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# STUDIES OF PHOTOIONIZATION IN LIQUIDS USING A LASER TWO-PHOTON IONIZATION CONDUCTIVITY TECHNIQUE*

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## Introduction

One-photon ionization studies of solute molecules in a liquid medium are limited by the absorption of the host medium. We developed a *laser two-photon ionization (TPI) technique* using a frequency tunable dye laser [1], whereby the photoionization threshold $I_L^1$ of a solute molecule was determined from the induced conductivity in the liquid medium under study due to electron-ion pair formation via two-photon ionization of the solute. The two-photon induced electron-ion current is measured as a function of the laser wavelength, $\lambda_{laser}$. In this paper, results are reported and discussed on the photoionization of N,N,N´,N´-tetramethyl-p-phenylenediamine (TMPD), pyrene and fluoranthene in liquid n-pentane (n-Pt).

## Experimental Apparatus

The experimental apparatus employed in the present study is shown schematically in Fig. 1. The beam from a frequency tunable nitrogen-laser-pumped dye laser is focused on the photoconductivity cell inducing two-photon transitions which result in ionization of the solute. The TPI signal from a parallel-plate charge-sensitive detector (maintained at a potential difference of 3 kV corresponding to an electric field of 15 kV cm$^{-1}$) after linear amplification is averaged using a box car integrator. The dye laser beam upon

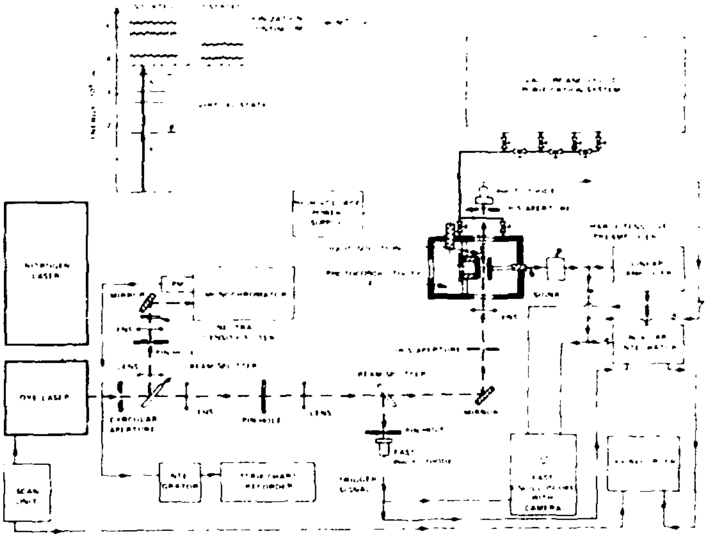

Fig. 1. [illegible] and principle of the laser two-photon ionization [illegible]

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exiting the cell is monitored by a photodiode of well-known spectral responsivity and is sampled by a second box car integrator. The output signals of both integrators after digitalization are fed into a PDP-10 computer for analysis. The TPI signal after intensity correction (division by the square of the light intensity after correction for the spectral responsivity of the photodiode [see Ref. 1 for discussion]) are plotted as a function of $\lambda_{laser}$. Due to the low $I_L^1$ value of TMPD, it was possible to measure the one-photon ionization (OPI) spectrum for this molecule in n-Pt near the ionization threshold. For this the apparatus was slightly modified to accommodate a frequency-doubling unit. The OPI current for TMPD in n-Pt near the threshold was measured as a function of the second harmonic of the dye laser generated in an angle-tuned KDP crystal.

## TPI Spectra

The TPI spectra of TMPD, pyrene and fluoranthene in n-Pt show two distinct features. (1) The photocurrent intensity declines sharply initially and then monotonically to a "zero level" as $\lambda_{laser}$ increases and (2) show distinct structure. These features can be seen from the data in Fig. 2 where the TPI spectrum of $\sim 5 \cdot 10^{-6}$ mol dm$^{-3}$ solutions of TMPD in n-Pt in the spectral range from 360 to ∿650 nm (corresponding to two-photon transitions from 180 to ∿325 nm) is shown. The TPI spectrum comprises 15 individual corrected spectra, combined by normalization in the respective regions of overlap. The TPI current for TMPD shows a monotonic slow increase with decreasing $\lambda_{laser}$ until, at $\lambda_{laser} \approx$ 425 nm, it rises very steeply. Such sharp rise is expected when one-photon resonant two-photon ionization is possible [1]. On the long wavelength side, the photocurrent approaches a "zero level" at $\lambda_{laser}$ = 639.1 ± 4.1 nm (see Fig. 2, curve 2). This corresponds to a two-photon energy

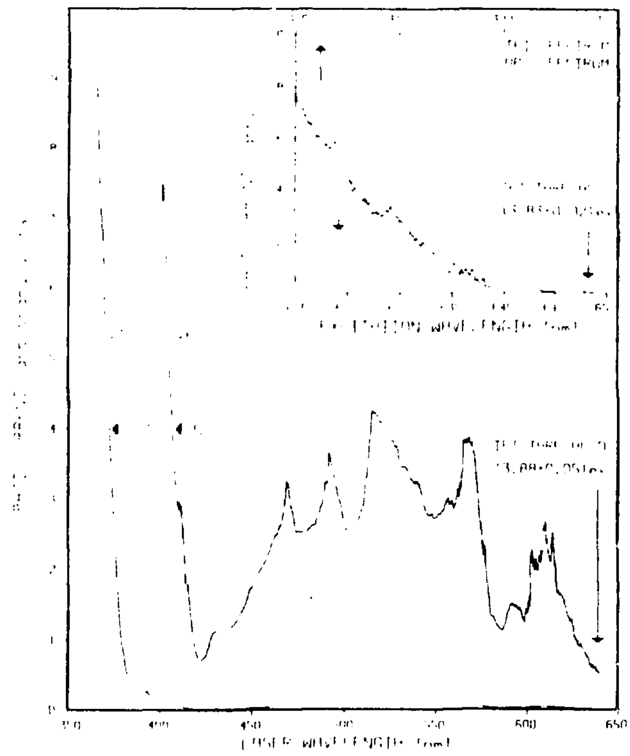

Fig. 2. Two-photon ionization (TPI) current as a function of the laser wavelength (curve 1). The section of this spectrum above 400 nm (curve 2) is magnified by a factor of 62. The arrow indicates the position of the photoionization threshold. The literature value of 4.89 eV [7] would have corresponded to $\lambda_{laser}$ = 507 nm. Insert: The one-photon ionization (OPI) current (dashed line) as a function of the laser wavelength (upper scale). The arrow indicates the OPI threshold. For comparison the TPI current (solid line) as a function of the laser wavelength (lower scale) is also presented.

of 3.88 ± 0.05 eV which we associate with the $I_L^1$ of TMPD in liquid n-Pt.

To ensure that the 3.88 eV value for the $I_L^1$ of TMPD in n-Pt, determined from the TPI spectrum, is not influenced by any higher-order multiphoton process we measured (as described in Section 2) the OPI spectrum of TMPD from 310 to 325 nm. This spectrum is shown by the dashed line in the insert of Fig. 2 where, for comparison, the TPI spectrum (solid line) is also presented. The OPI current decreases smoothly with increasing $\lambda_{laser}$, and it asymptotically reaches a "zero level" at 324 ± 3 nm. This "onset" corresponds to an $I_L^1$ value of 3.83 ± 0.02 eV, in agreement with the TPI $I_L^1$ value of 3.88 ± 0.05 eV.

Similar spectra were obtained for pyrene and fluoranthene. However, for fluoranthene the TPI spectrum declines sharply with increasing energy at energies corresponding to a two-photon transition, one-photon resonant with the first excited singlet state, and this is attributed to the molecular dissociation via this state [2]. From the TPI spectra of pyrene and fluoranthene we determined the $I_L^1$ values for those molecules listed in Table 1.

Table 1. Values of the photoionization threshold (in eV) of TMPD, pyrene and fluoranthene in n-Pt.

| Molecule | $I_L^1$ | $I_G^1$ a) | $\Delta I = I_G^1 - I_L^1$ |
|---|---|---|---|
| TMPD | 3.88 ± 0.05<br>4.89 b) | 6.75 | 2.87 |
| Pyrene | 4.80 ± 0.02 | 7.41 | 2.61 |
| Fluoranthene | 4.50 ± 0.05 | 7.72 | 3.22 |

a) References [4-6]

b) Reference [7]

The TPI spectra for all the molecules show distinct structure (see Fig. 2) due to autoionization. For molecules such as TMPD and pyrene with inversion symmetry, the observed structure is ascribed predominately to two-photon excitation of one-photon forbidden transitions. For molecules such as fluoranthene which do not possess center of symmetry, all the excited states are both one- and two-photon allowed [2].

## The Photoionization Threshold

Attention should be drawn to the much lower values of $I_L^1$ obtained by us compared with those obtained by Holroyd and Russell [7] (see Table 1). As in any measurement of a threshold quantity, the value determined is a function of the sensitivity of the method employed. We believe that our ability to detect very small signals (see Ref. 1) enables us to locate more accurately $I_L^1$. This advantage of our method removes the need of fitting assumed "threshold-law" functions to the data "close" to the threshold to infer $I_L^1$, as has been practiced by others [7-10]. Concerning the effect of the medium on the photoionization threshold value, attention is drawn to the following recent findings. (1) The $I_L^1$ of TMPD, pyrene and fluoranthene in n-Pt as measured with the present technique is, respectively, 2.87, 2.61, and 3.22 eV lower than the corresponding photoionization threshold in the gas phase (see Table 1). These differences are much larger than those inferred from other data on a number of molecules in nonpolar liquids (e.g., see Refs. 3, 7, 8). (2) Recent studies [11,12] using strongly electron attaching molecules at high concentrations to probe the photoionization process for solute molecules in dielectric liquids have shown that the value of $I_L^1$ depends on the time evolution of the photoionization and electron attachment processes. It was inferred from those studies that the photoejected electron is captured by the electron attaching additive at times of $\sim 10^{-14}$ s. (3) Dynamical studies of electron solvation, following photoionization in liquid water using laser picosecond techniques [13] indicated that the *visible* absorption spectrum of solvated electrons appears at times $<3 \times 10^{-13}$ s.

The aforementioned recent findings seem to suggest that the photoionization process for a solute molecule in a liquid medium is completed at times $<10^{-13}$ s *independently* of the nature of the medium. Studies of the photoionization threshold of molecules in polar liquids using the TPI technique are in progress.

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