Rapid Communication

Effects of polarons on static polarizabilities and second order hyperpolarizabilities of conjugated polymers*

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According to the one-dimensional tight-binding Su–Schrieffer–Heeger model, we have investigated the effects of charged polarons on the static polarizability, α_{xx}, and the second order hyperpolarizabilities, γ_{xxxx}, of conjugated polymers. Our results are consistent qualitatively with previous *ab initio* and semi-empirical calculations. The origin of the universal growth is discussed using a local-view formalism that is based on the local atomic charge derivatives. Furthermore, combining the Su–Schrieffer–Heeger model and the extended Hubbard model, we have investigated systematically the effects of electron–electron interactions on α_{xx} and γ_{xxxx} of charged polymer chains. For a fixed value of the nearest-neighbour interaction V, the values of α_{xx} and γ_{xxxx} increase as the on-site Coulomb interaction U increases for $U < U_c$ and decrease with U for $U > U_c$, where U_c is a critical value of U at which the static polarizability or the second order hyperpolarizability reaches a maximal value of $\alpha_{\max}$ or $\gamma_{\max}$. It is found that the effect of the e–e interaction on the value of α_{xx} is dependent on the ratio between U and V for either a short or a long charged polymer. Whereas, that effect on the value of γ_{xxxx} is sensitive both to the ratio of U to V and to the size of the molecule.

Keywords: polaron, nonlinear optics, conjugated polymer

PACC: 7138, 4265, 7865T

1. Introduction

Much research has focused on the nonlinear optical (NLO) properties of conjugated organic and polymeric materials largely for the development of new optical devices.[1] The organic NLO effects originate from the microscopic nonlinear polarization, which is mainly enhanced by π-electron conjugation and characterized by the hyper-polarizability. The first order hyperpolarizability is the largest non-linearity, and it exists only for materials without inversion symmetry. The second order hyperpolarizability, on the other hand, can be detected in any material. The quest for theoretical methods that provide reasonable descriptions of the NLO response for such materials is not only academically interesting but also acutely required by new material research.

So far, a large number of *ab initio*[2−10] and semi-empirical calculations[11−22] have been performed to calculate the (hyper)polarizabilities of π-conjugated systems. From these studies one can note that the microscopic and the macroscopic NLO responses of polymer chains are sensitive to the nature and the length of the conjugated skeleton, the position and the nature of the donor/acceptor substituents, and the presence and the level of dopant charge defects. It has been generally accepted that charges on polymer chains, introduced by photo-excitation, chemical doping, or injection, can lead to a great enhancement of the (hyper)polarizability, and that some charged defects such as solitons and polarons induce negative values of second order hyperpolarizability (γ_{xxxx}) for short and even medium chains.[11,12,15] For short conjugated systems, most of the *ab initio* and semi-empirical methods, especially those that include

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higher order electron correlation effects, can estimate the (hyper)polarizability values in equal or even better accuracy than the experimental techniques.[23,24] In these systems, although the structural conformations of the charged polymer chain were regarded as solitonlike,[8] such solitonic structures were highly distorted due to the confinement by the chain ends. So it is desired to study extended-chain cases, where the solitonic structures are relatively free from finite chain effects and the converged physical properties can be obtained.[25]

It is well known that for conjugated polymers, the basic physical process is determined by both electron–lattice and electron–electron interactions. Recently, some studies have focused on the role that the electron–electron interactions play in the NLO response of polymers.[26−28] Results from different methods all confirm that the e–e interactions markedly influence the NLO response and other properties of polymers, which implies a guideline to optimize the NLO properties. Consequently, it is valuable to study the effects of the e–e interactions on the NLO responses, furthermore, to study the collective effects of the various factors, such as chain lengths, topological defects, and the e–e interactions, on the NLO properties of conjugated systems. We have found that such collective study is apparently rare in the literature. In the present article, we will investigate how the e–e interactions affect the NLO responses of both short and long charged polymers based on the combination of the one-dimensional tight-binding Su–Schrieffer–Heeger (SSH) model and the extended Hubbard model (EHM). It has been shown that the EHM and the unrestricted Hartree–Fock (UHF) approximation are good approximations if the electron–electron interactions are not too strong. Due to the important role that the polaron plays in determining the charge injection, optical and transport properties of conducting polymers, many efforts have been made to study its static and dynamical properties.[29−33] Here we also take polarons as an example to reveal the effect of topological defects on NLO responses. Besides, we will also discuss the structure-property relationship by a local-view formalism that is based on the local atomic charge derivatives in order to provide a conceptually simple, quantitative understanding of the results obtained.

2. Model and method

Regarding a conjugated polymer with a charged polaron as a finite chain of N CH groups with $N+1$ (or $N-1$) electrons in the π band, the total Hamiltonian is given as

$$H = H_{\rm SSH} + H_{\rm e-e} + H_{F_x}, \tag{1}$$

where $H_{\rm SSH}$ represents the electron–phonon coupling and the elastic energy,[34] and is expressed as

$$H_{\rm SSH} = -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n)](c^{\dagger}_{n+1,s}c_{n,s} + {\rm h.c.}) + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2. \tag{2}$$

Here, t_0 is the transfer integral between the nearest neighbour sites in the undimerized system, α is the electron–phonon coupling, $c^{\dagger}_{n,s}$ ($c_{n,s}$) is the creation (annihilation) operator of an electron with spin s at the n-th site, u_n is the displacement of the n-th CH unit, and K is the spring constant of σ-bond.

$H_{\rm e-e}$ gives the electron–electron interactions,[35] which is expressed in the Hartree–Fock approximation as

$$H_{\rm e-e} = \frac{U}{2}\sum_{n,s}\left(c^{\dagger}_{n,s}c_{n,s} - \frac{1}{2}\right)\left(c^{\dagger}_{n,-s}c_{n,-s} - \frac{1}{2}\right) + V\sum_{n,s,s'}\left(c^{\dagger}_{n,s}c_{n,s} - \frac{1}{2}\right) \times \left(c^{\dagger}_{n+1,s'}c_{n+1,s'} - \frac{1}{2}\right), \tag{3}$$

where U represents the on-site Coulomb interactions, and V the nearest-neighbour interactions.

Finally, H_{F_x} is the additional potential energy induced by the applying electric field F_x and given as

$$H_{F_x} = F_x\sum_{n,s}|e|\,[na + u_n]\left[c^{\dagger}_{n,s}c_{n,s} - \frac{1}{2}\right], \tag{4}$$

where e is the electron charge, and a the lattice constant. In the calculation, the parameters are those generally chosen for polyacetylene:[34] $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, and $a = 1.22$ Å (1 Å=0.1 nm).

In the Wannier representation the electron wave function can be expressed as

$$\psi^s_{\mu} = \sum_n z^s_{n,\mu}\,|n\rangle\,. \tag{5}$$

The electron wave function ψ^s_{μ} and the energy spectrum ε_{μ} can be obtained by solving the eigenequation

$$H\psi^s_{\mu} = \varepsilon_{\mu}\psi^s_{\mu}. \tag{6}$$

The total energy is

$$E\left[\{u_n\}\right] = \sum_{\mu,s}^{\text{occ.}} \varepsilon_\mu\left[\{u_n\}\right] + \frac{k}{2}\sum_n \left[u_{n+1} - u_n\right]^2. \quad (7)$$

The lattice distortion u_n is determined by minimizing the total energy

$$u_{n+1} - u_n = -\frac{2\alpha}{K}\left[\sum_{\mu,s}^{\text{occ.}} z^s_{n,\mu} z^s_{n+1,\mu} - \frac{1}{N}\sum_{n=1}^{N}\sum_{\mu,s}^{\text{occ.}} z^s_{n,\mu} z^s_{n+1,\mu}\right]. \quad (8)$$

The ψ_μ, ε_μ and u_n can be obtained by self-consistently solving the combined equations (6) and (8).

In the present work, the static polarizabilities α_{xx} and the second order hyperpolarizabilities γ_{xxxx} of finite polymer chains are calculated by using the finite-field procedure[36] which has been described clearly in one of our previous papers.[9]

3. Results and discussion

3.1. Static polarizability

We initially calculate the values of static polarizability, α_{xx} of polymer molecules including charged polaron defects with different lengths based only on the SSH model, i.e., with $U = V = 0$. In our calculations, the starting geometry of a finite polymer chain with a charged polaron is obtained by considering the doping of an electron into a half-filled system based on the computational method mentioned above. Due to the low-dimensional nature of the electronic and lattice structures, the ground state system undergoes Peierls distortion with nonlinear defects. Many properties of conjugated polymers have been considered to be related to these nonlinear localized defects. The situation is the same for hole doping because of the electron–hole symmetry in the present model.

Shown in Fig. 1 are the chain-length dependences of α_{xx} for finite neutral polymers and charged polymers with negative polarons represented by $C_{2n}H_{2n+2}$ and $C_{2n}H^-_{2n+2}$ respectively. For short and medium chains, the values of α_{xx} of the two species clearly present super linear growth with chain length increasing, and the growth rate of α_{xx} for charged chain is much larger than that for the neutral chain. This is caused by an increase of electron delocalization which is associated with smaller bond length alternation (BLA) induced by charge defect. For the longer chains, the chain-length dependent enhancements of α_{xx} for both the charged and the neutral polymeric chains become less and less pronounced.

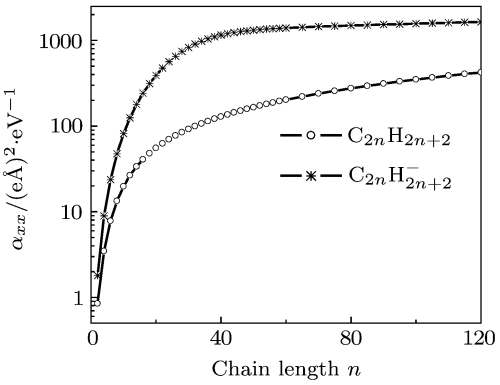


Fig. 1. Curves for static polarizability α_{xx} versus chain length n for $C_{2n}H^-_{2n+2}$ and $C_{2n}H_{2n+2}$.

The saturation of the chain-length dependent growth of α_{xx} for the two species is depicted in Fig. 2, where we plot the increment in α_{xx} due to the addition of a unit cell of C_2H_2 against the number of unit cells n contained in the molecule. The increment in α_{xx} for one additional unit cell is given by $\alpha_n - \alpha_{n-1}$, where α_n is the static polarizability of the polymers containing n repeat units. The horizontal asymptotes of the two species observed for large n indicate that the increment in α_{xx} due to an additional unit cell is a constant independent of the chain length. Therefore, the values of α_{xx} increasing with the chain length for the two species become linear for large n. Furthermore, because of the same asymptotic values for the two species, the increase of α_{xx} for long chains is not affected by the presence of the polaron, i.e., in the long chain limit, both the charged and the neutral polymer chains are expected to have the same dependences of the growth rate of α_{xx} on chain length. From the plots, we obtain a value of 3.79 $(\text{eÅ})^2/\text{eV}$ for $\alpha_n - \alpha_{n-1}$, which is equivalent to the static polarizability per unit cell, α_n/n, for an infinite chain. Meanwhile, it is obvious that the effect of the polaron simply amounts to a constant increment to α_{xx}. By comparing the values of α_{xx} of charged and neutral chains in the long-chain limit, we infer an approximate effective α_{xx} value of 1.2×10^3 $(\text{eÅ})^2/\text{eV}$ for a single charged polaron. The above results are consistent qualitatively with previous results[8–12,14,15] by *ab initio* and semi-empirical calculations.

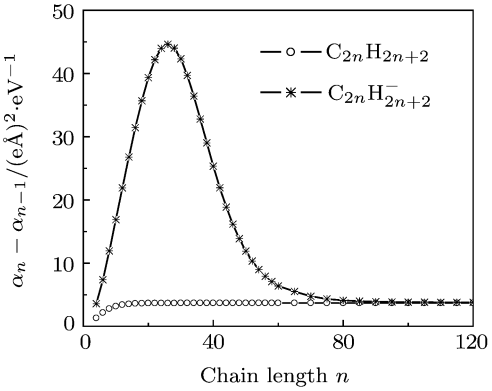


Fig. 2. Increments in α_{xx} due to one additional unit cell against the number of unit cells for $C_{2n}H^-_{2n+2}$ and $C_{2n}H_{2n+2}$.

In order to describe the effects of local variations, a local-view formalism was developed by Nakano *et al.*[14] and Geskin and Bredas.[37,38] In the view of the local-view formalism, the α_{xx} and γ_{xxxx} of a polymer molecule are approximated by a sum of contributions from individual partitioned point charges, which are conveniently taken to be the charges at the atomic sites:

$$\alpha_{xx} \approx \sum_i^{\text{atoms}} x_i \left.\frac{\partial q_i}{\partial F_x}\right|_{F_x=0} \equiv \sum_i^{\text{atoms}} x_i q_i^{(1)}, \quad (9)$$

$$\gamma_{xxxx} \approx \sum_i^{\text{atoms}} x_i \left.\frac{\partial^3 q_i}{\partial F_x^3}\right|_{Fx=0} = \sum_i^{\text{atoms}} x_i q_i^{(3)}, \quad (10)$$

where $x_i q_i^{(1)}$ and $x_i q_i^{(3)}$ are called the α-moment and γ-moment, and $q_i^{(1)}$and $q_i^{(3)}$ the α-charge and the γ-charge at the site i. The α-charge and the γ-charge are basically the first and third derivatives of the charge that is localized at an atomic site i with respect to applied electric field F_x. The distance x is along the long axis of the molecule. Figure 3 shows the α-charge profiles for charged and neutral long polymer chains with the chain-length being 140 carbon atoms. For the neutral molecule, the α-charge profiles within the central region of the chain are essentially flat, with the values at neighbouring sites being equal in magnitude but opposite in sign. For charged molecules with a polaron, the α-charge profiles within the central region of the chain are distorted due to the presence of the polaron, which causes contributions to α_{xx} from this region to increase. Meanwhile, the extent of the α-charge distortion induced by the polaron is limited to about 100 sites for long chains, and does not extend further with chain increasing. In the regions near the chain-ends, the α-charges for the charged and neutral cases are essentially identical at each site. Thus, in the α-charge picture, what happens as the molecule grows in length in the long-chain limit is that pairs of α-charge with equal magnitude and opposite sign are inserted anti-symmetrically into the flat region near the chain-end (such as I_1 and I_1', I_2 and I_2' in Fig. 3). The original α-charge profiles are pushed toward the ends without any change in shape. The increment in α_{xx} due to inserting pairs of α-charges is composed of two parts:[9] (a) the α-moments provided by the inserted pairs: the inserted α-charges I_1 (I_1') and I_2 (I_2') are +0.57 (–0.57) and –0.61 (+0.61) e^2Å/eV respectively, multiplied by their coordinate along the x direction; their net contribution is about 3.37 $(\text{eÅ})^2$/eV; (b) in the regions near the chain-ends, since the insertion of an additional pair translates the α-charge profile of each end outward, the increment in α_{xx} due to the contributions from sites in the regions near the chain-end is

$$\sum_i^{\text{end sites}} \Delta x q_i^{(1)} = \Delta x \sum_i^{\text{end sites}} q_i^{(1)}, \quad (11)$$

where Δx is the distance of translation of the α-charge profile, which is equal to half of the length of the x projection of a single bond and a double bond, i.e., 1.22 Å. The summation is over all the sites in the two end regions, which is 3.64 e^2Å/eV, so the contributions to α_{xx} from the two ends can be obtained to be 4.44 $(\text{eÅ})^2$/eV in total. Since the contributions of contributions (a) and (b) are independent of chain length, α_{xx} increases linearly with the chain length in the long-chain limit. Furthermore, the sum of the contributions (a) and (b) gives a net value of 7.82 $(\text{eÅ})^2$/eV for the insertion of two additional unit cells, i.e., 3.91 $(\text{eÅ})^2$/eV for $\alpha_n - \alpha_{n-1}$, which is remarkably close to the value of 3.79 $(\text{eÅ})^2$/eV from the finite-field calculation.

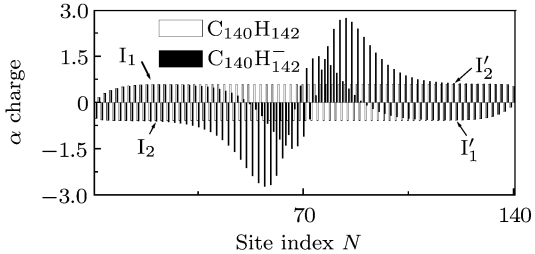


Fig. 3. The α-charge profiles for $C_{140}H^-_{142}$ and $C_{140}H_{142}$.

In the following, we will discuss the effect of e–e interaction on the α_{xx} of charged polymer with polaron by modifying the SSH model with the extended Hubbard model (EHM). To start with, we study the case of the simpler Hubbard model (HM), i.e., $V = 0$

in the EHM. Figure 4 shows that the value of α_{xx} for charged polymer varies with on-site Coulomb interactions U. One can see that both the Coulomb attraction ($U < 0$) and the repulsion ($U > 0$) reduce the α_{xx} of charged polymer, i.e., α_{xx} decreases monotonically with $|U|$ and reaches its maximum value at $U = 0$, from which we note that the on-site Coulomb interaction U weakens the response of the additional charge to external electric field.

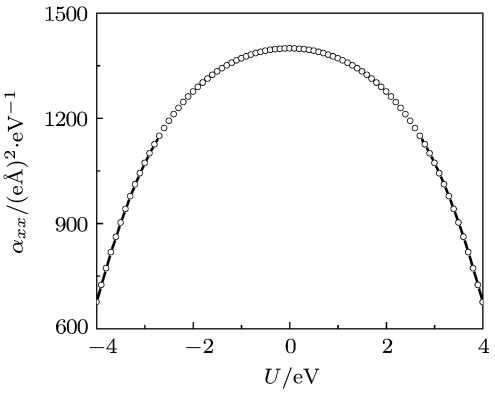


Fig. 4. Static polarizability α_{xx} as a function of U for charged polymer.

Next, we turn to consider both the on-site Coulomb interactions U and the nearest-neighbor interactions V, i.e., EHM. Only positive U and V are considered here because they are more relevant to real polymer materials. Figure 5 illuminates how the values of α_{xx} for long charged polymeric chains including 120 carbon atoms vary with U for several fixed values of V. It can be seen that the nearest-neighbour interaction V also reduces the α_{xx} of charged chain, and that for every fixed value of V, α_{xx} of the polymer chain increases as U increases from 0 to a critical value U_c, and reaches its maximum value $\alpha_{\max}$ at U_c. Beyond this point, α_{xx} decreases with U. These results indicate a competition between the on-site Coulomb interaction U and the nearest-neighbour interaction V, which means that they will counteract each other in the process of charge distribution. When $U < U_{\mathrm{c}}$, the nearest-neighbour interactions play a dominant role, the larger U weakens the tendency of V to reduce α_{xx}, and results in α_{xx} increasing with U. For $U > U_{\mathrm{c}}$, U plays a dominant role, and the larger U means a stronger reduction in α_{xx} for a fixed value of V. The result is that α_{xx} decreases with U. As a result, the value $U = U_{\mathrm{c}}$ is the position where U and V balance each other most effectively.

Meanwhile, the value of U_{c} presents a slowly and relatively decreasing trend with V increasing for a fixed chain. For example, for V=0.3, 0.7, 1.0, and 1.5 eV, the values of U_{c} are 2.40, 2.39, 2.35, and 2.27 times the value of V respectively for both the short and long chains, which shows that the effects of e–e interactions on α_{xx} of charged polymers are dependent only on the competition between U and V, i.e., the ratio between U and V, and are independent of the size of molecule.

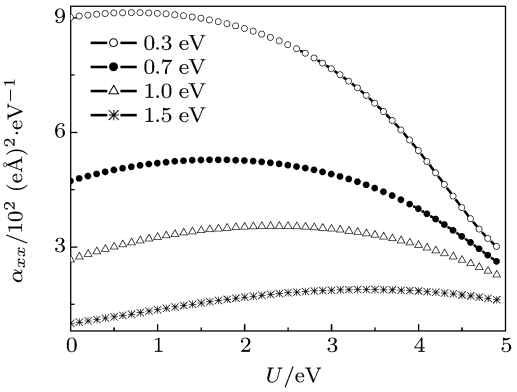


Fig. 5. Curves for static polarizability α_{xx} of charged polymer versus U for several fixed values of V in EHM.

3.2. Second order hyperpolarizability

Our numerical results show that the values of the second order hyperpolarizability γ_{xxxx} of charged polymers are also very sensitive to the presence of a polaron for the short and the medium chain-length cases, their long chain-length behaviours are essentially universal, like that of α_{xx}. We note that the γ_{xxxx} value of short chain (less than 6 carbon atoms) with a polaron is found to be negative in sign, like the case of a charged soliton. The above results are qualitatively consistent with previous results.[11,12,15]

Now we discuss the effects of e–e interactions on the values of γ_{xxxx} for charged polymeric chains. We also begin with considering the simpler Hubbard model (HM). Figure 6 shows the values of γ_{xxxx} for short (40 carbon atoms) and long (120 carbon atoms) chains with polarons as functions of on-site Coulomb interactions U separately. One can see that the on-site Coulomb interactions produce different effects on γ_{xxxx} for the short and the long chains. For a short chain, γ_{xxxx} increases with $|U|$ increasing from 0 to 3.4 eV and reaches its maximum value at $U = \pm 3.4$ eV. It then decreases with $|U|$ increasing. For a long chain, γ_{xxxx} decreases monotonically with $|U|$ and reaches its maximum value at $U = 0$.

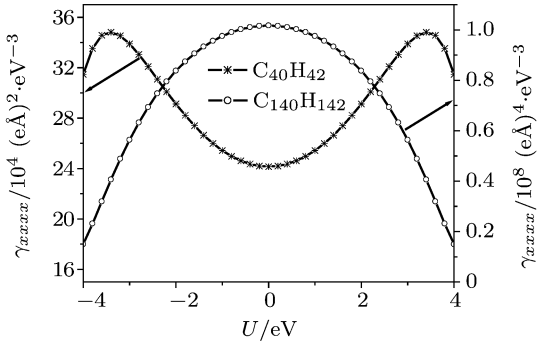


Fig. 6. Curves for the second order hyperpolarizability γ_{xxxx} versus U for charged chains.

Shown in Fig. 7 are the γ-charge profiles for short chains (40 carbon atoms) with polarons for $U = 0$, 3.3 and 4.0 eV. One can see that (a) the γ-charge distortions induced by the polaron occupy almost the whole chain, all γ-charge profiles can be divided into the abnormal polarization region within the central part of the chain, and the normal polarization regions on both outward sides of the abnormal polarization region; the former provides negative contributions for $U < 3.3 \sim 3.4$ eV, and positive ones for $U > 3.3 \sim 3.4$ eV, and the latter provides only positive contributions to γ_{xxxx}; (b) the existence of the abnormal polarization region is the origin of the negative values of γ_{xxxx} for a short chain with a polaron; (c) the on-site Coulomb interactions U reduce the values of the γ-charges in both the normal and the abnormal polarization regions, which decreases the absolute values of its negative contributions.

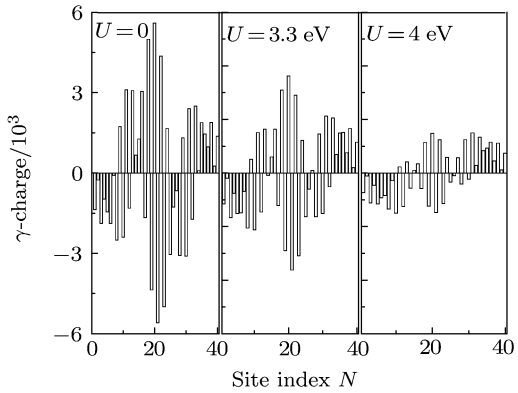


Fig. 7. The γ-charge profiles for short charged chains at different values of U.

For the case $U < 3.3 \sim 3.4$ eV, although the absolute values of the γ-charges of both the normal and the abnormal polarization regions decrease with U increasing, the absolute value of the decrement of the negative contribution from the abnormal polarization region is larger than that of the positive one from the normal polarization region. This results in γ_{xxxx} increasing with U. As for $U > 3.3 \sim 3.4$ eV, the effects of the abnormal polarization region on γ_{xxxx} become a smaller fraction due to the diminution of both its γ-charge values and its extent. The molecular second-order polarizability is mainly dependent on the variation of positive contribution from the normal polarization region and thus decreases with U.

For long chains the extent of abnormal polarization region is fixed and not affected by the increase of chain length. The positive contribution coming from the normal polarization region plays a dominant role while the negative contribution coming from abnormal polarization region accounts for only a small fraction and its effect may be neglected. Therefore, γ_{xxxx} decreases monotonically with U increasing. It is obvious that the different effects of U on γ_{xxxx} for short and the long chains are due to the existence of the abnormal polarization region, which means that the size of molecule plays an important role in the effect of e–e interaction on γ_{xxxx} of charged polymer.

Next, we turn to a consideration of both the on-site Coulomb interaction U and the nearest-neighbour interaction V. Figure 8 shows the values of γ_{xxxx} for short chain (40 carbon sites) as functions of U for several fixed values of V respectively. It can be seen that the nearest-neighbour interaction V also reduces γ_{xxxx} in polymer chain with polaron, and that, for each fixed value of V, γ_{xxxx} of the short chain increases with U increasing from 0 to a critical value U_c, and reaches its maximum value γ_{max} at U_c. It then decreases with U further increasing.

U_c for γ_{xxxx} also decreases relatively with V increasing for a fixed chain, which is similar to the case of static polarizability. For example, for $V = 0.3$, 0.7, 1.0, and 1.5 eV, the values of U_c are 10.3, 2.86, 2.4, 2.33 times the value of V for short chains (40 sites). We note that as V increases, the value of U_c's for either α_{xx} or γ_{xxxx} approaches $U = 2V$ where the ground state system undergoes a quantum phase transition between the charge-density-wave (CDW) for $U < 2V$ and the spin-density-wave (SDW) for $U > 2V$. The deviation of U_c's from the normal transition boundary is due to the electronic and lattice structure distortions induced by charged defects.

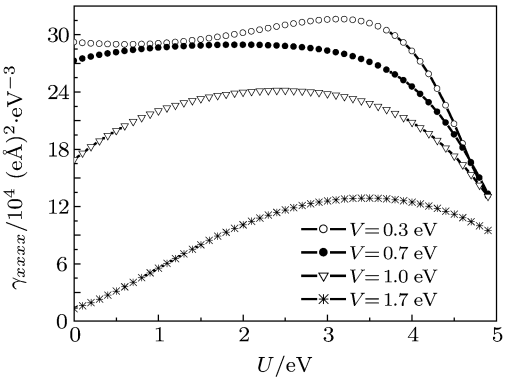


Fig. 8. Curves for the second order hyperpolarizability γ_{xxxx} of short charged chain versus U at several fixed values of V in EHM.

It should also be noted that U_c for γ_{xxxx} of long chains is smaller than that of the short chain for a fixed V. For example, for $V = 1$ eV, its U_c is 2.43, 2.38 and 2.37 times the value of V when the chain length is 40, 80 and 120 carbon sites respectively. In the long chain limit, U_c for γ_{xxxx} also approaches $2V$, i.e., $U = 2V$, which indicates that the effect of e–e interaction on γ_{xxxx} of polymer with polaron is dependent on the size of molecule. It is easy to see that with the chain length increasing, the region having distortions becomes a smaller and smaller fraction of the overall chain, and the deviation of U_c from the transition boundary becomes less and less pronounced.

As a result, the effect of e–e interaction on γ_{xxxx} of polymers with polarons is sensitive to both the ratios between U and V and the size of the molecule. Our results indicate the feasibility of optimizing the static polarizability and the second order hyperpolarizability of polymer by tuning the e–e interaction. In principle, polyenes consisting of different atoms may possess different correlation strengths.

4. Summary

Although both α_{xx} and γ_{xxxx} are very sensitive to the presence of a charged polaron for short and medium chain lengths, their long chain-length behaviours are essentially universal for both the neutral and the charged chains. Furthermore, for every fixed value of V, α_{xx} and γ_{xxxx} for polymer chains with polarons increase with U increasing for $U < U_c$ and decrease with U increasing for $U > U_c$. Here U_c is a critical value of U at which the largest static polarizability α_{max} or the largest second order hyperpolarizability γ_{max} occurs. Both U and V reduce the α_{xx} and γ_{xxxx} values of polymers with polarons, their collective actions on α_{xx} and γ_{xxxx} are dependent on their relative sizes because of the competition between them. Additionally, the effects of electron–electron interaction on the γ_{xxxx} of polymers with polarons is also sensitive to the molecular size. The theoretical results are expected to provide useful guidance in optimizing α_{xx} and γ_{xxxx} of polymers by tuning the e–e interactions.

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