

MULTIPHOTON IONIZATION AND EXCITATION SPECTROSCOPY OF MOLECULES IN LIQUIDS*

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ABSTRACT

The two-photon ionization and excitation spectra of fluoranthene in liquid n-pentane have been measured and together with laser power versus signal intensity measurements have been utilized to elucidate the multiphoton ionization mechanism for this and other molecules in liquids.

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The exact mechanism of multiphoton ionization of molecules in the liquid phase is a subject of much current discussion.¹⁻⁴ Earlier, we have shown^{1,4} that an aromatic molecule dissolved in a dielectric liquid can reach the "ionization continuum" by absorbing two photons either via a virtual intermediate state--coherent two-photon excitation process--or via a resonant state--stepwise excitation process. We have argued^{1,4} that the structure we observed in the two-photon ionization (TPI) spectra via a virtual intermediate state can be attributed to the final states in the "ionization continuum" reached by two-photon absorption. In this paper we report the first *direct* experimental proof for the above argument. We have studied the TPI and the two-photon excitation (TPE) spectra of fluoranthene (F) in liquid n-pentane (n-Pt) at room temperature using linearly polarized light, a TPI conductivity technique,^{1,4} and a TPE (fluorescence) apparatus.⁵ These spectra are shown in Fig. 1 as a function of the laser excitation wavelength (λ_{exc}) from 450 to 560 nm, corresponding to two-photon excitation energies from $\approx 44,400$ to $35,700 \text{ cm}^{-1}$ (≈ 5.5 - 4.45 eV).

The following observations can be made from the data in Fig. 1: (i) the TPI spectrum shows an onset, indicated by the arrow in Fig. 1 at $\lambda_{\text{exc}} \approx 551 \text{ nm}$, corresponding to a two-photon energy of 4.50 eV which we assigned to the ionization threshold of F in n-Pt; (ii) the TPI spectrum is structured; and (iii) the peaks in the TPI spectrum in the 480 to 551 nm spectral region, where a second order power dependence was measured, correspond to peaks in the

K. Siomos, MULTIPHOTON SPECTROSCOPY

TPE spectrum. Below $\lambda_{\text{exc}} = 480$ nm (in this region the power dependence measurements showed less than a second order dependence) the TPE spectrum cannot reveal (as does the TPI spectrum) as clear a structure as in the spectral region above $\lambda_{\text{exc}} = 480$ nm due to the two-photon excitation, because of the strong quenching of the one-photon fluorescence from the first singlet state of F. From the above observations, it can be concluded that (i) the peaks in the TPI spectrum below $\lambda_{\text{exc}} = 550$ nm can be attributed to autoionization of discrete states embedded in the "ionization continuum" and reached by two-photon absorption and (ii) two-photon ionization is in competition with internal conversion to the fluorescing first singlet state of F. Symmetry assignments for the states involved are presently not possible due to the incompleteness of our polarization studies. Measurements of the TPE spectrum of F in n-Pt using circularly polarized light are in progress.

The importance of the present studies together with power dependence measurements to elucidate the multiphoton ionization mechanism of molecules in liquids will be discussed.

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Figure Caption

Fig. 1. The two-photon ionization (1) and the two-photon excitation (2) spectra of fluoranthene in n-pentane. The arrow around 551 nm indicates the ionization onset. The polarization of the laser beam is linear and vertical to the direction of observation.

