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Two-Photon Ionization of Naphthacene in Hexane Excited by an Argon Ion Laser

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A continuous wave laser can induce two-photon ionization in solution. The conductivity signals of naphthacene in hexane excited by the 458-nm line of an argon ion laser were quadratically proportional to the laser power and linearly proportional to the solute concentration, indicating a two-photon process.

Laser multi-photon technique is a versatile method for ionizing a photoabsorbing solute molecule even in a non-polar hydrocarbon solvent,[1] and offers a sensitive analytical method useful in solutions.[2 - 4] A pulse laser has been used for ionization, because a nonlinear process is more efficient as the peak power of the laser is more intense. A continuous wave (CW) laser has been considered to be inefficient for exciting multi-photon processes[5] and no multi-photon ionization (MPI) in solution has been reported. However, a CW laser has a well-defined beam shape, oscillation mode and a stable laser power. A continuous excitation can achieve a steady-state between ionization and relaxation. These features are definite advantage of CW laser excitation for accurate measurements of absolute cross sections. In this letter we will report the first detection of the laser two-photon ionization signal in solution excited by a CW laser. We tried with naphthacene in hexane, because it has an intense absorption and is a suitable sample for the two-photon ionization by an argon ion laser.

The 458-nm beam from an argon ion laser (Lexel, model 95-4) was focused tightly into a cell with a set of concave (f=-25 mm) and convex (f=30 mm) lenses. The cell has a pair of parallel electrodes held 5-mm apart and quartz windows and the sample was flowing through to avoid photobleaching. The conductivity signal was measured by a current input preamplifier (NF, LI-76) and a lock-in amplifier (NF, 5610B) with the laser light intensity modulation. Naphthacene (guaranteed grade, Nacalai Tesque.) was used as received. Hexane (guaranteed grade, Kishida Chemicals) was used after refluxing with $CaCl_2$.

Two-photon ionization current signals are shown in Fig. 1 for 1.0 x10^{-4}-mol/l naphthacene in hexane.

The laser power was 200 mW, the applied electric field was 5000 V/cm, the modulation frequency was 200 Hz, and the time constant of the lock-in amplifier was 3 s. The current signal showed the highest signal-to-noise ratio at modulation frequencies of between 180 Hz and 240 Hz. The dc leak current of the solution was about 5 pA and this decreased to about 0.003 pA by the lock-in modulation. The current signal of the solution increased substantially upon laser irradiation, but that of the pure solvent (about 0.007 pA) changed little.

The conductivity signal from naphthacene in hexane was quadratically proportional to the incident laser power, as shown in Fig. 2. It was linearly proportional to the concentration of naphthacene for 0 - 1.0 x10^{-4} mol/l. Since the molar extinction coefficient of naphthacene is 1800 at 458 nm and the two-photon energy of the 458-nm radiation (2.7 x 2 = 5.4 eV) exceeds the ionization threshold of naphthacene (4.8 eV in hexane[4]), the observed current signal should be due to the stepwise two-photon ionization process of naphthacene via the singlet excitation state. This is the first report on the laser two-photon ionization in solution by a CW laser. The detailed analysis will be published elsewhere.

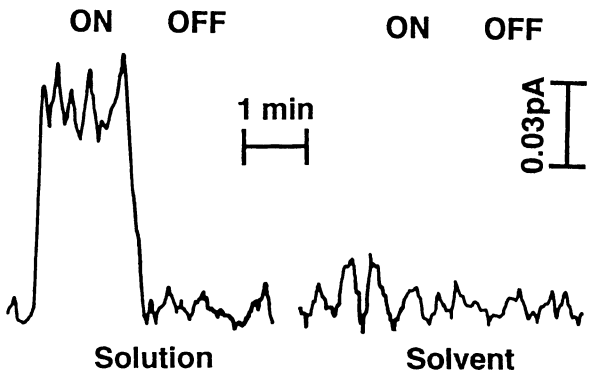

Fig. 1. Photoconductivity signal of naphthacene (1.0 x 10^{-4} mol/l) in hexane. ON: irradiating an argon ion laser light (458 nm), OFF: blocking the laser light.

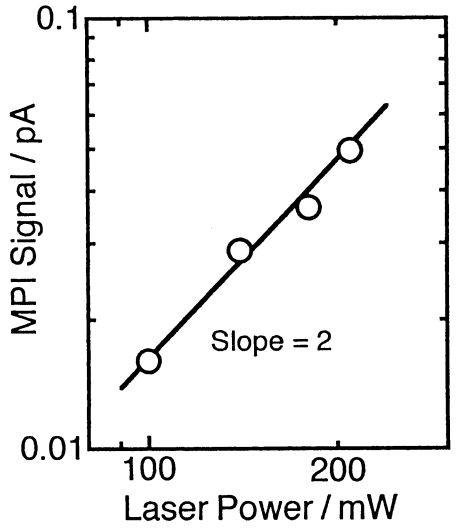

Fig. 2. Effect of laser power on photo-current. Sample: naphthacene (1.0 x 10^{-4} mol/l) in hexane. Solid line shows a quadratic dependence.

References

1)L. G. Christophorou and K. Siomos, "Electron-Molecule Interactions and Their Applications, Volume 2," ed by L. G. Christophorou, Academic Press, Orlando (1983), pp. 222 - 316.

2) S. Yamada and T. Ogawa, *Prog. Analyt. Spectrosc.*, **9**, 429 (1986).

3) T. Ogawa, M. Kise, T. Yasuda, H. Kawazumi, and S. Yamada, *Anal. Chem.*, **64**, in press (1992).

4) S. Yamada, N. Sato, H. Kawazumi, and T. Ogawa, *Bunkô Kenkyû*, **37**, 18 (1988).

5) W. D. Pfeffer and E. S. Yeung, *Anal. Chem.*, **58**, 2103 (1986).

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