

## Impurity clustering in doped polyacetylene

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We use an augmented Su-Schrieffer-Heeger model to study the changes that occur in polyacetylene in the low-doping regime as doping concentration is increased. The lowest-energy configurations are found to be those for which the impurities are clustered together. The clustering results from the net interaction between impurity atoms and pinned solitons. Clustering explains the doping-induced shifts observed in the infrared spectrum of iodine-doped samples. Infrared results for widely spaced impurities are in marked contrast with experiment.

An enormous amount of theoretical effort has been devoted to understanding the properties of doped polyacetylene,<sup>1</sup> but few investigators have explicitly included the effects of the dopant ions in their calculations. Experimentally, it is established that at low dopant concentrations, the impurities can be treated as being randomly distributed<sup>2</sup> and thus, models that assume one defect per chain and account for the impurity in a phenomenological way can adequately account for the data. Experiments, however, have shown that above  $\sim 0.5\%$  dopant concentration<sup>2</sup> the model of randomly distributed dopant ions no longer holds, and, in particular, x-ray studies of highly oriented samples suggest that acceptors form intercalated structures where columns of dopant ions displace  $(\text{CH})_x$  columns within the polymer planes,<sup>3,4</sup> while donors form channel structures along the chain direction.<sup>4,5</sup>

The above remarks make it clear that at dopant levels above about 0.5%, it is crucial to explicitly include the effects of the dopant ions, and, in almost all cases, to go beyond the model of randomly distributed dopants. It has been suggested that the strain energy plays an important role for the acceptors because of their large size.<sup>3</sup> However, as a first step towards understanding the formation of these structures, we have chosen to consider a single chain of  $(\text{CH})_x$  with multiple adjacent impurities. We do not restrict the impurities to any particular configuration, but adjust their separation so as to minimize the total adiabatic energy. In this regard we note that the reversibility of electrochemical doping implies easy mobility of the dopants, suggesting that the dopants may sit in their lowest-energy configurations. Although we neglect the specific structure of any particular dopant, we recall that the universal features of both the optical and infrared spectra imply that the added or deleted charge is an intrinsic property of the  $(\text{CH})_x$  chain, and thus, we choose to concentrate our efforts on the universal role that all dopants play, i.e., that of a Coulomb-pinning center.

Our model consists of the Su-Schrieffer-Heeger<sup>6</sup> (SSH) Hamiltonian augmented by an on-site Hubbard term treated in mean-field theory plus three terms that include the effect of the dopants treated as simple Coulomb

charges: the electron-dopant interaction, the dopant-lattice interaction, and the dopant-dopant interaction.<sup>7</sup> The program is to numerically solve for the self-consistent electronic-lattice ground state<sup>8</sup> for a given configuration of dopants and to then find that configuration which minimizes the system energy. To allow for different azimuthal positions of the impurities relative to the chain, we treat each impurity as a ring of positive charge with radius of 2 Å centered on the chain axis [the distance between  $(\text{CH})_x$  chains is known to be  $\sim 4$  Å]. The results presented are for chains with 100 sites and an even number of impurities, each of which is assumed to donate one electron to the chain.

The result of our numerical studies is that the lowest-energy solutions are those for which the impurities are clustered together with nearest-neighbor separation of 6–9 lattice constants depending on the strength of the on-site Hubbard term and the number of impurities present. The clustering persists for all values of the Hubbard on-site energy for which the mean-field theory converges and gives a lowering of the energy on the order of 0.1 eV relative to a configuration of widely separated impurities. For the remainder of the paper, we will be making comparisons between results obtained for the lowest-energy configuration and that for a typical configuration of widely separated impurities, which we choose to be one in which the impurities are equally spaced and centered on the chain so that the distance between either end and the nearest impurity is as close to the impurity-impurity separation as possible. We term this configuration *uniform*. Specifically, we find that in the absence of the Hubbard term the clustered configuration is lower in energy than the uniform one by 0.08 eV for 2% doping and 0.28 eV for 4% doping. With a Hubbard on-site energy of 4 eV we find that the clustered configuration is lower in energy than the uniform one by 0.06 eV for 2% doping and 0.18 eV for 4% doping. Since we consider chains with 100 sites, doping of 2% means two or four impurities, and thus, two or four electrons added to a chain. It may not be realistic to compare results of a single-chain model at a certain concentration of dopants with experimental results at the same concentration, since for any given average concentration there may

be regions of higher and lower concentration in the material, as well as chains of different length. Nevertheless, these results are suggestive of qualitative behavior that occurs as the dopant concentration is varied.

That clustering of impurities is the energetically favorable state is easy to understand within the context of our model. For simplicity, assume we just have two impurities which then create two charged solitons, each adjacent to one of the impurities. There are then six terms describing the Coulomb energy of such a state: the binding of each of the solitons to its impurity, the binding of each to its neighbor's impurity, the impurity-impurity repulsion, and the soliton-soliton repulsion. Note, however, that in the on-site Hubbard model, the soliton-soliton repulsion depends only on the extent to which the charge densities overlap. As the impurities approach, the impurity-impurity repulsion increases by roughly the same amount as the binding of each soliton to its neighboring impurity; thus, the net effect from these terms is a lowering of the energy. The system then favors clustering in the on-site Hubbard model as long as the charge-density overlap is not substantial. The use of the Hubbard interaction is considered justified because it accounts in a phenomenological way for on-chain screening of the electron-electron interaction. The off-chain interactions are reduced by the background dielectric constant, but are still long ranged.

Although clustering is clear in a mean-field on-site Hubbard model, it is not certain that such a model is sufficient for the ground-state properties of doped  $(\text{CH})_x$ . Previous work has shown that such a model gives a good description of the low-lying excited states of lightly doped  $(\text{CH})_x$ .<sup>9,10</sup> The question of how to properly treat the electron-electron interactions in  $(\text{CH})_x$  has been the subject of numerous investigations and seems, as yet, unsettled. In this paper, however, we are primarily interested in the linear response in the infrared as a function of impurity configuration, and thus, for a given configuration, we expect our model to give reasonable results. Whether or not clustering is energetically favorable in the real system cannot be decided with certainty on the basis of our model, although we will see that clustering provides a simple explanation of some aspects of the infrared data of iodine-doped samples.

Having studied the ground-state properties, let us now examine the linear response of this state to infrared radiation as we vary the dopant concentration and configuration. At low dopant concentrations ( $\lesssim 1\%$ ), the structure in the infrared consists of three peaks<sup>11,12</sup> at 900, 1260, and 1370  $\text{cm}^{-1}$  which are absent in undoped samples. For samples doped with iodine, the energy of both the lowest- (900  $\text{cm}^{-1}$ ) and highest- (1370  $\text{cm}^{-1}$ ) energy peaks decreases continuously with increased doping for concentrations in the range of  $\sim 1\%$  to  $\sim 5\%$  with the lowest-energy peak dropping in energy<sup>13</sup>  $\sim 100 \text{ cm}^{-1}$  and the highest-energy peak dropping<sup>14</sup> only  $\sim 10 \text{ cm}^{-1}$  in this range. At a dopant concentration of  $\sim 5\%$  there is a sharp decrease in the energy of both the low- and high-energy peaks<sup>13,14</sup> which has been attributed to the additional screening indicative of a transition to a metallic phase. Our aim in this paper is to understand the sub-

stantial decrease in energy of the low-energy peak below the transition, and thus, we expect the same model that is appropriate to the low-concentration regime to provide a good description of the infrared activity up to the transition. In this regard, recall that the peaks in the low-concentration regime have been successfully accounted for theoretically by attributing them to phonon modes that become infrared active in the presence of a single charged soliton created in the doping process.<sup>10,15,16</sup> In particular the lowest-energy peak is attributed to the translation mode of the localized charge and is the finite-frequency analog of a zero-frequency Goldstone mode.

To calculate the infrared response, one notes that the radiation couples much more strongly to the electrons than to the lattice because of the large mass difference. Thus the lowest-order coupling to the lattice is indirect through virtual electron-hole pairs, and, in the absence of the Hubbard term, it is found by evaluating the real part of the conductivity diagram shown in Fig. 1. In the presence of the Hubbard term the bare electron-hole bubbles become dressed by the on-site mean-field interaction.<sup>10</sup> To calculate the phonon modes, we allow a single degree of freedom for each lattice ion which is sufficient for understanding the lowest-energy peak.<sup>7</sup> We then follow the standard procedure of expanding the adiabatic energy to second order in small lattice displacements, and then, diagonalize the bilinear piece to obtain the phonon spectrum.

The results of our calculations are shown in Fig. 2. For the sake of brevity we have only shown the results for on-site Hubbard strength of 4 eV (the value that is in best agreement with low-concentration results) although the qualitative behavior is the same for all values used. Figure 2(a) shows the real part of the conductivity versus the wave number for the *uniform* dopant configuration, and Fig. 2(b) shows the conductivity for the lowest-energy configuration. The dashed line is for 2% doping, the dotted line for 4%, and we have included results for a single impurity adjacent to a 99-site chain (solid line) so that the spectra in the presence of multiple impurities can be compared to that for a single impurity. The dominant peak in each of the spectra can easily be identified with the translation mode of the soliton by examining the phonon spectrum and correlating it with the energy of the peak. Thus, it is clear that the clustered configurations are in qualitative agreement with the experimental results, whereas *uniform* configurations representing widely separated dopants are in marked contrast to those results. Upon closer examination of many configurations one finds behavior similar to the *uniform* configuration as



FIG. 1. Conductivity diagram for the infrared response. The bubbles represent virtual electron-hole pairs, and the wavy line is a real phonon.

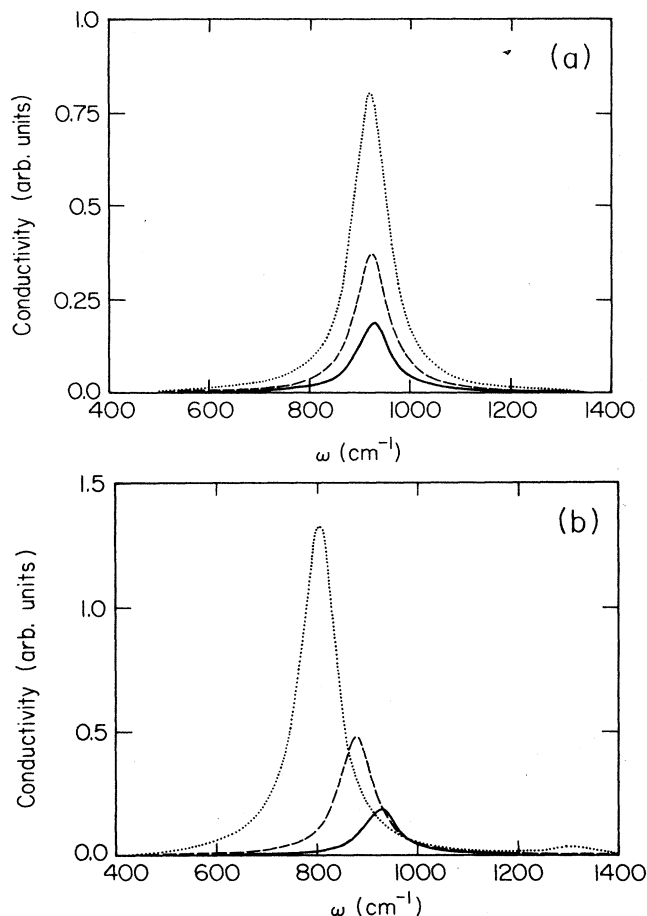


FIG. 2. Real part of the infrared conductivity (in arbitrary units) vs wave number for (a) the *uniform* configurations and (b) the lowest-energy configurations (clustered). The solid line in each figure is for a single impurity adjacent to a 99-site chain, the dashed line is for 2% doping, and the dotted line is for 4% doping.

long as the nearest-neighbor dopant separation is larger than the soliton width of  $\sim 12$  lattice constants, i.e., in that case the solitons hardly overlap and they behave as if each is sitting in an independent potential well almost

identical to that of a single soliton with a single dopant. This simple picture is further supported by the fact that the energy of the peak for the *uniform* configurations is almost identical to that for a single soliton and single dopant ion as shown in Fig. 2(a). In this regard we note that the spectra for the uniform configurations will resemble that for the clustered ones when the number of impurities placed on the chains is large enough that soliton-soliton overlap cannot be avoided. For the clustered configurations the potential wells of the separate dopants merge into an effective well which is much deeper than the wells of the individual dopants. Making use of the fact that the lowest-energy peak arises from a translation mode of the charge, one can think of the mode arising from the motion of a quantum particle in the well of the impurities.<sup>17</sup> The energy of the mode is then the energy to excite the particle from the ground state to first-excited state in the well and is related to the curvature at the bottom of the well. The shift towards lower energies as the impurity concentration is increased then arises because the effective well for the clustered configuration broadens more rapidly than it deepens.

In conclusion, we have shown that within a simple model of doped  $(\text{CH})_x$ , which explicitly includes impurity effects, the dopants are clustered in the ground state. The shift towards lower energies of the Goldstone mode with increased doping, below the transition to a metallic phase, seen in iodine-doped samples can be explained simply as a consequence of this clustering. The mechanism, however, underlying the sharp drop in energy of the Goldstone mode at the transition itself<sup>13</sup> requires a correct description of the microscopic nature of the metallic state, and is as yet an unresolved issue.

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