

made near the scattering center (detailed analysis of angularly resolved time-of-flight data would provide a more accurate radiative lifetime<sup>16</sup>). The measured time-integrated angular distribution is shown in Figure 2. From these data, it is apparent that at least one component of the observed emission is due to a fragment with low kinetic energy. Were the emission due solely to parent molecules, the angular distribution would lie, within experimental resolution, on the molecular beam axis. The only mechanism by which parent molecule emission could lead to an angular distribution resembling that in Figure 2 is the formation of van der Waals complexes in the expansion, and experimental conditions were chosen which strongly discriminate against this.

Model calculations on similar systems<sup>16</sup> indicate that angular distributions resembling that in Figure 2, with strong peaking at  $\theta = 0^\circ$ , are typical of unimolecular processes with no barrier along the reaction coordinate, such as simple bond fission. Our data are entirely consistent with this interpretation and suggest that, while we cannot eliminate the possibility of parent molecule emission, it must be at most a minor process. Nevertheless, previous reports suggest the possibility of parent and fragment emission at the high fluences employed in our experiment (radiative excited states 19–34 kcal mol<sup>-1</sup> below the ground-state dissociation limit of CrO<sub>2</sub>Cl<sub>2</sub> are well established, and internal conversion has been observed experimentally in this molecule by Heller and West<sup>17</sup>).

Of equal interest is the mechanism(s) whereby electronically excited fragments are formed. Halonbrenner et

al. identified transient absorptions of CrO<sub>2</sub> and CrO<sub>2</sub>Cl following flash photolysis of chromyl chloride vapor,<sup>15</sup> and others have also observed photodissociation of chromyl chloride although there is not general agreement concerning the energy required for the onset of photochemical action.<sup>10,15</sup> In our experiments, excitation and dissociation of chromyl chloride occurs overwhelmingly in the ground electronic state. There is no evidence for *nascent* electronic excitation in the photofragments from this process, as this would require a barrier to the production of ground-state species and we know of no good reason to anticipate such a barrier. Rather, the MPE of photofragments and  $V \rightleftharpoons E$  coupling in these photofragments is in accord with all of our observations, and requires no speculation about barriers along the reaction coordinate. The data shown in Figure 2 certainly indicate that no barriers were involved in the production of the emitting species, as  $I(\theta)$  vs.  $\theta$  would be much broader were a barrier present.

In summary, we have established unambiguously the existence of fragment emission in the collisionless IR MPE of chromyl chloride at fluences  $\sim 10^2$  J cm<sup>-2</sup>. We were unable to detect emission from parent chromyl chloride, and the issue of whether chromyl chloride electronic emission is detectable via IR MPE remains unresolved. We feel that a more thorough study of the dynamics of the MPE process using a molecular beam arrangement will provide the information required to make this determination. Efforts toward this end are presently underway in our laboratory.

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## Theoretical Study of Charge Transfer and Bond Alternation in Doped Polyacetylene

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Restricted Hartree-Fock calculations on lithium-doped polyacetylene chains are presented. We find that the bond alternation present in the undoped chain is dramatically reduced as the charge transfer from the lithium atoms increases. At  $\sim 0.1$  e transferred per CH unit, we predict equal bond lengths, a result which is consistent with the predictions of the soliton model at high dopant concentrations.

The discovery that doping can increase the conductivity of polyacetylene and some other conjugated polymers to near metallic levels has focussed much attention on these organic systems.<sup>1</sup> Of particular interest are the changes in the polymer electronic and geometric structures upon doping. In this note, we present a theoretical study of the effect of an alkali metal, Li, acting as a dopant on (i) the amount of charge transferred to the polymer chain, (ii) the bond length and bond order alternation in the chain, and

(iii) the band structure (and band gap) in the one-electron picture.

The key result of our calculations is that, at surprisingly small degrees of charge transfer, there are major changes

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TABLE I: RHFR Geometry Optimization Results (in au<sup>a</sup>) on trans-(CH)<sub>x</sub>, Using a Christoffersen Basis Set

	alternating chain	equal bond-lengths chain
$R_{C=C}$	2.555	2.589
$R_{C-C}$	2.623	2.589
C-C-C angle, deg	119.0	119.0
total energy (per C <sub>2</sub> H <sub>2</sub> unit)	-65.835103	-65.833870

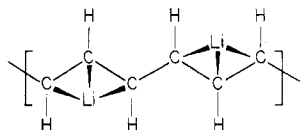
<sup>a</sup> 1 au (length) = 0.52917 Å. 1 au (energy) = 27.2 eV.

in the nuclear geometry of the chain and hence in its electronic structure. This casts serious doubts on the appropriateness of rigid band structure models in theoretical studies of dopant polymer interactions.<sup>2</sup> In fact, our results are consistent with the theoretical concepts based on solitons<sup>3</sup> for describing doped (CH)<sub>x</sub>.

We have performed ab initio crystal orbital calculations at the restricted Hartree-Fock-Roothaan (RHFR) level<sup>4</sup> on infinite single chains of *trans*-polyacetylene, (CH)<sub>x</sub>, with and without Li atoms at a variety of distances from the chain. In the case of doped systems, we present our data for (C<sub>6</sub>H<sub>6</sub>Li)<sub>x</sub> which represents a doping level of 33%. The reasons for our choice of this concentration are that (a) it is close to the experimentally achieved concentration of 30%;<sup>5</sup> (b) the unit cell, which is as large as we can handle on our computer, has the freedom for structural changes of the Peierls distortion<sup>6</sup> type; (c) the RHFR method can only easily handle closed-shell systems. Because of the size of the unit cell, we have used a subminimal Christoffersen basis set<sup>7a</sup> which has proved to give reliable results in conformational studies of polyacetylene as well as other cases.<sup>7b</sup> Long-range Coulombic interactions which are expected to be of particular importance in this charge-transfer system have been properly taken into account through a multipole based technique for lattice summation.<sup>8</sup>

The focus of this study involves ground-state properties, namely, the charge transfer and the geometry changes in the chain that occur on doping. We do not address quantitatively the questions related to metallic behavior or optical properties which require going beyond the one-electron picture.

The geometry of our system is as follows:



As a first step, we have optimized the "single" and "double" bond lengths and the C-C-C angle of the undoped chain (i.e.,  $R_{Li-C} = \infty$ ) while keeping the CH distance fixed at 2.04 au and the C-C-H angle as  $180^\circ - \frac{1}{2}(C-C-C \text{ angle})$ . The results are given in Table I. As expected, we find the alternating chain to be most stable, in agreement

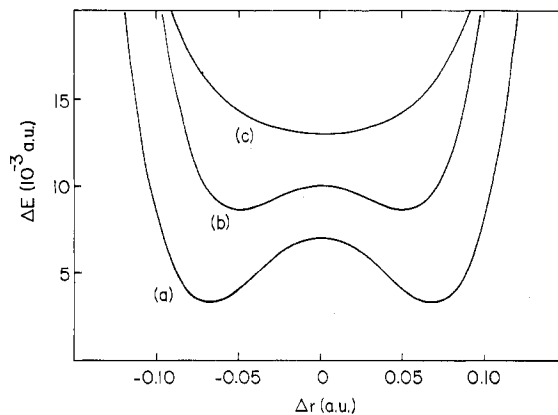


Figure 1. Relative total energies,  $\Delta E$ , of the lithium-doped chains as a function of bond alternation,  $\Delta r$ , and lithium-chain separation: (a)  $R_{Li-C} = \infty$ , (b)  $R_{Li-C} = 2.35$  Å, (c)  $R_{Li-C} = 2.00$  Å. The curves have been displaced and the zero of energy chosen arbitrarily for the three curves, in order to improve the clarity of presentation.

TABLE II: Total Energies,  $E$  (in au), and Charge Transfers per Lithium Atom, CT, for Lithium-Doped Polyacetylene, (C<sub>6</sub>H<sub>6</sub>Li)<sub>x</sub>, as a Function of Lithium-Carbon Distance

$\Delta r^a$	$R_{Li-C} = 2.000$ Å	$R_{Li-C} = 2.175$ Å	$R_{Li-C} = 2.350$ Å
0.068	$E = -209.642332$ CT = 0.298	$E = -209.680324$ CT = 0.196	$E = -209.702055$ CT = 0.104
0.034	$E = -209.644770$ CT = 0.303	$E = -209.681890$ CT = 0.205	$E = -209.702723$ CT = 0.117
0.000	$E = -209.645255$ CT = 0.306	$E = -209.681660$ CT = 0.212	$E = -209.701710$ CT = 0.129
$\Delta r_{min}^b$	0.000	0.036	0.050

<sup>a</sup>  $\Delta r$  indicates the degree of bond-length alternation (in au). <sup>b</sup> Found by fitting the potential to a form  $a + b(\Delta r)^2 + c(\Delta r)^4$ .

with previous RHFR extended basis set geometry optimization by Karpfen and Petkov (KP).<sup>9</sup> The degree of alternation (C-C bond length difference)  $\Delta r = r_{C-C}^{long} - r_{C-C}^{short}$  we find is rather low (0.068 au), less than half that found by KP, which can be understood from our use of the Christoffersen basis which is known to give rather short C-C single bonds.<sup>10</sup> However, our overall results for undoped polyacetylene, and in particular the potential curve (Figure 1a), agree well with the more extended calculations of KP. Note that the optimized C-C distance for the equal bond length case is exactly midway between the single and double bond lengths in the lowest energy configuration.

In the doped chains, each Li is positioned equidistant from three carbon atoms in analogy with the structure found in the lithium intercalated graphite compound.<sup>11</sup> The two lithium atoms are placed one above and one below the plane of the chain. We have considered three lithium-carbon distances,  $R_{Li-C}$ , and optimized the energy by allowing the difference between single and double bond lengths ( $\Delta r$ ) to vary again keeping the CH distances fixed, and the C-C-H angle as  $180^\circ - \frac{1}{2}(C-C-C \text{ angle})$ . The range of lithium-carbon distances is chosen to be in accord with crystal packing calculations, which show that the interchain carbon-carbon distance (in the cis polymer) is

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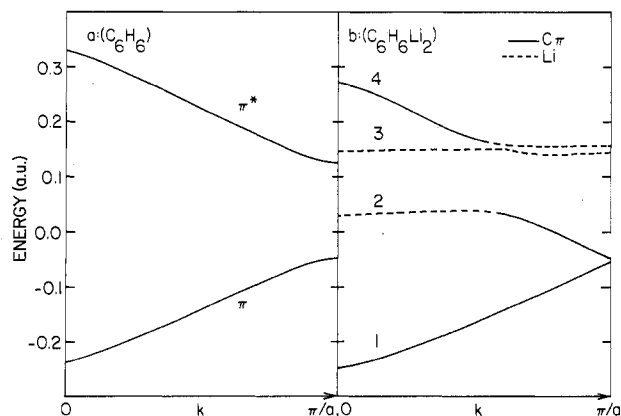
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**Figure 2.** Electronic structure of highest occupied and lowest unoccupied bands in (a) undoped and (b) doped ( $\text{C}_6\text{H}_6\text{Li}_2$ ,  $R_{\text{Li-C}} = 2.00 \text{ \AA}$ ,  $\Delta r = 0$ ) chains. The states with predominantly lithium ( $\text{C}-\pi$ ) character are represented by dashed (solid) lines. The energies are plotted vs.  $k$  ( $= \pm\pi p/a$  where  $1 > p \geq 0$ , and  $a$  is the unit cell length).

$\sim 4.4 \text{ \AA}$ .<sup>12</sup> The charge transfer is computed by using the Mulliken population analysis as a measure of atomic charges.<sup>13</sup> We do not address the question of system stability with respect to lithium-chain separation since this would require consideration of three-dimensional effects including the Madelung energy. (In fact, we do not find a minimum in energy as a function of lithium-carbon separation.) The questions addressed herein are: given a particular Li-chain separation, what is the charge transfer and what is the equilibrium chain geometry? The results are displayed in Table II and Figure 1.

As expected, the charge transfer from the lithium to the chain increases as the lithium-chain separation decreases. The most important feature of our results is that the bond alternation is greatly reduced, to the point that, at a distance of  $2 \text{ \AA}$ , we predict the equal bond length case to be the lowest energy configuration. Thus even with a small charge transfer of  $\sim 0.035 \text{ e}$  per carbon atom, the alternation is reduced substantially and vanishes for charge transfer of  $\sim 0.1 \text{ e}$  per carbon atom. An independent optimization allowing the length of the central C-C bond in the unit cell to vary independently of the others again yields the equal bond length structure at  $R_{\text{Li-C}} = 2 \text{ \AA}$ . This indicates that the reduction of alternation persists throughout our structure, and is likely to be a long-range effect.

The possibility of geometrical change upon doping has been of great interest to many investigators; those who support the soliton picture in doped  $(\text{CH})_x$  predict a vanishing of the alternation,<sup>3</sup> while others<sup>14</sup> claim that a bond length alternation persists although it is less than in the undoped chain. In organic  $\pi$  molecular systems, it is known that ionization can substantially change the nuclear geometry.<sup>15</sup> Our results for this polymer  $\pi$  system

are dramatic in that even modest charge transfer drastically alters chain geometry.

In Figure 2, the electron band structures of the highest filled and lowest unfilled bands are given for the optimized chain geometries at  $R_{\text{Li-C}} = \infty$  (alternating chain,  $\Delta r = 0.068 \text{ au}$ ) and  $R_{\text{Li-C}} = 2 \text{ \AA}$  (equal bond lengths). In the undoped case the total  $\pi$  band width is  $\sim 10 \text{ eV}$  and the band gap is  $\sim 4.8 \text{ eV}$ . (The latter is too high as has to be expected for the RHFR method; the experimental band gap is  $1.4\text{--}1.9 \text{ eV}$ .<sup>16</sup>) The presence of the lithium introduces two  $2s$  bands in the gap, which mix strongly with the  $\pi^*$  band, at  $k \sim 2\pi/3a$ , pushing it down in energy. The lithium bands are nearly flat since the smallest Li-Li distance is  $\sim 5 \text{ \AA}$ .<sup>17</sup> The present calculation predicts nonmetallic behavior for  $(\text{C}_6\text{H}_6\text{Li}_2)_x$  because of the one dimensionality of the model and the inability of the Hartree-Fock method to describe properly a metallic situation where correlation is important. In order to discuss the conductivity quantitatively, we would have to include correlation and interchain interactions. In the case of equal C-C bond lengths, there is a screw axis symmetry element in the geometric structure so that the bands should become degenerate at the Brillouin zone boundary and bands 2 and 4, in Figure 2b, should cross (leading to a metallic situation). However, in the RHFR method, the self-consistent wave functions can lower their energy by breaking this symmetry, for instance by the formation of a bond order alternating state (a charge density wave (CDW) instability).<sup>18</sup> As a result, all crossings and degeneracies are lifted and a nonmetallic situation is obtained. Note that the  $\pi$  and  $\pi^*$  bands are nearly degenerate at the zone edge, a result which indicates a rather weak CDW instability. In other systems, we have found evidence for more dramatic instabilities which we will discuss more thoroughly in a future publication.

In summary, the principal conclusion we draw from RHFR calculations on isolated trans- $(\text{CH})_x$  chains doped by Li atoms is that even a small degree of charge transfer dramatically alters the chain geometry and, as a consequence, its electronic structure. We suggest that these results imply strong electron-phonon coupling (even in the undoped chain). This will tend to localize optical excitations, and have substantial effects on transport properties.

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