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LASER TWO-PHOTON IONIZATION AND AUTOIONIZATION SPECTROSCOPY OF MOLECULES
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ABSTRACT

The observation of autoionizing states of molecules in the *liquid phase* together with one- and two-photon ionization threshold measurements obtained using a laser conductivity technique are reported. Coherent versus resonant (stepwise) two-photon excitation in the photoionization process in solutions is discussed.

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LASER TWO-PHOTON IONIZATION AND AUTOIONIZATION SPECTROSCOPY OF MOLECULES
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Laser-induced multiphoton ionization of molecules in the gaseous phase has been the subject of many experimental and theoretical investigations recently. However, little attention has been given to similar processes in the liquid phase. In this paper we report and discuss results obtained with a conductivity technique [1,2] on (1) the photoionization of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in liquid hydrocarbons, (2) autoionizing states of fluoranthene in liquid n-pentane, and (3) the effect of coherent versus resonant (stepwise) two-photon excitation in the photoionization process in solutions.

In the laser conductivity technique the photocurrent, I_{pc} , is measured as a function of the laser excitation wavelength, λ_{Laser} , or photon energy, $h\nu_{exc}$, from the ionization threshold, I_L , to energies $h\nu_{exc} \lesssim E_1$, where E_1 is the energy of the first-excited singlet state of the liquid medium. Figure 1 shows the two-photon ionization (TPI) spectrum of TMPD in neohexane. The one-photon ionization (OPI) spectrum of TMPD in neohexane has also been measured using the second harmonic of a frequency-doubled dye laser [3]; the latter spectrum is also shown in Fig. 1 (curve 5). The photocurrent in Fig. 1 declines sharply initially and then slowly to a "zero level" as λ_{Laser} increases. From the TPI data in Fig. 1, the I_L of TMPD in liquid neohexane at $T = 295$ K was estimated to be 3.65 ± 0.20 eV and found to be independent of the solute concentration. The OPI data gave a value for I_L equal to 3.80 ± 0.20 eV, in agreement with the TPI result.

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Figure 2 shows the TPI spectrum of fluoranthene in n-pentane. It shows distinct structure attributed to autoionization of discrete states embedded in the ionization continuum and reached by two-photon absorption. The fluoranthene molecule has a C_{2v} symmetry and does not possess center of inversion; all excited states might therefore be both one- and two-photon allowed, although the spectral distribution for one- and two-photon excitation might be different due to vibronic coupling. It can be seen from the data in Fig. 2 that while the peaks in the TPI spectrum for $h\nu_{\text{exc}} \lesssim 42,000 \text{ cm}^{-1}$ correspond to peaks in the one-photon absorption spectrum, above $42,000 \text{ cm}^{-1}$ the two spectra deviate, indicating the biphotonic character of the transitions in this energy range. Symmetry assignment for the states involved are presently not possible because of the lack of two-photon polarization spectra such as, for example, measured for similar compounds by Dick and Hohlneicher [5]. The high sensitivity, $I_{\text{pc}} \lesssim 10^{-14} \text{ A}$, of our laser conductivity technique provides a unique method to study two-photon excitation in liquids.

The exact mechanism of multiphoton ionization both in the gaseous and the liquid phases [2,4] is a point of much discussion. An aromatic molecule dissolved in a liquid can reach the "ionization continuum" by absorbing two-photons [2]. The I_{pc} increases greatly (see Fig. 1 for $\lambda_{\text{Laser}} \lesssim 400 \text{ nm}$) if there is a molecular state resonant with the one-photon energy. In this case one speaks of one-photon resonant two-photon ionization process or a stepwise excitation process. In the case of a virtual intermediate state--coherent two-photon excitation process--the observed TPI spectra resemble the final excited states in the "ionization continuum" reached by two-photon absorption. The differentiation

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between the two ionization mechanisms is possible by measuring the dependence of I_{pc} on the laser power, I_{Laser} , at different excitation wavelengths, provided that great care is exercised concerning the spatial characteristics of the laser-beam profile (see Fig. 3) as well as space-charge effects. If I_{pc} depends on I_L as $I_{pc} \propto I_{Laser}^\alpha$, then for a coherent two-photon excitation, α should be 2, while in the case of the two-photon stepwise excitation $1 \leq \alpha \leq 2$ [4]. In an effort to separate the two ionization mechanisms we studied systematically the power dependence of the I_{pc} on I_{Laser} for TMPD at two concentrations in liquid neohexane. The results obtained are shown in Fig. 3. They show that the quadratic dependence of I_{pc} on I_{Laser} is exhibited only for $\lambda_{Laser} \gtrsim 450$ nm. For $\lambda_{Laser} \lesssim 450$ nm, $1 \leq \alpha \leq 2$. This is due to the fact that the tail of the first absorption band of TMPD extends to ~ 450 nm (unpublished results). In conclusion the laser two-photon conductivity technique allows accurate determination of the photoionization threshold of a molecule in the liquid phase and provides most valuable new spectroscopical data on autoionizing transitions of molecules in the liquid phase.

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FIGURE CAPTIONS

Fig. 1. Photoionization currents as a function of the one- and two-photon laser wavelengths for TMPD in neohehexane. The TMPD concentrations were $c = 5 \times 10^{-6} \text{ mol dm}^{-3}$ curves 1, 2, and 3, and $c = 10^{-3} \text{ mol dm}^{-3}$ curve 4. Curve 5 represents the one-photon ionization spectrum for $5 \times 10^{-6} \text{ mol dm}^{-3}$ of TMPD in neohehexane. The spectra are not normalized to each other.

Fig. 2. Two-photon ionization spectrum of $5 \times 10^{-6} \text{ mol dm}^{-3}$ fluoranthene solution in neohehexane (dashed line). The solid line represents the one-photon absorption spectrum.

Fig. 3. Variation of α with λ_{Laser} for TMPD in neohehexane. $\circ$: $5 \times 10^{-6} \text{ mol dm}^{-3}$; Δ : $10^{-3} \text{ mol dm}^{-3}$. The insets represent the laser-beam spatial profiles; the solid curves through the experimental data are the theoretical Gaussian distributions.

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