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Origin of the 0.89 eV peak in $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of polyacetylene: Electron correlation effects

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The third-order optical susceptibility $\chi^{(3)}$ of polyacetylene is calculated by the Lanczos-based density-matrix renormalization group. The theoretical results now remarkably agree with two different sets of experimental data: both the positions of two major peaks and their relative intensities. The 0.89 eV peak, originally assigned to a two-photon resonance, is actually a three-photon resonance due to the nB_u state. This state lies above the band-edge state jB_u which itself accounts for a hidden hump on the right shoulder of the 0.6 eV peak. The electron correlation effect is the main origin of these rich features.

Nearly a decade ago, Fann *et al.*[1] measured the whole spectrum of the third-order optical susceptibility $\chi^{(3)}$ in *trans*-polyacetylene (PA). Two distinctive peaks at 0.6 and 0.89 eV were identified. The 0.6 eV peak was quickly assigned to the three-photon resonance as the gap E_g in PA is around 2.0 eV. However, the assignment of the 0.89 eV peak has been controversial. An early attempt was to attribute it to a two-photon resonance, as suggested by the peak position.[2] A noninteracting theory[3] did show a cusp around 0.89 eV, which seemingly supported the above assignment, but later it was proved to be an artifact of the zero damping. Wu and Sun[4] deliberately demonstrated that the cusp cannot survive a small damping. Its amplitude is too small, at least one order of magnitude smaller than the experimental data. Yu *et al.*[5] did not even observe the so-called ''two-photon'' resonance peak for a reasonably long chain. From the symmetry consideration, such assignment is even more questionable since this transition is precisely forbidden unless one assumes a two-photon state near the band edge. Other mechanisms, such as the conjugation length effect,[4] special damping factors,[6] lattice fluctuation,[7] and interchain coupling effect,[8] have been proposed, but their relative roles are less clear. The correlated-electron calculations in small polyenes[9,10] improved theoretical results, but they are not fully consistent with the experimental observation in both the peak positions and the relative ratio of the intensities. In particular, one has to worry about the finite-size effect in these calculations. Up to now, this issue has not been resolved completely[9–11] though better experimental measurements are available.[12] It is our present aim to explain the $\chi^{(3)}$ spectrum and finally settle on the origin of the 0.89 eV peak.

In this paper, we do not invoke the interchain coupling nor other special mechanisms, but only employ a generic correlated model with the common parameters of PA to demonstrate in a long chain that the theoretical spectrum, both peak positions and relative intensities, is in remarkable agreement with two different sets of experimental data[1,12] within the experimental errors. Our results clearly show that the 0.89 eV peak is not a two-photon resonance as speculated by the earlier studies,[1–3] nor the resonance of the band-edge state and mA_g state conjectured by the finite-cluster calculations,[9,10] but a three-photon resonance due to the nB_u state. This nB_u state lies above the band-edge state jB_u and can survive in the long chain limit and in the presence of a finite damping. The jB_u is responsible for a hidden hump on the right shoulder of the 0.6 eV peak. This rationalizes the exciton binding energy. The electron correlation is the main reason for these rich features.

We begin with the generic Peierls-extended Hubbard model,[10,13]

$$\hat{H}=-t\sum_{i,\sigma}\,[1+(-1)^i\delta](c^{\dagger}_{i+1,\sigma}c_{i,\sigma}+\text{H.c.})+U\sum_i\, n_{i\uparrow}n_{i\downarrow}+V\sum_i\, n_i n_{i+1}, \tag{1}$$

where all the operators have their usual meanings. Hereafter, the on-site and intersite electron interactions U and V are in units of the hopping integral t which is chosen to be 1. We only use a generic set of parameters for PA, namely, the dimerization $\delta=0.07$, $U=4$ and the ratio $V/U=0.4$.[14] There is no additional parameter which can be adjusted in our well-defined model. The half-filling case is considered. The numerical calculation is done with the Lanczos-based density-matrix renormalization group method[15] (LDMRG) until the results are well-converged.[16] 220 eigenstates of density matrices are kept in each block with the truncation error less than 10^{-9} and the relative error around 10^{-2}.[17] The essence of the LDMRG success is that the scheme skips over numerous intruder states and avoids the targeting catastrophe.[18] The technical details can be found in Ref. 15. Our results will be compared with two different sets of experimental data.[1,12] This constitutes an objective and challenging check of the model and parameters used since we have no additional parameters to tune. As one will see soon, the LDMRG scheme indeed gives a very accurate spectrum.

To have some flavor of our results, in Fig. 1 we plot the calculated $\chi^{(3)}$ spectrum for PA, together with the experimental data taken from Ref. 1 (see filled boxes and error bars), where the linear absorption is shown in the inset. For clarity, as usual, the whole spectrum is illustrated as a function of Z: $Z\equiv\hbar\omega/E(1B_u)$, where $\hbar$ is Planck's constant over 2π, ω is the incident photon frequency (fundamental), and $E(1B_u)$ is the $1B_u$ state energy.[19] A damping factor of 0.05t is used in the spectrum. Since we are only interested in the relative ratio of peak intensities, we rescale the theoretical

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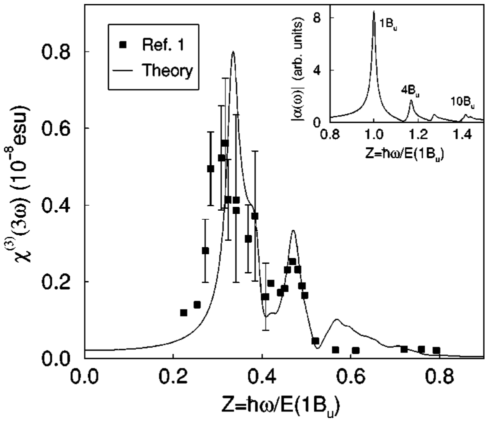

FIG. 1. Dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in polyacetylene. The solid curve refers to the theoretical results. The filled boxes with error bars are the experimental data from Ref. 1. A remarkable agreement is reached between theory and experiment. In the inset is the linear absorption spectrum.

amplitudes in order to make an easy comparison with the experimental data. Figure 1 demonstrates a noticeable agreement between the theoretical and experimental results. For example, on the low-energy side, though the experimental error bars are quite large, the theoretical curve exhibits a correct tendency as indicated by the experimental data points. There are two main peaks plus a small peak in the theoretical spectrum and no additional peak exists below the optical gap, which is in line with the experimental observation. Fann *et al.*[1] noted that no other structure of comparable intensity and width appears in the energy range extending down to 1/4 of the optical gap. The intensity ratio between two major peaks is 2.4 as compared to the experimental ratio 2.3 (0.6/0.26). The positions of two peaks are at $Z=0.33$ and $Z=0.47$, which can be compared to the experimental values at $Z=0.32$ and $Z=0.47$, respectively.

The good accordance with the experimental results is not only at these two peaks, but also in other regions. For instance, in the area with $Z\geqslant 0.4$, our theoretical curve closely follows the experimental points. In particular, two valleys around $Z=0.41$ and 0.53 are correctly reproduced; a nearly symmetrical structure of the second peak is also observed in the theoretical curve. In addition, the experimental data on the right-shoulder of the main peak suggest a possible hump, which now can be seen clearly in our theoretical curve. Actually, this hidden hump had already appeared experimentally in an oriented PA sample,[12] but did not attract much attention. In Fig. 2, we made another direct comparison with the experimental data by Halvorson *et al.*[12] One can notice that the hump almost precisely appears at the theoretically predicted location. Note that this hump has an important consequence as soon seen. The relative intensity between two major peaks and their respective positions are again in keeping with the theoretical results. The theoretical curve on the high-energy side also correctly reproduces the experimental trend (see Fig. 2). Probably due to the disorders,[12] such small structures were smeared out in Ref. 1 (see Fig. 1). In view of experimental uncertainties and numerical truncation errors, such good consistency between theory and experiment is remarkable. The most important thing here is that we do not have any adjustable parameters to fit the experimental data, which gives one an objective and unbiased comparison.

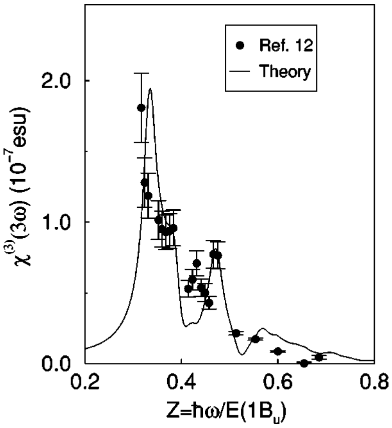

FIG. 2. A comparison with another experimental set of data (filled circles) from Ref. 12 on an oriented PA sample. A clearer agreement between theory and experiment is found around the hump on the right shoulder of the main peak. The second peak is also consistent with the theoretical prediction. On the high-energy side, the theoretical curve correctly reproduces the experimental tendency.

In the following, we begin to pinpoint the origins of these peaks one by one. Analogously, the biggest peak is also attributed to a three-photon resonance due to the $1B_u$ state. One naive way to check this is to see whether the peak lies at one-third of the $1B_u$ peak energy in the linear absorption spectrum (see the inset of Fig. 1). However, as noted by McWilliams *et al.*,[20] such assignment simply from energy resonances without regard to intensities is extremely risky, when the states are congested. A more rigorous way is to isolate different contributions explicitly, which could be difficult to do experimentally, but is easy to achieve theoretically. When we exclude the contribution from the $1B_u$ state while keeping the rest intact, the peak disappears; otherwise, the peak is always there. This proves that the peak indeed corresponds to the three-photon transition of the $1B_u$ state.

As aforementioned, there is a hump on the right shoulder of the main peak in both the theoretical and experimental curves. We find that this hump is a three-photon resonance due to the jB_u (here $j=4$) which lies above the $1B_u$. To see it clearly, states with large transition moments are schematically shown in Fig. 3. The odd-parity states are represented by short lines, while the even-parity ones by long lines. The $1A_g$ is the ground state. The first dipole-allowed excited state is $1B_u$. Some dominant excitation channels are marked with double-arrow lines. The greatest significance of the jB_u is that it is a conduction-band edge state, from which the continuum starts. We can prove this by the standard scheme of Ref. 10. Namely, through the $1B_u$, we first locate the mA_g ($m=42$ in the present case) by looking for states with the maximal transition-matrix element. Likewise, starting from the mA_g, we search for the band-edge state. Through this procedure, we can unequivocally identify that the jB_u is such state. It is not surprising that due to the finite and realistic U and V, the continuum is naturally overlapped with the exciton states, which is also observed experimentally.[21] Its direct consequence is that besides the band-edge state, other states can survive in the long chain limit, an essential point for

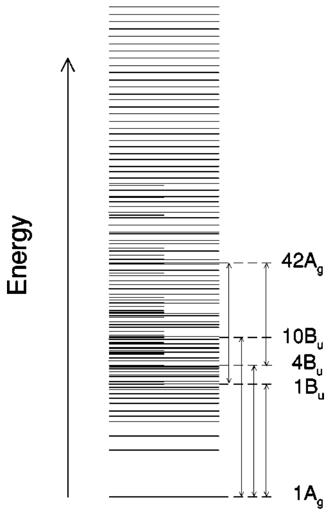

FIG. 3. Energy spectrum. Only optically relevant states are displayed. The long lines denote A_g states while the short ones B_u states. The ground state is $1A_g$. The continuum band starts from the $4B_u$ state. Some dominant excitation channels are shown in double-arrow lines.

understanding the $\chi^{(3)}$ spectrum, which was not clear in the finite-size calculations[9,10] since artificially large U and V pushed this band-edge state up to the very high energy side and its corresponding peak was then interpreted as the *partial* ''second peak'' of $\chi^{(3)}$. Doing so, one faces a surprisingly large exciton-binding energy in PA, on the order of ~ 1 eV,[22] which cannot be easily explained within existing theories. It is clear now that the band-edge state does not account for the second peak, but for the hump or the continuum. This yields a reasonable exciton-binding energy $\sim 0.2-0.3$ eV, in agreement with the experimental estimation.[23]

Of course, the most difficult task is the assignment of the second peak in Figs. 1 or 2. The peak energy is roughly at 2/3 of the optical gap, which misled one to ascribe it to the ''two-photon'' absorption. Here we demonstrate that this is not the case. First, we turn off the $1B_u$ contribution while keeping the rest unchanged and find that the second peak is still there, which indicates that the $1B_u$ is not responsible for the second peak. Contrary to the early speculation,[1–3] there is no such two-photon state with a large transition element in the vicinity of the $1B_u$, which is also the reason why the $1B_u$ does not account for the second peak. In particular, in analogy to the finding in a short chain,[10] the $2A_g$ has nearly no effect on the spectrum at all. However, if we eliminate the nB_u contribution (in the present case, $n=10$, see Fig. 3) while retaining the components of the $1B_u$ and other states, the peak disappears. This crosscheck establishes that the second peak results from the nB_u, not from the $1B_u$ or mA_g as originally believed. This assignment can be further justified by its location. The second peak energy in Fig. 1 is accurately at one-third ($=0.47/1.41$) of the $10B_u$ energy (see the inset). This concludes that the second peak is due to the three-photon resonance of the $10B_u$ state. Note that for the same reason (see above), such nB_u was not obvious in the previous finite-cluster calculation.

From Fig. 3, one sees that the $10B_u$ is above the band-edge state $4B_u$ and its linear absorption peak appears near the end of the spectrum (see the inset of Fig. 1). Although it has a quite large transition-matrix element to the ground state (about one-third of that associated with the $1B_u$ state), the high-energy excitation reduces its amplitude greatly. However, due to the three-photon process, the $10B_u$ contribution (the second peak) is much more highlighted in the $\chi^{(3)}$ spectrum. Importantly, in contrast to the noninteracting case, the second peak is genuine;[16] it can survive a finite damping factor and a chain elongation, which can be verified by the gradual increase of the transition-matrix element, an evidence which is not easily revealed from a small-cluster calculation. Specifically, we find that the intensity of the second peak is increased about 1.6 times as one goes from $N=30$ to 40. Such persistence of the increment ensures that even in a much longer chain, the nB_u state and subsequently the second peak still can be observed. Now comparing with the previous noninteracting results,[5] one can tell an important role of the electron correlation in the $\chi^{(3)}$. Previously, it was known that the electron correlation rectifies the relative ordering between the $1B_u$ and $2A_g$ states while a noninteracting model always predicts the opposite to the experimental observation in PA.[24] Spectrally, we know that the electron interaction does not favor a single peak and always tries to ''split'' a peak into several small ones. Its unique role here is that it pushes states, in particular, the nB_u state to the high-energy side and enhances its intensity to be visible in the nonlinear optical spectrum. Having observed the failure of the noninteracting theory and the success of the correlated theory to reproduce the experimental results such as (1) the profile of the $\chi^{(3)}$ spectrum, (2) the major peak positions, (3) their relative intensities, (4) the continuum-band edge or the hump, and (5) the reasonable exciton-binding energy, together with the correct ordering of $1B_u$ and $2A_g$ states, we have a good reason to believe that the 0.89 eV peak, among others, manifests the importance of the electron-correlation effect in polyacetylene.

In conclusion, we have employed the LDMRG method to accurately calculate the $\chi^{(3)}$spectrum in polyacetylene. A remarkable agreement is found between two different experimental data and our theoretical results: both the positions of two major peaks and their relative intensities. We locate a hidden hump on the right shoulder of 0.6 eV peak, which stems from the continuum-band-edge state jB_u. This gives a reasonable binding energy. Our results shed light on the origin of the 0.89 eV peak. It is unambiguously shown that this peak is a three-photon resonance due to the nB_u state, not a two-photon resonance as originally assigned. Comparing with the noninteracting results, we suggest that the appearance of the 0.89 eV peak is another manifestation of the electron correlation effect in polyacetylene. Our conclusion is made on the generic correlated model Hamiltonian with the generic parameters in a long chain without invoking other mechanisms or assumptions. Thus, this appears to be a most natural explanation of the physical origin of the 0.89 eV peak of the $\chi^{(3)}$in polyacetylene.

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[16] We have carefully checked and compared the whole spectra as the chain length increases. For example, from $N=30$ to 40, no clear change of the spectrum can be detected and both energies and transition elements are well converged. The susceptibility gradually exhibits a linear dependence on the system size, an evidence of saturation. The finite-size effect is negligible if any. All the results are presented for $N=40$.

[17] We estimated it (a) at $U=V=0$ and (b) by keeping different number of states of density matrices. The experimental error is never smaller than this.

[18] Shuai *et al.* [J. Chem. Phys. **109**, 2549 (1998)] performed a similar calculation, but they did not investigate the origin of the 0.89 eV peak nor compare theory with experiment. They only trusted their results up to 20 sites. As we pointed out recently [G. P. Zhang, Phys. Rev. B **60**, 11 482 (1999)], several technical difficulties associated with the usual DMRG method prevented them from going further. Within the LDMRG, not only the results are more accurate, but also the system size can be much larger. We can calculate the system size up to 40 sites and make a detailed comparison with experimental results. The big merit of LDMRG is also exemplified by a recent paper [Chandross *et al.*, Phys. Rev. B **59**, 4822 (1999)].

[19] Experimentally, the optical gap E_g is roughly around 2 eV, but here we need a more precise value since we are making a quantitative and accurate comparison. E_g or $E(1B_u)$ that Ref. 1 used is 1.8 eV as they quoted the reference [D. Moses *et al.*, Phys. Rev. B **26**, 3361 (1982)]. However, these latter authors were more careful to conclude that their $E_g \sim 1.7-1.8$ eV with uncertainty limited by the model. In an earlier paper reported by the same latter group [N. Suzuki *et al.*, Phys. Rev. Lett. **45**, 1209 (1984)], E_g is 1.4 eV. Thus there is some arbitrariness. Maybe a more accurate and easy way is simply to use the peak energy of the absorption band since both experimentally and theoretically the peak is unique and well-defined. Experiments [see the above reference and C. R. Fincher *et al.*, Phys. Rev. B **20**, 1589 (1979)] showed that $E(1B_u)=1.90\pm0.05$ eV. In the present model, the theoretical $E(1B_u)$ is 1.386 t.

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[23] Based on the implicit assumption of the weak correlation, Fincher *et al.* [Phys. Rev. B **20**, 1589 (1979)] estimated the binding energy about 0.1 eV, which can be considered as a lower bound. The upper bound must be smaller than the binding energy in polydiacetylene, 0.5 eV.

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