PHYSICAL REVIEW B VOLUME 48, NUMBER 12 15 SEPTEMBER 1993-II

Optical response of conjugated polymers

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(Received 29 March 1993)

We present a simple model for the description of the linear and nonlinear optical response of conjugated polymers, where the π electrons are confined in a periodic system composed of anharmonic potential wells. We calculate the optical band gap, the polarizability, and the second hyperpolarizability as a function of the molecular length for the oligomers of thiophene and benzene, adjusting the model parameters to two band-gap measurements. We find them to be in fair agreement with experimental data. Furthermore, the length dependencies are discussed and compared with experimental and theoretical reported values. The model is very suitable for studying the sensitivity of the optical response to conformational disorder.

I. INTRODUCTION

The current developments in optical information processing technology require materials with high optical nonlinearities combined with good physical properties for processability purposes. Conjugated molecules, which possess an extended delocalized π-electron cloud along the chain axis are considered to be very promising organic materials for optical signal processing applications because of their large, ultrafast nonlinear optical response, their high laser damage threshold, and their relatively easy deposition in the form of thin films on a wide range of different substrates.[1,2] Many theoretical efforts have been focused on the chain length (or electronic delocalization length) dependence of the optical properties of this class of one-dimensional semiconductors.[3–6] They range from classical, Drude-like models[3] to detailed quantum-chemical *ab initio* calculations.[5,6] However, either they use extensive fitting to experimental data[3] or they are very elaborate and sensitive to the choice of the orbital basis sets.[7,8] The latter calculations explicitly account for the details of the molecular structure and the electron-electron interaction, but are, however, limited to molecules containing typically less than 20 carbon atoms because of computational limitations.[9] Some systematic experimental investigations of the length dependence of the molecular optical response of thiophene and phenyl oligomers have been published.[10,11] It is noted by Thienpont *et al.*[10] that conformational disorder influences the effective delocalization of the π electrons and hence the optical response of the molecules to an unknown but probably not negligible extent. A good understanding of the important electronic and conformational parameters determining the optical properties of these molecules should be a very useful tool for guiding synthesis and device engineering efforts. This paper aims at the construction of a self-consistent semiempirical model which could give a better insight into the role of the latter parameters.

The free-electron model, first used to model the optical absorption of conjugated molecules,[12] was further developed because of the simple physical picture it provides. Rustagi and co-workers[13,14] calculated the polarizability and the second hyperpolarizability considering the whole polyene molecule as an infinite rectangular potential well for the π electrons. Most recently, Kuhn[15] modeled the carbon-carbon bonds as finite potential steps, calculated the optical properties of polyacetylene, and demonstrated the electron-phonon coupling in this molecule. He also pointed out that electron correlation effects can be treated in an effective manner with his model. We present here a different approach by merging the classical Drude picture to the particle in a box treatment, reminiscent of the successful Kronig-Penney model in semiconductor physics. Our model consists of a set of anharmonic oscillators quantum mechanically coupled by tunneling. We calculate the optical band gap E_g, the polarizability α, and the second hyperpolarizability γ from the energy eigenvalues and the delocalized wave functions. We present our model in Sec. II and discuss the principal physical phenomena involved. In Sec. III, we calculate the optical response of the thiophene oligomers as a function of the number of repeat units and discuss the role of conformational disorder. In addition, the model calculations are also applied to the *p*-phenylene oligomeric series. In Sec. IV, we draw conclusions and give some remarks on the validity and physical significance of our model.

II. MODEL PRESENTATION

We consider one repeat unit of the one-dimensional conjugated chain as a system of two π electrons confined to an anharmonic-oscillator potential well. The influence of the molecular structure of the monomer (nuclei and *bounded* electrons) is modeled by the two parameters of the potential well [Eq. (1)], i.e., the oscillator pulsation ω_0 and the anharmonicity coefficient b:

$$V(x)=\tfrac{1}{2}m\omega_0^2x^2+\tfrac{1}{4}mbx^4\ , \tag{1}$$

where m is the electron mass and x the coordinate along the molecule backbone. To model the different oligomers (number of repeat units $N > 1$), we approach the monomer anharmonic oscillators to a distance 1_d (the monomer delocalization length) from each other in order to couple them by means of tunneling through the potential barrier (Fig. 1). It is clear that in a potential well with N repeat units, the original energy levels of the monomer will split up to form *bands* of N discrete energies, and delocalized states will occur (e.g., Ref. 16). We calculate the solutions of the steady-state Schrödinger equation of a free electron in this potential by sampling the potential profile and applying the well-known transfer-matrix technique,[17] while imposing evanescent wave functions at the borders of the potential well as boundary conditions. If we introduce two electrons per repeat unit according to the Pauli exclusion principle, the optical band gap is given by

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} = E_{N+1} - E_N \ , \tag{2}$$

where we assume that the $2N$ electrons fill the N energy levels of the lowest "energy band," i.e., we consider the system at 0 K (LUMO is the lowest unoccupied molecular orbital, HOMO is the highest occupied molecular orbital). Next, we apply a uniform, static electric field E parallel to the chain axis and calculate the shifted energy levels and modified wave functions in order to evaluate the expectation value of the electric dipole:

$$\langle \hat{\mu} \rangle = \sum_{n=1}^{N} \langle \psi_n | q\hat{x} | \psi_n \rangle \ , \tag{3}$$

where the summation runs over the occupied energy levels, and q is the electric charge in each occupied level of the potential well. For different, but not too intense, electric fields we obtain a linear relationship between $\langle \hat{\mu} \rangle / E$ and E^2 [Eq. (4)], from which we can identify α and γ:

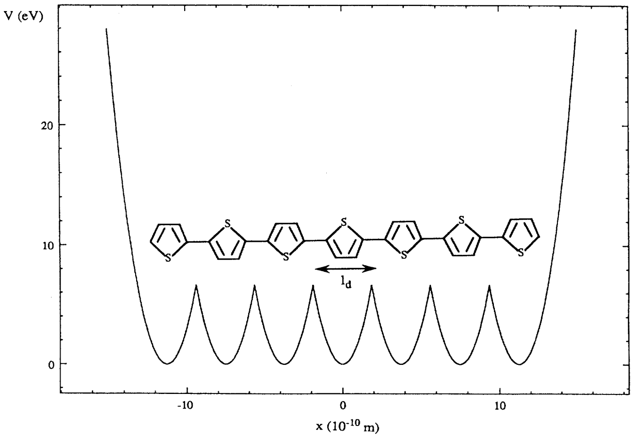

FIG. 1. The potential-energy profile V [Eq. (1)] for the thiophene heptamer as a function of the coordinate along the molecule backbone x (parameters: $\omega_0^2 = 6.55 \times 10^{31}$ s^{-2}, $b = 6.20 \times 10^{49}$ m^{-2}s^{-2}, and $l_d = 3.75 \times 10^{-10}$ m). The molecular structure is shown in the inset.

$$\frac{\langle \hat{\mu} \rangle}{E} = \varepsilon_0(\alpha + \gamma E^2) \ , \tag{4}$$

where ε_0 is the vacuum permitivity and where the term proportional to E is canceled because of the centrosymmetry of the potential profile. Note that in this approach, we consider the *entire* monomer as one repeat unit, i.e., one anharmonic oscillator, which allows us to study the interplay between the π-electron delocalization and the *anharmonicity* of the monomer in a clear and physically meaningful manner.

III. RESULTS AND DISCUSSION

A. Thiophene oligomers

We now apply this model to study the optical properties of the thiophene oligomers. We obtain $\omega_0^2 = 6.55 \times 10^{31}$ s^{-2} and $b = 6.20 \times 10^{49}$ m^{-2}s^{-2} from fitting the calculated values of the band gap to two experimental data points, i.e., $E_g(N=1) = 5.39$ eV and $E_g(N=5) = 3.00$ eV,[11] using $l_d = 3.75 \times 10^{-10}$ m. Note that the anharmonicity coefficient b is in good agreement with the one found by Prasad, Perrin, and Samoc[3] in their perturbative Drude-like treatment of this problem. It accounts for less than 2% of the total potential energy. The monomer length l_d is close to the one calculated by Aime *et al.*[18] The unidimensionality of our model only allows for the determination of the tensor components α_{xx} and γ_{xxxx} parallel to the chain axis. Figures 2(a)–2(c) show the length dependence of E_g, α, and γ, respectively, in comparison to the available experiment data.[10,11] The calculated band gap is in very good agreement with the experimental data and tends to 2.46 eV for large N, in excellent agreement with the measurements of Brédas *et al.* [$E_g = 2.5$ eV (Ref. 19)], Vardeny *et al.* [$E_g = 2.6$ eV (Ref. 20)], and Dorsinville *et al.* [$E_g = 2.7$ eV (Ref. 21)]. The experimental polarizability and second hyperpolarizability are orientationally averaged values $\langle \alpha(\omega) \rangle$ and $\langle \gamma(\omega) \rangle$, which we reduced to their static limit following Eqs. (5a)–(5c),[22] neglecting damping and using the corresponding experimental band gap to obtain ω_0. Following the arguments of Zhao *et al.*,[23] we used the two-level classical anharmonic oscillator model in order to obtain a first assessment of the dispersion of the experimental values:

$$\langle \alpha(0) \rangle = \langle \alpha(\omega) \rangle \frac{\omega_0^2 - \omega^2}{\omega_0^2} \ , \tag{5a}$$

$$\langle \gamma(0) \rangle = \langle \gamma_{\text{EFISHG}}(\omega) \rangle \frac{(\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)}{\omega_0^6} \ , \tag{5b}$$

$$\langle \gamma(0) \rangle = \langle \gamma_{\text{DFWM}}(\omega) \rangle \frac{(\omega_0^2 - \omega^2)^4}{\omega_0^8} \ , \tag{5c}$$

where EFISHG stands for "electric-field-induced second-harmonic generation" and DFWM for "degenerate four-wave mixing." It is clear that this procedure cannot fully account for the divergence of the experimental results. For instance, the sample preparation is completely different in the two experiments [thin films of thiophene oligomers in a poly(methl methacrylate matrix on quartz substrates[10] vs the solution in tetrahydrofurane (Ref. 11)]. Furthermore, it was pointed out by Dirk and Kuzyk[24] that, even in the off-resonance wavelength region, the effect of damping can be important. For example, for the thiophene pentamer ($N=5$) the visible absorption is centered around $\lambda_{\max}=412$ nm with a half width half maximum of about 50 nm.[25] Neglecting the effect of damping in the analysis of the EFISHG measurement at $\lambda=1.064$ μm results in an approximate error $>6\%$ in the determination of γ. In recent DFWM experiments by Unroe and Reinhardt[26] on similar compounds, important imaginary components for γ were found. Because of the inherent limitation of our calculation to the longitudinal components of the polarizability and hyperpolarizability tensors, an in-depth analysis of the experimental data is not relevant for our purposes.

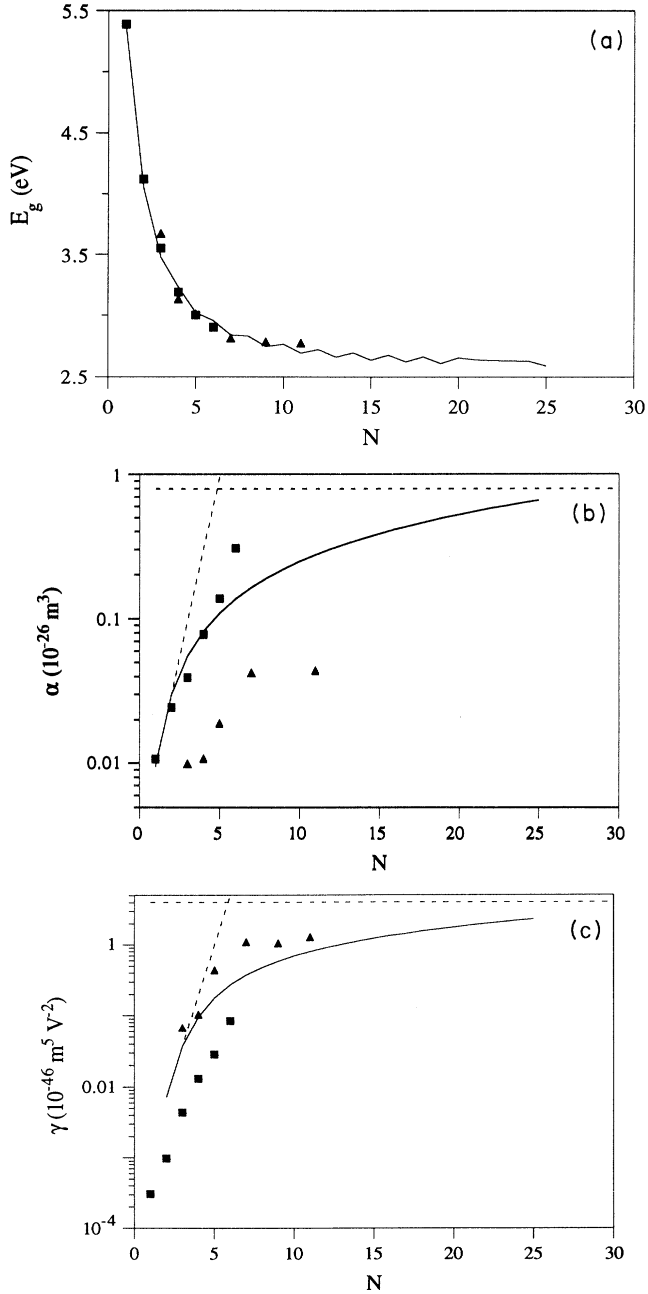

FIG. 2. (a) Optical band gap E_g (eV) vs the number of repeat units N for thiophene oligomers. (b) Polarizabiltiy α (m^3) vs the number of repeat units N. (c) Second hyperpolarizability γ (m^5 V^{-2}) vs the number of repeat units N. Calculations: plain line; experimental values: triangles (Ref. 10) squares (Ref. 11).

In addition, we have estimated the $\chi^{(3)}$ value for polythiophene (very large N) from our calculated curves. A fit of our curves following Eq. (6) yields the asymptotic values: $\log_{10}\alpha(0)\cong-26.1$ and $\log_{10}\gamma(0)\cong-45.4$.

$$\log_{10}A=a+b/N+c/N^2 \qquad (6)$$

[A stands for $\alpha(0)$ or $\gamma(0)$; a, b, and c are fitting parameters]. Approximating the molecular density $\rho=10^{27}$ m^{-3},[27] Eqs. (5a), (5c), (7a), and (7b) yield a refractive index $n\cong2.1$ and a macroscopic third-order nonlinear susceptibility $\chi^{(3)}_{\mathrm{DFWN}}\cong1.956\times10^{-19}$ m^2/V^2 at $\lambda=1.064$ μm, in fair agreement with the experimental values of Dorsinville *et al.*[21] [n between 1.9 and 2.1, $\chi^{(3)}_{\mathrm{DFWM}}=(4.19\pm2.8)\times10^{-19}$ m^2/V^2]:

$$\chi^{(1)}=\alpha_{xx}\rho\langle\cos^2\theta\rangle\ , \qquad (7a)$$

$$\chi^{(3)}=\gamma_{xxxx}\rho\langle\cos^4\theta\rangle\ , \qquad (7b)$$

where $\langle\cos^2\theta\rangle=\frac{1}{3}$ and $\langle\cos^4\theta\rangle=\frac{1}{5}$ for samples which exhibit three-dimensional macroscopic conformational disorder. It must be stressed that the fairly good agreement between our model calculations and the experiments is obtained with fitting to only *two* band-gap measurements.

B. Length dependence

Figure 3 shows the explicit *length dependence of the optical response* as a function of the length of the thiophene oligomers, given by the following definitions:

$$c=\frac{d}{d\ln N}(\ln\alpha)\ , \qquad (8a)$$

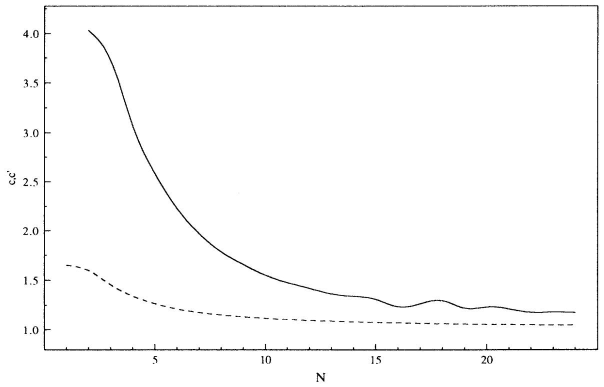

FIG. 3. $c=d\ln\alpha/d\ln N$ (dashed line) and $c'=d\ln\gamma/d\ln N$ (plain line) vs the number of repeat units N.

$$c'=\frac{d}{d\ln N}(\ln\gamma)\ . \tag{8b}$$

For long molecules ($N\rightarrow\infty$) both c and c' tend to 1. This is the so-called *thermodynamic limit* which implies that the optical response per unit length becomes independent of the length of the molecule when this length tends to infinity. In the short-chain limit we obtain $c=1.65$ and $c'=4$. An overview of the length dependencies is shown in Table I, along with the fitted values of c and c' for the experimental data for the oligothiophenes.[10,11] Most of the theoretical work has been focused on the polyene oligomers. However, it seems meaningful to compare the length dependencies obtained with these theories with the ones we calculated, because the essential features of the conjugation and the π-electron delocalization are the same in both molecules. However, the additional sulphur atom in the thiophene ring can increase the anharmonicity of the monomer repeat unit, resulting in a different length dependence. It should be noted that the commonly used fitting function $\alpha,\gamma\propto N^{c,c'}$ does not provide a general description of the length dependence since c and c' are functions of N.[28,29] The free-electron model (particle in a box), proposed by Kuhn[12] and further developed by Rustagi and Ducuing,[13] predicts $c=3$ and $c'=5$ for large N. In the short-chain limit, *ab initio* calculations by Hurst, Dupuis, and Clementi[8] found c to vary from 1.51 over 1.61 (at $N=6$) to 1.41 (at $N=11$) and c' from 3.67 over 3.98 to 3.04. Other *ab initio* results reported by Chopra *et al.*[30] for polyenes, predict c in the range 1.36–1.44 and c' between 3.14 and 3.27, whereas the semiempirical INDO (intermediate neglect of differential overlap) calculation by Pierce[31] gives $c'=4.3$. In a CNDO (complete neglect of differential overlap) modelization of thiophene oligomers Fichou *et al.*[32] also obtained $c'=4.3$. A simple Hückel model yields $c=2.8$ and $c'=5.3$,[33] and with the Pariser-Parr-Pople (PPP) approach de Melo and Silbey[34] found $c'=4.25$. Shuai and Brédas[9] obtained $c'=4.32$ in a Su-Schrieffer-Heeger (SSH) calculation, without accounting for electron-electron interaction. Heflin *et al.*[35] found $c'=4.6$ while pointing out that electron-correlation effects have a strong impact on the optical properties of conjugated polymers. Recently, Mukamel and Wang[28] developed a coupled anharmonic-oscillator picture from the PPP model. They found a maximum of $c'=6$ at $N=7$, and also established the importance of Coulomb interaction between π electrons. In addition, in Figs. 2(b) and 2(c) we show the intersection between the short-chain and long-chain limits. This intersection can be seen as a conjugation or saturation length where the optical response of the molecules becomes linearly dependent on the number of repeat units.[28] From our calculations we infer that this transition is situated at around five repeat units for α and six for γ, which agrees well with the experiments of Thienpont *et al.*[10]

TABLE I. Length dependencies of α and γ in the short-chain limit (except for Ref. 13) for different model calculations and experiments on polyenes[a-i] and oligothiophenes[j-l].

Theory	c	c'
particle in a box[a]	3	5
Hückel[b]	2.8	5.3
SSH[c]		4.32
PPP		4.25[d]
		6[e]
Ab initio	1.41–1.61[f]	3.04–3.98[f]
	1.36–1.44[g]	3.14–3.27[g]
		4.6[h]
		4.3[i]
		4.3[j]
This work	1.65	4.0
Experiment		
Thienpont *et al.*[k]	2.4	4.6
Zhao *et al.*[l]	1.69	4.05

[a] Reference 13.
[b] Reference 32.
[c] Reference 9.
[d] Reference 33.
[e] Reference 28.
[f] Reference 8.
[g] Reference 29.
[h] Reference 34.
[i] Reference 30.
[j] Reference 31.
[k] Reference 10.
[l] Reference 11.

C. Conformational disorder

Viallat and co-workers[36] pointed out the importance of the interplay between *electronic* (optical) properties of conjugated molecules and their *conformation.* They calculated the statistical properties of polythiophene and polyene molecules in solution using a modified Hückel model to include a rotational degree of freedom around the σ bond *between* the repeat units. This rotation can be caused by steric hindrance of side groups and by temperature. Their calculations clearly show the interrelation between the π-electron delocalization and the twisting of the molecule backbone. To study the influence of this type of conformational disorder, we consider a local increase of a potential barrier in the conjugated chain. Hence, the effective delocalization (tunneling probability) of the electrons in the well decreases. Figures 4(a)–4(c) show the influence on the optical properties of the doubling of the potential barrier at different bonds in the chain. The enhancement of the band gap and the reduction of α and γ is much more pronounced if the increased barrier is situated in the middle of the potential well (e.g., for $N=6$, the third barrier equals 13.3 eV instead of 6.65 eV: $\Delta E_g/E_g=+0.16$, $\Delta\alpha/\alpha=-0.18$, and $\Delta\gamma/\gamma=-0.69$) than if it is near the border [e.g., for $N=6$, the first barrier equals 13.3 eV instead of 6.65 eV: $\Delta E_g/E_g=+0.03$, $\Delta\alpha/\alpha=-0.12$, and $\Delta\gamma/\gamma=-0.33$]. Note that the influence of this conformational effect is much more important for α and γ (the most sensitive) than it is for the band gap. In view of the different sample preparation mentioned earlier, this gives an additional clue about the good agreement between the band-gap measurements and the much poorer agreement between the α and γ experimental data. It is clear that there exists a lower limit to α and γ, because at a certain barrier height the potential well will become effectively uncoupled in two *separate* potential wells. Our calculations show that this lower limit is reached for barrier heights somewhat lower than the doubled potential we used to illustrate these conformational effects.

D. Benzene oligomers

Let us now briefly outline the results of the model calculations applied to the *p*-phenylene oligomers. From the measured band gaps $E_g(N=1)=6.11$ eV and $E_g(N=2)=5.04$ eV,[36] we obtain $\omega_0^2=8.56\times10^{31}\ \mathrm{s}^{-2}$ and $b=2.97\times10^{49}\ \mathrm{m}^{-2}\mathrm{s}^{-2}$, using $l_d=4.25\times10^{-10}$ m. Figures 5(a)–5(c) show the length dependence of E_g, α, and γ, respectively, in comparison to the measured values reported by Zhao *et al.*[23] Again, we used Eq. (5c) to reduce the experimental DFWM data to their static limit. The calculated asymptotic value for the optical band gap is $E_g(N\rightarrow\infty)=3.95$ eV, in fair agreement with the experiments [$E_g=3.61$ eV (Ref. 19)]. In addition, we have calculated the length dependencies c and c' in the short-chain limit and obtained $c=1.35$ and $c'=2.6$. From the experimental values, Prasad, Perrin, and Samoc[3] derived $c'=3.2$.

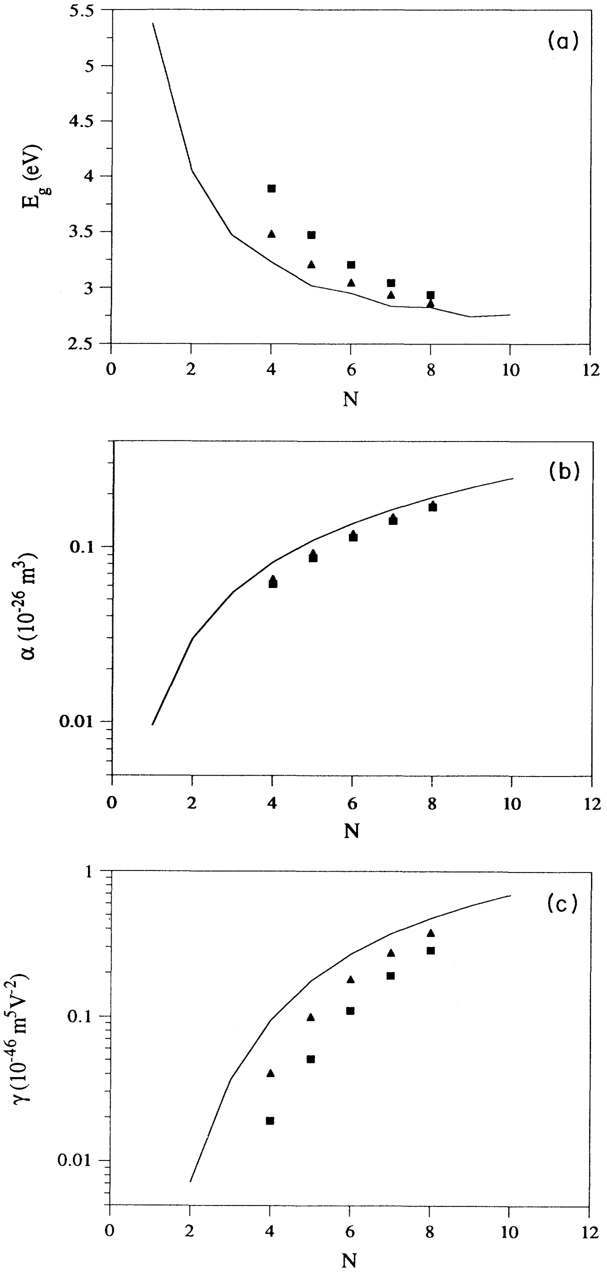

FIG. 4. (a) Optical band gap E_g (eV) vs the number of repeat units N for thiophene oligomers. (b) Polarizability α (m^3) vs the number of repeat units N. (c) Second hyperpolarizability γ (m^5 V^{-2}) vs the number of repeat units N. The height of the first (triangles) or second (squares) barrier is doubled in comparison with the *ideal* structure (plain line), i.e., 13.3 instead of 6.65 eV.

E. Final remark

As a final remark, we once again want to draw attention to the importance of π-electron delocalized states in the description of the optical response of conjugated polymers. Spano and Mukamel[37] calculated the second hyperpolarizability of an aggregate of two-level molecules with only nearest-neighbor dipole-dipole coupling. In the off-resonant regime, they obtained γ *proportional* to the number of molecules N in the aggregate. This is in clear contradiction with the theory and experiments discussed here.

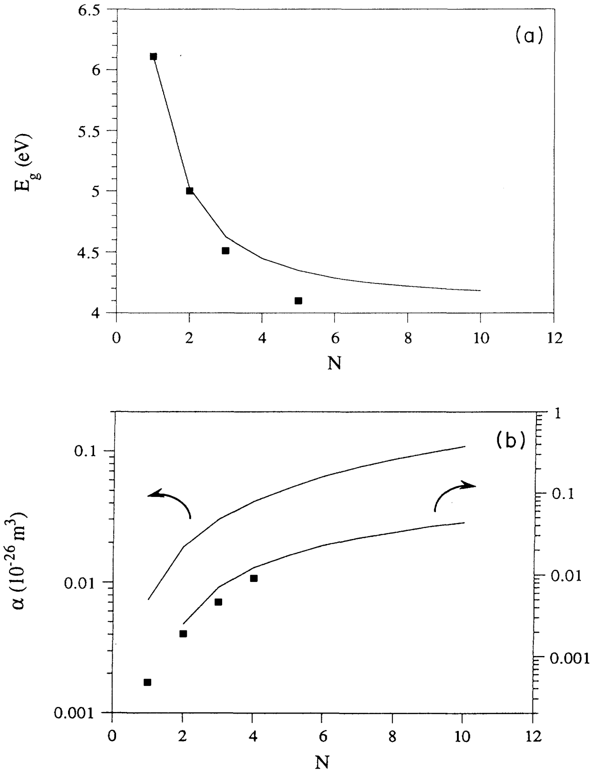

FIG. 5. (a) Optical band gap E_g (eV) vs the number of repeat units N for benzene oligomers. (b) Polarizability α (m^3) and second hyperpolarizability γ (m^5 V^{-2}) vs the number of repeat units N. Calculations: plain line; experimental values (Ref. 23): squares.

IV. CONCLUSION

In this paper, we have presented a quantum mechanically coupled anharmonic-oscillator model for the calculation of optical properties of conjugated polymers. By combining the classical Drude picture and the particle in a box treatment, we calculated the optical band gap for different polythiophene (and poly-*p*-phenylene) molecular lengths fitting the two model parameters to two band-gap measurements. They are in very good agreement with experiments. The calculated longitudinal polarizability and second hyperpolarizability tensor components are in fairly good agreement with the scarce available experimental data. A twist in the molecular backbone is modeled by a local increase of the potential-energy barrier between neighboring repeat units. The band gap is rather insensitive to this phenomenon, but α and γ can vary strongly. The reduction of their values depends on the location and magnitude of the increased barrier. This model can easily be extended in order to take into account the overall reaction of the π-electron cloud on the applied electric field. The calculated wave functions under the static electric field generate an electron density which induces a correction to the potential-energy well. Reiterating our calculations in this new potential well should yield a correction to the wave functions, the electric dipole, and, hence, the polarizability and second hyperpolarizability of the conjugated molecule.

In conclusion, we have found that a physically simple periodic structure of truncated anharmonic oscillators can give meaningful predictions about the linear and nonlinear optical properties of conjugated polymers from the measurements of the optical band gap of two oligomers with different length, without the need for supercomputing power. The model provides a clear picture of the combined effect of the anharmonicity of the monomer repeat unit, the effective π-electron delocalization, and the conformational effects influencing this delocalization. It is well suited for predicting length dependencies and limiting values of the nonlinear optical response. Hence, it can be a valuable tool for guiding synthesis efforts.

ACKNOWLEDGMENTS

Y.V., H.T., and I.V. gratefully acknowledge fruitful discussion with their colleagues P. Geerlings, M. Gielen, and especially B. Van Mele, who initiated the collaboration between their department and Philips Research Laboratories. Y.V. is particularly indebted to G. Vitrant (LEMO, Grenoble, France) and M. Kull for their interest in the problem and many valuable suggestions.

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