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Methodology for measuring two-color two-photon photoacoustic spectra of chemical species in liquid solutions.

Shiori Sakurai[1†], Miki Isoda[1], and Akira Harata[1] ([1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu Univ.)

1. Introduction

Two-photon absorption is an important nonlinear optical processes: unlike the one-photon process, a molecule is excited from its ground state to an excited state by simultaneous absorption of two photons. Two-photon absorption processes can produce molecules excited by longer wavelengths of light than one-photon process. In addition, spatial selectivity is improved in the two-photon absorption process. Because of these properties, two-photon absorption has a wide variety of potential applications, including optical data storage, fluorescence microscopy, and photodynamic therapy. Two-photon fluorescence has been frequently investigated.

Photoacoustic (PA) spectroscopy is a technique that observes changes in thermal energy generated by light irradiation, as acoustic waves associated with heat generation. Photo-absorption properties of almost all of target molecules can be investigated with PA spectroscopy, one of the highly sensitive photothermal calorimetric techniques. As an ideal measurement tool of weak two-photon absorption of non- or less-fluorescent solute molecules in liquid solutions, PA spectroscopy has a great potential.

In this study, an apparatus to measure two-photon absorption photoacoustic spectra of chemical species in liquid solutions is designed and tested with tunable laser light.

2. Experimental Section

2.1 Materials

Para-nitrophenol was selected as the central asymmetric molecule and diphenylacetylene as the central symmetric molecule. Para-nitrophenol (Kishida Chemical Co., LTD. >98.5%) was dissolved in acetonitrile (for HPLC-grade, >99.5%). Diphenylacetylene (FUJIFILM Wako Pure Chemical Co., LTD. >98.0%) was dissolved in hexane (Kishida Chemical Co., LTD. 96.0%).

2.2 Apparatus

A schematic diagram of the newly developed equipment is shown in **Fig.1**.

A diode pumped Q-switched optical parametric oscillator (OPO) laser (EKSPLA, NT230; vertical polarization, pulse duration ~3 ns) were used as the excitation sources. Intensity of the laser light was adjusted using a half wave plate (λ/2) and a polarizing beam splitter (PBS) and monitored with a power meter (COHERENT, PM2). Laser beams were focused into a quartz glass cell (optical path length 10 mm) using an achromatic focusing lens (100 mm).

A piezoelectric transducer (PZT) was attached to the liquid sample cell, which fixed to a cell holder with an aluminum plate between the cell and PZT. The cell was housed in a black-painted aluminum box. The signals from PZT were fed into a preamplifier (KEITHLEY, 428) and averaged by a digital oscilloscope (Tektronix, TBS2102B).
One-photon absorption spectra were with a UV/Vis spectrophotometer (Shimadzu, UV-2600). All the measurements were carried out at room temperature.

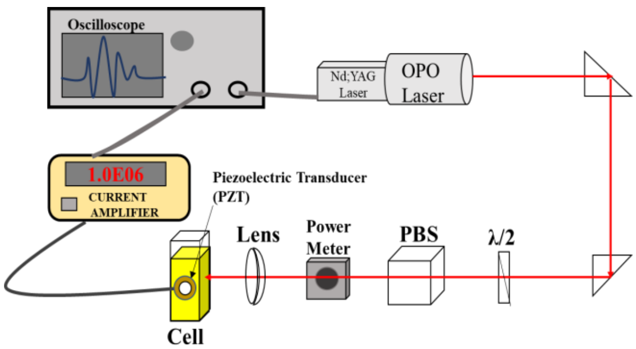

Fig. 1 Experimental setup for nonlinear photoacoustic spectroscopy.

3. Results

3.1 One-and two-photon absorption spectra for para-nitrophenol

One-photon absorption (1P) and monochromatic two-photon absorption (2P) spectra of para-nitrophenol are shown in **Fig. 2**. (2P wavelength range 550~650 nm). Intensity of the excitation laser is adjusted to 20 mW, selected from the results obtained from the two-photon absorption PA signal Intensity dependence.

The bottom and left axis show the one-photon absorption spectrum (1P wavelength vs. molar absorption coefficient). The top and right axis show the two-photon absorption spectrum (2P wavelength vs. photoacoustic signal intensity). 2P wavelength is just twice the 1P wavelength.

The two-photon absorption peak of para-nitrophenol was observed at 620 nm (2P Wavelength), and one-photon absorption peak at 310 nm (1P Wavelength). A good matching was observed for this molecule.

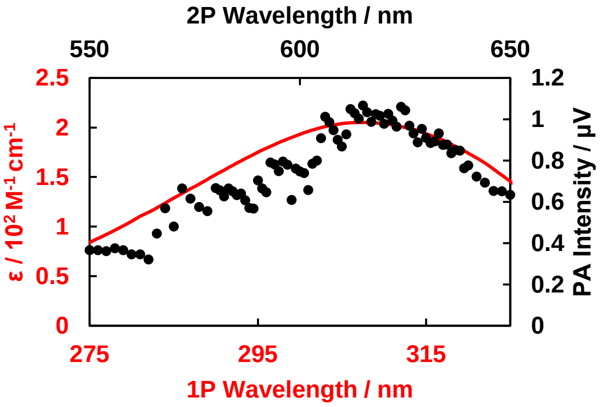

Fig. 2 Two-photon photoacoustic and one-photon absorption spectra of para-nitrophenol in acetonitrile (4.4×10^{-4} M): two-photon absorption spectrum (2P wavelength: top vs. PA signal intensity: right axes, black dots); and one-photon absorption spectrum (1P wavelength: bottom vs. molar absorption coefficient (ε): left axes, red curve).

3.2 One-and two-photon absorption spectra for diphenylacetylene

One-photon absorption and monochromatic two-photon absorption spectra of diphenylacetylene are shown in **Fig. 3**. (2P wavelength range 405~690 nm).

Intensity of the excitation laser is adjusted to 20 mW, selected from the results obtained from the two-photon absorption PA signal intensity dependence. The two-photon absorption peak of diphenylacetylene was observed at 405nm and 475nm (2P Wavelength), and one-photon absorption peak at 280 nm and 297nm (1P Wavelength). The results are consistent with the one- and two-photon absorption spectra of diphenylacetylene reported by Isozaki et al.[1]

None good matching between the one and two-photon absorption spectra was observed for this molecule. The Laporte rule[1], a spectroscopic selection rule that applies only to center-symmetric molecules (those with inverted centers), dominates the spectrum. For the center-symmetric molecules, strong two-photon absorption peaks are observed at shorter wavelengths shorter than twice wavelengths of the one-photon absorption peaks.[2]

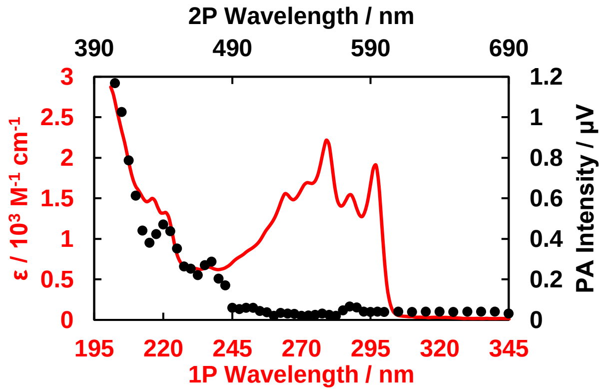

Fig. 3 Two-photon photoacoustic and one-photon absorption spectra of diphenylacetylene in hexane(1.1×10^{-4}M): two-photon absorption spectrum (2P wavelength: top vs. PA signal intensity: right axes, black dots); and one-photon absorption spectrum (1P wavelength: bottom vs. molar absorption coefficient (ε): left axes, red curve).

4. Conclusion

Simultaneous two-photon absorption of para-nitrophenol in acetonitrile and diphenylacetylene in hexane were investigated by means of PA spectroscopy technique with a newly developed apparatus.

Two-photon absorption photoacoustic spectra of para-nitrophenol and diphenylacetylene are compared with their one-photon absorption spectra. Good or poor matching was observed depending on the molecular species. This is consistent with the selection rules for one-photon allowed and two-photon allowed transitions (Laporte's rule)[1] Preliminary results of nondegenerate (two-color) two-photon absorption photoacoustic spectra will be presented for further discussion.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research (KAKENHI) [No. JP18H03915] from the Japan Society for the Promotion of Science.

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