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Development of a Photoacoustic Spectrometer for Two-Photon Absorption Using a Femtosecond Laser

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

1. Introduction

Two-photon absorption is a phenomenon in which a molecule absorbs two photons simultaneously and is excited. It is characterized by its high spatial resolution and low damage to the sample due to the use of long-wavelength light. However, the probability of two-photon absorption is extremely low, so a method capable of high-sensitivity detection is required. Photoacoustic spectroscopy is a highly sensitive measurement method that detects acoustic waves emitted by a sample that has absorbed light. It can easily measure absorption spectra of not only thin films and opaque solids, but also weakly fluorescent materials. Using a femtosecond laser as the excitation light, the probability of two-photon absorption can be increased while minimizing damage to the sample. In this study, we developed a two-photon photoacoustic spectrometer using a femtosecond laser and evaluated its performance in order to realize two-photon absorption spectrum measurement of weakly fluorescent chemical species for solute chemicals samples.

2. Equipment Development

Figure 1 shows a schematic diagram of the photoacoustic signal detector. The excitation light was a femtosecond pulse trains of fundamental (790 nm) or second harmonic (400 nm) from an Nd:YVO4/SHG laser-pumped femtosecond Ti:sapphire laser.

The excitation light was modulated by a chopper (107 Hz), focused by a lens (focal length 40 mm), and irradiated into a quartz cuvette (optical path length 1 cm) filled with sample solution. The quartz cuvette was a cell with a lid, on which grease was applied to prevent air bubbles from entering the cell. The piezoelectric transducer was fixed to the side of the quartz cuvette with an aluminum foil between them using adhesive. The acoustic waves emitted by the sample were received by the piezoelectric transducer, amplified by a preamplifier, and observed with an oscilloscope. To confirm the photoacoustic signal due to two-photon absorption, dependence of the photoacoustic signal on the excitation light intensity at two excitation wavelengths was measured with an ethanol solution of coumarin 480. The results are shown in Fig. 2.

The photoacoustic signal intensity is linearly proportional to excitation light intensity at 400 nm excitation and showed nonlinear behavior with an exponent of 1.79 at 790 nm excitation. This indicates that coumarin 480 shows one-photon absorption at 400 nm excitation and by two-photon

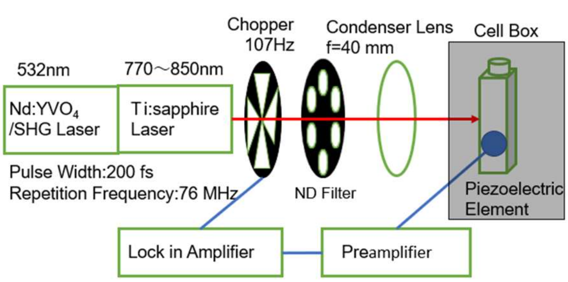

Figure1 Two-photon photoacoustic measurement system

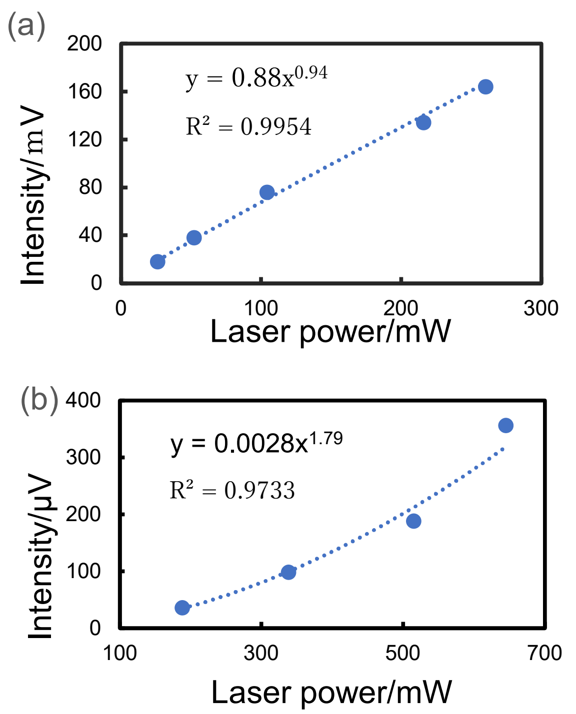

Figure2 Excitation light intensity dependence of photoacoustic signal intensity for coumarin 480 (a)Wavelength: 400 nm Concentration: 10^{-5} M (b)Wavelength: 790 nm Concentration: 10^{-2} M

tomimaru.kazuki.468@s.kyushu-u.ac.jp

absorption at 790 nm excitation. This result makes us confirm the feasibility of two-photon absorption measurement with this system.

3. Measurement of Two-photon Absorption Photoacoustic Spectrum

Measurement of two-photon absorption photoacoustic spectrum with the apparatus developed was tested using coumarin 540, for which there is a report of two-photon fluorescence spectrum (1). The laser wavelength was tuned 770~850 nm. Excitation light intensity was adjusted to 262 mW at each wavelength using an ND filter. For the measurement, a lock-in amplifier was used to extract only the signal synchronized with the chopper for high sensitivity.

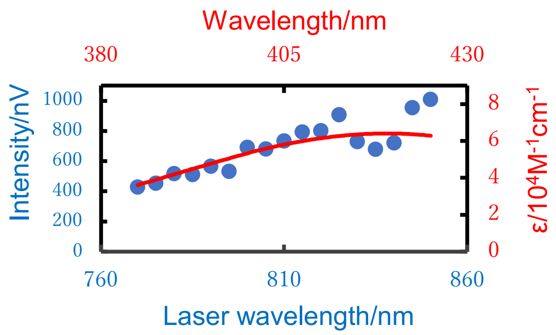

Figure3 Two-photon absorption photoacoustic spectra (dots) of coumarin 540/acetonitrile(10^{-2}M). A red curve shows molar absorption coefficients in the half of the wavelength region.

Figure 3 shows the two-photon absorption photoacoustic spectrum of coumarin 540. Absorption spectrum measured with a UV-visible spectrometer is plotted against the laser wavelength with the wavelength axis halved. The photoacoustic spectrum in Fig. 3 is consistent with the reported [(1)]. We conclude that two-photon photoacoustic spectra can be measured with this system.

Almost all of two-photon absorption measurements have been performed mainly by fluorescence methods, which are highly sensitive but targets have been limited to fluorescent chemicals. Therefore, 1-nitropyrene, a weakly fluorescent substance is a challenging target for whith there are no report before, using a laser wavelength of 770 to 830 nm and an excitation light intensity of 645 mW.

Figure 4 shows the photoacoustic spectra of the 1-nitropyrene solution. The shapes of the one-photon and two-photon absorption spectra do not necessarily coincide, but a similar trend was observed for 1-nitropyrene although combining two spectra in the short wavelength region results in a mismatch in the long wavelength region (>405 nm). Two-photon absorption cross section for 1-nitropyrene was calculated to be 19 cm^4s/photon at 800 nm by comparing the photoacoustic signal intensities in Fig. 3 and 4 and using the two-photon absorption cross section of 45 cm^4s/photon at 800 nm for coumarin 540.

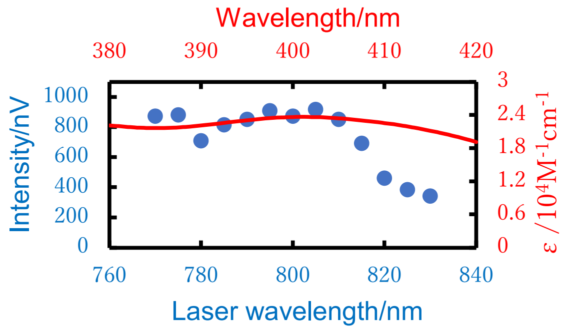

Figure4 Two-photon absorption photoacoustic spectra of coumarin 540/acetonitrile(5×10^{-5} M). A red curve shows molar absorption coefficients in the half of the wavelength region.

4. Conclusion

A two-photon absorption photoacoustic spectrometer is developed and tested for liquid samples. Two-photon absorption photoacoustic spectrum of a weakly fluorescent 1-nitropyrene solution, is measured for the first time to our knowledge. Two-photon absorption cross section is also reported. Since all materials can be measured by photoacoustic spectroscopy, new developments are expected in the understanding and application of two-photon absorption processes, which have different selection rules from those of single-photon absorption.

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References

(1) Joseph W. Perry, Mariacristina Rumi. *Advance in Optics and Photonics* **2,** 451-518(2010)