

## Structural and electronic properties of polymeric fullerene chains

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Properties of polymeric fullerenes are studied theoretically using a semiempirical model that treats only the  $\pi$  electrons explicitly but allows for lattice relaxations. Both neutral and charged systems are studied, and both the isolated  $C_{60}$  molecule as well as the polymer. In agreement with experiments, the model predicts the elongation of certain intraball bonds upon polymerization as the most significant structural relaxation. This is found both for the neutral and the charged system. For the latter, we observe symmetry reductions, and it is suggested that polaronlike distortions or charge-density waves may act as charge carriers. The distortions are predicted to induce extra phonon modes that should be observable experimentally.

Despite its recent discovery, a large amount of information about the physical and chemical properties of  $C_{60}$  has been collected. In particular, alkali-doped crystalline  $A_n C_{60}$ ,  $n = 1-6$  ( $A$  being an alkali atom) have been at the center of the interest (see, e.g., Ref. 1), with the systems for  $n = 3$  being those that have been studied most intensively due to the discovery of superconductivity in them.<sup>2,3</sup> However, recently the compounds with  $n = 1$  have attracted some attention. It has been argued that polymeric chains are formed in the solid state upon photoexcitation.<sup>4-6</sup> In this case the chain is supposed to carry one extra electron per  $C_{60}$ . But also the production of longer neutral  $(C_{60})_n$  oligomers has been reported.<sup>7</sup>

The most recent study of these materials<sup>6</sup> reports results of x-ray scattering experiments for  $A = Rb$  or  $K$ . These clearly indicate the formation of covalent bonds between the  $C_{60}$  molecules as well as a significant elongation of some of the intra- $C_{60}$  covalent bonds. Referring to Fig. 1, the lengths of the 1-59 and 2-60 inter- $C_{60}$  bonds were found to be  $1.44 \pm 0.15$  Å for  $A = Rb$  and  $1.65 \pm 0.20$  Å for  $A = K$ . The lengths of the 1-2 and 59-60 intra- $C_{60}$  bonds were, on the other hand, found to be  $1.90 \pm 0.15$  and  $1.74 \pm 0.20$  Å for the two compounds. Since the typical bond length of  $C_{60}$  is around 1.39 Å, these results clearly indicate the formation of covalent

inter- $C_{60}$  bonds and breaking of intra- $C_{60}$  bonds for  $A = Rb$ , whereas the situation appears to be less clear for  $A = K$ .

There have been some calculations on the neutral  $(C_{60})_2$  dimer (see Ref. 8 and references therein). These have suggested that all the bonds around the inter- $C_{60}$  link (the 1-2, 1-59, 2-60, and 59-60 bonds in the notation of Fig. 1) are relatively long (1.55–1.60 Å) but not broken, in agreement with the experimental results for  $A = K$  above. However, little is known about larger polymers and charged systems and there exist few theoretical studies devoted to polymeric systems.<sup>9-11</sup> Surján and Németh<sup>9</sup> applied a model conceptually similar to ours (to be described below) and used it both for neutral and charged chains. Some of the results differ, however, markedly from ours, as shall be discussed below, and we believe that in certain aspects their model is inaccurate. Also Tanaka *et al.*<sup>10</sup> studied the electronic properties of a neutral and a charged chain using a semiempirical model. They studied, however, neither structural nor vibrational properties. Finally, Adams *et al.*<sup>11</sup> used a first-principles molecular-dynamics method but only for neutral chains. They studied electronic, structural, and vibrational properties.

It is the purpose of the present paper to report results of a theoretical study devoted to structural, electronic, and vibrational properties of neutral and charged, infinite  $C_{60}$  polymers. We shall put special emphasis on whether the 1-2 and 59-60 intra- $C_{60}$  bonds can be considered broken and the 1-59 and 2-60 inter- $C_{60}$  bonds are covalent. Moreover, we shall explore to which extent the results depend on the charge of the system. In addition, we shall focus on the type of the charge carriers. Recent microwave experiments<sup>5</sup> suggest that the material is metallic. Finally, we shall study bond-stretch vibrations of the material.

We have adapted a slightly modified single-particle model that recently has been developed and used for isolated  $C_{60}$  molecules.<sup>12-14</sup> The total Hamiltonian  $\hat{H}$  of the system is written as a sum of one term,  $\hat{H}_\pi$ , treating one

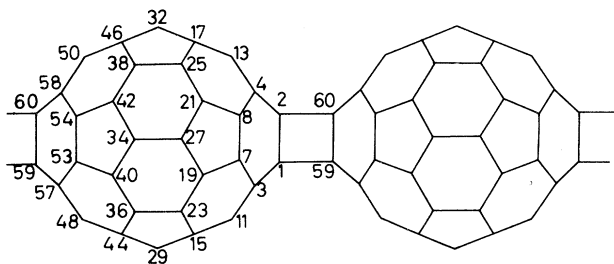


FIG. 1. Schematic representation of the structure of the  $C_{60}$  chain. The numbering of about half the atoms of one unit is also shown.

( $\pi$ ) electron per site (carbon atom) and a remainder  $\hat{H}_\sigma$ . Since the frontier orbitals of the  $C_{60}$  systems essentially are constructed from carbon  $p$  functions pointing along the radii of the  $C_{60}$  sphere, a one-electron-per-site approximation is good. We shall also assume that only nearest-neighbor hopping integrals  $t$  are nonvanishing and that they are linear functions of the bond lengths. Denoting the creation and annihilation operators  $\hat{c}_{i,s}^\dagger$  and  $\hat{c}_{i,s}$ , respectively, we have

$$\hat{H}_\pi = - \sum_{(i,j)} \sum_s t_{ij} \hat{c}_{i,s}^\dagger \hat{c}_{j,s}, \quad (1)$$

where  $(i,j)$  denotes nearest-neighbor sites and  $s$  is a spin variable.  $t_{ij}$  obeys

$$t_{ij} = t_0 - \alpha d_{ij}, \quad (2)$$

where  $t_0$  is the value at some reference bond length, and  $d_{ij}$  is the deviation of the  $i$ - $j$  bond length from the reference value. As has been found realistic,<sup>12,14</sup> we use  $t_0 = 2.5$  eV and  $\alpha = 6.31$  eV/Å.

Satpathy *et al.*<sup>15</sup> have used first-principles linear-muffin-tin-orbital (LMTO) calculations to obtain the parameters for a similar model. They assume a more complicated dependence of  $t_{ij}$  on  $d_{ij}$ , but their values result in  $t_0 = 2.53$  eV and  $\alpha = 3.19$  eV/Å when using a reference bond length of 1.39 Å. Thus, the values of  $t_0$  agree well, but we use a much larger value of  $\alpha$ . This difference may be responsible for smaller quantitative differences in the conclusions when modifying the model correspondingly, but we do not believe that the qualitative conclusions will be altered. Moreover, our values have been estimated by others as giving a correct description of the frontier orbitals.

In contrast to the earlier work<sup>12-14</sup> we write  $\hat{H}_\sigma$  as

$$\hat{H}_\sigma = \sum_{(i,j)} (K_1 d_{ij} + K_2 d_{ij}^2). \quad (3)$$

$K_1$  and  $K_2$  are adjusted so that the neutral  $C_{60}$  molecule has double- and single-bond lengths characterized by  $d_{ij} = -0.03$  and  $+0.06$  Å, respectively. These are the typical lengths found for *trans*-polyacetylene, when using that the reference bond length for the structure with all bond lengths equal is 1.39 Å (see, e.g., Ref. 16). We found  $K_1 = -7.603$  eV/Å and  $K_2 = 18.68$  eV/Å<sup>2</sup>.

Earlier studies have used  $K_1 = 0$  and  $K_2 = 24.85$  eV/Å<sup>2</sup> together with the constraint  $\sum_{(i,j)} d_{ij} = 0$ .<sup>12,14</sup> We found it, however, less obvious how to impose such a constraint in the present study for which the number and types of bonds are not clear, and modified therefore the model as described.

In our model we treat all intra- and inter- $C_{60}$  bonds equivalently, thereby neglecting that the atoms closest to the inter- $C_{60}$  links experience somewhat different surroundings than the others. But since these bonds have lengths comparable to those of typical covalent bonds—according to the experiments quoted above—we consider it a reasonable first approximation that of course can be improved in future studies. We do, however, not believe that our general conclusions thereby will be altered.

The studies of the infinite chains were performed by

imposing periodic boundary conditions on an oligomer consisting of a smaller finite number ( $N$ ) of  $C_{60}$  units. In a band-structure picture this corresponds to using only  $k=0$  in the  $k$ -space sampling. We thus do not calculate the complete band structure.

In order to optimize the structure we used first-order perturbation theory and calculated hence the forces according to (see, e.g., Ref. 17)

$$-F_{ij} = \frac{\partial E_{\text{tot}}}{\partial d_{ij}} = K_1 + 2K_2 d_{ij} + \alpha \sum_{n=1}^{\text{occ}} (c_{ni}^* c_{nj} + c_{ni} c_{nj}^*), \quad (4)$$

where  $c_{ni}$  is the coefficient of the  $n$ th eigenfunction of  $\hat{H}_\pi$  to the basis function of the  $i$ th site. The  $n$  summation runs over all occupied orbitals. Once the forces are obtained, the bond lengths are updated according to  $d_{ij} \rightarrow d_{ij} + \xi F_{ij}$ , and we used  $\xi = 0.01$  in the units of the present work (i.e., energies in eV, lengths in Å, and masses in units of that of an isolated carbon atom).

Finally, we studied neutral and singly charged isolated  $C_{60}$  molecules as well as neutral and charged chains consisting of periodically repeated units of  $N = 1, 2, 3, 4$ , and 5  $C_{60}$  molecules. Here, the charged systems contain one extra electron per  $C_{60}$ , as should be the case for the  $A_1 C_{60}$  systems.

We have numbered the 60 C atoms per  $C_{60}$  molecule as indicated in Fig. 1. Subsequently, we have numbered all nearest-neighbor interatomic bonds, i.e., 90 bonds for the isolated  $C_{60}$  and 92 bonds per  $C_{60}$  unit for the chain. The numbering is not important for the present work and shall therefore not be discussed further here, except for mentioning that bonds number 91 and 92 per unit are the inter- $C_{60}$  bonds and that the 1-2 and 59-60 bonds are given numbers 1 and 90, respectively, per unit.

In Fig. 2(a) we show the bond lengths of the neutral, isolated  $C_{60}$  molecule. Only two values are found, as expected. The corresponding density of states is shown in Fig. 3(a). The uppermost occupied orbital (HOMO) is tenfold degenerate (including spin), whereas the lowest unoccupied (LUMO) is sixfold degenerate. The gap is calculated to be 2.43 eV, which is a reasonable value for this system (experimental values between 1.9 and 2.6 eV have been reported<sup>18</sup>). The electron distribution is completely homogeneous as expected [Fig. 4(a)].

Figure 2(b) shows the bond lengths for the isolated  $C_{60}$  molecule with one extra electron and Fig. 3(b) the density of states. A comparison between Figs. 2(a) and 2(b) shows that the main effect of the extra electron is to make some of the single bonds shorter and some of the double bonds longer. In agreement with results of previous studies<sup>8-10</sup> we find that the lattice distortion is mainly located at a ring around the  $C_{60}$  equator. As Fig. 4(b) shows, the extra electron is spread out over most of the ball. The lowering of the symmetry upon doping leads to a more structured density of states. Most important are the changes around the Fermi level, and it turns out that of the fivefold (neglecting spin) degenerate HOMO's in Fig. 2(a) one orbital is moved into the gap, similar to what happens to one of the threefold degenerate LUMO's. This reduces the gap to 1.99 eV, but the Fermi level is actually centered at the former LUMO.

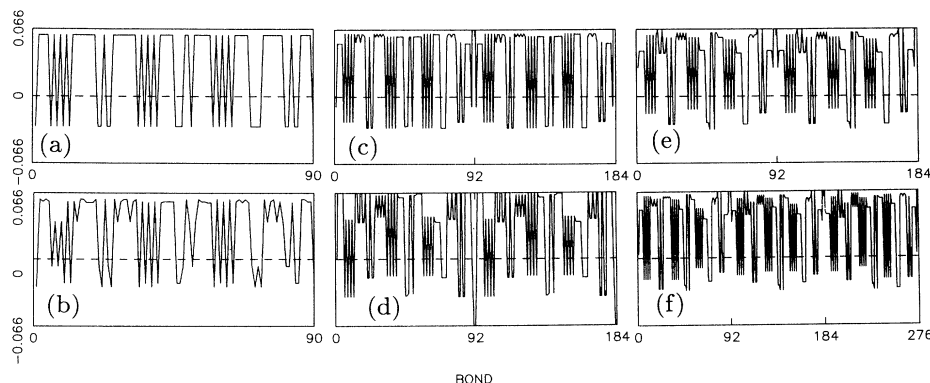


FIG. 2. Relative bond lengths (in Å) for various  $C_{60}$  systems. (a) and (b) The isolated molecule, (c)–(e) [(f)] the chain modeled through a system of periodically repeated units of two [three]  $C_{60}$  molecules. (a) and (b) have 90 bonds per unit, whereas the others have 92. (b), (e), and (f) correspond to charged systems with one extra electron per  $C_{60}$ , and the others to neutral systems. The system of (d) differs from that of (c) by the assumption that the 1-2 and 59-60 intra- $C_{60}$  bonds are assumed broken.

Turning to the chains we show in Fig. 2(c) the optimized structure for the system consisting of periodically repeated units of two  $C_{60}$ . There are some smaller differences for the system formed by repeating only one  $C_{60}$ , whereas the results for the large systems essentially are unchanged, indicating that the properties of the system are converged already with two units. Compared with the isolated, neutral  $C_{60}$  molecule, the largest changes occur for the bonds close to the inter- $C_{60}$  link (i.e., the bonds with the indices around  $n \times 92 \pm 15$ ,  $n$  being an integer). This is in contrast to the case of the isolated, charged  $C_{60}$  molecule. Moreover, the bond lengths in Fig. 2(c) are less regular than in Fig. 2(a), which can be ascribed to the lower symmetry. Finally, the inter- $C_{60}$  bonds are relatively long, with  $d_{ij}$  being about 0.16 Å. On the other hand, the 1-2 and 59-60 intra- $C_{60}$  bonds close to the link are slightly elongated, with  $d_{ij} \approx -0.01$  Å [compared with  $-0.03$  Å in Fig. 2(a)].

Despite the lowering of symmetry, the charge density [Fig. 4(c)] is spread out almost uniformly over all 60 carbon atoms per unit. The density of states [Fig. 3(c)] is qualitatively similar to that of the isolated  $C_{60}$  but with a number of extra peaks. The most important difference is the occurrence of two extra gap levels in Fig. 3(c). These levels lead to a reduction of the band gap to 1.48 eV, i.e., a reduction of about 1 eV. Although one may intuitively think of these levels as due to orbitals mainly confined to the regions of the inter- $C_{60}$  bonds, this is only partially true: the corresponding wave functions (not shown) have the main components near the links, but have also large components on the rest of the atoms of the  $C_{60}$  units.

We tried alternatively to assume that the 1-2 and 59-60 intra- $C_{60}$  bonds were broken and removed therefore the pairs (1,2) and (59,60) from the summation in Eqs. (1) and (3). This led to significantly larger changes in the bond lengths [cf. Fig. 2(d)] and to much stronger inter- $C_{60}$  bonds, for which  $d_{ij}$  becomes even smaller ( $-0.07$  Å) than those of standard double bonds. Also the density of states [Fig. 3(d)] differs more from that of the isolated neutral  $C_{60}$  molecule than that of Fig. 3(c). Nevertheless,

the electron density remains fairly uniform [Fig. 4(d)]. The results appear, however, to be unrealistic (in particular the occurrence of very short bonds), and we therefore believe that it is incorrect to assume that the 1-2 and 59-60 intra- $C_{60}$  bonds are completely broken.

In their study, Surján and Németh<sup>9</sup> assumed, however,

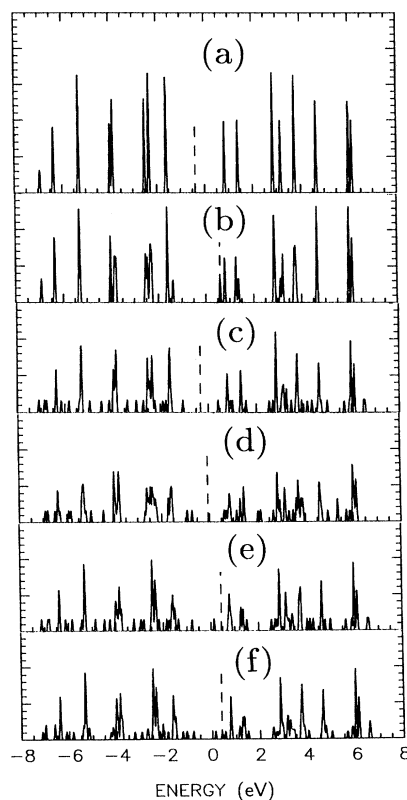


FIG. 3. Electron density of states (in arbitrary units) for the same systems as in Fig. 2. The Fermi levels are marked by the vertical dashed lines, and the isolated levels have been broadened by Gaussians of width 0.05 eV.

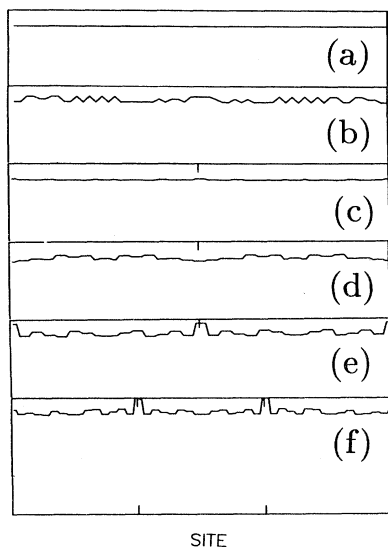


FIG. 4. Electron density as a function of site index for the same systems as in Fig. 2. In the ideal, homogeneous, neutral case all sites have one electron. The tick marks are placed at every 60 atoms. The y-axis scale is defined such that the constant value in (a) equals 1 and the upper top of that panel equals 1.1.

that the 1-2 and 59-60 intra- $C_{60}$  bonds were broken. This resulted in inter- $C_{60}$  bond lengths equal to 1.41 Å, i.e.,  $d_{ij}=0.02$  Å. The same method applied on an isolated  $C_{60}$  molecule gave, on the other hand, bond lengths of 1.402 and 1.446 Å, i.e., more regular than what we have assumed. The band gap of the polymer was found to be very small, only 0.35 eV, which we consider unrealistic, when taking our results as well as those of Tanaka *et al.*<sup>10</sup> and of Adams *et al.*<sup>11</sup> into account.

Tanaka *et al.*<sup>10</sup> found for a fixed geometry with 1-2 and 59-60 intra- $C_{60}$  bond lengths of 1.62 Å ( $d_{ij}=0.23$  Å) and 1-59 and 2-60 inter- $C_{60}$  bond lengths of 1.56 Å ( $d_{ij}=0.17$  Å) a band gap of 1.15 eV, which is in better agreement with our results.

Finally, Adams *et al.*<sup>11</sup> found that the gap for the neutral system is reduced only by some few tenths of an eV upon polymerization, compared with that of the neutral  $C_{60}$  molecule, and that the gap of the latter is slightly less than 2 eV.

When adding one electron per  $C_{60}$  unit several things happen. For the undistorted system one band will be exactly half filled, and a Peierls distortion may be expected. Since we, however, only use  $k=0$  in the  $k$ -space sampling, this effect will be most significant for systems with  $N$  being odd. But let us start by discussing the results for chains consisting of repeated units of two or four  $C_{60}$ .

First of all, the lengths [cf. Fig. 2(e)] of the 1-2 and 59-60 intra- $C_{60}$  bonds become elongated ( $d_{ij}=0.03$  Å), although they are far from being so long as they would be within a broken-bond picture. Compared to the neutral chain, the inter- $C_{60}$  bonds are shortened, i.e.,  $d_{ij}=0.12$

Å. In addition to those most significant changes we also notice that in general, most of the double bonds become longer, thereby losing a smaller part of their double-bond character. By analyzing the electron distribution [Fig. 4(e)] it turns out that the extra electron is located in the regions of the links. This is in contrast to the findings for the isolated  $C_{60}$  molecule. Actually, the extra electron occupies an orbital that has bonding inter- $C_{60}$  components and antibonding 1-2 and 59-60 intra- $C_{60}$  components, thereby directly explaining the most significant changes in the bond lengths.

The density of states is shown in Fig. 3(e). Due to the extra electron, the Fermi level has moved upwards in energy and is, due to the dimerization, placed at the center of another gap. Compared with Fig. 3(c), the most significant change is the shift of the two "gap levels" at  $-1.06$  and  $0.42$  eV in Fig. 3(c) towards each other in Fig. 3(e), where they occur at  $-0.79$  and  $0.14$  eV. This leads to an increase of the gap around the Fermi level in Fig. 3(e) where its size becomes 0.59 eV.

The results are somewhat different for the chain with an odd number of electrons. In the case of noninteracting  $C_{60}^-$  ions, the Fermi level will fall in the middle of the sixfold degenerate LUMO in Fig. 3(a). Turning on the inter- $C_{60}$  interactions will split the LUMO into more peaks and lead to a smaller broadening of the levels. But as long as the  $C_{60}$  units are equivalent, the Fermi level for the systems with an odd number ( $N$ ) of  $C_{60}$  units will fall at a peak with a degeneracy of at least  $N$ . Reducing the symmetry (i.e., making the  $C_{60}$  units inequivalent) may lower the density of states at the Fermi level. Such a symmetry reduction is clearly seen in our calculations. Figure 2(f) shows the bond lengths for the chain with  $N=3$ , and in particular the bonds closest to the inter- $C_{60}$  links are not equivalent. The inter- $C_{60}$  bonds remain long for  $N=3$ , i.e.,  $d_{ij}=0.11-0.13$  Å.

Figure 4(f) confirms that the structure is no longer homogeneous; i.e., the extra electrons are in this case mainly concentrated to the atoms close to the inter- $C_{60}$  links between units 1 and 2 and units 2 and 3. Finally, Fig. 3(f) shows that the density of states is split up into a large number of separate peaks due to the symmetry lowering. For the sake of completeness, we finally add that similar results were found for  $N=5$ .

Despite the differences in the models, also Surján and Németh<sup>9</sup> found a symmetry-lowering distortion for a charged chain. They suggested that this corresponds to a charge-density wave. They calculated the full band structures for the system with  $N=2$ , and the charge-density wave was found to induce a gap of 0.13 eV.

Our model may also be used in calculating frequencies and patterns of bond-stretch phonons. We expand the total energy  $E_{\text{tot}}$  around the equilibrium structure, defined by the bond lengths  $\{d_{ij}^{(0)}\}$ , to second order,

$$E_{\text{tot}} = \sum_{(ij),(kl)} \frac{1}{2} k_{ij,kl} (d_{ij} - d_{ij}^{(0)}) (d_{kl} - d_{kl}^{(0)}) . \quad (5)$$

The force constants  $k_{ij,kl}$  can be calculated by using second-order perturbation theory for the Hamiltonian of Eqs. (1) and (3), or, alternatively (which is the approach

we have used), by directly calculating the changes in  $E_{\text{tot}}$  when varying one or two bond lengths (we choose  $d_{ij} - d_{ij}^{(0)} = \pm 0.001 \text{ \AA}$ ). Exploratory calculations on the neutral  $C_{60}$  molecule gave that besides diagonal terms [( $ij$ )=( $kl$ )] it was necessary to include also up to third-nearest-neighbor interactions: some of the corresponding force constants were roughly 5% of the diagonal terms. Having calculated the force constants, the squares of the phonon frequencies and the displacement patterns can be calculated as the eigenvalues and eigenvectors, respectively, of the dynamic matrix containing  $k_{ij,kl}/\mu$ , where  $\mu$  is the reduced mass of a  $C_2$  unit.

Related models for a  $C_{60}$  molecule were originally introduced by Wu, Jelski, and George.<sup>19</sup> They included also out-of-plane vibrations but no off-diagonal bond-stretch constants. They suggested  $k_{ij,ij} = (1.0 - 1.1) \times 10^6$  dyn/cm. By varying all short or long bond lengths simultaneously we found a considerably smaller value, around  $0.4 \times 10^6$  dyn/cm. Also Weeks and Harter<sup>20</sup> have suggested to use a smaller value, i.e.,  $0.76 \times 10^6$  dyn/cm. It turns out that the earlier studies lead to too high frequencies compared with experiments, so that we consider our values more realistic.

Including off-diagonal couplings results in on-diagonal force constants of  $0.49 \times 10^6$  dyn/cm for the long bonds and  $0.42 \times 10^6$  dyn/cm for the short bonds. The largest off-diagonal values are  $0.064 \times 10^6$  dyn/cm, i.e., about 15% of the diagonal terms.

In Fig. 5(a) we show the resulting density of states for the isolated, neutral  $C_{60}$  molecule. Antropov, Gunnarsson, and Liechtenstein<sup>21</sup> have also calculated phonon frequencies, but using first-principles LMTO calculations. Their highest  $H_g$  mode appears at  $1462 \text{ cm}^{-1}$ , slightly lower than the experimental value, but higher than our highest value for  $H_g$  modes at  $1292 \text{ cm}^{-1}$ . The lowest  $H_g$  mode we find at  $814 \text{ cm}^{-1}$ , whereas Antropov, Gunnarsson, and Liechtenstein find the lowest mode with little radial character at  $785 \text{ cm}^{-1}$ .

Also Adams *et al.*<sup>11</sup> have calculated these modes. They show a larger width than ours and than those of Antropov, Gunnarsson, and Liechtenstein and also than the experimental values. In total our values appear thus as reasonable, especially when taking the spread of the values of other studies into account (see, e.g., Ref. 21). But the interatomic interactions as well as the off-diagonal force constants may be somewhat underestimated in our model. The uncertainty (of the order of 10%, we estimate) is, however, not larger than our conclusions remain valid.

As discussed above, the structure of the isolated  $C_{60}$  molecule relaxes upon adding an extra electron. This relaxation results in a symmetry lowering. Therefore, the phonon spectrum gets broader [Fig. 5(b)]. In particular, extra modes between  $900$  and  $1000 \text{ cm}^{-1}$  appear. We suggest that these are used in experimental studies of this system.

Also the polymerization is predicted to lead to extra modes in the gap around  $900$ – $1000 \text{ cm}^{-1}$ . Similar effects were observed in the study of Adams *et al.*<sup>11</sup> However, a characteristic gap around  $900 \text{ cm}^{-1}$  remains [cf. Figs.

5(a), 5(c), and 5(d)] for the neutral system, and only for the charged system is it reduced considerably [cf. Figs. 5(b), 5(e), and 5(f)]. According to recent experiments<sup>22,23</sup> extra modes are in fact seen for the charged polymeric system. We finally notice that the phonon spectrum is much less sensitive to the size of the system than the electronic density of states [cf. Figs. 5(e) and 5(f)].

In conclusion, we have shown that a simple phenomenological model supports the experimental findings that polymeric  $C_{60}$  chains can be formed in  $A_1C_{60}$ . In contrast to the case for the isolated fullerene molecules, the extra electron is not delocalized along the equator of the buckyball but localized to the regions of the inter- $C_{60}$  bonds. Thereby, these get a covalent character, although the bond lengths found here suggest that the bonds are slightly longer (weaker) than the intra- $C_{60}$  single bonds. Simultaneously, the nearest intra- $C_{60}$  bonds are significantly elongated, although not so much that one may talk about broken bonds. Our results thus agree best with the experimental results for  $A=K$ , as well as with the theoretical results on neutral  $(C_{60})_2$ , but less with the experimental results for  $A=Rb$ . The most important

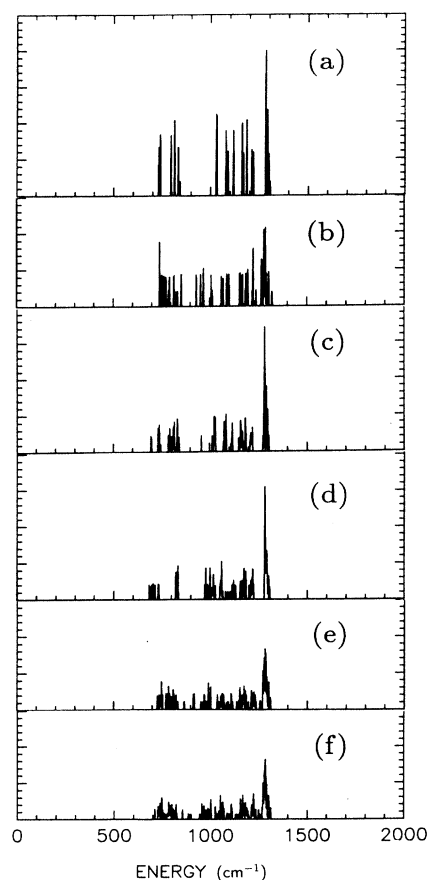


FIG. 5. Density of vibrational states (in arbitrary units) for the same systems as in Fig. 2. Only bond-stretch vibrations are considered.

finding is that the structure for the charged chains becomes distorted and has a reduced symmetry. Our results indicate the formation of polarons or a charge density wave, such that the metallic behavior of the system as observed in experiments may be explained as due to the propagation of polarons or the charge density wave. Fi-

nally, also extra phonon modes show up for the polymers, and in particular a characteristic phonon gap is reduced for the charged system.

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