4764 *J. Phys. Chem. A* **2000,** *104,* 4764−4766

Intermolecular Effects on the Two-Photon Absorption Spectrum of DEANST Crystal[†]

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Received: January 7, 2000; In Final Form: March 7, 2000

The two-photon absorption (TPA) spectrum of 4-(*N,N* diethylamino)-β-nitrostyrene (DEANST) crystal has been characterized in the 760−1300 nm spectral range. It presents a broad (~7000 cm^{-1}) absorption band that cannot be described by any molecular resonance. In particular, it does not display the strong molecular TPA resonance that is due to the internal charge-transfer transition. Davydov splittings as large as 5400 cm^{-1} are observed in the linear absorption spectrum. Thus, dipole coupling between transition dipole moments are very strong in DEANST crystal. The linear and nonlinear absorption spectra are analyzed using the framework of Frenkel-Davydov exciton theory.

Introduction

The recent development of nonlinear optical applications, such as optical power limiting and fluorescence up-conversion, is steering new interests on the nonlinear absorption properties of organic molecular crystals. Most earlier studies have focused on the nonresonant nonlinear optical properties of organic crystals, a spectral region for which intermolecular effects can be neglected.[1] In contrast, two-photon absorption (TPA) is a resonant process, and its properties are strongly dependent on intermolecular coupling effects on electronic states.[2]

Conjugated molecules, such as 4-(*N,N* diethylamino)-β-nitrostyrene (DEANST), have been engineered for their high hyperpolarizabilities that originate from large permanent and transition dipole moments. The strong interaction that occurs between these dipole moments in the crystal phase leads to new electronic states, i.e., excitonic states.[3,4] Thus, the resonant linear and nonlinear responses of the crystal do not correspond to the molecular responses.[5]

Previous papers on optical properties of DEANST have reported on its molecular hyperpolarizabilities,[6] nonresonant third-order susceptibilities,[7] two-photon up-conversion fluorescence ($\lambda_{\text{laser}} = 1064$ nm),[8] and molecular TPA spectrum.[9] In this work, we investigate the TPA spectrum of DEANST crystal in the 750−1200 nm spectral range.

Experimental Section

DEANST molecules were synthesized according to the procedure proposed by Kurihara et al.[7] Large crystals ($20 \times 15 \times 3$ mm^3) were obtained in a few weeks by solvent evaporation from a high concentrated solution in ethyl acetate. The most developed face is a (001) plane with *a* axis parallel to the longest edge. *b* and *c* directions correspond to crystal edges. The crystal structure was published elsewhere.[10]

The TPA spectrum was measured by the up-converted fluorescence technique. The laser source was a frequency tripled Nd:YAG laser associated with an optical parametric oscillator. The pulse duration was 2.6 ns (fwhm), and the wavelength range was 760−1300 nm. During the wavelength scanning, the laser intensity was constantly maintained , at about 50 MW/cm^2, within the quadratic fluorescence regime. The up-converted fluorescence was collected at 90° by an optical-fiber spectrometer. The spectral resolution was limited to 15 nm by the 400 μm diameter of the collecting optical fiber.

Measurements were made at normal incidence on the (001) crystallographic plane with a linearly polarized incident beam.

Results and Discussion

In Figure 1, we recall the linear absorption spectrum and the TPA spectrum of DEANST molecule in a tetrahydrofuran solution.[9] Both spectra have a strong resonance centered at 22800 cm^{-1}. It corresponds to the internal charge transfer transition (ICT) that usually dominates the linear and nonlinear optical response of bisubstituted donor -acceptor conjugated molecules. It is one-photon and two-photon allowed because of the noncentrosymmetric molecular structure.

The crystal TPA spectrum that was characterized in this work is shown on Figure 2 (squares). It presents a broad (~7000 cm^{-1}) absorption band in the near-infrared spectral range. The amplitude calibration was obtained by z-scan measurements using picosecond pulses at $\lambda = 1064$ nm, i.e., $\beta = 4.7 \pm 1.2$ cm/GW.[11] For completeness, the corresponding linear absorption spectrum of DEANST crystal is displayed in Figure 2 (dashed curve). This polarized spectrum was previously obtained by a Kramers-Kronïg and Fresnel analysis of reflectivity data.[12] Clearly, these crystal linear absorption and TPA spectra are very different from their corresponding spectra in solution. Therefore, the oriented gas model cannot be used to describe these crystal data from the microscopic optical properties of molecules.

In a previous work,[12] we have theoretically discussed the optical properties of DEANST crystal using the framework of Frenkel-Davydov exciton theory. In the first level of perturbation and for negligible intermolecular charge transfer, the interaction Hamiltonian is

$$\mathrm{H} = \sum_{\mathbf{m},\alpha} H_{\mathrm{m}},\alpha + \frac{1}{2} \sum_{\substack{\mathbf{m},\alpha,\mathbf{n},\beta \\ \{\mathbf{m},\alpha\}\neq\{\mathbf{n},\beta\}}} \mathrm{V}_{\mathbf{m},\alpha,\mathbf{n},\beta}$$

[†] Part of the special issue "Electronic and Nonlinear Optical Materials: Theory and Modeling."

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10.1021/jp000102b CCC: $19.00

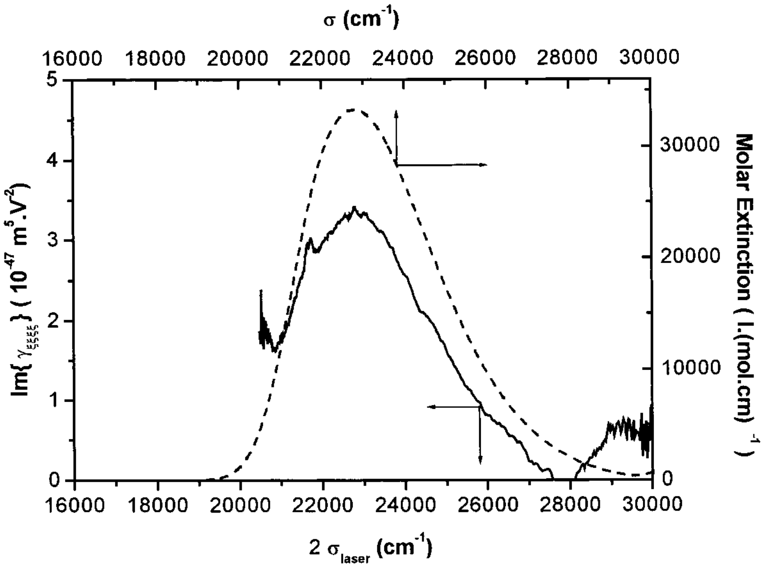

Figure 1. Linear absorption spectrum (dashed line) and two-photon absorption spectrum (solid line) of DEANST molecule in THF solvent. Adopted from ref 9. Copyright 1997 Optical Society of America.

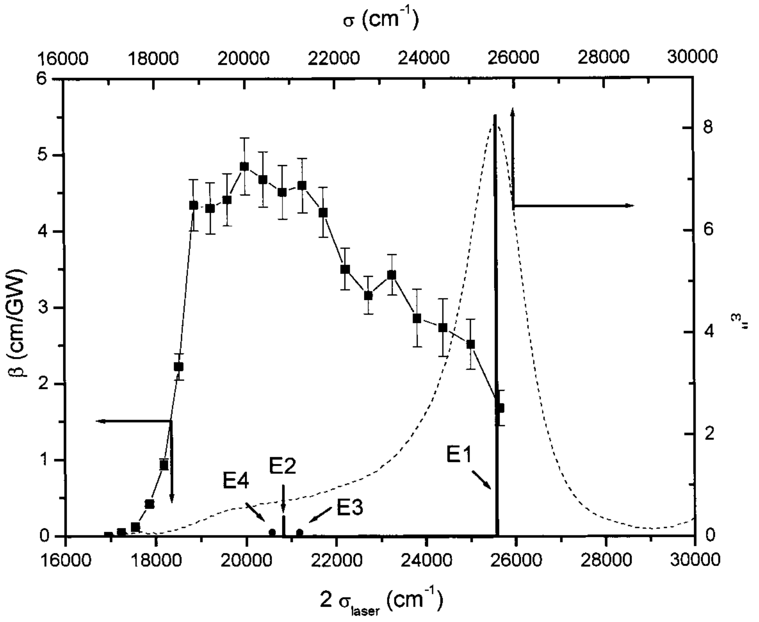

Figure 2. Linear absorption spectrum (dashed line) and two-photon absorption spectrum (square) of DEANST crystal.

where $H_{\mathbf{m},\alpha}$ is the energy operator linked with the molecular eigenstates, and $V_{\mathbf{m},\alpha,\mathbf{n},\beta}$ corresponds to the interaction between molecule α in the cell **m** and molecule β in the cell **n**.

After introduction of the quasi-wave-vector **k**, the Hamiltonian diagonalization is reduced to the diagonalization of submatrices which dimension is the number $N_{\mathbf{m}}$ of molecules per unit cell. These submatrices are written as

$$\Delta H(\mathbf{k}) = D + L(\mathbf{k})$$

where D corresponds to the permanent dipole moment interaction and L corresponds to the transition dipole moment interaction.

The D term leads to a global shift of transitions, and the L term leads to a splitting of a molecular transition into $N_{\mathbf{m}}$ crystalline transitions. Neglecting exciton-vibration interaction, it can be shown[3] that a photon can only interact with an exciton of the same wavevector. Thus, the optical transitions correspond to the eigenvectors of ΔH in the limit $\mathbf{k} \rightarrow 0$.

Let us consider the basis corresponding to the excitation on the molecules located on one site of the elementary cell. On this basis, D is diagonal and given by

$$D_{\alpha,\alpha} = \sum_{\substack{\beta,\mathbf{m}\\ \beta\neq\alpha \text{ if } \mathbf{m}=0}} \mathbf{M}_{0\alpha,\mathbf{m}\beta}(\mu_{11}^{\alpha},\mu_{00}^{\beta}) - \mathbf{M}_{0\alpha,\mathbf{m}\beta}(\mu_{00}^{\alpha},\mu_{00}^{\beta})$$

where $\mathbf{M}_{0\alpha,\mathbf{m}\beta}(\mu_{ii}^{\alpha},\mu_{00}^{\beta})$ is the interaction energy between the permanent dipole moment μ_{ii}^{α} of the molecule $\{0,\alpha\}$ in its i state ($i = 0$: ground state. $i = 1$: excited state) and the permanent dipole moment μ_{00}^{β} of the molecule $\{\mathbf{m},\beta\}$ in its ground state.

In the same basis, $L(\mathbf{k})$ is given by

$$L_{\alpha,\beta} = \sum_{\substack{\mathbf{m}\\ \mathbf{m}\neq 0 \text{ if } \alpha=\beta}} \mathbf{M}_{0\alpha,\mathbf{m}\beta}(\mu_{01}^{\alpha},\mu_{01}^{\beta}) \exp(i\mathbf{k}(\mathbf{m}+\mathbf{r}_{\beta}-\mathbf{r}_{\alpha}))$$

where μ_{01}^{α} and μ_{01}^{β} are the transition dipole moments between

TABLE 1: Calculated Energies and Transition Dipole Moments for Excitonic Transitions in DEANST Crystal: Wave Vector Direction k = [001]

excitonic transition	relative energy (cm^{-1})	transition dipole (D)
E1	0	6.14
E2	−4750	0.84
E3	−4400	0.02
E4	−5000	0.01

the ground and excited states of molecule $\{0,\alpha\}$ and $\{\mathbf{m},\beta\}$, respectively. $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ are respectively the position of molecule $\{0,\alpha\}$ and $\{0,\beta\}$.

In this work, the dipole interaction is calculated using a generalization of the extended-dipole model:[13]

$$\mathbf{M}_{0\alpha,\mathbf{m}\beta}(\mu_\alpha,\mu_\beta) = \frac{1}{4\pi\epsilon_0}\sum_{\mathbf{a}\in\alpha\ \mathbf{b}\in\beta}\frac{Q_\mathrm{a}Q_\mathrm{b}}{\mathbf{r}_{\mathbf{m},\mathbf{a}(\alpha),\mathbf{b}(\beta)}}$$

where Q_a is the net atomic charge of atom a on molecule α. It is the net atomic charge associated with either a given electronic state or a transition dipole moment depending on the nature of μ_α: permanent or transition dipole moment. The same convention holds for the net atomic charge Q_b of atom b on molecule β. Finally, $\mathbf{r}_{\mathbf{m},\mathrm{a}(\alpha),\mathrm{b}(\beta)}$ is the distance between atom a and atom b. The net atomic charges are obtained from the quantum chemistry calculation.

After the computation of the perturbative Hamiltonian, its diagonalization leads to the excitonic energies. Then, the transition dipole moments are calculated from the computed eigenvectors. Table 1 summarizes the calculated relative energies and transition dipole moments of excitonic transitions. The molecular base is site 1, site 2, symmetric of site 1, symmetric of site 2. The molecular ICT transition leads to four excitonic transitions in the crystal: two of them (E1 and E2) are one-photon allowed and two-photon forbidden, and the other two (E3 and E4) are one-photon forbidden and two-photon allowed. This results from the DEANST crystal structure that has two centrosymmetric couples of independent molecules per unit cell. The selection rules for transitions among molecular states, and among exciton states are imposed by the molecule symmetry and the crystal symmetry, respectively. This explain why linear absorption and TPA spectra have distinct electronic resonances for the centrosymmetrical crystal while they have the same resonances for the noncentrosymmetrical molecule.

The calculated excitonic transitions are displayed in Figure 2 with the relative energy scale adjusted on the experimental E1 transition, i.e., 25600 cm^{-1}. For linear absorption, calculations predict a 4750 cm^{-1} Davydov splitting between the E1 and E2 transitions. This is in good agreement with the observed 5400 cm^{-1} experimental splitting. Similarly, the crystal TPA spectrum cannot be directly described by molecular resonances. In particular, it does not display the strong TPA resonance that is due to the internal charge-transfer transition in the molecular TPA spectrum. The calculations in ref 12 predict two TPA resonances at E3 and E4 energies. As shown on Figure 2, the experimental TPA resonance is effectively centered in the same spectral region, but it is much larger than the 600 cm^{-1} expected splitting. This broadening could arise from molecular vibrations that are not being taken into account in calculations. Note that the density of excitonic states is very high in this spectral range and that excitations can easily be localized through exciton-vibration interactions.

Conclusion

The linear and nonlinear absorption spectra of DEANST molecule in solution, and of DEANST crystal are compared in Figures 1 and 2, respectively. In solution, the absorption resonances correspond to the same molecular transition, the so-called internal charge transfer transition. In contrast, the one-photon and two-photon crystal resonances correspond to different electronic transitions, which are also different from molecular transitions. This work confirms that resonant crystal features cannot be trivially deduced from the molecular features. For this type of highly nonlinear molecules, the oriented-gas model fails because of strong intermolecular interactions that result from the coupling of transition dipole moments. However, calculations within the framework of Frenkel−Davydov exciton theory give a good rationalization of experimental spectra.

Acknowledgment. We thank Dominique Block for theoretical help and Fabrice Gillot for participating with us on our experimental work.

References and Notes

(1) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987.
(2) Knoester, J.; Mukamel, S. *Phys. Rev. A.* **1989**, *39*, 1899.
(3) Davydov, A. S. Theory of Molecular Excitons; Plenum: New York, 1971.
(4) Pierre, M.; Baldeck, P. L.; Block, D.; Georges, R.; Trommsdorff, H. P.; Zyss, J. *Chem. Phys.* **1991**, *156*, 103.
(5) Munn, R. W. *J. Chem. Phys.* **1997**, *106*, 3870.
(6) Keshari, V.; Karna, S. P.; Prasad, P. N. *J. Phys. Chem.* **1993**, *97*, 3525.
(7) Kurihara, T.; Kanbara, H.; Kobayashi, H.; Kubodera, K.; Matsumoto, S.; Kaino, T. *Opt. Commun.* **1991**, *84*, 149.
(8) He, G. S.; Zieba, J.; Bradshaw, J. T.; Kazmierczak, M. R.; Prasad, P. N. *Opt. Commun.* **1993**, *104*, 102.
(9) Feneyrou, P.; Doclot, O.; Block, D.; Baldeck, P. L.; Delysse, S.; Nunzi, J. M. *Opt. Lett.* **1997**, *22*, 1132.
(10) Suchod, B.; Baldeck, P. L. *Acta Crystallogr., Sect. C* **1995**, *51*, 432.
(11) Doclot, O. Ph.D. Thesis, Université J. Fourier (Grenoble 1), Grenoble, France, 1996.
(12) Feneyrou, P. Ph.D. Thesis, Université J. Fourier (Grenoble 1), Grenoble, France, 1998.
(13) Czikklely, V.; Forsterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 207.