



Electronic versus vibrational optical nonlinearities of push-pull polymers

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Abstract

The electronic and nuclear contributions to the second-order polarizabilities of donor/acceptor substituted polymers are calculated in the intermediate frequency regime relevant for optical material applications (laser frequency high compared to nuclear and low compared to electronic transitions). We find that the purely electronic contribution is positive and vibrations only make a ~ 5 –10% negative correction. This is in marked contrast with the static (zero frequency) response where both contributions are positive and have comparable magnitudes. Despite recent suggestions to the contrary, purely electronic structure/polarizability relations provide a useful guide for the synthesis of new materials. © 2000 Published by Elsevier Science B.V. All rights reserved.

Conjugated polymers constitute an important class of optical materials [1,2]. Their unusually large polarizabilities have long been attributed to the delocalized nature of electronic excitations. Numerous experimental and theoretical studies had forged a pretty good understanding of their electronic and optical characteristics. This created a firm platform for the wide-spread use of organic polymers in field-effect transistors [3–6], light-emitting diodes [7,8], solid-state lasers [9,10], and other electroluminescent devices [11,12].

Standard simulations and structure/polarizability relations assume that the electronic response to the applied laser field constitutes the dominant mecha-

nism of optical nonlinearities [13–22]. However, a series of recent studies had challenged this common wisdom by raising the possibility that vibrational contributions may be as important as their electronic counterparts [23–28]. These nuclear effects arise from geometry deformations induced by the external field. π -electron delocalization and polymer non-rigid energy potential surface strongly enhances this vibrational contribution. Computations using semiempirical and finite field techniques unambiguously established the important role of nuclear contributions to the purely static (zero-frequency) polarizabilities [25–27,29,30]. If true, this should radically change the structure/property relations and require a major revision of well established synthetic strategies.

Our key point is that these results are not necessarily relevant for optical materials applications. The static limit applies when the characteristic frequency ω_L of the driving field is low compared to both

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electronic (Ω_e), and vibrational (Ω_N), frequencies. In this limit electronic and nuclear dynamics are fast, and both have enough time to adjust to the instantaneous value of the driving field. To avoid dissipative losses, optical devices should operate in the range where field frequencies are kept off resonant with respect to electronic and vibrational resonances. In conjugated materials Ω_e vary in the range 2–4 eV whereas the highest vibrational frequencies are $\Omega_N \sim 0.25$ eV. An ideal readily accessible field frequency is therefore $\omega_L \sim 0.7$ eV [13–15]. In this intermediate frequency regime (IFR) the laser field can be considered as static with respect to electronic motions and fast compared to the nuclear degrees of freedom.

Computing of the dynamical (finite frequency ω) response is a much more complicated task since it involves the excited states as well as the ground state of the system and the finite field method is no longer applicable. We have developed a new method for computing the optical response in the intermediate frequency regime based on expanding the dynamical variables in powers of the inverse nuclear mass M^{-1} [31]. It should be noted that the static response is independent of M . The method treats the optically driven electronic degrees of freedom within the time-dependent Hartree–Fock (TDHF) approach, whereas the nuclear motions are calculated classically [32]. The equations for the nuclear coordinates and the deviation $\delta\rho(\tau)$ of the single-electron density matrix from its value $\rho_0(\tau)$ in a system with the fixed molecular geometry are solved perturbatively in M^{-1} . Expanding the solution in the driving field yields the IFR vibrational corrections to the optical polarizabilities. The expressions for the corrections only involve the Hamiltonian parameters, their derivatives with respect to nuclear positions, and the eigenmodes of the linearized TDHF equation, all taken at the ground state geometry. This allows numerically inexpensive computations of the vibrational contributions in large conjugated systems. In this report we consider a simple two-states model of push-pull polyene introduced in [33,34] to study the nonlinearities and solvent effects of push-pull polyenes to demonstrate that vibrational contributions may be large at zero frequency, and only provide a minor correction in the intermediate frequency regime, which is relevant for optical materi-

als applications. A good estimate of optical nonlinearities is therefore possible by neglecting nuclear contributions altogether.

The model includes a neutral $|\psi_{\text{VB}}\rangle$ and a charge transfer (zwitterionic) $|\psi_{\text{CT}}\rangle$ diabatic state linearly coupled to a single bond-length alternation vibrational mode r with mass M . The energies of these states are $E_{\text{VB}}(r) = \frac{1}{2}k(r+Q)^2$ and $E_{\text{CT}}(r) = \frac{1}{2}k(r-Q)^2 + E_0$ where $2Q$ represents the displacement between the diabatic surfaces. The coupling of these electronic states is J , and the permanent dipole μ_{CT} in the zwitterionic state is the only non-vanishing component of the dipole. The two adiabatic states obtained by diagonalizing this Hamiltonian will be denoted $|g\rangle$ with $|e\rangle$. This model has been shown to capture the essence of the underlying physics of second order polarizabilities in a variety of conjugated molecules [28]. For this model the electronic and the vibrational contributions turn out to be exactly the same [28].

The resulting second Harmonic generation polarizability obtained using the expressions of [31] is given by a sum of an electronic (β_E) and vibrational (β_V) contributions.

$$\beta_E = \frac{\beta_0}{3} [I_0(\omega) + I_1(\omega)], \quad (1)$$

where $\beta_0 = 6(\mu_{eg})^2(\mu_{ee} - \mu_{gg})/\Omega^2$ is the electronic contribution to the static polarizability, and we have used the following notation:

$$I_0(\omega) \equiv \frac{\Omega^2}{\Omega^2 - \omega^2};$$

$$I_1(\omega) = \frac{\Omega^2}{\Omega^2 - 4\omega^2} \frac{4\omega}{\Omega - \omega}. \quad (2)$$

The vibrational-induced contribution adopts the form:

$$\beta_V = -\beta_E \frac{\kappa_{\text{eq}}}{M\omega^2\Omega} [4I_0(\omega) + \frac{1}{2}I_0(2\omega)], \quad (3)$$

where $\kappa_{\text{eq}} = (kQ)^2/(\varepsilon^2 + 1)$, $\varepsilon = [E_{\text{CT}}(r^*) - E_{\text{VB}}(r^*)]/2J$, r^* is an equilibrium geometry, and $\Omega = 2J(\varepsilon^2 + 1)^{1/2}$ is the transition frequency at the equilibrium geometry.

We have calculated the electronic and vibrational polarizabilities in the IFR regime. The parameters were adopted from [28]: $J = E_0 = 1$ eV, $k = 33.55$ eV/Å², $Q = 0.12$ Å. Assuming vibrational fre-

quency $\nu = 1500 \text{ cm}^{-1} = 0.186 \text{ eV}$ gives for the reduced mass: $M_{\text{red}} = k/\nu^2 = 970 \text{ (eV} \cdot \text{\AA}^2)^{-1}$. Straightforward minimization of the ground state energy gives the optimal coordinate $r^* = -0.075 \text{ \AA}$ and ground state energy $E_g(r^*) = -0.446 \text{ eV}$. We then computed the electronic and vibrational polarizabilities using Eqs. (1)–(3) with $\kappa_{\text{eq}} = 3.14 \text{ eV/\AA}$ and $\varepsilon = 0.8$. The results are shown in Fig. 1. The electronic polarizability β_E is positive, whereas the vibrational contribution β_V is negative and small compared to β_E . At low frequencies $\omega \sim 0.2 \text{ eV}$ we approach vibrational resonance spectroscopy regime, where the perturbative treatment of the nuclear degrees of freedom does not hold. At high frequencies $\omega \rightarrow 1 \text{ eV}$ we approach the two-photon (2 eV) resonance and enter to the electronic resonance spectroscopy regime. Our calculations show that in the IFR ($0.2 \text{ eV} < \omega < 1 \text{ eV}$) the purely electronic contribution dominates and vibrational corrections only slightly reduce the total polarizability. The relative nuclear contribution (dash-dotted line) decreases from 18% (low frequencies) to $\sim 4\%$ (high frequencies).

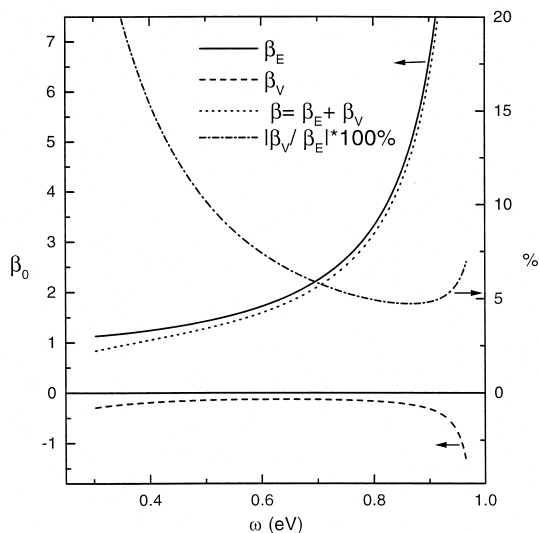


Fig. 1. The variation of electronic (solid line), vibrational (dashed line), and total (dotted line) second order polarizabilities in the intermediate frequency regime for a two-level model coupled to a single vibrational mode. The absolute values of polarizabilities are given in the units of β_0 (static limit for electronic polarizability). The relative magnitude of the vibrational contribution (%) is shown by the dash-dotted line. For other parameters see text.

At the characteristic laser frequency $\omega = 0.7 \text{ eV}$ commonly used for material applications the vibrational contribution accounts for $\sim 5\%$.

The different roles of the vibrational contribution to the optical polarizabilities in the static versus IFR originate from the relative magnitudes of the driving frequency ω_L and the vibrational frequency Ω_N . In the static limit ω_L is located below the electronic and vibrational resonances and both contributions to the polarizabilities have therefore, the same sign. Furthermore, all degrees of freedom have enough time to respond to the external field and make comparable contributions to the response. The current study shows that the IFR is drastically different from the static limit [24–27,29,30]. Here the optical frequency is low compared to the electronic frequencies. This implies that the electronic degrees of freedom still have enough time to respond and their behavior is similar to the static limit. The situation with the vibrational degrees of freedom is absolutely different. Since the nuclei are driven at a higher frequency compared to the vibrational frequency. The driving field is too fast to generate a substantial response from the vibrational degrees of freedom. The amplitude of the driven oscillations is small, this response is weak and negative and in some cases may be neglected in estimating the polarizabilities of optical materials. These general arguments hold not only for the second-order polarizability β but for higher-order polarizabilities (e.g. γ) as well.

Finally, we note that a 5–10% correction is obtained for a simple model [33,34] of a polyene. For different models, this corrections may become more important [35]. However, the small value of β_V found here for the relevant frequencies, validates the IFR expansion for other models as well. The expansion is not only numerically inexpensive, but also provides with a direct estimate of the vibronic contributions in terms of the parameters of the model and the purely electronic response.

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