Nonlinear spectroscopy as a probe for correlated frequency disorder
Durrant, James; Wiersma, Douwe A.; Knoester, Jasper

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Chainlength dependence of cubic optical non-linearities in polyene oligomers: saturation and scaling law.

H. D. W. Samuel, Isabelle Ledoux, Christophe Dhennaut, Joseph Zyss, Howie Fox, Richard R. Schrock, Robert J. Silbey, France Telecom-CNET-Centre Paris B Laboratoire de Bagneux, 126 avenue Henri Ravera, 92210 Bagneux, France

Early theoretical and experimental 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. We report here investigations that would be required to validate these models remained limited to short-length oligomers, owing to the poor stability of polymeric molecules beyond a limited number N of carbon-carbon double bonds, and to solubility problems occurring 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. We report here γ measurements for 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 acceptor) on γ values.

Hyperpolarizabilities γ were measured by third-harmonic generation (THG) in tetrahydrofuran solutions. The excitation beam at 1.907 μm was generated by a hydrogen Raman cell pumped at 1.064 μm by a Nd:YAG laser. The third-harmonic wavelength at 653 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^-16 esu) for N=240. Contrary to the case of short oligomers, 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 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 uni-dimensional compounds. The graph of γ/N versus N (Fig. 1) clearly evidences a saturation for large N. This behaviour is quite different from the simple power law dependence γ ∝ kNα (where α is constant) predicted and observed for shorter polyene oligomers. The plot of α = d[ln(γ)]/d[ln(N)] as a function of chainlength is measured by third-harmonic generation at 1.907 μm.

Table 1. Summary of data for model polyene oligomers: N is the average number of double bonds in the sample; λ2w is the wavelength of maximum of the absorption in tetrahydrofuran solution: γ(3w;w,w,w) is measured by third-harmonic generation at 1.907 μm.

<table>
<thead>
<tr>
<th>N</th>
<th>γ(3w;w,w,w)</th>
<th>λ2w (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.10^-15</td>
<td>665</td>
</tr>
<tr>
<td>20</td>
<td>2.10^-15</td>
<td>653</td>
</tr>
<tr>
<td>30</td>
<td>1.30^-15</td>
<td>650</td>
</tr>
<tr>
<td>40</td>
<td>9.10^-16</td>
<td>648</td>
</tr>
<tr>
<td>50</td>
<td>7.10^-16</td>
<td>646</td>
</tr>
<tr>
<td>60</td>
<td>5.10^-16</td>
<td>644</td>
</tr>
<tr>
<td>70</td>
<td>4.10^-16</td>
<td>642</td>
</tr>
<tr>
<td>80</td>
<td>3.10^-16</td>
<td>640</td>
</tr>
</tbody>
</table>

Fig. 1. Values of γ(3w;w,w,w)/N as a function of number of double bonds N for the model polyene oligomers.

Fig. 2. Plot of d[ln(γ)]/d[ln(N)] as a function of chainlength for the data in Fig. 1.

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 non-linear 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 is small and has no intermolecular correlations, the aggregate linear absorption spectrum is monotonically narrowed and has a typical width 2Δa/N with N the number of molecules in the aggregate. However, monotonous 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...
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 (multie exciton states). In the weak disorder (motional narrowing) limit it is possible to obtain analytic expressions for the disorder averaged nonlinear polarizabilities of arbitrary order. 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 $a$, and a large correlation length, in the order of the exciton delocalization length (Fig. 1).

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 prove useful for other nanostructures as well, e.g., in the distinction between segment and continuous disorder models of polymers.