Nonlinear Optical Spectroscopy

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We have developed a femtosecond pump probe method that allows the determination of the nondegenerate nonlinear absorption spectra of materials over a broad wavelength range. Such spectra can be used to determine the dispersion of the associated nonlinear refraction via Kramers-Kronig relations under certain circumstances. The two-photon absorption spectra and excited satae absorption spectra of a number of materials including organic molecules using this femtosecond continuum nonlinear spectrometer are reported. The data on organics show interesting structure/property relations in addition to resonance enhancement of the third-order nonlinearity which is consistent with simple models.

We are investigating the nonlinear optical properties of materials using our femtosecond pump, continuum probe nonlinear spectrometer. In this talk we emphasize its use for determining the two-photon absorption (2PA) spectra of organic materials. In addition, since tow independently tunable sources are used for the pump and probe, we can examine the role of intermediate states in the 2PA process.

Organic materials are useful for applications using two-photon absorption (2PA) because their material properties can be tailored through molecular engineering. We developed a spectroscopic technique for measuring the nondegenerate nonlinear absorption spectrum using a pump-probe optical geometry where the probe is a broadband femtosecond continuum. This "white-light continuum" (WLC) probe pulse spans from 350-1700nm. The transient absorption is monitored via transmittance of this probe following excitation of the sample with a strong ultrashort pulsed pump at a different frequency. The tunability of the pump beam is also useful for measuring these spectra in a variety of materials. The effects of solvism, electron-withdrawing character, conjugation length, and symmetry on the 2PA properties of these molecules can be determined. In particular, we use our femtosecond pump, WLC probe nonlinear spectrometer to measure nondegenerate 2PA spectra.[1]

The fact that we measure the nondegenerate 2PA spectrum as opposed to the more commonly measured degenerate 2PA allows us to "tune" the probe toward a resonant intermediate state as shown in Fig. 1. In the simple 3-level model often used to describe 2PA in organic materials, the third-order polarizability γ (related to the 2PA coefficient) can be written as a simple expression including only three terms. This expression shows that intermediate state resonances may be exploited to maximize an organic molecule's 2PA properties. Prior work has been devoted to this goal; however since these experiments used degenerate 2PA, several molecules with slightly different structures had to be studied to show the resonance enhancement.

As an example we study a symmetric fluorene derivative whose synthesis can be found in reference [2]. In order to compare the resonant enhancement we performed two types of measurements. For the degenerate case we employed the well-known method of two-photon induced fluorescence (2PF). For the nondegenerate case we used our WLC nonlinear spectrometer.

Intermediate state resonance is illustrated by Fig. 1. S_0, S_1, and S_2 denote the positions of the excited states. The dashed line indicates the virtual transition created by the 2PA process and Δ is the detuning between this transition and the real state S_1. As this transition approaches S_1, or equivalently as Δ decreases, there should be an enhancement in the imaginary part of γ. Figure 1a denotes the schematic representation of D-2PA (2PF method) whereas Figs. 1b-1d are representations of ND-2PA (WLC method) where the pump and probe energies are varied.

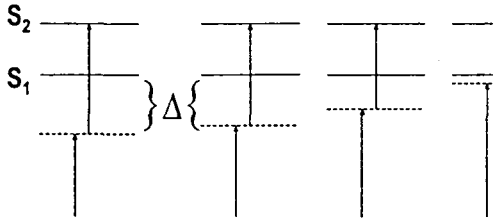

Fig. 1 Schematic representation of experiments performed. (a) denotes D-2PA and (b)-(d) denote ND-2PA.

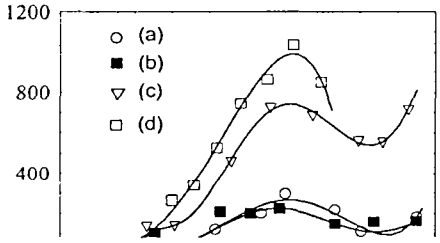

Fig. 2: 2PA Spectra. Cross-sections are plotted versus the sum of the energies of the two photons.

Figure 2 shows the 2PA spectra for the experiments depicted in Fig. 1 for the symmetric fluorene derivative. Organic 2PA molecules are often classified by their 2PA cross-section δ , which is given in cm^4 sec/photon and is related to the Im (γ). In Fig. 2, δ's are plotted versus the sum of the photon energies. Figure 2a shows the degenerate 2PA measurement (2PF) where Δ =1.21eV. Figures 1b-1d show nondegenerate 2PA (WLC) with the following detunings: (b) Δ =0.88eV, (c) Δ =0.61eV, (d) Δ =0.26eV. The experimental data verifies that the 2PA cross-sections show enhancement as resonance is approached. Using a simplified 3-level approximation for Im(γ) we were able to compare the theoretical model to this experimental data (experiment, theory): (b) 0.9, 1.0; (c) 2.8, 1.6; (d) 4.0, 4.6, showing good agreement. These results are promising since prediction of resonance enhancement in organics provides the possibility of maximizing the nonlinear properties of the molecule.

References

[1] Negres RA, Hales JM, Kobyakov AK, Hagan DJ, Van Stryland EW, IEEE JQE 38 (9), 1205-1216 (2002).

[2] K. D. Belfield, K. J. Schafer, W. Mourad, B. A. Reinhardt, J. Org. Chem., vol. 65, pp. 4475-4481, 2000.