Nonlinear spectroscopy as a probe for correlated frequency disorder

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quadratic hyperpolarizability ever reported, thus confirming the validity of the octupolar molecular engineering scheme.

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QTuM3   1745

Chainlength dependence of cubic optical nonlinearities in polyene oligomers: saturation and scaling law

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Early theoretical[1-6] and experimental[1,2,7,8] studies have pointed out the interest of highly extended conjugated molecules (e.g., polyenes) for optimization of non-linear quadratic (β) and cubic (γ) hyperpolarizabilities at the molecular level. The role of the conjugation length, of the bond alternation, and the influence of side or chain-end substituents was intensively explored using various theoretical methods. However, the experimental investigations that would be required to validate these models remained limited to short-length oligomers, owing to the poor stability of polyenic moieties beyond a limited number N of carbon-carbon double bonds, and to solubility problems occuring with long-chain conjugated compounds. Therefore, nonlinear optical studies remained limited to oligomeric species up to N = 16.
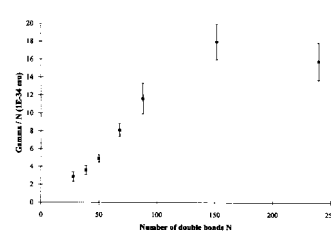
The controlled synthesis of long-chain conjugated oligomers with satisfactory stability and solubility became recently possible using living polymerization techniques.[9] We report here γ measurements as a function of N of soluble long-chain polyene oligomers (see Table 1), with up to 240 double bonds. We will also discuss the effect of the nature of the end groups (donor or acceptors) on γ values.

Hyperpolarizabilities γ were measured by third-harmonic generation (THG) in tetrahydrofurane solutions. The excitation beam at 1.907 μm was generated by a hydrogen Raman cell pumped at 1.064 μm by a Nd^{3+}:YAG laser. The third-harmonic wavelength at 633 nm is just below the onset of the electronic absorption band of the molecules.

Experimental results are reported in Table 1 and Fig. 1. Giant γ values were evidenced (up to 3.10^{-31} e.s.u.) for N = 240. Contrary to the case of short oligomers,[8] there is no evidence of significant modification of γ values, for similar Ns, upon introduction of donor or acceptor end groups at the extremities of the conjugated chain. It must be pointed out that

QTuM3 Table 1. Summary of data for model polyene oligomers: N is the average number of double bonds in the sample; λ_{max} is the wavelength of maximum of the absorption in tetrahydrofuran solution; $\gamma_{THG} = \gamma(-3\omega; \omega,\omega,\omega)$ is measured by third-harmonic generation at 1.907 μm.

N (R=H)	γ(R=H) (10^{-34} e.s.u.)	N (R=CN)	γ(R=CN) (10^{-34} e.s.u.)	N (R=NMe₂)	γ(R=NMe₂) (10^{-34} e.s.u.)
				16	111
		18	51		
		21	92		
28	81				
		34	97		
39	141				
				41	174
				43	180
50	247			50	270
		52	256		
68	553				
88	1025				
		101	765		
				117	657
152	2731				
240	3794				

QTuM3 Fig. 1. Values of $\gamma(-3\omega;\omega,\omega,\omega)/$N as a function of number of double bonds N for the model polyene oligomers.
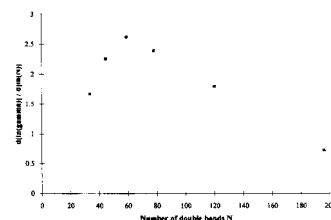
QTuM3 Fig. 2. Plot of d[ln(γ)]/d[ln(n)] as a function of chainlength for the data in Fig. 1.

the relevant parameter to be chosen for proper estimation of the effective nonlinear response of large molecules is the hyperpolarizability per molecular volume unit, i.e., γ/N in the present case of unidimensionnal compounds. The graph γ/N versus N (Fig. 1) clearly evidences a saturation for large Ns. This behaviour is quite different from the simple power law dependence $\gamma = kN^\alpha$ (where α is constant) predicted and observed for shorter polyenic oligomers. The plot of $\alpha = $ d[ln(γ)]/d[ln(N)] vs N displayed in Fig. 2 reveals a rather complex behaviour of γ(N). There is a maximum of α for N $\approx$ 60, followed by a decrease towards 1 (i.e., $\gamma \approx$ N) for the largest molecules.

To our knowledge, this is the first ob-

servation of a saturation of γ with chain-length in polyenes. The shape of Figs. 1 and 2 qualitatively resembles the predictions of several theories,[5-6] but the number of double bonds corresponding to the onset of saturation or to the maximal value α_{max} of α is much larger than these theories suggest. Furthermore, α peaks at 2.6, compared with 6 calculated in Ref. 5, or 3.6 as measured on shorter polyenes.[8] We consider that conformational effects may contribute to the observed behaviour. The unambiguous experimentals trends reported here could only be enhanced in closer-to-ideal systems. This suggests that existing calculations performed on isolated "model" polyenes may not be fully adequate to account for the experimental NLO properties of real molecules.

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QTuM4 (Invited)   1800

Nonlinear spectroscopy as a probe for correlated frequency disorder

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The collective optical response of molecular aggregates has attracted much attention over recent years. Due to the exciton delocalization in these structures, giant transition dipoles may occur leading to ultrafast spontaneous emission and large nonlinear polarizabilities. Disorder in the transition frequencies of the molecules that make up an aggregate plays a crucial role in the exciton delocalization and, therefore, strongly affects the optical response. If the disorder a_0 is small and has no intermolecular correlations, the aggregate linear absorption spectrum is motionally narrowed and has a typical width $a_0\sqrt{N}$, with N the number of molecules in the aggregate.[1] However, motional narrowing can be strongly reduced if the inhomogeneous frequency offsets of the molecules within an aggregate are correlated. Although correlations in solvent-induced shifts of neighboring molecules are very likely, one mostly assumes totally uncorrelated disorder in
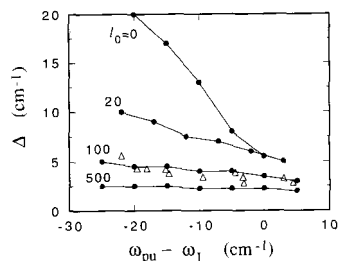
QTuM4 Fig. 1. The splitting Δ between induced one- to two-exciton absorption and ground state to one-exciton bleach as a function of the detuning of the pump frequency from PIC's red absorption maximum (ω_J = 17361 cm^{-1}). The lines are results of numerical simulations with correlation lengths 0, 20, 100, and 500 lattice constants (a_0 = 58, 15, 13.5, and 13 cm^{-1}, respectively). The triangles are the experimental data obtained with narrow bandwidth laser pulses.

tinction between segment and continuous disorder models of polymers.

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model studies. The reason is that experimentally no independent information on the size and the degree of correlation of the disorder can be obtained from the width of the linear absorption spectrum.

In this paper, we show that nonlinear optical techniques can provide the answer to the question of the unknown correlation length. To this end, we analyze the nonlinear optical response of linear J-aggregates described by the Frenkel-exciton Hamiltonian with Gaussian molecular frequency disorder with arbitrary spatial correlations. We use exact response theory that correctly accounts for states with more than one excitation quantum shared by the molecules on a chain (multiexciton states). In the weak disorder (motional narrowing) limit it is possible to obtain analytic expressions for the disorder averaged nonlinear polarizabilities of arbitrary order.[2] Application of the general theory to two-color pump—probe spectroscopy shows that the distance between the one-exciton bleach peak and the induced one- to two-exciton absorption peak as a function of pump frequency is an excellent probe for the disorder correlation length; the size of the disorder then follows from the width of the linear absorption band or the induced absorption feature. The practical potential of this novel approach is further demonstrated by numerical simulations of the pump—probe spectrum for larger, more realistic, sizes of the disorder, for which the perturbative approach breaks down. Pump—probe spectra of the J-aggregates of pseudo-isocyanine (PIC) in a glassy host are analyzed on the basis of this model and show that the molecular disorder has a surprisingly small size a_0 and a large correlation length, in the order of the exciton delocalization length (Fig. 1).[3]

We finally note that the general method proposed here, namely to obtain information on molecular frequency correlations from correlations in exciton transitions, measured in pump—probe spectroscopy, may proof useful for other nanostructures as well, e.g., in the dis-