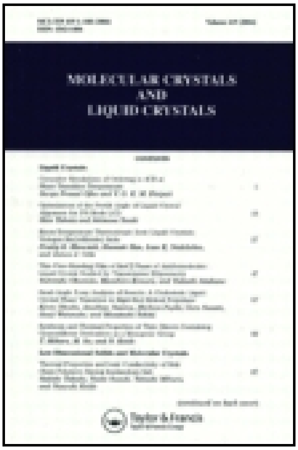

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Optical Absorption of Molecular Chains: Influence of Conformational Disorder

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OPTICAL ABSORPTION OF MOLECULAR CHAINS: INFLUENCE OF CONFORMATIONAL DISORDER

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Abstract The optical absorption line shape of a polymeric chain under the influence of conformational disorder is investigated. In the model consecutive segments of the polymer chain are allowed to be randomly oriented in space. Intrinsic disorder is taken into account phenomenologically in the Green's function of the chain. A comparison shows that the contribution of conformational disorder on the line width may be considerable.

INTRODUCTION

In recent years many experimental and theoretical investigations have considered the influence of static and dynamic disorder on spectroscopic properties such as optical line shapes. In the case of static disorder[1–4] it is assumed that disorder gives rise to fluctuations of the excitation energy or the transfer matrix elements. These models are then treated either analytically using ATA or CPA treatments, or by numerical methods. In the case of dynamic disorder phonons create time dependent fluctuations of the excitation energies and the transfer matrix elements. This dynamic disorder is either treated fully quantum mechanically[5] by treating the phonons as a heat bath[6], or by modelling the influence of the phonons by a stochastic process with white or colored noise[7–9].

In a series of linear polymers optical properties are commonly described in terms of Frenkel excitons propagating along these chains. Disorder and its influence on optical absorption of such systems has been considered along two lines. One is analogous to the treatment of static disorder described above[10]. In the second model it is assumed that the polymeric chain is composed of segments of various lengths on which an electronic excitation is localized[10,11]. In both treatments a broadening of the optical line shape is obtained. However, both treatments neglect conformational disorder, which gives rise to a random orientation of optical transition dipole moments. It is the purpose of this contribution to show that this conformational disorder also gives rise to a considerable broadening of the optical line shape.

HAMILTONIAN AND EXPRESSION FOR THE OPTICAL LINE SHAPE

The Hamiltonian of our model consists of two parts, $\mathcal{H} = H + H_{int}$, where H is the Hamiltonian of the exciton propagating along the polymeric chain (in presence of intrinsic static and dynamic disorder) and

$$H_{int} = -\sum_{n}(\vec{\mu}_n\vec{E})\left[a_n^+ e^{i\vec{q}\vec{r}_n} + h.c.\right] \tag{1}$$

describes the interaction with the light field. Here $\vec{\mu}_n$ is the transition dipole moment, a_n^+ and a_n are creation and annihilation operators for excitons, $\vec{r}_n$ is the position vector of the nth monomer of the polymeric chain, $\vec{q}$ is the wave vector and $\vec{E}$ the amplitude of the light wave. Furthermore, we write $\vec{\mu}_n = \mu\vec{e}_n$, where $\vec{e}_n$ is the unit vector along the transition dipole moment of the nth monomer. Using Fermi's Golden Rule the probability for an optical transition under the influence of the light field is given by

$$W(\epsilon) = \frac{2\pi}{\hbar}\sum_{\nu}|\langle\nu|H_{int}|0\rangle|^2\delta(\epsilon-\epsilon_\nu). \tag{2}$$

In Eq. (2) ν enumerates the eigenstates of the Hamiltonian H and ϵ_ν are their energies measured with respect to the energy E_0 of the lowest excited state, $\epsilon = \hbar\omega - E_0$ is the energy of the photons normalized to the energy of the gap between ground and lowest excited state. With H_{int} from Eq. (1) we obtain the following expression for the transition probability:

$$W(\epsilon) = \frac{2\pi\mu^2}{\hbar}\sum_{n,m}(\vec{E}\vec{e}_n)(\vec{E}\vec{e}_m)e^{i\vec{q}(\vec{r}_n-\vec{r}_m)}\sum_{\nu}\langle 0|a_m|\nu\rangle\langle\nu|a_n^+|0\rangle\delta(\epsilon-\epsilon_\nu) \tag{3}$$

which may also be written in the following way

$$W(\epsilon) = \frac{i\mu^2}{\hbar}\sum_{n,m}(\vec{E}\vec{e}_n)(\vec{E}\vec{e}_m)e^{i\vec{q}(\vec{r}_n-\vec{r}_m)}\left[G^R(m,n;\epsilon) - G^A(m,n;\epsilon)\right]. \tag{4}$$

The retarded and advanced Greens functions, G^R and G^A, respectively, are defined by

$$G^{\overset{R}{A}}(m,n;t) = \mp\frac{i}{\hbar}\Theta(\pm t)\langle 0|\left[a_m(t), a_n^+(0)\right]|0\rangle. \tag{5}$$

This expression depends on the specific realization of the disorder of the polymeric chain. The quantity of experimental interest is the average over the ensemble of realizations. Having in mind the purpose of this contribution, that is the investigation of conformational disorder on the optical lineshape, we neglect the influence of this disorder and of "large loop interactions" on the wave functions and energies of the electronic states. For conformational disorder with large persistence length l it could be shown that the influence of these interactions on the optical absorption is small by some power of the parameter a/l as compared to the mechanism taken into account below (a is the length of the repeat unit). The average over disorder decomposes with these assumptions into two averages over conformational and intrinsic disorder, respectively. The first average is relevant only for the factor containing the transition dipole moments, whereas the second results in an averaged Green's function $\overline{G}^R(m-n;\epsilon)$. Carrying out these averages, we arrive at

$$W(\epsilon) = -\frac{2\mu^2}{\hbar}\sum_{n,m}\langle(\vec{E}\vec{e}_n)(\vec{E}\vec{e}_m)e^{i\vec{q}(\vec{r}_n-\vec{r}_m)}\rangle Im\overline{G}^R(m-n;\epsilon). \qquad (6)$$

Because the averaged expressions depend only on the difference of the site vectors, we can perform one summation. The resulting expression is written in the following way (N is the total number of repeat units in a given chain)

$$W(\epsilon) = -\frac{2\mu^2 N E^2}{3\hbar}\sum_{n=-\frac{N}{2}}^{\frac{N}{2}} F(n) Im\overline{G}^R(n;\epsilon) \qquad (7)$$

with

$$F(n) = \frac{3}{E^2}\langle(\vec{E}\vec{e}_0)(\vec{E}\vec{e}_n)\rangle. \qquad (8)$$

Following Flory [12] we consider successive coordinate systems $(1),(2),\ldots,(i),\ldots$ connected with monomer number $(1),(2),\ldots,(i),\ldots$. For an arbitrary vector $\vec{v}$ the connection between its components in the frames (i) and $(i+1)$ is given by

$$v_\alpha^{(i)} = T_{\alpha\beta}^{(i+1)} v_\beta^{(i+1)}. \qquad (9)$$

The matrix T^{i+1} is explicitly given in Ref.(12) and depends on the polar and and azimutal angles describing the relative orientations of frames (i) and $(i+1)$. Applying this relation in an iterative manner, we express the components of the vector $\vec{e}_n$ in the 0th coordinate system by its components in the nth system:

$$(\vec{e}_n^{(0)})_\alpha = \left[T^{(1)}...T^{(n)}\right]_{\alpha\beta}(\vec{e}_n^{(n)})_\beta. \qquad (10)$$

Assuming that the orientation of the nth coordinate system is such that its 1-axis coincides with the direction of $\vec{e}_n$, i.e. $(\vec{e}_n^{(n)})_\beta = \delta_{1\beta}$ we get

$$F(n) = \frac{3}{E^2}\langle E_\beta^{(0)} e_{0\beta}^{(0)} E_\alpha^{(0)} e_{n\alpha}^{(0)}\rangle = \frac{3}{E^2}\langle E_1^{(0)} E_\alpha^{(0)}\rangle\langle T^{(1)}...T^{(n)}\rangle_{\alpha 1}. \qquad (11)$$

We now average over the arbitrary orientation of the frame (0) and obtain

$$\langle E_\alpha^{(0)} E_1^{(0)} \rangle = \frac{E^2}{3} \delta_{\alpha 1}. \tag{12}$$

Using this result in (11) the expression for $F(n)$ reads

$$F(n) = (\langle T \rangle^n)_{11}. \tag{13}$$

When averaging the tensor T, we assume a constant distribution for the azimutal angle. The only non vanishing components of the averaged tensor are $\langle T \rangle_{11} = \langle \cos\theta \rangle$ and $\langle T \rangle_{12} = \langle \sin\theta \rangle$ and for the matrix element occurring in Eq.(13) we get $(\langle T \rangle^n)_{11} = \langle \cos\theta \rangle^n$. The function $F(n)$ may then be written in the following form

$$F(n) = \exp(-\frac{|n|a}{l}), \tag{14}$$

where the correlation (persistence) length l is defined by

$$\frac{1}{l} = \frac{1}{a} \ln \frac{1}{\langle \cos\theta \rangle}. \tag{15}$$

For small angles θ we may write $\langle \cos\theta \rangle \approx 1 - \langle \theta^2 \rangle / 2$ and therefore $l^{-1} \approx a^{-1} \langle \theta^2 \rangle / 2$. If we Fourier transform Eq. (7) we get

$$W(\epsilon) = -\frac{2\mu^2 N E^2}{3\hbar} \int \frac{dk}{2\pi} F(k) Im \overline{G}^R(k,\epsilon). \tag{16}$$

On account of Eq.(14) the Fourier transform $F(k)$ is

$$F(k) = \frac{2}{l} \frac{1}{k^2 + \frac{1}{l^2}}. \tag{17}$$

In the limit of an infinite correlation length ($l \to \infty$) Eq. (17) is a representation of $\delta(k)$. Therefore in the limit of a completely ordered chain we get the well known k-vector selection rule.

At the moment we are not interested in the detailed description of intrinsic disorder. Therefore we use for the averaged Green's function the simplest approximation

$$\overline{G}^R(k,\epsilon) = \frac{1}{\epsilon - \epsilon_k + \frac{i\hbar}{2\tau_\epsilon}} \tag{18}$$

where $1/\tau_\epsilon$ is the (generally energy dependent) scattering rate caused by intrinsic disorder. We assume that this scattering is weak, that is $\epsilon\tau_\epsilon \gg 1$. Furthermore we describe the excitonic energy in the effective mass approximation, i.e. $\epsilon_k = \hbar^2 k^2 / 2m$. In this way we get the following expression for the probability of optical absorption

$$W(\epsilon) = \frac{8\mu^2 N E^2 m}{3\hbar^3 l} Im \int \frac{dk}{2\pi} \frac{1}{k^2 + \frac{1}{l^2}} \frac{1}{k^2 - \frac{2m}{\hbar^2}(\epsilon + \frac{i\hbar}{2\tau_\epsilon})}. \tag{19}$$

The absorption coefficient is given by (ω is the frequency of light measured from the ground state)

$$\alpha(\epsilon) = 2\pi\hbar\omega n\frac{W(\epsilon)}{cE^2} \tag{20}$$

with n denoting the concentration of polymer molecules. Evaluating the integral in Eq. (19) with the help of residuum calculation from Eq. (20) we get ($\overline{N}$ is the average number of repeat units)

$$\alpha(\epsilon) = \frac{4\pi\omega\mu^2 n\overline{N}}{3c}\left[\frac{1}{\epsilon+\epsilon_0}\sqrt{\frac{\epsilon_0}{\epsilon}} + \frac{\hbar}{2\tau_\epsilon}\frac{1}{(\epsilon+\epsilon_0)^2+\frac{\hbar^2}{4\tau_\epsilon^2}}\right] \tag{21}$$

where $\epsilon_0 = \hbar^2/2ml^2$.

DISCUSSION

Obviously the expression for the optical absorption consists of two contributions: $\alpha(\epsilon) = \alpha_c(\epsilon) + \alpha_i(\epsilon)$. The first describes the influence of configurational, the second the influence of intrinsic disorder. Because of the approximation used for the Green's function, both expressions hold only for $\epsilon > 0$, i.e. for absorption within the energy band. Both kinds of disorder result in a broadening of the optical absorption line. In the first expression this broadening is caused by conformational disorder and vanishes with increasing correlation length l resulting in a δ-shaped line in the limit $l \rightarrow \infty$. The width of the second expression is caused by the intrinsic disorder scattering of the excitons. This part of the absorption line has a Lorentzian shape with vanishing width in the limit $\tau_\epsilon \rightarrow \infty$.

The ratio of intrinsic to configurational disorder is given by

$$\frac{\alpha_i}{\alpha_c} \sim \frac{\hbar}{\tau_\epsilon(\epsilon+\epsilon_0)}\sqrt{\frac{\epsilon}{\epsilon_0}} \tag{22}$$

and for $\epsilon \geq \epsilon_0$ we get

$$\frac{\alpha_i}{\alpha_c} \sim \frac{\hbar}{\tau_\epsilon\sqrt{\epsilon\epsilon_0}} \sim \frac{l}{l_\epsilon} \tag{23}$$

where $l_\epsilon = \tau_\epsilon v_\epsilon \sim \tau_\epsilon\sqrt{\epsilon/m}$. This result shows that the configurational absorption term is dominant if $l \ll l_\epsilon$. A rough estimate of τ_ϵ for scattering by random potential gives

$$\tau_\epsilon^{-1} \sim \langle\delta V^2\rangle\rho_1(\epsilon) \sim Const/\sqrt{\epsilon} \tag{24}$$

where $\sqrt{\delta V^2}$ describes the strength of the impurity potential fluctuations and $\rho_1(\epsilon)$ is the 1–dimensional density of states. Approximately we therefore can write

$$\tau_\epsilon^{-1} = \tau_0^{-1}\sqrt{\epsilon_B/\epsilon}. \tag{25}$$

In this expression ϵ_B is the half width of the energy band and τ_0^{-1} describes the scattering rate at energy $\epsilon \approx \epsilon_B$. Within this estimates for the first term we get $\alpha_c(\epsilon) \sim \epsilon^{-3/2}$ and for the second one $\alpha_i(\epsilon) \sim \tau_\epsilon^{-1}\epsilon^{-2} \sim \epsilon^{-5/2}$. So analyzing the absorption line shape one can distinguish two mechanisms of its broadening. Taking into account that in the case of phonon scattering τ_ϵ and l_ϵ are also functions of the temperature, we could expect a crossover of $W(\epsilon)$ between two different regimes at $l_\epsilon(T) \simeq l$.

In conclusion, we have demonstrated the importance of conformational disorder for light absorption, i.e. for linear optical process, in polymers. At present nonlinear optical phenomena in disordered media are also of considerable interest (see, e.g. Ref.(13)) and references therein). For such phenomena in polymers one could expect also an important influence of conformational disorder.

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