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光検出光音響分光法を用いた二光子吸収断面積の高感度測定

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Measurements of two-photon absorption cross-sections using highly sensitive optical-probing photoacoustic spectroscopy

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[Introduction]

Two-photon absorption, which is related to the imaginary part of third-order nonlinear susceptibility, is one of the important nonlinear optical processes. Conjugated organic molecules with large two-photon absorption cross-section are of interest in diverse applications such as microfabrication, photodynamic therapy of cancer, two-photon microscopy, optical power limiting, and optical data storage. Diphenylacetylene (DPA) and diphenylbutadiyne (DPB) are highly symmetric π-conjugated molecules and are attracting much attention as building blocks for two-photon absorption materials. The study of two-photon absorption is mostly based on the observation of direct absorption and radiative transitions, *i.e.* open-aperture Z-scan and two-photon excited fluorescence. However, because of the small two-photon absorption cross-section and subsequent weak fluorescence of DPA and DPB, the two-photon absorption cross-sections are difficult to obtain. Photoacoustic spectroscopy (PAS), a highly sensitive photothermal calorimetric technique, is ideal for the measurement of a variety of weak two-photon absorption phenomena in liquids. We applied the PAS technique detecting a transient angular deflection of the probe beam, so-called optical-probing PAS (OPPAS), to the measurement of two-photon absorption.

[Experimental]

An optical parametric oscillator (OPO) laser pumped by the third harmonic of a Nd^{3+}:YAG laser and a He-Ne laser were used as the excitation and the probe sources, respectively. An acoustic wave resulting from absorption was observed as a transient angular deflection of the probe beam. The temporal intensity profile of the probe light through a 200-μm pinhole was detected by a photomultiplier tube. Heat action spectra were measured by plotting the prompt photoacoustic signal amplitude U_{OPPAS} against the excitation wavelength.

[Results and Discussion]

The heat conversion efficiency to generate the prompt photoacoustic signal was obtained by one-photon absorption at 266 nm. The prompt photoacoustic signal amplitude U_{OPPAS} resulting from one-photon absorption can be described as;

$$U_{\mathrm{OPPAS}} = K_{266} I_{266} (1 - 10^{-A}) \alpha_{266},$$

where K is the instrument function, I is the incident laser power, A is the absorbance of the sample at 266 nm, and α is the heat conversion efficiency. The incident laser power dependence of the OPPAS signal intensity was measured, and linear regression of the plots provides the slope $U_{\mathrm{OPPAS}} / I_{266}$, which

is equivalent to K_{266} $(1-10^{-A})$ α_{266}. The heat conversion efficiency of the samples was obtained with respect to a calorimetric standard (2-hydroxybenzophenone (2HBP); α_{266} = 1)[1] by cancelling the instrument function. The α_{266} values for DPA and DPB were determined to be 0.49 and 1.0, respectively.

The prompt photoacoustic signal amplitude U_{OPPAS} resulting from the two-photon absorption can be described as;

$$U_{\mathrm{OPPAS}} = K\sigma^{(2)}cI_{\mathrm{OPO}}^{2}\alpha,$$

where K is the instrument function, α is the heat conversion efficiency, and $\sigma^{(2)}$ is the two-photon absorption cross-section. The heat conversion efficiency for the two-photon absorption was assumed to be identical with that for the one-photon absorption at 266 nm. The OPPAS signal intensity depending on the incident laser power at 472 nm is presented in Fig. 1. Fitting curves of the plots using the 2nd-order term of the polynomial function provide U_{OPPAS} / I_{OPO}^{2}, which is equivalent to $K\sigma^{(2)}c\alpha$. The two-photon absorption cross-sections of DPA and DPB at 472 nm was estimated using a reference molecule (BPEB; $\sigma^{(2)}$ = 76 GM at 476 nm)[2] by cancelling the instrument function. The $\sigma^{(2)}$ values for DPA and DPB were successfully determined to be 30 and 67 GM, respectively.

The relative magnitude of the two-photon absorption cross-section can be recognized as the interaction of the ground state with upper two excited states. In centrosymmetric molecules, one-photon transition properties, *i.e.* detuning energy and transition dipole moment, often play an important role in the frequency dispersion of the two-photon absorption activity even if the intermediate state is not populated by the transition. As the laser frequency approaches the one-photon transition frequency, the contribution of the detuning energy to the two-photon absorption cross-section increases. The increasing contribution results in the enhancement of the two-photon absorption cross-section near the resonance frequency of the one-photon absorption. The significant enhancement of the two-photon absorption cross-section for the 472 nm transition of DPB was related to the resonance effect with the red-shifted one-photon allowed transition.

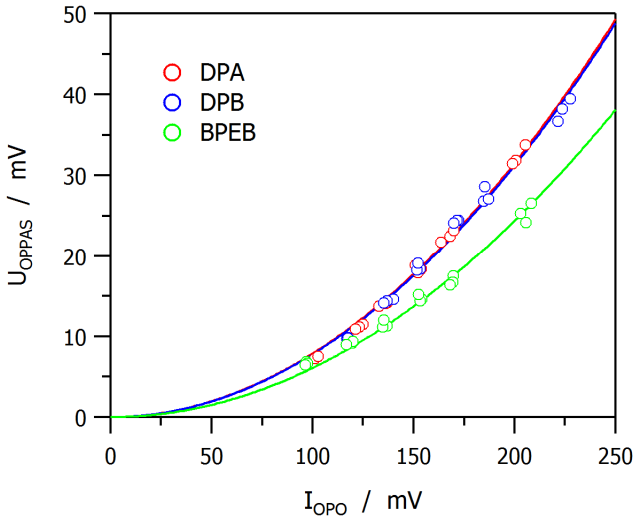

Fig. 1 Dependence of the OPPAS signal intensity on the incident laser power at 472 nm.

References

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