side of the 0-0 transition (-150 cm^{-1}) and the 14_0^1 peak (1390 cm^{-1}) are due to sequence structure unresolved in the liquid (Vasudev and Brand, 1979a).

3.6. Two-Photon Excitation of Fluoranthene

Fluoranthene has been studied in the past with a two-photon ionization (TPI) technique (Siomos et al., 1981), and the two-photon excitation study was undertaken in order to compare the information obtained with the two processes. It should be noted that no other two-photon studies of fluoranthene exist.

Fluoranthene belongs to the C_{2v} symmetry group, and since it has no center of symmetry all excited states are in principle accessible by both one- and two-photon excitation. The TPE spectrum of fluoranthene in a dilute solution of n-pentane ($\sim 10^{-3}$ M) was measured over the $420 \text{ nm} < \lambda_{\text{exc}} < 860 \text{ nm}$ range, and is shown in Figure 3.25 plotted together with the ionization spectrum. The one-photon resonant portion of the ionization spectrum for $\lambda_{\text{exc}} < 450 \text{ nm}$ is plotted at the corresponding two-photon resonant wavelengths to allow a comparison of the TPI and TPE spectra. In general, there is a fairly good agreement between the two spectra in the areas of mutual overlap. Table 3.6 contains the energy levels of fluoranthene as determined from the TPE studies. The 0-0 level of the transition to the S_1 state was found at $\lambda_{\text{exc}} \approx 806 \text{ nm}$ (24800 cm^{-1}), in good agreement with the value found with OPA in 3-methylpentane at 77°K (24750 cm^{-1}) by Kolc et al. (1974). The red-shift with respect to the gas phase, where the 0-0 transition has been located at 25217 cm^{-1} (Chan and Dantus, 1985), is $\sim 417 \text{ cm}^{-1}$. In the energy region under study (24000 cm^{-1} - 42000 cm^{-1}) the six lowest singlet excited states of fluoranthene can be observed. The 0-0 levels of the first five were located at 24800 (24750), 27840 (27750),

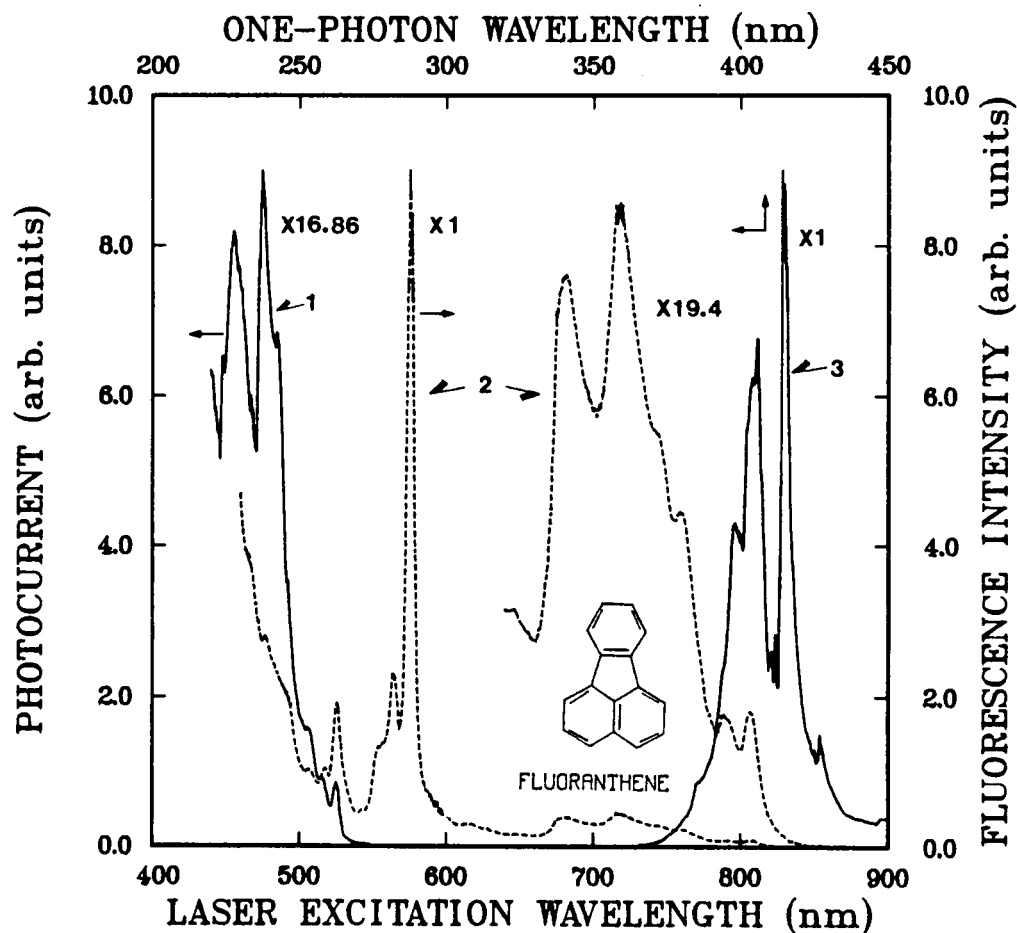


Figure 3.25. The two-photon excitation (2) and two-photon ionization (1, 3) spectra of fluoranthene in *n*-pentane. The one-photon resonant two-photon ionization (TPI) spectrum (3) is plotted at the corresponding two-photon wavelengths to allow comparison with the two-photon excitation (TPE) spectrum; its excitation wavelength is given by the upper axis. The TPI spectrum is from Siomos et al. (1981).

Table 3.6. Positions (in cm^{-1})^a of the Maxima of the TPE Spectrum of Fluoranthene in n-Pentane

	S_1	S_2	S_3	S_4	S_5	S_6
0-0 Level	24800	27840	30950	34764	38037	--
	25250	29380	32440	35460		38640
	25400			35945		39487
	25620			36100		40650
	25850			36343		41929
	26320			36812		
	26875			37390		

^aThe error in the determination of the energies is $\sim \pm 100 \text{ cm}^{-1}$.

30950 (30950), 34764 (34700), 38037 (38000) cm^{-1} , where the numbers in parentheses are the corresponding OPA values measured in 3-methylpentane at 77°K (Kolc et al., 1974). The 0-0 level of the sixth singlet state (OPA value 38350 cm^{-1}) could not be identified in the TPE spectrum. For wavelengths below ~ 480 nm, the fluorescence signal rises very steeply, because the observation and the excitation wavelengths (see Section 2.5) lie very close to each other and there is progressively an admixture of one-photon fluorescence and scattered light with it.

3.7. Signal vs. Intensity Measurements

Although in TPE measurements theoretically the signal should exhibit a quadratic dependence on the laser intensity, often this is not the case due to saturation effects. The saturation of the signal¹ occurs at relatively high photon fluxes, when and if the number of excited molecules becomes a significant fraction of the population of ground state molecules. Then the approximation that the number of ground state molecules in the interaction volume (N_0) is constant is not valid any more and N_0 becomes a function (usually decreasing) of the intensity of the exciting light. In this case Eq. 1.2.3 becomes:

$$S_F = (A \tau \beta \cdot \delta) N_0(I) \cdot I^2 \quad (3.7.1)$$

¹Instrumental saturation, i.e., photomultiplier or amplifier saturation, is not considered here.

where S_F is the fluorescence signal, I is the laser intensity and the other quantities are constants as specified in Section 1.2; as a result the dependence of the signal (S_F) on the laser intensity (I) is not quadratic any more. Obviously, this effect will be more pronounced when a strong transition is resonant; saturation therefore will tend to wash out the structure in a spectrum and alter the relative intensities of the peaks. To this extent, saturation is undesirable in two-photon studies (see page 53).

One artifact that can also lead to subquadratic intensity dependencies is the admixture with the real TPE signal of one-photon signals (i.e., scattered light or one-photon fluorescence). To ensure that none of these effects was in any way affecting the TPE signal during the course of these studies, a series of signal vs. laser intensity measurements was undertaken at different wavelengths. Figures 3.26 through 3.29 show these measurements plotted on log-log axes for benzene in n-pentane and various perfluorocarbon solvents (Figures 3.26 and 3.27, respectively), for toluene in various solvents (Figure 3.28) and for fluoranthene in n-pentane (Figure 3.29). The slope of each line is the exponent of the intensity dependence and reveals the apparent order of the process. All these measurements have a slope, $S = 2 \pm .2$. The only exceptions are the measurements of benzene in n-pentane at $\lambda_{exc} = 357$ nm (Figure 3.25) and of fluoranthene in n-pentane at $\lambda_{exc} = 460$ nm (Figure 3.29) with slopes $S = 1.52$ and $S = 1.42$, respectively. The reason in both cases is that, in the corresponding wavelengths, the filters used start transmitting and

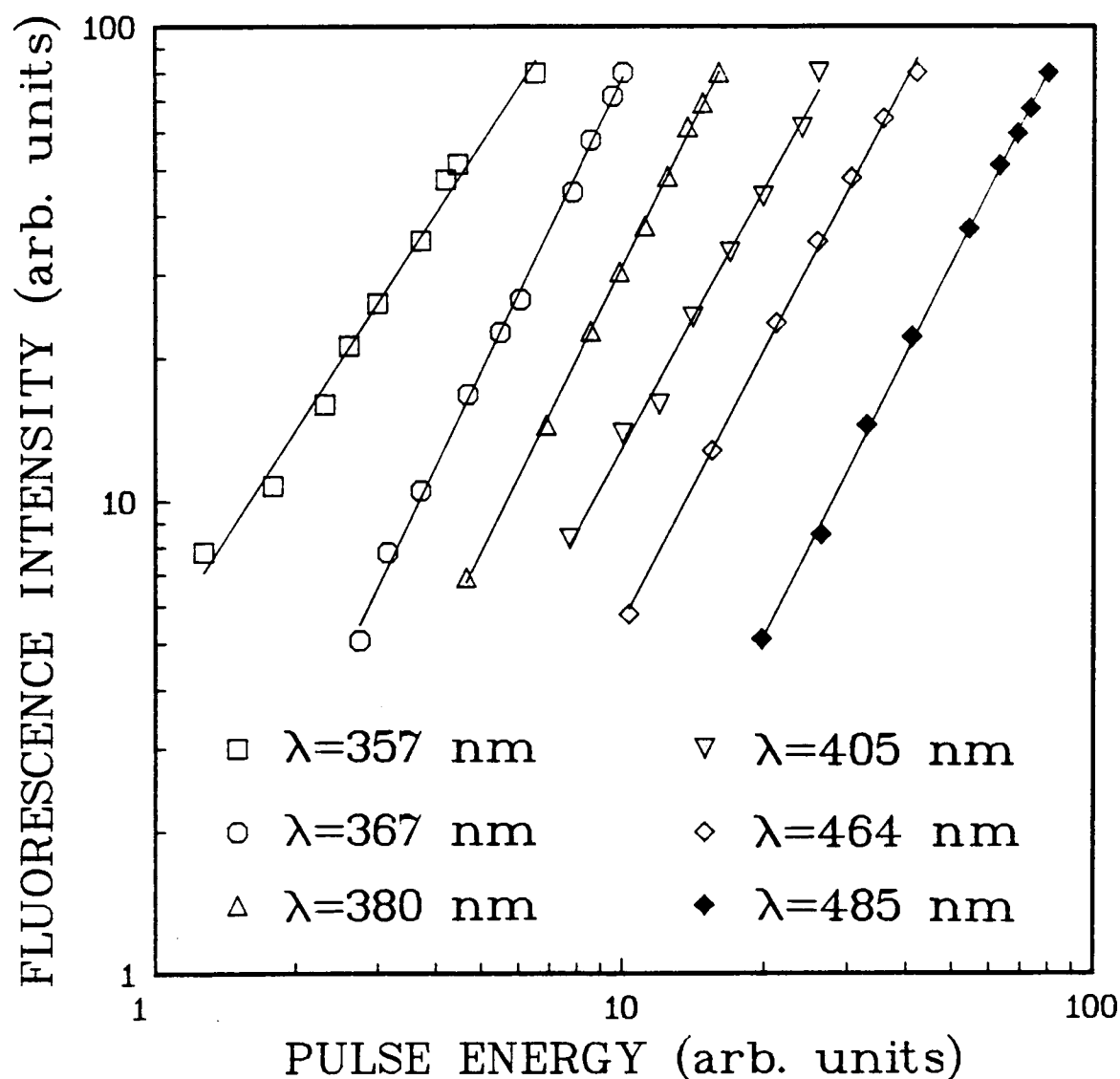


Figure 3.26. Signal vs. laser intensity measurements of the two-photon excitation of benzene in n-pentane at different excitation wavelengths. The slopes, S , are: S (357 nm) = 1.52, S (367 nm) = 2.06, S (380 nm) = 2.00, S (405 nm) = 1.82, S (464 nm) = 1.91, S (485 nm) = 1.98. The slope at $\lambda_{\text{exc}} = 357$ nm is strongly subquadratic because of admixture of laser scattered light with the fluorescence light signal. See text.

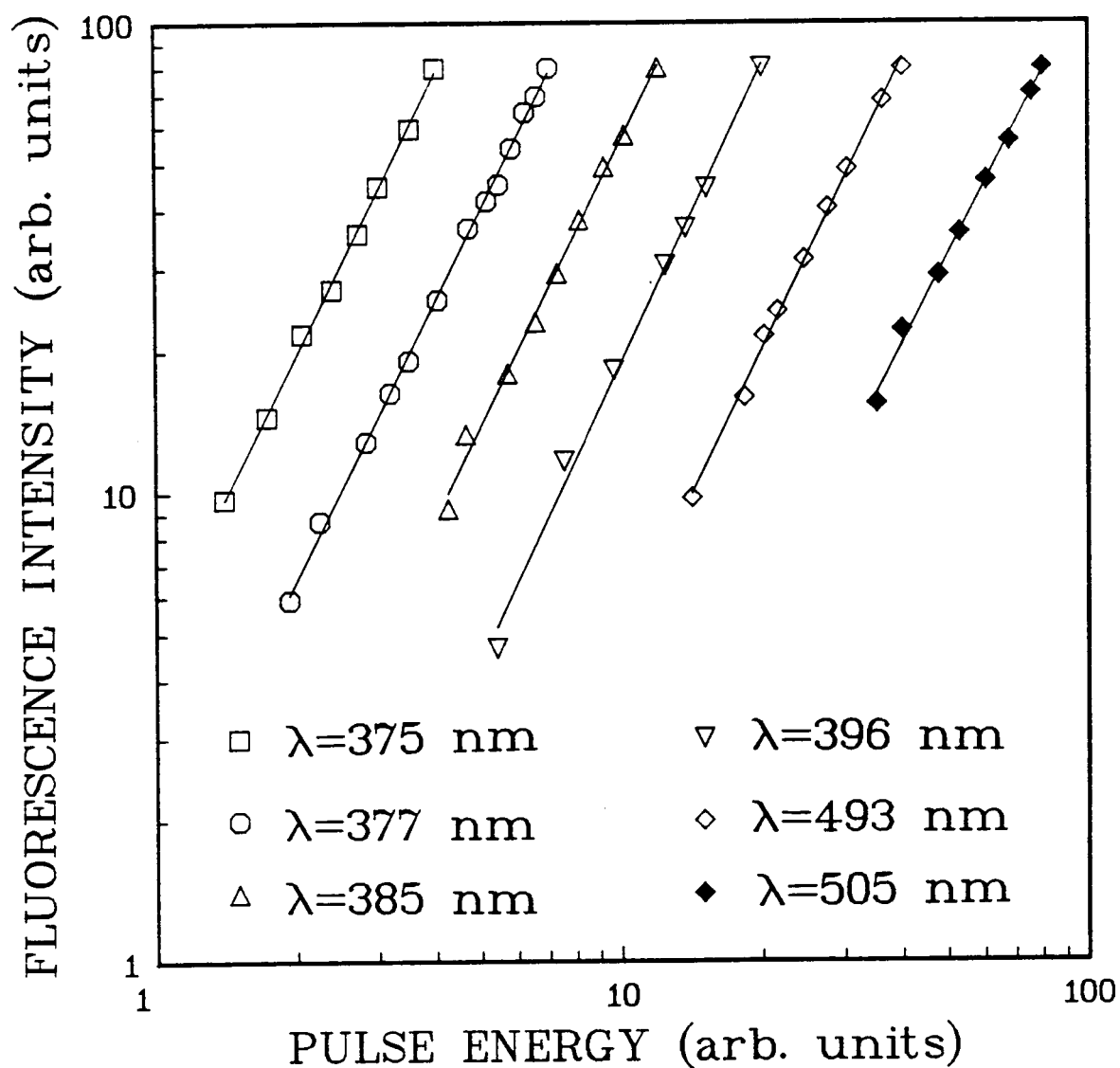


Figure 3.27. Signal vs. laser intensity measurements of the two-photon excitation of benzene in various perfluorocarbon solvents at different wavelengths. The slopes, S , are:
 S (375 nm) = 1.99 (c-C₇F₁₄), S (377 nm) = 1.98 (n-C₆F₁₄),
 S (385 nm) = 2.06 (c-C₆F₁₂), S (396 nm) = 2.10 (n-C₆F₁₄),
 S (493 nm) = 2.01 (n-C₆F₁₄), S (505 nm) = 1.93 (n-C₆F₁₄).

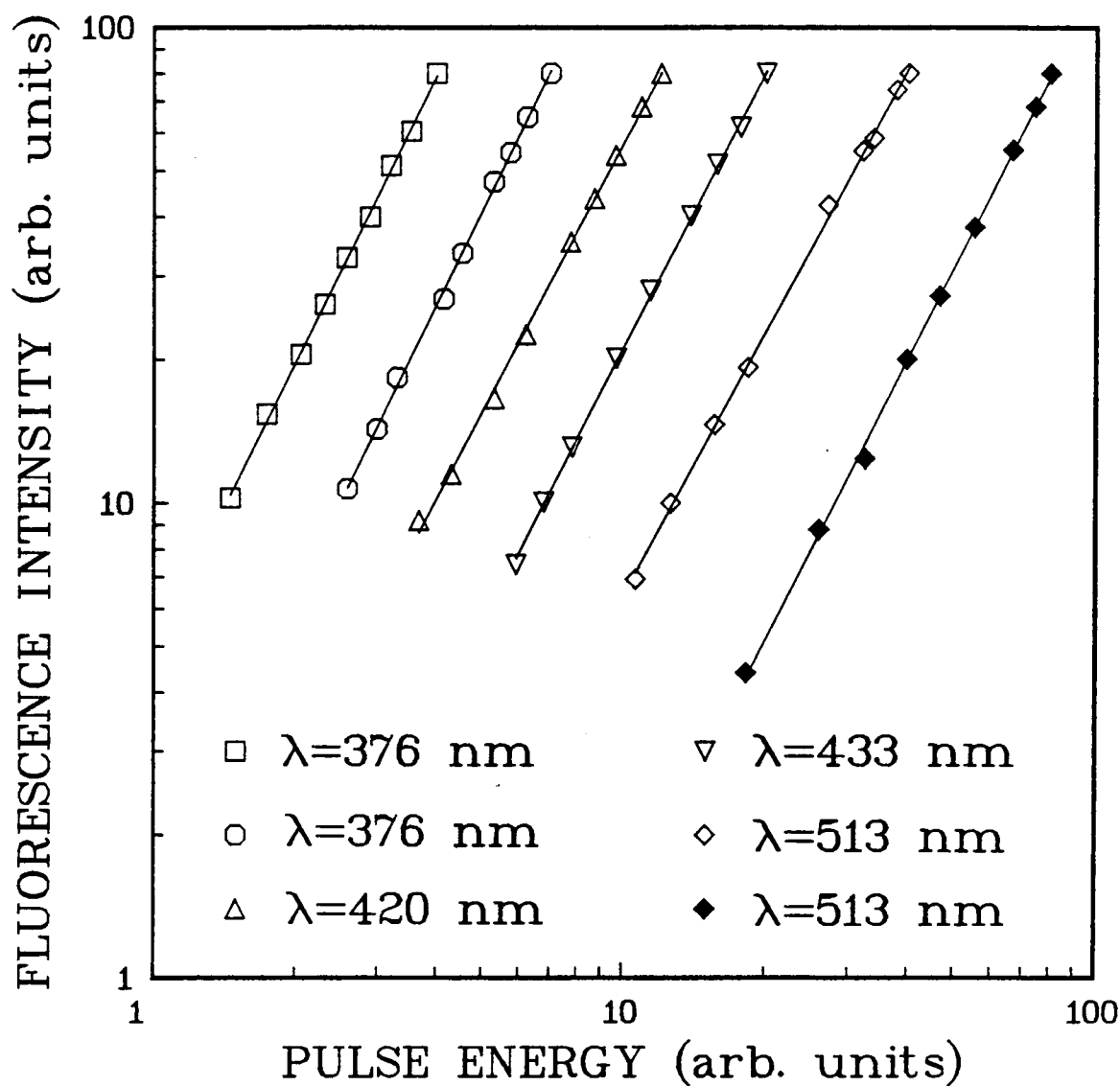


Figure 3.28. Signal vs. laser intensity measurements of the two-photon excitation of toluene in various solvents at different excitation wavelengths. The slopes, S , are: $\square$ S (376 nm) = 2.00 (n-pentane), $\circ$ S (376 nm) = 2.02 (TMSi), $\triangle$ S (420 nm) = 1.88 (n-C₆F₁₄), ∇ S (433 nm) = 1.94 (TMSi), $\diamond$ S (513 nm) = 1.85 (n-C₆F₁₄), $\blacklozenge$ S (513 nm) = 1.97 (c-C₆F₁₂).

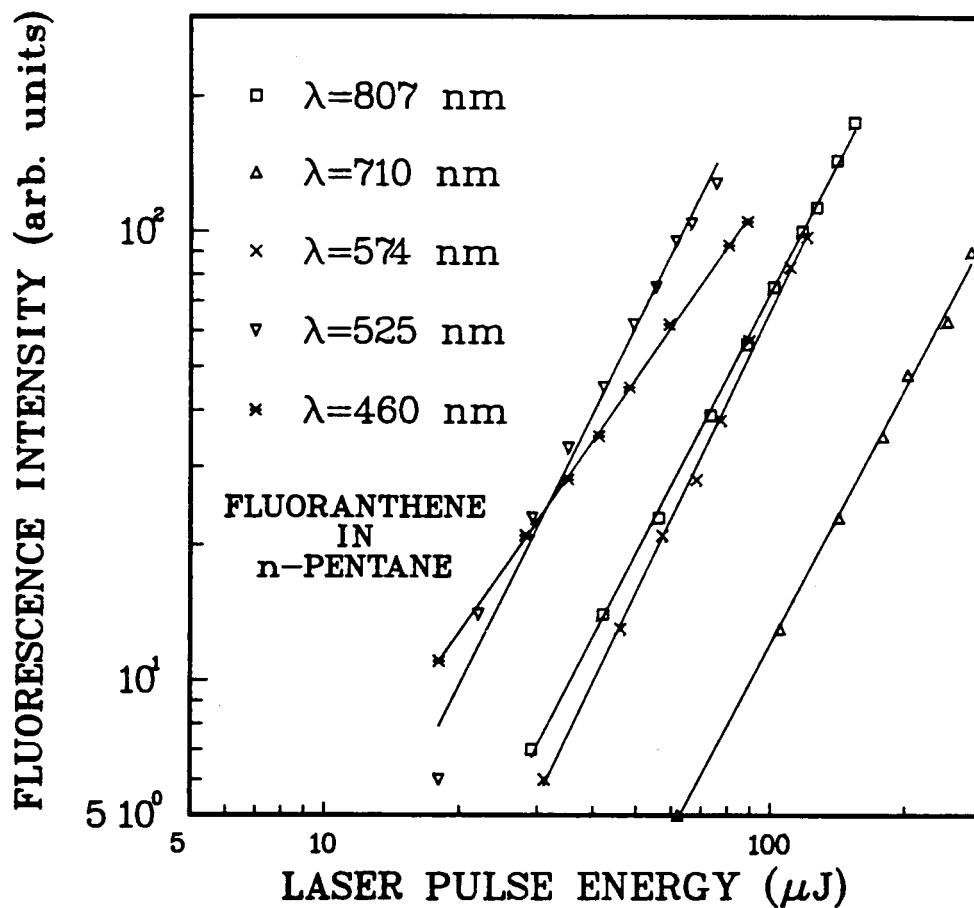


Figure 3.29. Signal vs. laser intensity measurements of the two-photon excitation of fluoranthene in n-pentane at different excitation wavelengths. The slopes, S , are: S (460 nm) = 1.42, S (525 nm) = 2.05, S (574 nm) = 2.09, S (710 nm) = 1.88, S (807 nm) = 1.96. The slope at $\lambda_{\text{exc}} = 460$ nm is strongly subquadratic because of admixture of scattered light with the fluorescence light signal.

laser scattered light from the interaction volume is detected by the photomultipliers.

Intentionally saturated measurements, by using high laser intensities and tight focusing, of benzene in n-pentane at $\lambda_{\text{exc}} = 508, 496 \text{ nm}$ and $\text{n-C}_6\text{F}_{14}$ at $\lambda_{\text{exc}} = 504, 482 \text{ nm}$ are shown in Figure 3.30. At relatively low intensities the slope is 1.8 in all cases, slightly saturated but still close to the expected value of 2. At higher intensities, however, a difference becomes apparent; the n-pentane measurements show a slight increase in saturation ($S = 1.6$) while the $\text{n-C}_6\text{F}_{14}$ measurements reveal an extremely strong saturation with a sublinear intensity dependence ($S = 0.5$), although in both cases the laser and the signal intensities are approximately the same. Since the two-photon transition probability is a molecular property it should be the same in both solvents and therefore the question arises as to why this difference in the saturation behavior between n-pentane and $\text{n-C}_6\text{F}_{14}$. The following considerations explain this behavior.

Once the molecule is excited to the two-photon state, there is a high probability that it will absorb an additional photon and become ionized since the last step is a one-photon bound continuum transition. Following ionization, geminate recombination occurs within a few picoseconds—the halflife of geminate pairs in n-hexane is 9 ps (Braun and Scott, 1983)—in n-pentane. In $\text{n-C}_6\text{F}_{14}$, however, the electron is captured by the solvent at times shorter than 1 ps (Siomos et al., 1980) and therefore recombination will be much more slow and weak. Since recombination replenishes the population of ground state molecules, the lack of

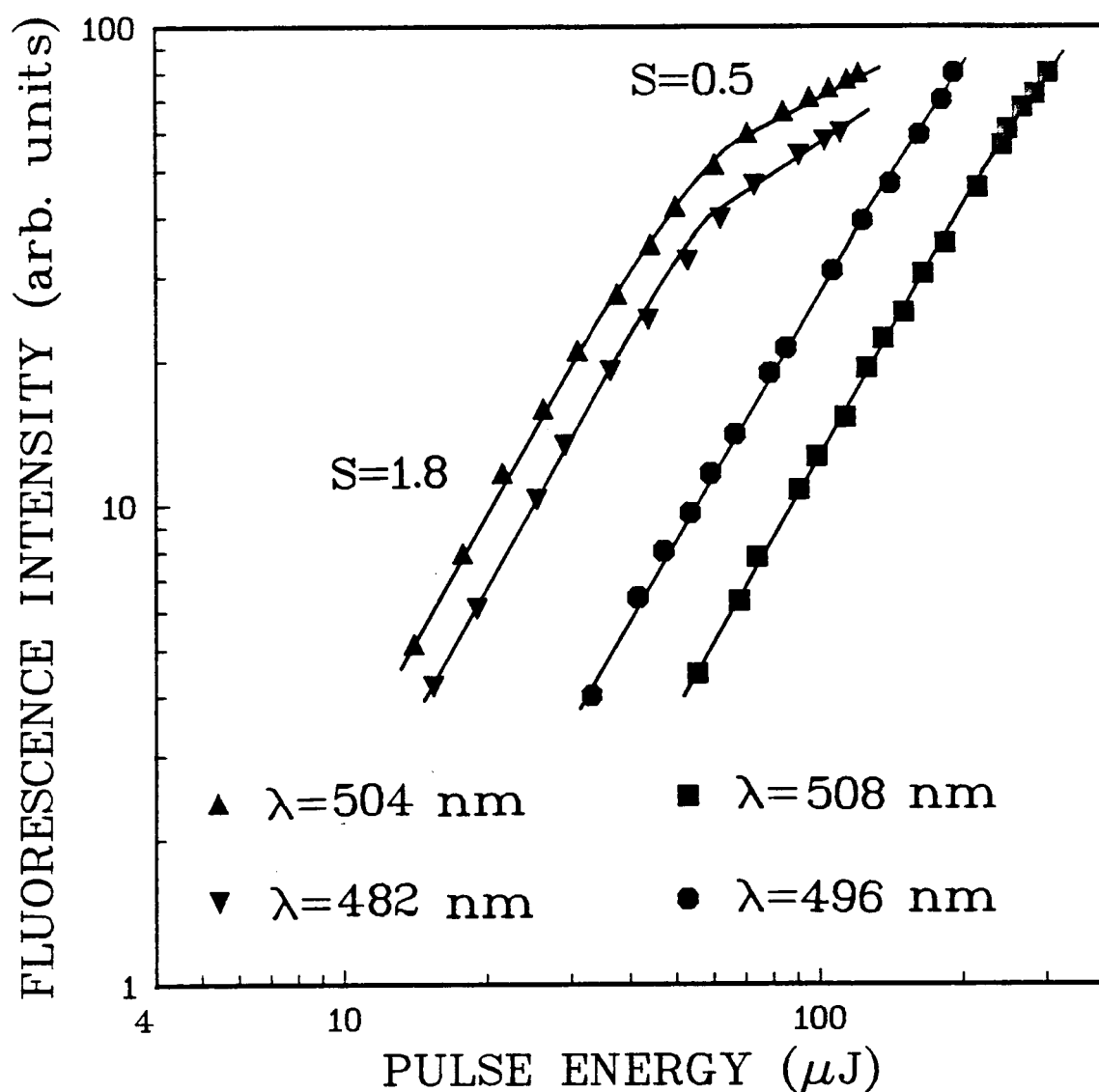


Figure 3.30. Signal vs. laser intensity measurements of the two-photon excitation of benzene in perfluoro-n-hexane ($\lambda_{\text{exc}} = 504 \text{ nm}$, 482 nm) and in n-pentane ($\lambda_{\text{exc}} = 508 \text{ nm}$, 496 nm) exhibiting saturation. Note the sublinear dependence ($S = 0.5$) of the signal on the laser intensity at high intensities for the measurements in perfluoro-n-hexane.

efficient recombination in $n\text{-C}_6\text{F}_{14}$ depletes the ground state to a great extent, while this depletion is almost imperceptible in $n\text{-pentane}$.

A simplified mathematical model was used to account for the saturation observed in $n\text{-C}_6\text{F}_{14}$, based on the assumption that the excited molecules do not return to the ground state within the laser pulse duration. This is a realistic assumption considering the short laser pulse duration ($\tau = 5$ ns), the much longer fluorescence lifetime (~ 30 ns) and the high probability of ionization and electron capture.

From Eq. 1.2.1 modified for a TPE process the fluorescence signal S_F will be:

$$S_F = A \int_t N(t) \cdot \delta \cdot I^2(t) dt \quad (3.7.2)$$

where A is a constant, $N(t)$ is the number of ground state molecules as a function of time, δ the two-photon transition probability, and $I(t)$ the laser intensity (in $\text{cm}^{-2} \cdot \text{s}^{-1}$).

The rate equations that need to be solved to obtain $N(t)$ are

$$\begin{aligned} \dot{N} &= -N \delta I^2 + f N_1 + g N_2 \\ \dot{N}_1 &= N \delta I^2 - (\sigma I + f) N_1 + g' N_2 \\ \dot{N}_2 &= N_1 \sigma I - (g + g') N_2 \end{aligned} \quad (3.7.3)$$

where a three level system is assumed (see Figure 1.1b, p. 7), with N_1 the population of the two-photon resonant state and N_2 the population of the ionization continuum. g and g' are the relaxation rate constants from the continuum to the ground and excited states, respectively, f is the total relaxation rate (radiative and nonradiative) from the

two-photon resonant excited state to the ground, and σ the ionization probability from that state. With the simplifying assumptions, however, mentioned above, the quantities fN_1 and gN_2 are negligible compared to $N \delta I^2$ and therefore:

$$\dot{N} = -N \delta I^2$$

and

$$N(t) = N_0 \cdot e^{-\delta I^2 t} \quad (3.7.4)$$

where $N_0 = N(t=0)$. Assuming a square pulse of duration τ and substituting in Eq. 3.7.2, after integration we have:

$$S_F = AN_0(1 - e^{-\delta \tau I^2}) \quad (3.7.5)$$

The slope, S , then will be:

$$\begin{aligned} S &= \frac{d \log S_F}{d \log I} \\ &= 2 \delta \tau I^2 \frac{(e^{-\delta \tau I^2})}{(1 - e^{-\delta \tau I^2})} \end{aligned} \quad (3.7.6)$$

or

$$S = 2X^2 \frac{e^{-X^2}}{1 - e^{-X^2}} \quad \text{where } X = \sqrt{\delta \tau I^2} \quad (3.7.7)$$

Figure 3.31 shows the slope S derived from Eq. 3.7.7 plotted as a function of the intensity in units of $(\delta \tau)^{-1/2}$. The solid symbols represent the experimentally determined slopes from the signal vs.

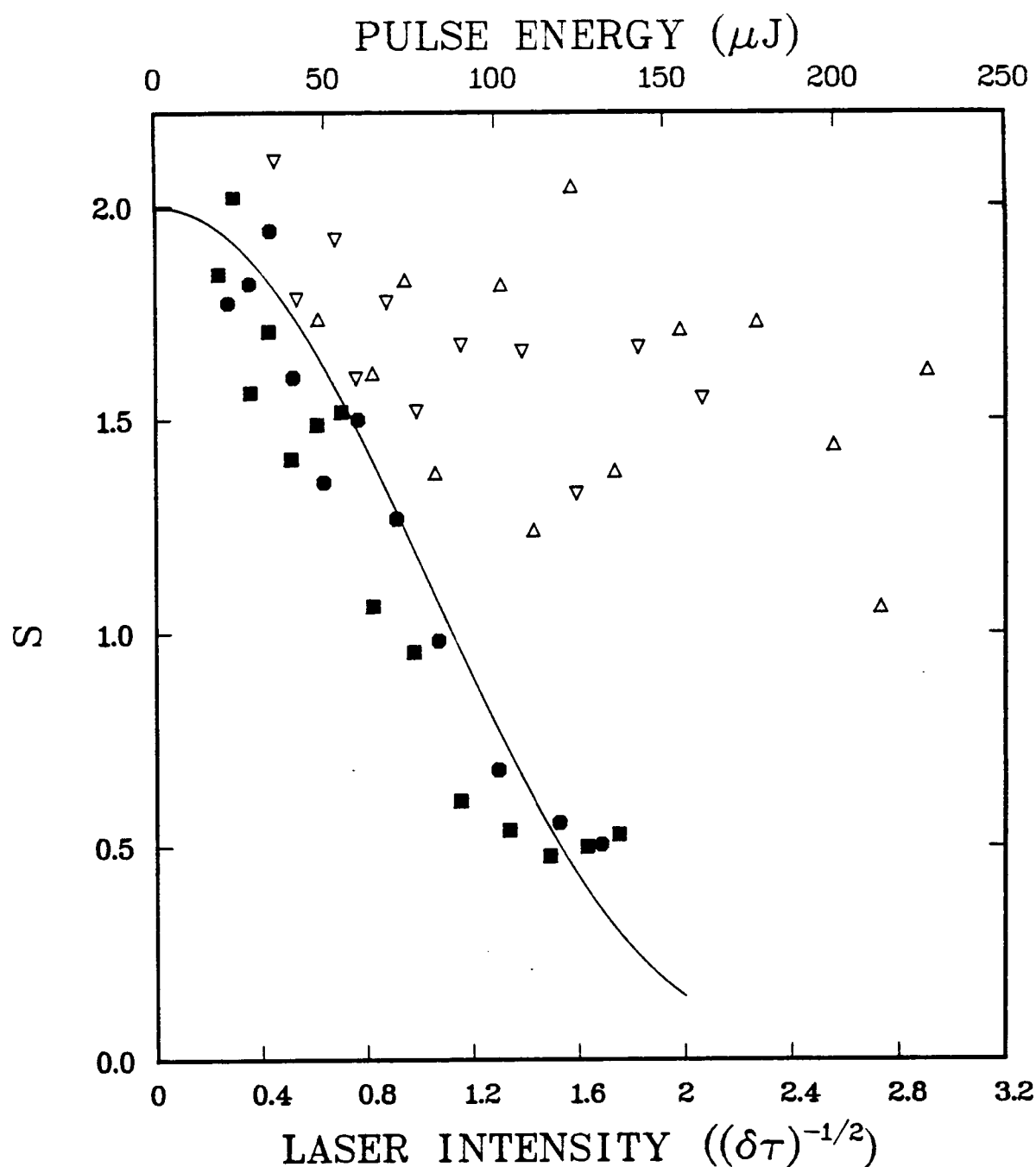


Figure 3.31. Plot of the slope vs. laser intensity in units of $1/\sqrt{\delta\tau}$ derived from the equation $S = 2I^2(e^{-I^2})/(1-e^{-I^2})$. The symbols represent the experimentally determined slopes vs. laser pulse energy from the measurements shown in Figure 3.30. Solid symbols are for benzene in perfluoro-n-hexane and open for benzene in n-pentane. See text.

intensity measurements in $n\text{-C}_6\text{F}_{14}$. The open symbols represent the corresponding slopes in $n\text{-pentane}$. They were derived by applying the following equation to successive points of the signal vs. intensity measurements.

$$S\left(\frac{I_i + I_{i+1}}{2}\right) = \log(S_{Fi+1}/S_{Fi})/\log(I_{i+1}/I_i)$$

where the subscript i indicates the i th point. The fit with the theoretical curve (Eq. 3.7.7) was obtained assuming that the intensity of $3.2 (\delta\tau)^{-1/2}$ corresponds to a laser pulse of $\sim 250 \mu\text{J}$. For the specific experimental conditions (see Section 2.3) this pulse energy corresponds to an intensity $I = 10^{28} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Then $10^{28} \text{ cm}^{-2} \cdot \text{s}^{-1} = 3.2/\sqrt{\delta \cdot 5 \times 10^{-2}} \text{ s}$, which yields a value of δ of the order of $10^{-46} \text{ cm}^4 \cdot \text{s}$.

3.8. Conclusions

The studies discussed in this chapter demonstrated the high sensitivity of the TPE technique, on one hand, and its complementarity both with one-photon and gas phase two-photon studies, on the other. Comparison of one- and two-photon studies elucidates the effect of symmetry on molecular transitions, while the two-photon liquid phase studies extend the wavelength range of transitions that have been studied in the gas phase. We were thus able to make a complete vibrational assignment over the entire wavelength range of the ${}^1\text{B}_{2u}$ (${}^1\text{B}_2$) state of benzene (toluene), including the hot bands, and study the polarization behavior of individual peaks. We were also able to

locate the position of the 0-0 band of the $^1B_{2u}$ state of benzene in different solvents and determine its polarization ratio ($\Omega = 0.7$); this is especially important, since this band has not been observed in gas or one-photon studies.

A very interesting feature of this work was the observation of the unusual solvent dependence of the upper states of benzene and toluene. Especially the peak of benzene at $\lambda_{exc} \approx 380$ nm exhibited a very strongly nonvalence behavior. Obviously the definitive assignment of this state will have to await, first, for the theoretical treatment of nonvalence and especially Rydberg states in the liquid phase, and second, for the establishment of sharp criteria (if they exist) that can be used to differentiate between neighboring valence and nonvalence states. Tentatively, however, and in the lack of alternative assignments, the benzene 380 nm peak was assigned to the $(3s)^1E_{1g}$ Rydberg state which is observed in the gas phase at $\lambda_{exc} \approx 391$ nm.

CHAPTER IV

MULTIPHOTON IONIZATION OF BENZENE

4.1. Introduction

Multiphoton ionization in the liquid phase is a process which, presently, is not very well understood. The multiphoton ionization of benzene in the liquid phase in particular has been the subject of a long controversy (see Section 1.3). In general the n -photon non-resonant transition probability per second ($W^{(n)}$) can be written as

$$W^{(n)} = \sigma^{(n)} I^n \quad (4.1.1)$$

where $\sigma^{(n)}$ is the n -photon absorption cross-section (in $\text{cm}^{2n} \cdot \text{s}^{n-1}$) and I is the laser intensity (in $\text{cm}^{-2} \cdot \text{s}^{-1}$). The excitation for such a process (case a in Figure 1.1, p. 7) is assumed to proceed through virtual states whose lifetime is typically 10^{-15} s and the photocurrent produced is proportional to I^n .

For a three-photon nonresonant ionization the cross-section $\sigma^{(3)}$ is given by (Parker et al., 1978)

$$\sigma^{(3)} = A \left| \sum_i \sum_j \frac{\langle f | \vec{r} \cdot \vec{\epsilon} | j \rangle \langle j | \vec{r} \cdot \vec{\epsilon} | i \rangle \langle i | \vec{r} \cdot \vec{\epsilon} | g \rangle}{(E_j - E_g - 2\hbar\omega)(E_i - E_g - \hbar\omega)} \right|^2 \quad (4.1.2)$$

where A is a constant, g and f are the ground and final (continuum) states, i and j are the virtual intermediate levels, $\vec{r} \cdot \vec{\epsilon}$ is the molecule-radiation interaction Hamiltonian and $\hbar\omega$ is the laser photon

energy. When the laser photon energy is tuned to a one- or two-photon resonance ($E_j - E_g = 2\hbar\omega$ or $E_i - E_g = \hbar\omega$), the denominator approaches zero and Eq. 4.1.2 diverges. Then a phenomenological damping constant $i\gamma$ is added to the energy in the denominator and the infinity is avoided (Parker et al., 1978; Zakheim and Johnson, 1978).

Generally there are two ways that the m -photon resonant n -photon ionization process can be envisaged. It can be thought of as an n -photon simultaneous process in which the m -photon resonant state serves as an intermediate and determines the observed structure in the spectrum. Alternatively it can be considered as a "two-step" process. In this context a two-step process is a process in which the second transition retains no memory of the first transition (Lambropoulos, 1974). In the two-step mechanism the molecule is first excited to the resonant state with m -photons and then the excited molecule absorbs the additional $n-m$ photons and is ionized. In this case the two absorption processes can be considered as independent. Which process—the one- or the two-step—is more appropriate to describe the ionization mechanism depends on parameters such as the relative lifetimes and bandwidths of the resonant state and the laser pulse, and the laser intensity. In the liquid phase, however, where collisional relaxation is very fast, the "two-step" process is usually thought to describe the multiphoton ionization mechanism.

Different types of studies can be used to provide information on the ionization mechanism. The use of ultrashort laser pulses, with lifetime shorter than the lifetime of the resonant state, is one way

of investigating the ionization mechanism. The study of the dependence should be proportional to I^n for the one-step process and between I^n and I^m for the two-step mechanism (Ito and Mikami, 1980). Polarization studies can also be used to obtain information on the ionization mechanism. The multiphoton ionization polarization ratio depends on factors such as the laser intensity, the nonradiative relaxation rate and the degree of anisotropy of the postresonant transition (Berg et al., 1978). At relatively low laser intensities the polarization ratio for a two-photon resonant, three-photon ionization process can be written as (Robin, 1980):

$$\Omega_{\text{MPI}} = \frac{\sigma_{\text{gr}}^{\text{cir}}}{\sigma_{\text{gr}}^{\text{lin}}} \frac{\sigma_{\text{rf}}^{\text{cir}}}{\sigma_{\text{rf}}^{\text{lin}}} = \Omega(2) \frac{\sigma_{\text{rf}}^{\text{cir}}}{\sigma_{\text{rf}}^{\text{lin}}} \quad (4.1.3)$$

where $\sigma_{\text{gr}}^{\text{cir}}$, $\sigma_{\text{gr}}^{\text{lin}}$ and $\sigma_{\text{rf}}^{\text{cir}}$, $\sigma_{\text{rf}}^{\text{lin}}$ are the transition cross sections, for circularly and linearly polarized light, from the ground to the resonant and from the resonant to the final (continuum) states, respectively, and $\Omega(2)$ is the polarization ratio of the two-photon resonant state. When the conditions (i.e., resonant state and laser pulse lifetimes, laser intensity and medium effect) are such that the two-photon resonant transition is the rate determining step and the anisotropy of the resonant state is destroyed before the second step takes place, then the MPI polarization ratio is determined by the symmetry of the two-photon resonant state ($\sigma_{\text{rf}}^{\text{cir}}/\sigma_{\text{rf}}^{\text{lin}} = 1$ and $\Omega_{\text{MPI}} = \Omega(2)$).

A number of different mechanisms have been proposed for the multiphoton ionization of benzene (and other molecules) in solution.

It has been suggested that ionization follows geminate ion-electron pair formation, very fast recombination and creation of an excited state, such as the first excited singlet, or triplet or an excimeric state. Excimer formation cannot be the case for dilute solutions (of benzene at least), having a concentration $C \lesssim 10^{-2}$ M (Nakashima et al., 1980b). On the other hand, in the time available for recombination (10^{-11} , 10^{-12} s) the electron and positive ion, which were generated as a singlet pair, retain their spin correlation and therefore recombination will populate, initially at least, only singlet states (Lipsky, 1981). Triplet formation then proceeds rather slowly, compared to the laser pulse duration; the triplet formation rate constant for benzene is $\sim 10^7 \text{ s}^{-1}$ (Cundall et al., 1977; Nakashima et al., 1980b).

Comparison of the two-photon excitation spectra and the corresponding multiphoton ionization spectra can also be used to provide information on the ionization mechanism. The photocurrent signal, (S_I), assuming that the ionization totally proceeds through two-photon resonant states, can be expressed as a function of the laser excitation wavelengths (see Section 1.2) by:

$$S_I(\lambda_{\text{exc}}) = A[\delta(\lambda_{\text{exc}}) \cdot \tau I^2] \cdot [\sigma^{(n-2)}(\lambda_{\text{exc}}) \cdot \tau I^{n-2}] \quad (4.1.4)$$

while the fluorescence signal (S_F) by:

$$S_F(\lambda_{\text{exc}}) = A'[\delta(\lambda_{\text{exc}}) \cdot \tau I^2] \cdot [\beta(\lambda_{\text{exc}})] \quad (4.1.5)$$

where the notation is that introduced in Section 1.2 and $\sigma^{(n-2)}(\lambda_{\text{exc}})$ is the transition cross-section from the two-photon resonant state to the ionization continuum involving absorption of $n-2$ photons. The photocurrent signal, therefore, should reveal the same structure as the fluorescence signal, modulated by the factor $\sigma^{(n-2)}/\beta$.

The determination of the ionization threshold of a molecule in the liquid phase (I_L) is one of the objectives of multiphoton ionization spectroscopy. Usually I_L is related to the gas phase ionization energy (I_G) by:

$$I_L = I_G + P_+ + V_0 \quad (4.1.6)$$

where P_+ and V_0 are the energies of the positive ion and the electron in the liquid, minus their energy in the gas phase, respectively. Often P_+ is thought of as the electronic polarization energy of the positive ion and V_0 as the "bottom" of the conduction band in the liquid. The I_L of benzene, in particular, is not exactly known. Indirectly and for neat liquid benzene it has been estimated to be ~ 7 eV (Fuchs and Voltz, 1973; Schwarz and Mautner, 1982). In the gaseous phase the ionization potential is a very accurately determined quantity. In the liquid phase, however, because of solvent-molecule interactions, there may not be a distinct ionization energy, but rather an apparent ionization threshold. The ionization potential of a solute in a liquid, therefore, is operationally defined as the threshold energy for the generation and observation of a current (Lipsky, 1981). Although this definition is convenient from an

experimental standpoint, it should be used with caution and consideration should be given to all the parameters which influence the experimentally determined threshold (see discussion in Sections 4.4 and 4.5).

In the present work the multiphoton ionization of benzene in two nonpolar liquids (n-pentane and TMSi) was studied for the $360 \text{ nm} < \lambda_{\text{exc}} < 570 \text{ nm}$ range, that is, a wavelength range coinciding with that of the TPE studies. In the following sections the MPI spectra and the polarization and signal vs. intensity measurements will be presented and their implications on the ionization mechanism and the ionization threshold of benzene in these liquids will be discussed.

4.2. The Multiphoton Ionization Spectra of Benzene in Tetramethylsilane and n-Pentane

The MPI spectrum of a $7 \cdot 10^{-3} \text{ M}$ solution of benzene in TMSi is shown in Figure 4.1, while Figure 4.2 shows the same spectrum plotted together with the corresponding TPE spectrum. Certain similarities but also differences are immediately apparent in the two spectra. The 380 nm peak (386 nm in TMSi) is observed in both cases at exactly the same wavelength and with the same sharpness. Similarly, the structure of the ${}^1\text{B}_{2\text{u}}$ state for the $470 \text{ nm} < \lambda_{\text{exc}} < 540 \text{ nm}$ range is identical in both spectra. The major difference is that in the MPI spectrum the structure is sitting on a continuously and steeply rising background. As a result, the weak ${}^1\text{B}_{1\text{u}}$ state ($400 \text{ nm} < \lambda_{\text{exc}} < 420 \text{ nm}$) is merely seen as a shoulder in the MPI spectrum, while the low intensity peaks on the high energy side of the ${}^1\text{B}_{2\text{u}}$ state

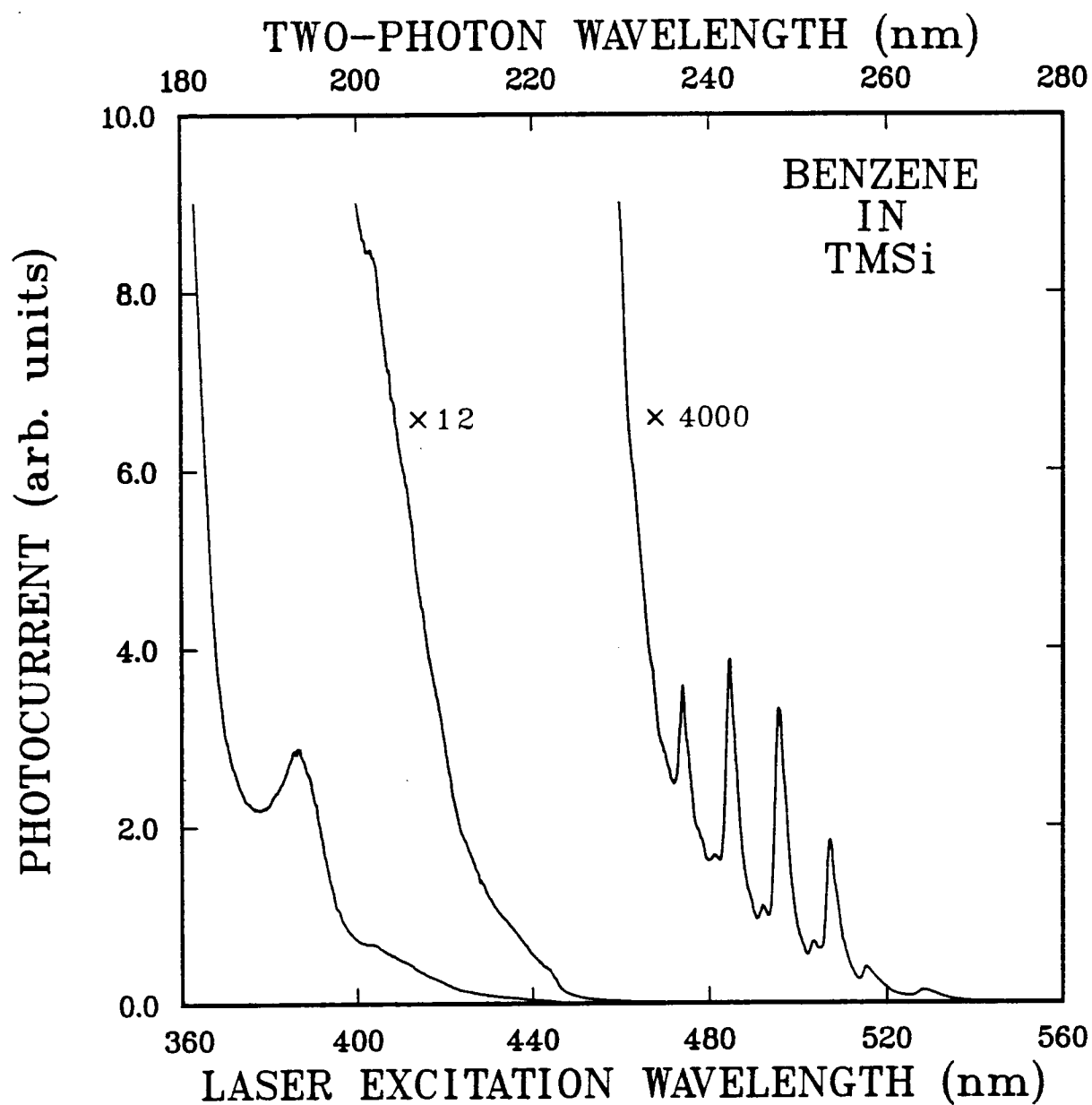


Figure 4.1. Multiphoton ionization spectrum of benzene in tetramethylsilane (TMSi).

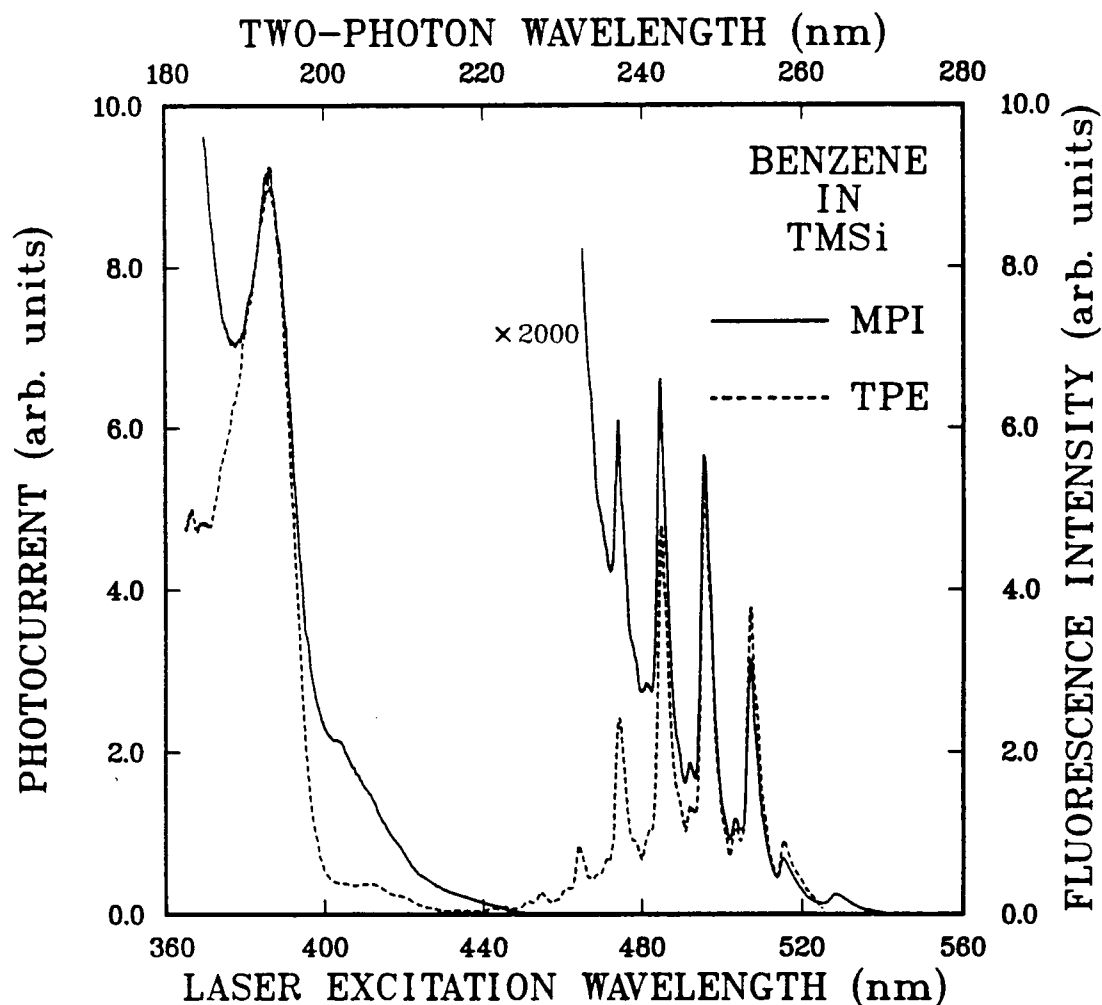


Figure 4.2. The multiphoton ionization (MPI) and the two-photon excitation (TPE) spectra of benzene in tetramethylsilane. The two spectra have been normalized at the peak intensity of $\lambda_{\text{exc}} = 386$ nm. The ${}^1B_{2u}$ state portion of the ionization spectrum was amplified 2000 times to reach the intensity of the excitation spectrum.

($\lambda_{\text{exc}} < 470 \text{ nm}$), disappear into the rising continuum. Moreover, while in the TPE spectrum the peak at 386 nm and the peak of the ${}^1\text{B}_{2\text{u}}$ state at $\lambda_{\text{exc}} = 496 \text{ nm}$ have comparable intensities (their ratio is ~ 1.59), in the MPI spectrum the ${}^1\text{B}_{2\text{u}}$ state is more than three orders of magnitude weaker than the 386 nm peak.

Polarization studies of the MPI of benzene in TMSi were also undertaken over the $465 \text{ nm} < \lambda_{\text{exc}} < 540 \text{ nm}$ range. Figure 4.3 shows the spectra measured with circularly and linearly polarized light and the corresponding polarization ratio. The polarization behavior is the expected one for a process involving a two-photon resonant transition to the ${}^1\text{B}_{2\text{u}}$ state and an isotropic second step to the ionization continuum. The polarization ratios of the MPI of benzene in TMSi, measured at relatively low laser intensity (see Section 4.3), and the TPE in n-pentane are plotted together in Figure 4.4 for the sake of comparison. The similarity between the two ratios is striking and indicates two things. First, that the ionization totally proceeds through the two-photon resonant ${}^1\text{B}_{2\text{u}}$ state, and second, that the two-photon resonant step is dominating the polarization behavior. Certain differences of course can be seen in that the peaks of the polarization ratio (the $18_0^1 1_0^n$ progression) are higher, and the valleys ($14_0^1 1_0^n$ progression) are lower, in TPE than in MPI. These differences are especially pronounced at wavelengths below $\sim 485 \text{ nm}$ and they will be discussed in detail in the next section.

The multiphoton ionization of benzene was also studied in n-pentane ($C = 3 \cdot 10^{-3} \text{ M}$) with the same qualitative results, as in

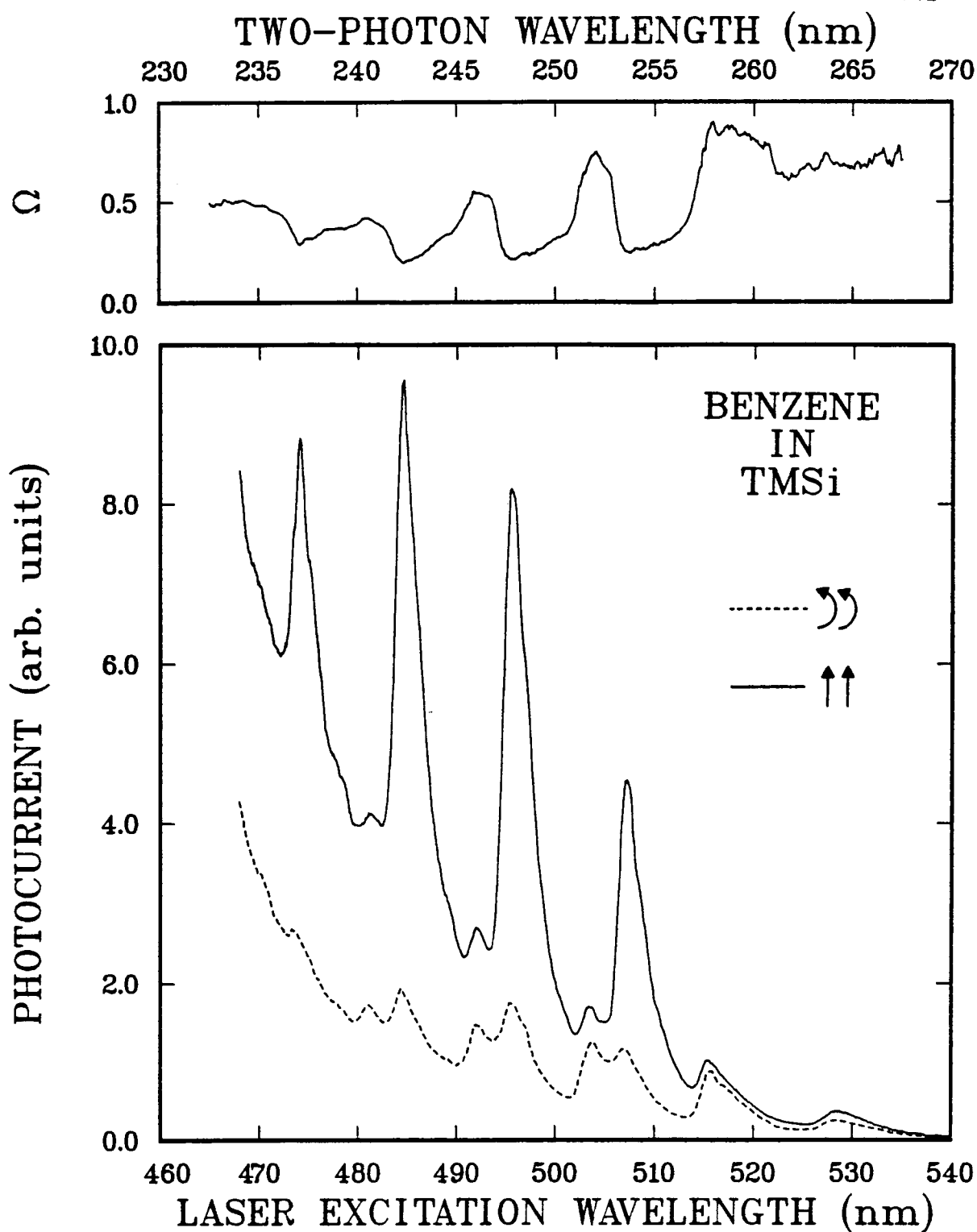


Figure 4.3. The multiphoton ionization spectra of benzene in tetramethylsilane (TMSi) using circularly (---) and linearly (—) polarized light. The corresponding polarization ratio, Ω , is shown exactly above.

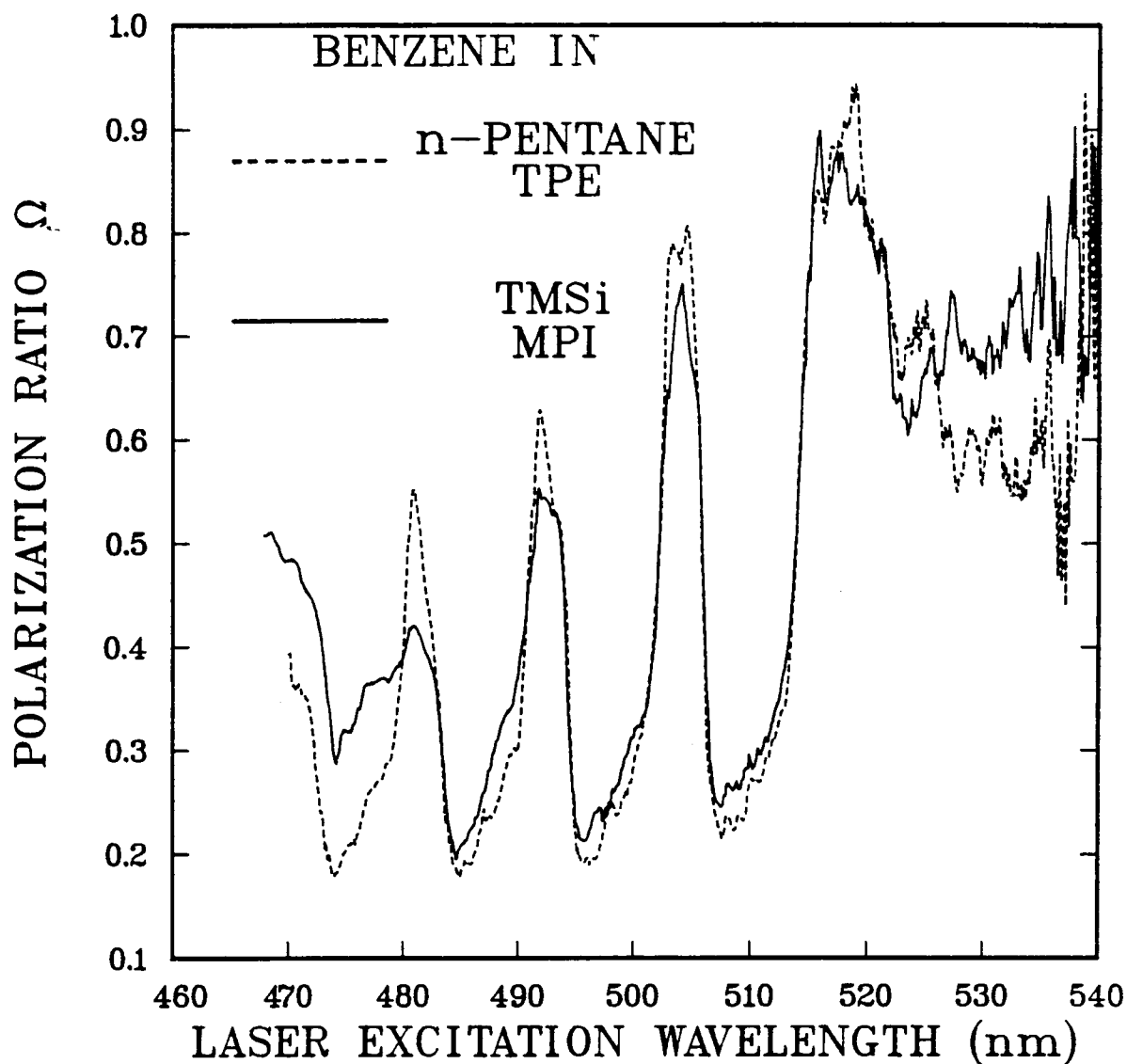


Figure 4.4. The polarization ratios, Ω , of the multiphoton ionization (MPI) of benzene in tetramethylsilane (TMSi) and of the two-photon excitation (TPE) in n-pentane. Note the excellent coincidence of the two ratios for $\lambda_{\text{exc}} \approx 490$ nm, and their gradual differentiation at shorter wavelengths.

TMSi, as far as the spectral characteristics are concerned. Certain differences associated with the signal vs. intensity measurements and the characteristics of the photocurrent signal will be discussed in Section 4.4. Figure 4.5 shows a portion of the MPI spectrum of benzene in n-pentane, together with the corresponding TPE spectrum, over the $440 \text{ nm} < \lambda_{\text{exc}} < 540 \text{ nm}$ range. As in TMSi, there is a high similarity between the two spectra and a rising background can be observed in the MPI spectrum.

4.3. The Ionization Mechanism of Benzene and the Channel 3

The differences referred to previously between the MPI and the TPE spectra of benzene below $\sim 485 \text{ nm}$ are also observed between MPI spectra measured at different laser intensities. Figure 4.6 shows three such MPI spectra of benzene in TMSi plotted together with the TPE spectrum; directly above are the corresponding polarization ratios of the MPI in TMSi (for the two higher laser light intensities) and of the TPE in n-pentane. The symbols represent the nonradiative relaxation rate constants for different vibrational levels of the ${}^1\text{B}_{2\text{u}}$ state of benzene in the gas phase, taken from Formosinho and Dias da Silva (1974) and Callomon et al. (1972). The sharp increase of the relaxation rates between 485 nm and 490 nm marks the onset of the channel 3 (see Section 1.3). It should be noted that although the channel 3 is especially apparent in the gas phase, it is also operating in the liquid phase, even though its onset is less sharp (Cundall and Pereira, 1973; Birks, 1973).

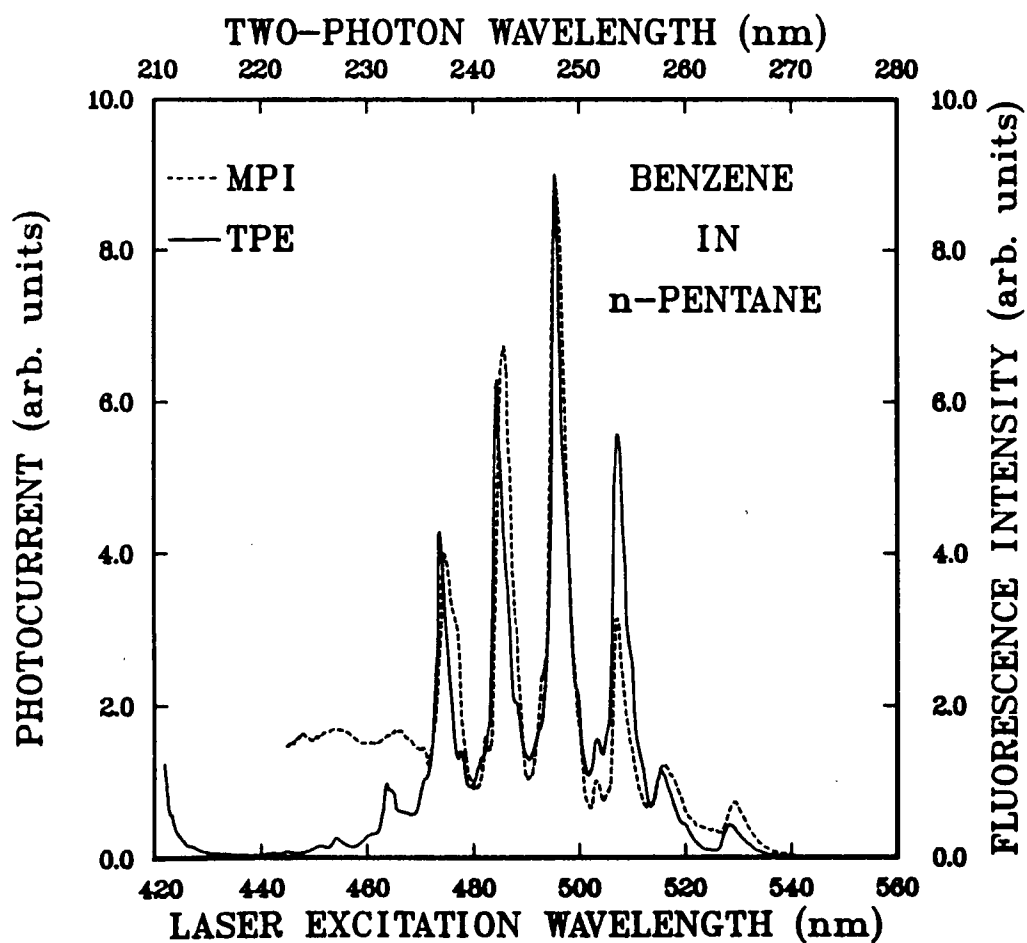


Figure 4.5. Multiphoton ionization (MPI) and two-photon excitation (TPE) spectra of benzene in n-pentane.

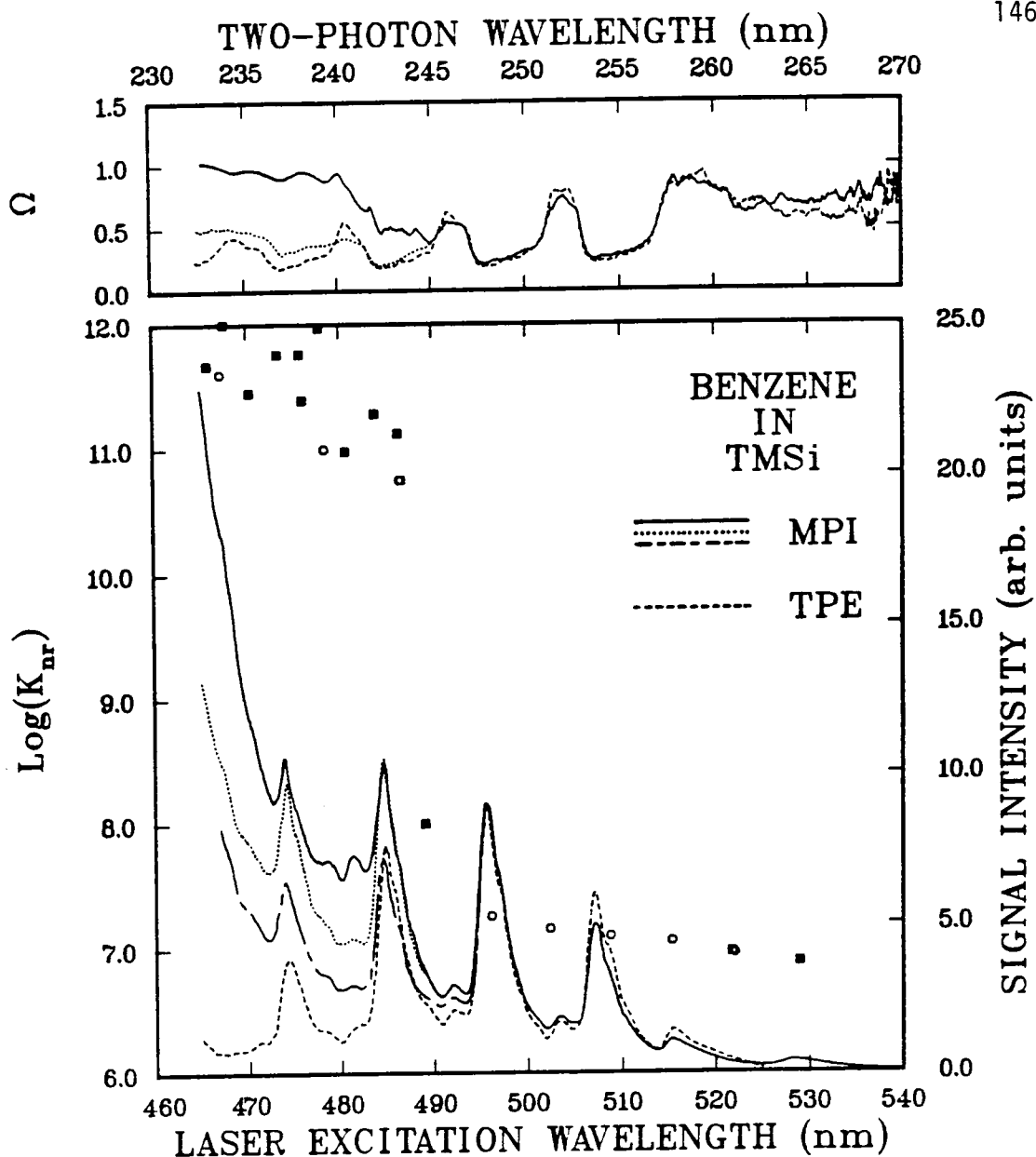


Figure 4.6. The two-photon excitation (TPE) spectrum of benzene in tetramethylsilane (TMSi), and the multiphoton ionization (MPI) spectra measured at successively lower laser intensities (— 150 $\mu\text{J/pulse}$, ... 120 $\mu\text{J/pulse}$, - - - 70 $\mu\text{J/pulse}$). The corresponding polarization ratios are shown directly above. The TPE ratio is that of benzene in n-pentane. The symbols represent the nonradiative relaxation rate constants from different vibrational levels of the $^1\text{B}_{2u}$ to the ground state, in the gas phase (■ from Dias da Silva, 1974; ○ from Callomon et al., 1979).

It is immediately apparent (from Figure 4.6) that the differences in the behavior between the TPE and the MPI spectra, associated with the rising background, are more pronounced the higher the laser intensity used to measure the spectrum. It should be noted that the spectra have been corrected for variations of the laser intensity. Some of the original uncorrected spectra that were combined to obtain the spectra of Figure 4.6 are shown in Figures 4.7 and 4.8. Figure 4.7 demonstrates the coincidence of the MPI and TPE spectra for $\lambda_{\text{exc}} \gtrsim 490$ nm, while Figure 4.8 shows the effect of the laser intensity on the ionization spectrum. The laser pulse energy for the three spectra, at the peak ($\lambda_{\text{exc}} \approx 480$ nm) of the laser-dye gain profile, was ~ 150 μJ , ~ 120 μJ and ~ 70 μJ , respectively. Especially conspicuous is the noise exhibited by the photocurrent signal, measured at high laser intensity, although it is an order of magnitude stronger than the others. The reason that this spectrum is so noisy is that it is produced by a high order multiphotonic process, so that the slight instabilities of the laser intensity are highly amplified and appear as noise. The existence of this high order process is demonstrated by the signal vs. intensity measurements shown in Figure 4.9. The slope (S) has a value $S = 3$ at relatively low intensities, at all wavelengths, but increases with intensity, and although the increase is only slight at $\lambda_{\text{exc}} = 496$ nm (from 3 to 4), it is rather significant at 485 nm and 468 nm where slopes 7 and 9 are reached respectively. The total energy of that many photons, in this wavelength region, exceeds twice the gas phase ionization threshold of benzene ($I_G = 9.24$ eV, while $9 \times 2.65 = 23.85$ eV).

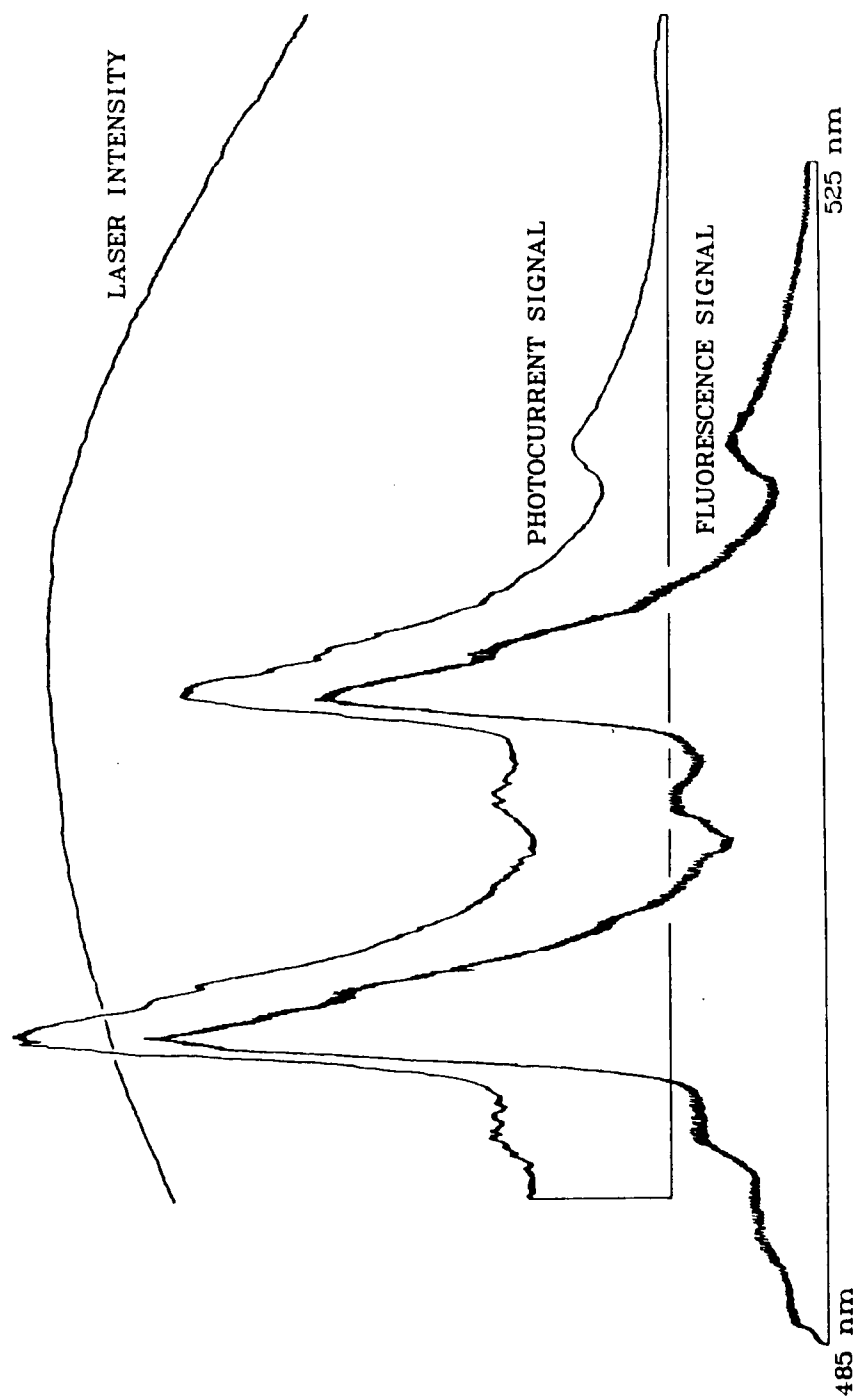


Figure 4.7. The original, uncorrected for laser intensity variations, multiphoton ionization (photocurrent signal) and two-photon excitation (fluorescence signal), spectra of benzene in tetramethylsilane. Above them is the corresponding laser intensity profile. The laser pulse energy on the peak of the laser profile is $\sim 150 \mu\text{J}$.

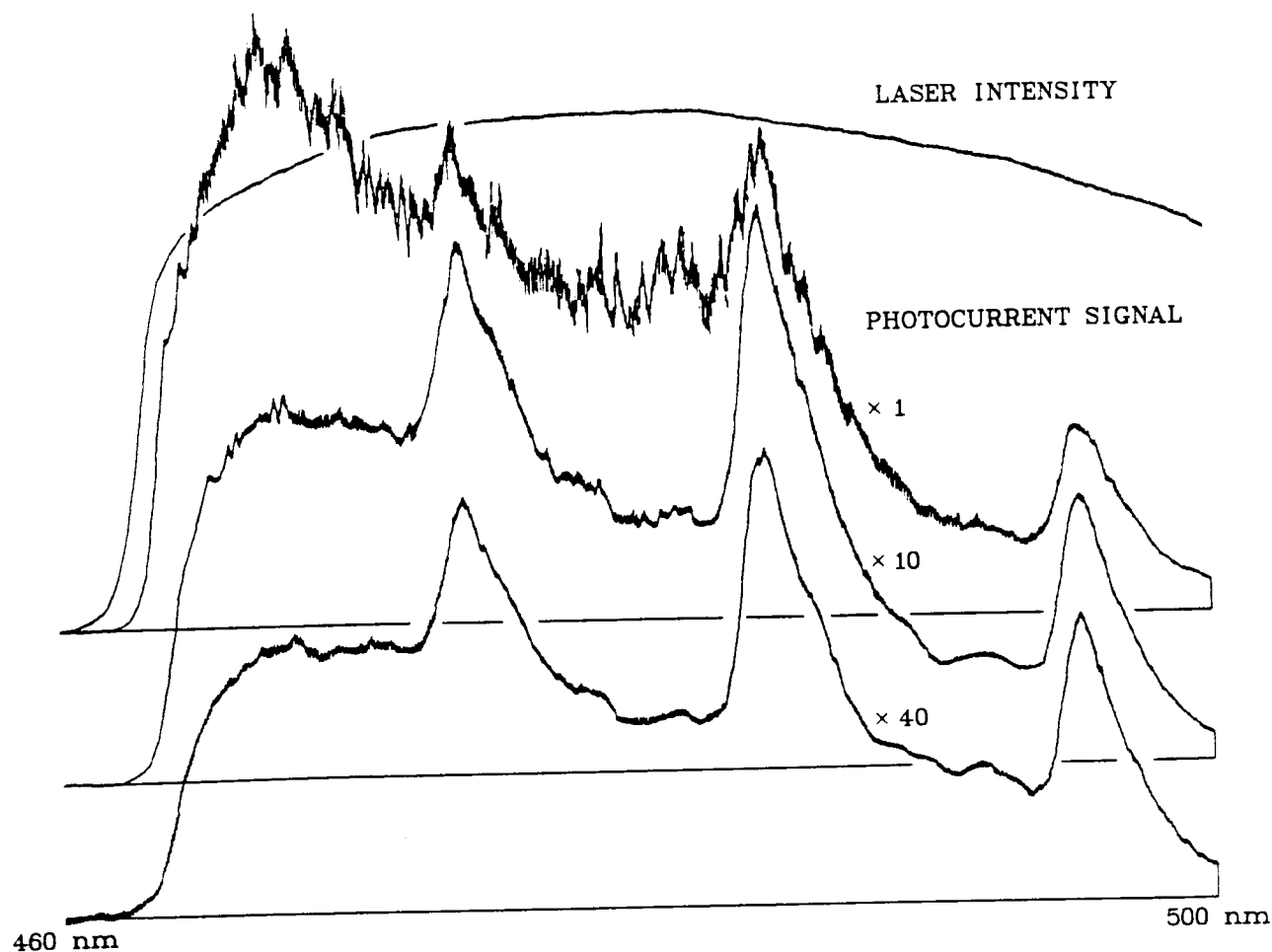


Figure 4.8. The original, uncorrected for laser intensity variations, multiphoton ionization (photocurrent signal) spectra of benzene in tetramethylsilane, measured at successively lower laser intensities. The laser pulse energy on the peak of the intensity profile was $\sim 150 \mu\text{J}$ for the upper, $\sim 120 \mu\text{J}$ for the middle and $\sim 70 \mu\text{J}$ for the lower spectrum. The photocurrent signal intensities of the two lower spectra were reduced, compared to the upper one, by a factor of 10 and 40 correspondingly. Note the high noise in the upper spectrum.

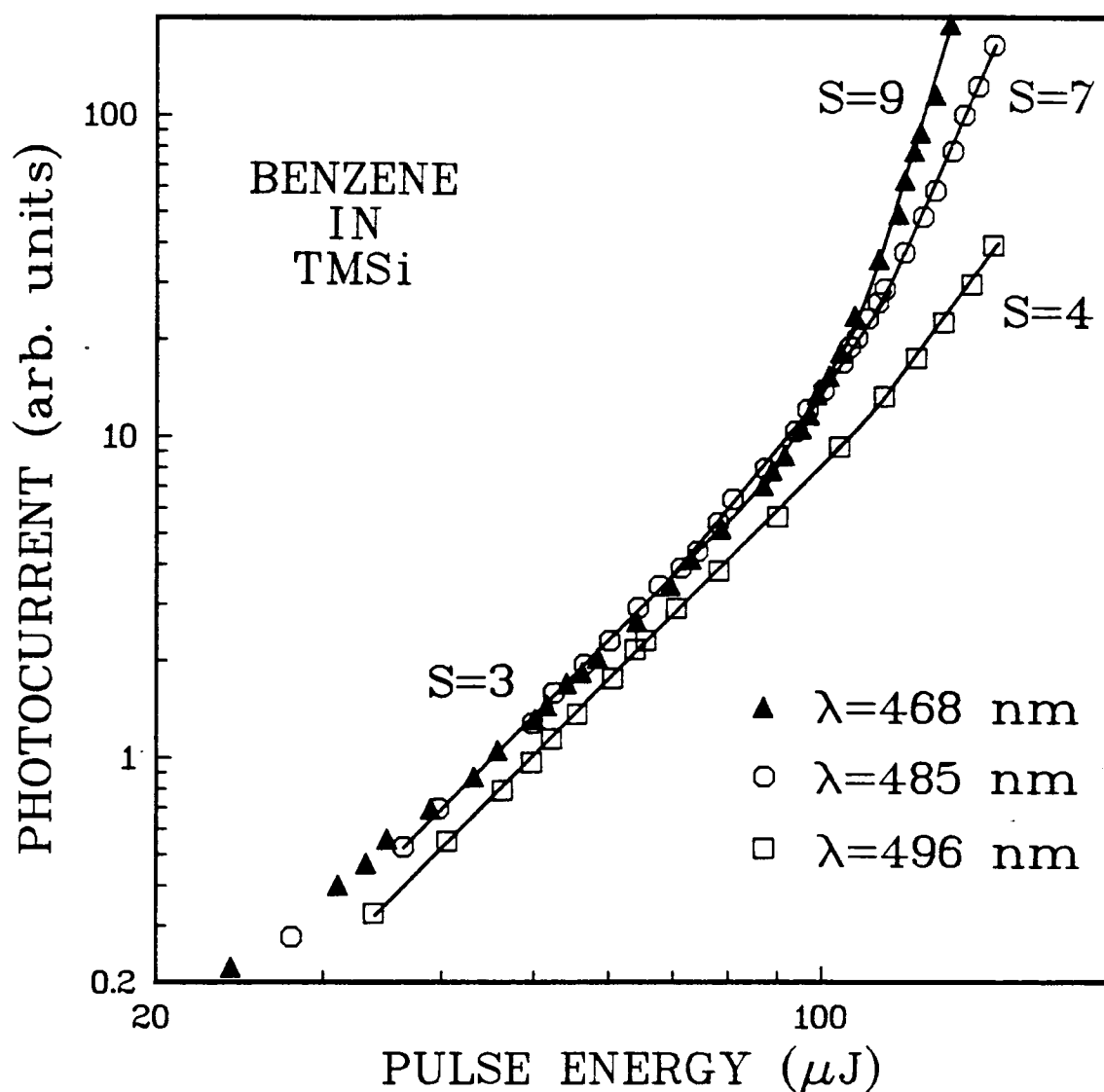


Figure 4.9. Signal vs. laser intensity measurements of the multiphoton ionization of benzene in tetramethylsilane. At low laser intensities the slope is three at all wavelengths. At higher intensities it increases gradually and reaches values of nine (at 468 nm), seven (at 485 nm) and four (at 496 nm).

The increase, therefore, of the background really reflects the onset below ~ 490 nm of a highly intensity dependent ionization channel. This is indicated also by the polarization ratio (see Figure 4.6). At relatively low laser intensities the MPI polarization ratio deviates slightly from the TPE ratio for $\lambda_{\text{exc}} < 490$ nm. At higher intensities, however, the two polarization ratios depart completely from each other and the MPI ratio approaches a value $\Omega = 1$, which means that this process is insensitive to the polarization of the exciting photons.

It appears, therefore, that for relatively high laser intensities and/or wavelengths below ~ 490 nm the ionization signal and spectrum undergo certain changes. Namely, a rising, intensity dependent, background sets in the spectrum, the MPI and TPE spectra deviate from each other, the apparent order of the ionization process increases dramatically and the signal loses its polarization sensitivity. The apparent onset of all these changes coincides with the onset of the well-known channel 3.

These observations lead to the proposal of two different processes for ionization. The first process, which is responsible for the observed structure in the spectrum, is the expected two-photon resonant, three-photon ionization which dominates at relatively low intensities and/or wavelengths exceeding ~ 490 nm. This process has a signal vs. laser intensity dependence of third order ($S = 3$) and preserves the polarization characteristics of the resonant $^1B_{2u}$ state. The other process, which will be called "the channel 3 ionization mechanism," appears at relatively higher intensities and at wavelengths

below ~ 490 nm. This, as the name implies, operates in the channel 3 region and involves transitions within the $^1A_{1g}$ state vibrational manifold. Such transitions, according to Ziegler and Hudson (1982), are two-photon allowed.

According to the second process, a molecule is excited by two-photons to the practically continuum of the high lying vibrational levels of the ground state (which are responsible for channel 3) and then it is subjected to two competing processes: photon absorption due to the intense radiation field within the levels of this dense vibrational ladder, and nonradiative relaxation which transfers vibrational energy to the environment. The molecule, therefore, "oscillates" up and down in energy, absorbing photons and relaxing, until it is either ionized (if it acquires enough energy) or back to the ground state. This process will occur more times the higher the laser field is, so that an intensity dependence of increasing apparent order (or slope) with intensity will be observed.

The "channel 3 ionization mechanism" sets in gradually, as indicated by the maximum slopes of the signal vs. intensity measurements at different wavelengths and the progressive loss of structure of the polarization ratio. It has, therefore, a wavelength dependence similar to that of channel 3 relaxation, which is expected, since it utilizes the same vibrational ladder. Of course the two distinct ionization processes—the "channel 3 ionization" and the two-photon resonant, three-photon ionization—are not mutually exclusive and they do co-exist at intermediate intensities and wavelengths (~ 485 nm).

They do not also exclude a third and mixed process, operating in the transitional wavelength region, whereby two photons excite the molecule to the $^1B_{2u}$ state and channel 3 relaxation brings it to the vibrational ladder from where additional photons, leading to ionization, are absorbed.

4.4. The Signal vs. Intensity Measurements

4.4.1. Results

During the course of the multiphoton ionization studies a series of signal vs. intensity measurements at different wavelengths was undertaken, both in TMSi and n-pentane, in order to obtain information on the ionization mechanism and locate the ionization threshold of benzene. Some of these measurements for benzene in TMSi and n-pentane are shown in Figures 4.10 and 4.11, respectively. The slopes thus obtained are summarized in Table 4.1. One striking observation is that, in any wavelength region, the slope—that is, the apparent order of the ionization process—measured in n-pentane is by one unit higher than that in TMSi, implying that one more photon is required to ionize benzene in n-pentane. This behavior is illustrated in Figure 4.12 where S is plotted as a function of the wavelength. The solid symbols connected with continuous lines represent the slopes obtained at laser intensities low enough so that neither saturation (for $\lambda_{exc} < 420$ nm) nor "channel 3 ionization" (for $420 \text{ nm} \lesssim \lambda_{exc} \lesssim 490$ nm) was observed. The dashed line arrows, originating on the points corresponding to the measurements in TMSi indicate the spread

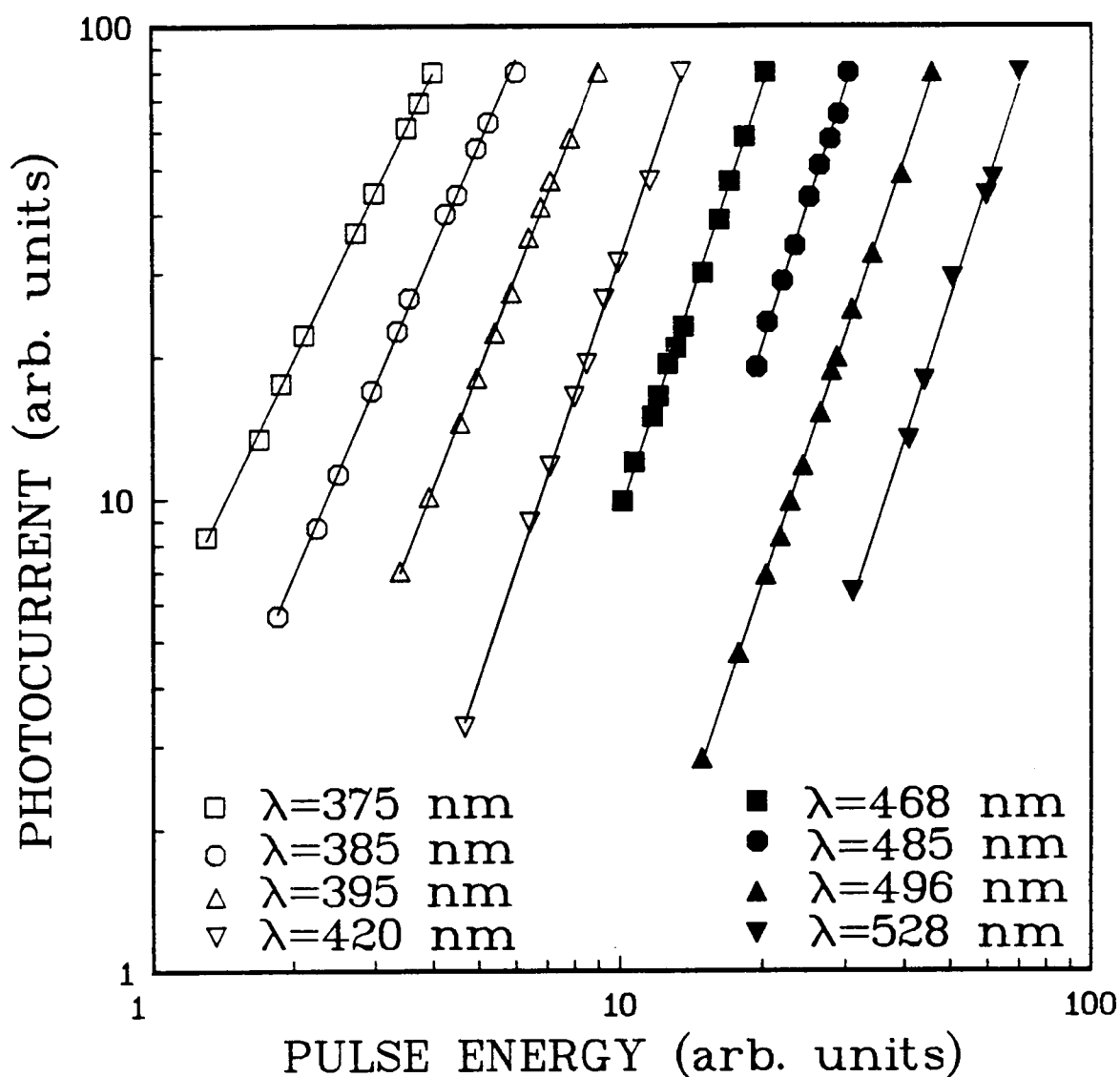


Figure 4.10. Signal vs. laser intensity measurements of the multiphoton ionization of benzene in tetramethylsilane at different wavelengths. The slopes are: S (375 nm) = 2.0, S (385 nm) = 2.3, S (395 nm) = 2.5, S (420, 468, 485, 496, 528 nm) = 3.0. The slope $S = 3$ at 468, 485 and 496 nm represents the low intensity limit.

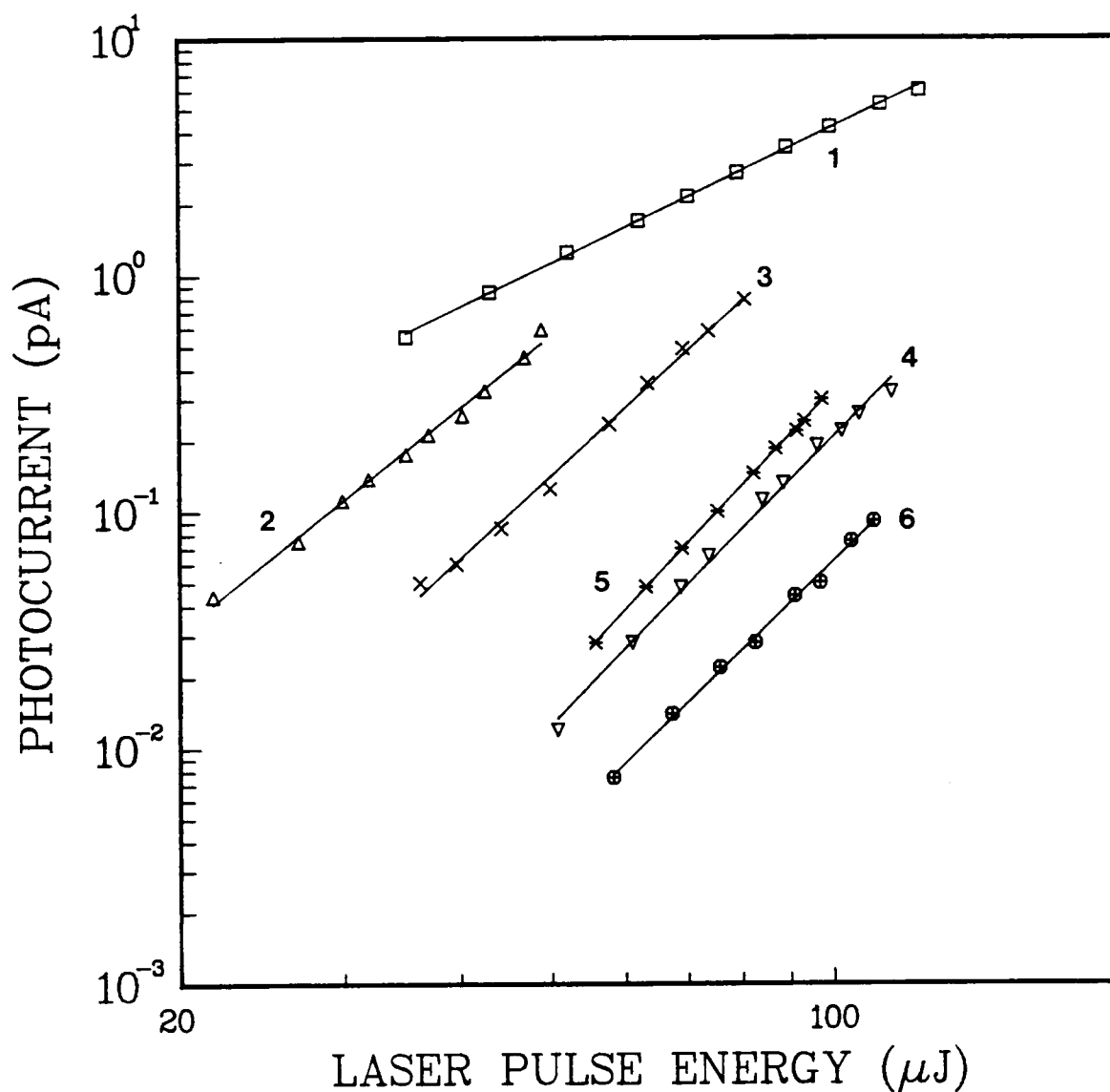


Figure 4.11. Signal vs. laser intensity measurements of the multiphoton ionization of benzene in n-pentane at different wavelengths. The slopes are: 1 ($S = 1.91$, $\lambda_{\text{exc}} = 337$ nm), 2 ($S = 3.13$, $\lambda_{\text{exc}} = 365$ nm), 3 ($S = 3.62$, $\lambda_{\text{exc}} = 386$ nm), 4 ($S = 4.02$, $\lambda_{\text{exc}} = 455$ nm), 5 ($S = 4.22$, $\lambda_{\text{exc}} = 496$ nm), 6 ($S = 4.0$, $\lambda_{\text{exc}} = 508$ nm).

Table 4.1. Slopes of the Signal vs. Intensity Measurements of the Multiphoton Ionization of Benzene in Tetramethylsilane and n-Pentane

Benzene in TMSi		Benzene in n-Pentane	
λ_{exc} (nm)	S	λ_{exc} (nm)	S
		337	1.95
		365	3.12
375	2.02	377	3.14
385	2.29	386	3.6
395	2.53		
420	2.98	421	4.44
		437	4.51
		455	4.02
468	3.0/9.5 ^a	475	4.0/5.8 ^a
485	3.0/7.0 ^a		
496	3.0/4.0 ^a	495	4.0/5.0 ^a
		508	4.0/5.0 ^a
528	3.0	529	4.0

^aMaximum slope obtained at the highest laser intensities reached.

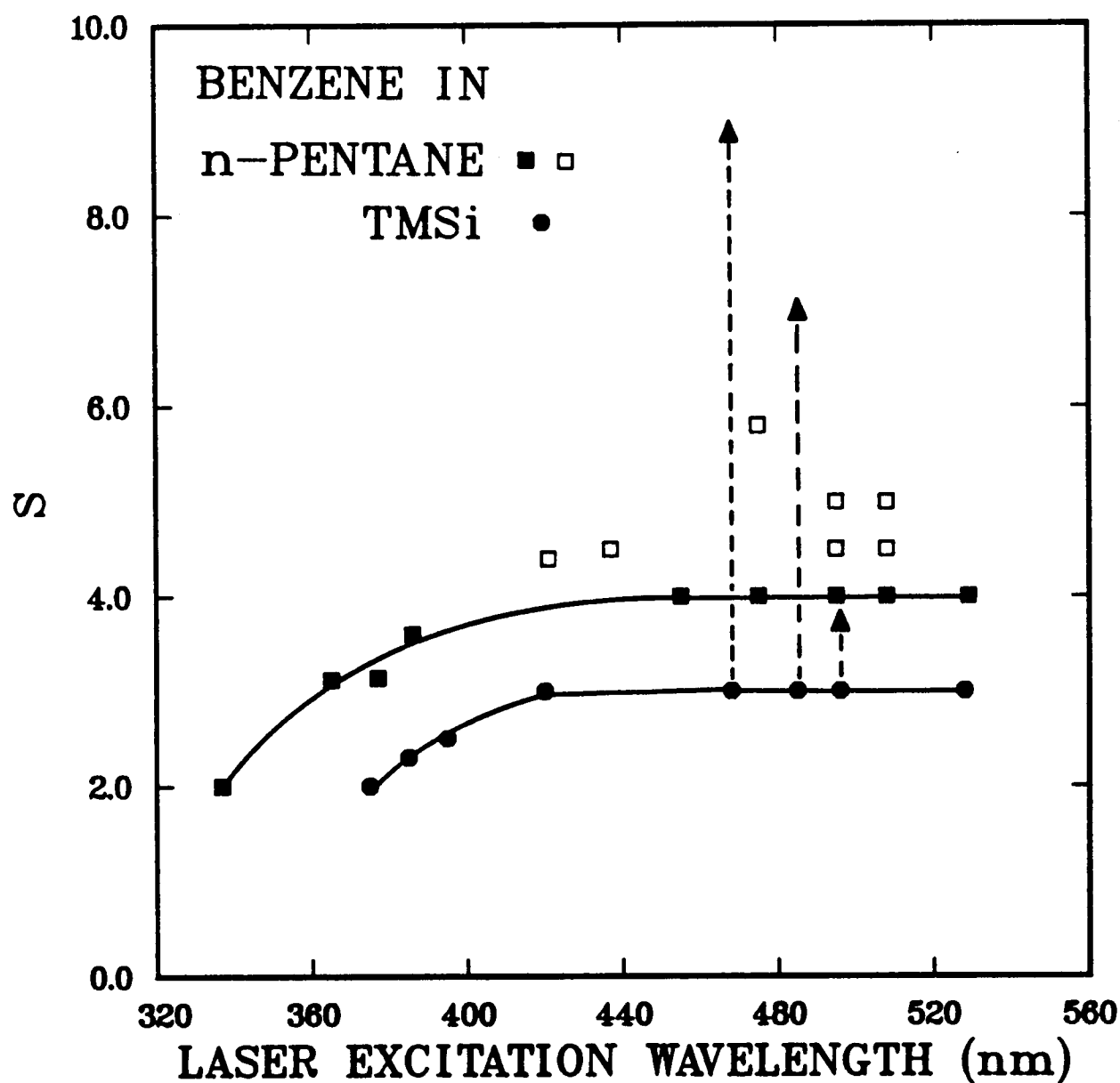


Figure 4.12. The slopes of the signal vs. laser intensity measurements of benzene in tetramethylsilane (TMSi) and n-pentane. The solid symbols connected with lines represent the slopes obtained at low laser intensities. The dashed line vectors indicate the spread of the slopes as the intensity increases in TMSi. The open squares represent slopes obtained in n-pentane at higher laser intensities.

of the slopes as the laser intensity is increased and up to the highest intensities reached. Similarly the open squares indicate slopes measured in n-pentane at higher laser intensities. Below $\lambda_{\text{exc}} \approx 420$ nm the slope gradually decreases and in TMSi it reaches a value of $S = 2$ at $\lambda_{\text{exc}} = 375$ nm, while in n-pentane it becomes $S = 3$ at $\lambda_{\text{exc}} = 365$ nm and $S = 2$ at $\lambda_{\text{exc}} = 337$ nm.

Figure 4.13 illustrates schematically all the different ionization mechanisms, in different wavelength regions, as revealed by the signal vs. intensity measurements in TMSi. The straight upward pointing arrows indicate photon absorption while the downward wavy ones represent nonradiative relaxation; the curved lines indicate the total energy of one, two, three and four photons as a function of wavelength. At $\lambda_{\text{exc}} = 375$ nm, two-photon ionization is observed setting thus an upper limit on the ionization threshold at 6.6 eV ($I_L < 6.6$ eV). At $\lambda_{\text{exc}} = 420$ nm, however, three-photons are required for ionization and therefore $I_L > 5.9$ eV. For the $420 \text{ nm} < \lambda_{\text{exc}} < 490 \text{ nm}$ range the "channel 3 ionization mechanism"—discussed extensively in Section 4.3—is observed, while for wavelengths above ~ 490 nm three-photon dependencies are again measured. The onset of the three-photon ionization signal was located at $\lambda_{\text{exc}} \approx 572$ nm (three-photon energy = 6.47 eV). Using similar arguments, the following limits can be set for the ionization threshold of benzene in n-pentane; the I_L should be less than 7.35 eV (= two-photon energy at 337 nm) and more than 6.8 eV (= two-photon energy at 365 nm).

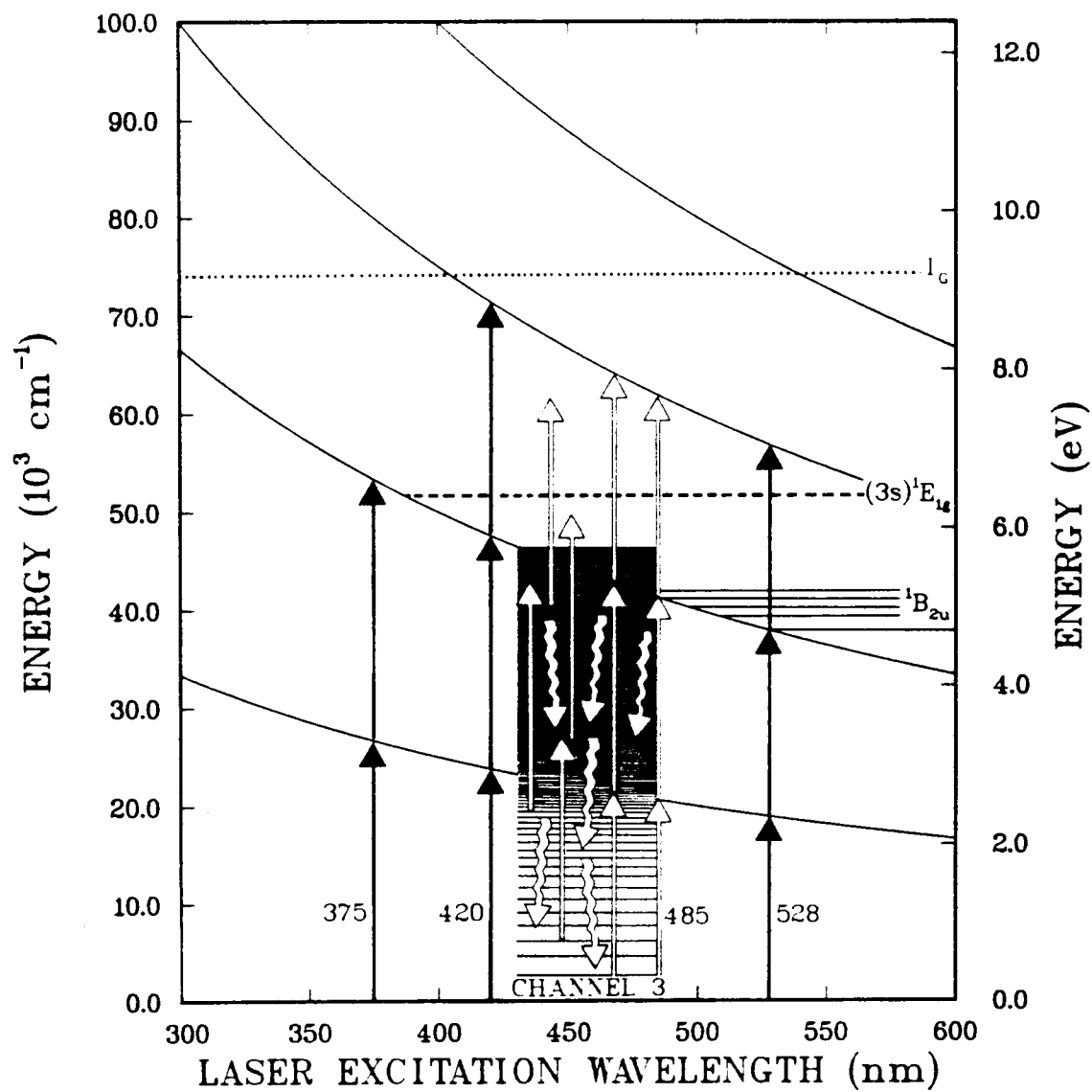


Figure 4.13. Ionization mechanisms of benzene in tetramethylsilane in different wavelength regions. See text.

4.4.2. Discussion

The results of the signal vs. intensity measurements seem to pose two different questions. First, where exactly the ionization threshold of benzene in the two liquids is located, and second, where do the significant differences between the measurements in TMSi and n-pentane arise from.

In the past, the liquid phase ionization thresholds of a number of aromatic molecules had been determined (Christophorou and Siomos, 1984) using a two-photon ionization (TPI) technique. In these measurements, the TPI onset, that is, the minimum energy at which a measurable photocurrent was observed, was identified as the I_L . In the present studies, however, no TPI onset for benzene can be observed. Instead (for benzene in TMSi), there is a smooth transition from a pure two-photon ($\lambda_{exc} = 375$ nm) to a pure three-photon ($\lambda_{exc} = 490$ nm) ionization, with a mixed ionization process in between ($S = 2.3$ at 385 nm and $S = 2.5$ at 395 nm). The ionization threshold, therefore, can be anywhere between 6.6 and 5.9 eV. Acceptance, however, of the definition for the I_L of the TPI technique would place the I_L at $6.0 \pm .1$ eV, that is, the two-photon energy at $\lambda_{exc} = 410$ nm, the longest wavelength at which a two-photon signal is observed, and just above the onset of the pure three-photon ionization signal. This value is also indicated by the appearance of the MPI spectrum for $\lambda_{exc} < 440$ nm. If one ignores the structure due to the 386 nm peak and the $^1B_{1u}$ resonance, and extrapolates the steeply rising background below 390 nm towards longer wavelength (see Figure 4.1, p. 139), the

curve will go asymptotically down to zero at $\lambda_{\text{exc}} \approx 410 \pm 10$ nm yielding thus an ionization threshold energy (for benzene in TMSi) of ~ 6 eV.

Concerning the ionization of benzene in n-pentane, it is a fact that one more photon than in TMSi needs to be absorbed in order to observe a measurable photocurrent in all wavelength regions. This could be due to two different reasons: (a) the ionization threshold of benzene in n-pentane is sufficiently higher than that in TMSi so that one more photon is required; (b) because the ionization signal in n-pentane consists of two ionic components and is very weak (see Section 2.4), higher laser intensities and possibly additional photon absorption are required to produce a measurable signal; at higher intensities, however, the "channel 3 ionization" becomes dominant and produces artificially higher order signal vs. intensity dependencies.

The first possibility is rather unlikely, because it would imply that the I_L in n-pentane is more than 2.5 eV higher than that in TMSi. For example, at $\lambda_{\text{exc}} = 421$ nm the three-photon energy is 8.83 eV and still a fourth photon is required for ionization in n-pentane. Since, however, a two-photon ionization is observed at $\lambda_{\text{exc}} = 337$ nm, the I_L cannot exceed 7.35 eV. On the other hand, it is known (Christophorou and Siomos, 1984) that differences in the I_L of a particular molecule in various solvents, due to different V_0 values, do not generally exceed 1 eV. The second possibility, therefore, appears more likely in view of the different photocurrent signals observed in the two liquids.

4.5. Conclusions

The present work is the first multiphoton ionization and polarization study of benzene in solution and especially the first ionization study of the $^1B_{2u}$ state. It revealed the existence of a resonance at $\lambda_{exc} = 386$ nm (in agreement with the TPE studies), tentatively assigned to the $(3s) ^1E_{1g}$ Rydberg state. It revealed also the operation in a wavelength region grossly corresponding with the channel 3 relaxation of a particular ionization mechanism—presently characteristic of benzene—, which was called the "channel 3 ionization mechanism."

The ionization threshold of benzene in TMSi and n-pentane was estimated to lie between 6.6 and 5.9 eV and 7.35 and 6.8 eV, respectively. For benzene in TMSi, in particular, the TPI threshold most likely lies at 6.0 ± 0.1 eV. It should be noted, however, that no distinct TPI onset was determined, because of the overlap of the two- and the three-photon ionization mechanisms. Attention should also be brought to the fact that the results of the threshold determination by TPI techniques require careful interpretation and analysis before conclusions can be drawn.

The threshold determined by TPI techniques (and any technique for that matter) depends on the sensitivity (minimum observable current) of the particular instrumentation being used. Parameters, therefore, that affect the magnitude of the generated current will also affect the value of the determined threshold. Such parameters are: the laser intensity, the solute concentration, the external applied

electric field and the drift velocity of the charge carriers in the solution. Moreover, it is possible—as the present measurements on benzene have demonstrated—that the n -photon ionization threshold is overlapping with the $(n+1)$ -photon ionization region. It is important therefore that careful signal vs. intensity measurements are conducted in the n -photon threshold region before a threshold is determined. Ultimately the ionization probability as a function of the absorbed energy might be a more suitable quantity to describe the ionization in the liquid phase.

CHAPTER V

SUMMARY AND CONCLUSIONS

The spectroscopy and the photophysics of aromatic molecules in nonpolar solvents have been studied using two experimental techniques: the multiphoton ionization and the two-photon excitation technique.

The multiphoton ionization of benzene in solutions of n-pentane and tetramethylsilane was studied using laser excitation wavelengths ranging from 360 nm up to 570 nm. No direct two- or three-photon ionization thresholds could be observed, because of a smooth transition in the wavelength region between 380 nm and 420 nm, from a two- to a three-photon ionization mechanism (for benzene in tetramethylsilane) or from a three- to a four-photon mechanism (for benzene in n-pentane). Based on the results of the signal vs. laser intensity measurements the ionization threshold of benzene in n-pentane and tetramethylsilane was located between 7.35 and 6.8 eV and 6.6 and 5.9 eV, respectively. Indirectly and with qualifications the ionization thresholds in TMSi was estimated to be 6.0 ± 0.1 eV.

There were important differences in the ionization signals obtained in the n-pentane and the TMSi solutions. The signal in n-pentane consisted of two ionic components—interpreted to be positive and negative benzene ions—and was much weaker than the signal in TMSi, while the latter exhibited a strong electronic component. Moreover, the signal vs. laser intensity measurements in n-pentane revealed

a higher order ionization process than that in TMSi at all wavelengths. On the basis of these measurements it appears that one more photon is required to ionize benzene in n-pentane over the whole wavelength region under investigation.

These differences were attributed to the high mobility of the electrons in TMSi compared to that in n-pentane to the more efficient ion-electron geminate pair recombination in n-pentane and to the capture of electrons by neutral benzene molecules in n-pentane. All these effects render the ionization signal in n-pentane much weaker than that in TMSi and make the use of high laser intensities and the absorption of additional photons necessary for the observation of an adequate signal.

A particular ionization behavior, observed up to now only in benzene, was apparent in a wavelength range corresponding to the well-known channel 3 nonradiative relaxation region. The number of photons absorbed—that is, the apparent order of the process—appeared to be increasing with increasing laser intensity. Thus the measurements of the dependence of the signal on the laser intensity in TMSi have shown that while at low intensities three-photon processes are mainly responsible for the signal, at higher laser intensities, up to ninth order processes dominate the signal. Similarly, for benzene in n-pentane dependencies of fourth order, at low laser intensities, reaching up to sixth order, at higher intensities, were measured. The total energy of that many photons ($6 \text{ to } 9$) in the wavelength range where this effect is apparent ($\sim 430 \text{ nm} < \lambda_{\text{exc}} < 490 \text{ nm}$) well exceeds

the gas phase ionization threshold of benzene. In the same wavelength region the structure in the spectrum corresponding to the $^1B_{2u}$ state was sitting on a steeply rising background which was increasing with increasing laser intensity.

The polarization studies also revealed an intensity and wavelength dependence of the polarization ratio in MPI. At relatively low intensities the MPI and the TPE polarization ratios were very similar. This indicated that the ionization process involved a coherent two-photon resonant excitation to the $^1B_{2u}$ state and then a third photon absorption, leading to ionization. This process was dominant at low intensities and for excitation wavelengths over 490 nm. At high laser intensities, however, and for excitation wavelengths below ~ 490 nm the polarization sensitivity of the photocurrent signal was gradually lost and the polarization ratio was tending towards a value of one.

This behavior of the ionization signal was interpreted as indicating a different ionization process, which was called the "channel 3 ionization mechanism." In the channel 3 region there is a competition between radiative excitation and nonradiative deexcitation, which results in alternating photon absorption and relaxation many times over, before the molecule is eventually ionized or returns back to the ground state.

The two-photon excitation of benzene and toluene in nonpolar solvents, differing in their physicochemical properties, was also studied. The solvents were n-pentane, tetramethylsilane and a number

of perfluorocarbons. The latter have a high electron affinity and are well-known electron scavengers; they differ also from the hydrocarbons in that they have lower indices of refraction and polarizabilities and generally a more "gas like" behavior. The spectra obtained in perfluorocarbon solutions permitted a detailed vibrational analysis of the first excited singlet states of benzene and toluene up to energies that had not been reached in gaseous phase spectra. More specifically, energies 9000 cm^{-1} and 7000 cm^{-1} above the origin of the $^1B_{2u}$ state of benzene and the 1B_2 of toluene were reached, respectively. The high resolution of these spectra permitted the study of effects, such as the bearing of the number of the vibrational quanta on the relative intensity of different peaks, and spectral features, such as the hot bands, which up to now only in the gas phase had been observed and analyzed.

Detailed polarization studies were also performed over the $^1B_{2u}$ state, which yielded a polarization ratio that was very close to the theoretically calculated one, after correction for the congestion background of the spectra. Polarization ratios of 1.5, ~ 0.2 and ~ 0.7 were the measured for the 18_0^1 , 14_0^1 and 0-0 bands, respectively.

A structure was observed in both the benzene and toluene spectra at energies lying in the vicinity of the third excited singlet state ($^1E_{1u}$ or 1E_1). The transition corresponding to this structure was apparently two-photon allowed and the state reached exhibited a strong "extravalence" character as indicated by the unusual, for a valence state, spectral shifts and the variations of its relative intensity in

different solvents. The polarization ratio of this peak is $\Omega = 3/2$, which points towards a $^1E_{2g}$ or $^1E_{1g}$ assignment. On the basis of all available evidence, and in the absence of any alternatives, this peak of the benzene spectrum was assigned to the $(3s) ^1E_{1g}$ Rydberg state.

The TPE of fluoranthene in n-pentane was also studied over the 420 nm-860 nm laser excitation wavelength range. The 0-0 bands of the five lowest singlet excited states of fluoranthene were identified in the above region.

Extensive signal vs. laser intensity measurements were performed for all the TPE studies at different excitation wavelengths. Generally a quadratic dependence of the signal on the laser intensity was observed. At relatively high laser intensities a very strong saturation was observed in the measurements of benzene in perfluoro-n-hexane, but not in n-pentane. This difference was interpreted in terms of a process involving ionization and electron capturing in perfluoro-n-hexane, while ionization and geminate recombination occurs in n-pentane.

Finally, the following suggestions can be made regarding experiments that might provide additional information on the processes studied in this work:

a. TPE studies of benzene in mixtures of TMSi and a perfluoro-carbon having different relative concentrations could further clarify the nature of the 380 nm peak.

b. MPI studies of benzene (toluene) in TMSi over the $^1B_{2u}$ (1B_2) state with subnanosecond laser pulses would provide information on the ionization mechanism, the nonradiative relaxation processes, and channel 3.

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APPENDIX

APPENDIX

THE PHOTOCURRENT BETWEEN TWO PARALLEL PLATE ELECTRODES

Let $n_+(x,y,z,t)$, $n_-(x,y,z,t)$ be the positive and negative charge carrier concentrations (in cm^{-3}) where x is the direction normal to the plane of the electrodes, y , z the lateral coordinates and t the time. The following coupled differential equations describe the movement and the population variations of the two species.

$$\begin{aligned}\vec{\nabla} \cdot \vec{J}_+ + \frac{\partial n_+}{\partial t} &= -K \cdot n_+ \cdot n_- \\ \vec{\nabla} \cdot \vec{J}_- + \frac{\partial n_-}{\partial t} &= -K \cdot n_+ \cdot n_-\end{aligned}\tag{A.1}$$

where $\vec{J}_+(x,y,z,t)$, $\vec{J}_-(x,y,z,t)$ = cation, anion fluxes (in $\text{cm}^{-2} \cdot \text{s}^{-1}$) and K = recombination rate constant (in $\text{cm}^{-3} \cdot \text{s}^{-1}$). The ion fluxes are given by:

$$\begin{aligned}\vec{J}_+ &= -D_+ \vec{\nabla} n_+ + \mu_+ n_+ \vec{E} \\ \vec{J}_- &= -D_- \vec{\nabla} n_- - \mu_- n_- \vec{E}\end{aligned}\tag{A.2}$$

where D_+ , D_- = diffusion coefficient for cations, anions;

μ_+ , μ_- = mobility of cations, anions (in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$); and

$\vec{E}(x,y,z,t)$ = electric field (V/cm).

Substituting A.2 into A.1, we get

$$\begin{aligned}\frac{\partial n_+}{\partial t} &= D_+ \nabla^2 n_+ - \mu_+ \vec{E} \cdot \vec{\nabla} n_+ - \mu_+ n_+ \vec{\nabla} \cdot \vec{E} - K \cdot n_+ \cdot n_- \\ \frac{\partial n_-}{\partial t} &= D_- \nabla^2 n_- + \mu_- \vec{E} \cdot \vec{\nabla} n_- + \mu_- n_- \vec{\nabla} \cdot \vec{E} - K \cdot n_+ \cdot n_-\end{aligned}\quad (\text{A.3})$$

where

$$\vec{\nabla} \cdot \vec{E} = \frac{e}{\epsilon \epsilon_0} (n_+ - n_-)$$

e = electron charge and ϵ , ϵ_0 are the relative permittivity and the permittivity of free space.

Then the current along the x direction due to the external electric field will be:

$$i(x,t) = e \int_t \int_z (n_+ \mu_+ + n_- \mu_-) E_x dydz \quad (\text{A.4})$$

and the average current along x will be:

$$i(t) = \frac{e}{d} \int_y \int_z \int_0^d (n_+ \mu_+ + n_- \mu_-) E_x dydzdx \quad (\text{A.5})$$

where d is the electrode separation and E_x the electric field along x .

Generally, Eqs. A.3 need to be solved to obtain n_+ and n_- and substitute into A.5. Assuming however that: (a) no recombination occurs during the drift time ($K \cdot n_+ \cdot n_- = 0$), (b) the number of charges created is small enough so that no space charge effect is created ($\vec{\nabla} \cdot \vec{E} = 0$) and $E_x = \text{const.}$, Eq. A.5 can be integrated and:

$$i(t) = \frac{e}{d} (N_+ W_+ + N_- W_-) \quad (\text{A.6})$$

where N_+ , N_- = total number of cations, anions created and W_+ , W_- =
 $\mu_+ \cdot E$, $\mu_- \cdot E$ = drift velocity of cations, anions.

VITA

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