

Photoionization dynamics of a phenylenediamine derivative in condensed phase induced by multiphoton ionization

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Photoionization is one of the most important primary processes of photochemical reactions. Polarization of surrounding media by solvation plays an important role in photoionization process in solvent where the ionization energy of the solute is lower than that in the gas phase. In order to elucidate their effect on photoionization process, we have investigated multiphoton ionization dynamics of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD, Figure 1) in polar and non-polar solvents by means of femtosecond transient absorption spectroscopy under the double pulse excitation.

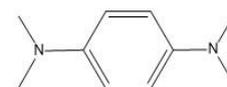


Figure 1. Molecular structure of TMPD.

A femtosecond dual NOPA/OPA laser system was used for transient absorption spectroscopy. The output of a femtosecond Ti:sapphire laser was amplified by using a regenerative amplifier. The amplified pulse was divided into two pulses. One was guided into an OPA system and converted to 1180-nm pulse, which was focused into 2-mm CaF₂ plate to generate a white-light continuum covering the wavelength region from 400 to 1000 nm. This white light was used as a probe pulse. The other pulse was guided into a NOPA system which was tuned at 680 nm and was frequency-doubled with a 100- μ m BBO crystal. The SHG (340 nm) was used as the first pump pulse (Pump 1) and remaining 680-nm pulse was used as a second pump pulse (Pump 2). Pump 1 at 340 nm was resonant with the S₁-S₀ transition of TMPD and Pump 2 at 680 nm was resonant with the S_n-S₁ transition. Pump1 was introduced into the sample 10 ps before Pump 2 and the delay time (Δt) is defined as the time interval between Pump 2 and probe pulse.

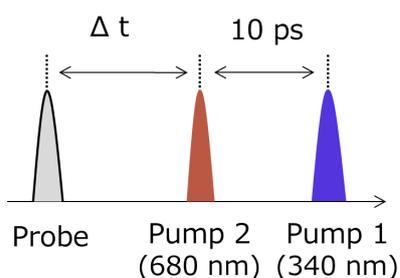


Figure 2. Pump-pump-probe pulse sequence used in double-pulse excitation experiment.

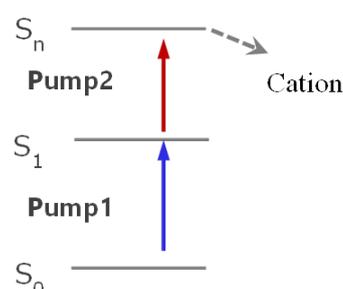


Figure 3. Schematic diagram of photoionization via higher excited state

Transient absorption spectra of TMPD in ethanol solution under the double-pulse excitation condition are shown in Figure 3. Negative signal at 635-800 nm appearing immediately after the irradiation of the pump 2 (at 0 ps in the figure) is attributed to the bleaching of the S_1 state. And positive signal at 800-1000 nm is attributed to S_1 vibrationally excited state (S_1 hot band.) On the other hand, positive signal around 500-600 nm exhibits unique behavior. The fast component < 200 fs region is attributed to the absorption of the S_n state. The decay time of this signal in ethanol is estimated to be 70 fs, which is faster than that in n-hexane. This indicates that additional reaction occurs from S_n state in ethanol. After this fast signal has almost decayed, the new signal appears gradually in the same wavelength region, which has the characteristic peaks at 560 and 610 nm. This slow component is attributed to TMPD radical cation and exhibits a gradual rise in the time scale of 5 ps, which is slower than the lifetime of S_n state. This indicates that photoionization does not take place directly from the higher excited state but via specific intermediate.

At the conference site, we will discuss effects of solvent polarity and excitation wavelengths on the ionization process.

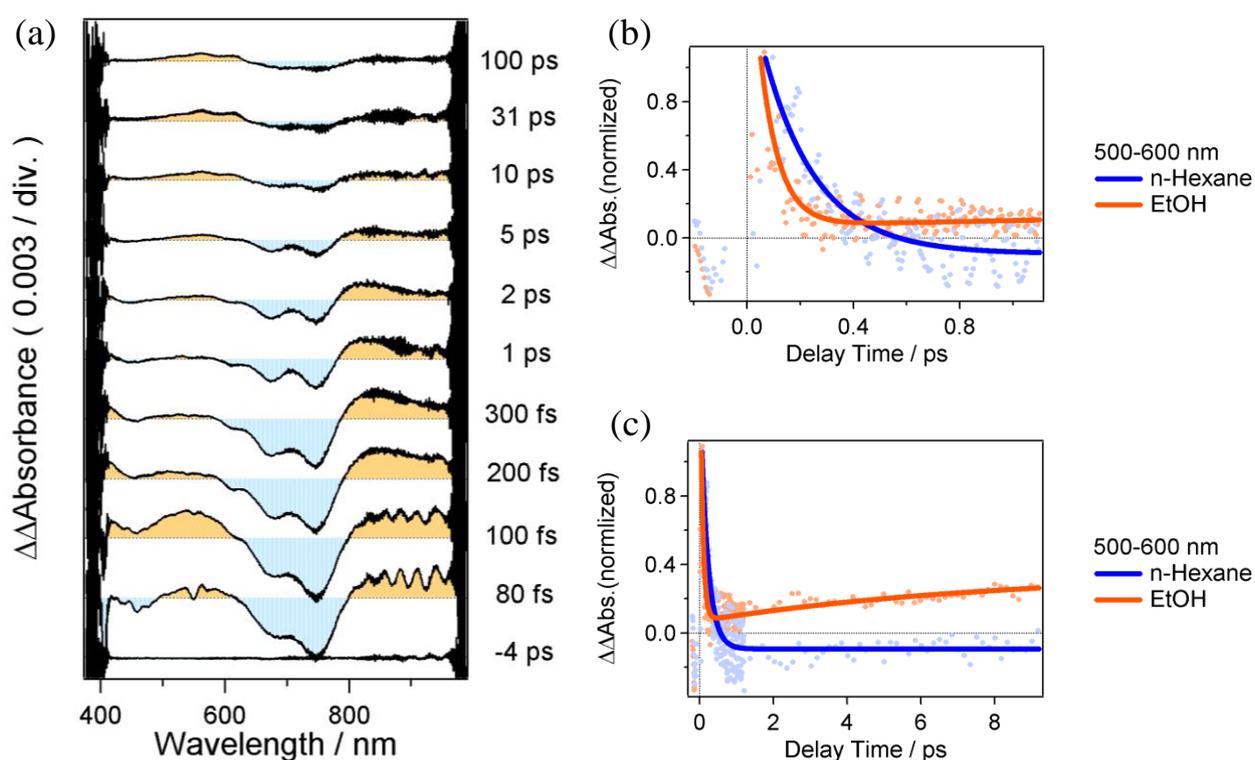


Figure 4. (a) Transient absorption spectra of TMPD in Ethanol solution excited with pump1 (340 nm, 320 μ W) and pump2 (680 nm, 740 μ W). The delay time was a time interval between pump2 and probe pulses. The delay of pump1 was fixed to be -10 ps. (b), (c) Time profiles of transient absorbance in ethanol (orange lines) and n-hexane (blue lines) averaged over 500-600 nm.

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