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Sliding Mechanisms of Soliton Lattice and Vibrational Coupling for Trans-Polyacetylene

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To study the solitons in heavily doped trans-polyacetylene, the dynamics of a charged soliton lattice have been calculated. First, the structure has been optimized and it shows a soliton lattice. Next, an electric field has been applied. The soliton lattice has begun to slide slowly and finally the speed is saturated to a constant value. The final speed is determined by a coupling where the soliton passing is synchronized with a C-C stretching motion. It is also found that the period of the passing solitons is able to be synchronized with the two or three times of the period of the C-C stretching vibration.

Keywords: polyacetylene; soliton; vibration; molecular orbital

INTRODUCTION

Heavily doped trans-polyacetylene has been studied with various aspects for nearly twenty years. The intrinsic electronic structure is, however, still under discussion. A number of experimental works[1-3] have asserted that a soliton lattice is preferable to a metallic structure. And some theoretical studies[4-7] employing Coulomb interaction show that the optimized structure is a soliton lattice. In this report, it is also a soliton lattice and the dynamic motion of the lattice is studied. As regards the soliton sliding, a single soliton has been studied theoretically[8,9], and the saturated speed *etc.* has been discussed. But the sliding mechanism of a multi soliton system has not yet been clarified. In this work, the geometry is optimized and the vibrational modes for the soliton lattice structure are calculated with a semi-empirical MNDO method. After that, dynamic simulations are carried out. The sliding speed and the coupling between the soliton sliding and the C-C stretching vibration are studied.

LATTICE STRUCTURE AND SLIDING MODE DISPLACEMENTS

A program named MOPAC and a semi-empirical MNDO method have been used to calculate the soliton lattice structures. Compared with SSH calculation, this method includes more than one-dimensional effect of the carbon and hydrogen atoms. And the Coulomb interaction is taken into account within the semi-empirical Hartree Fock method. With this program, the geometry is optimized. The model molecule is a single periodic chain where even numbers of charges are included, *i.e.* *unit* = $(C_nH_n)_m^{m+}$ (m : even, n = 7 - 24). According to this optimization, the solitons in the chain form a soliton lattice for any soliton density in the model. This is consistent with some previous calculations[4-7]. The vibrational modes have been calculated by using force constant matrix. One of the modes is found to be a soliton lattice sliding mode. This mode is shown in Fig. 1. It corresponds to the translational mode[10,11] of a single soliton. The displacement vectors in Fig. 1 indicate that double and single bonds interchange on the right side of each soliton. This makes all solitons translate together to the right.

The displacement vectors shown in Fig. 1 imply a sort of coupling between the sliding and the C-C stretching mode as the soliton sliding is not a simple movement along a normal coordinate. The process is shown in Fig. 2. If the carbon atoms at a soliton are accelerated too much in the soliton sliding process, the excess energy still remains on the same carbon atoms even after the soliton has passed away and it becomes the potential energy of the C-C bonds as with (b) in Fig. 2. After that, the carbon atoms release the potential energy as in Fig. 2(c) and let another soliton pass from the left to the right as shown in Fig. 2(c,d). This implies that the period of the C-C stretching vibration becomes the same as the period of the passing solitons. This phenomenon occurs in the simulations described below.

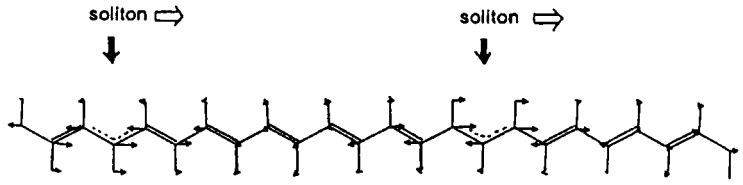

FIGURE 1 The displacement vectors of the soliton lattice sliding mode.

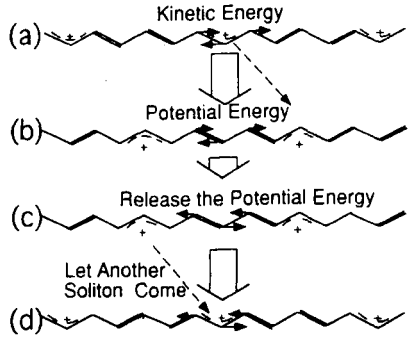

FIGURE 2 An explanation of the coupling between the passing soliton and the C-C stretching vibration.

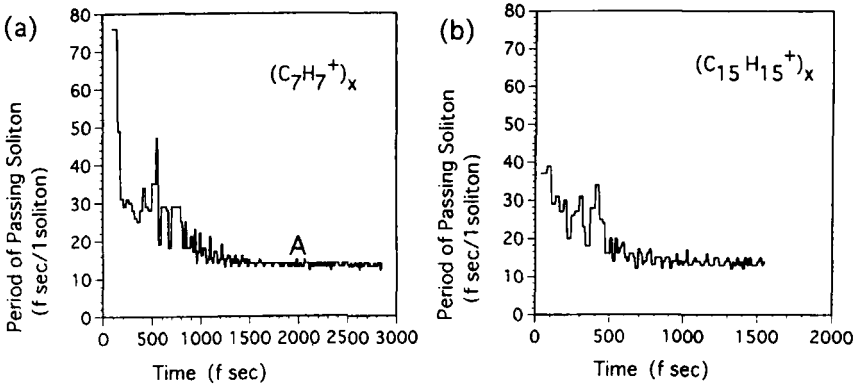

FIGURE 3 The period for solitons passing one after another at one point on the chain. (a) $(C_7H_7)^+_x$ and (b) $(C_{15}H_{15})^+_x$.

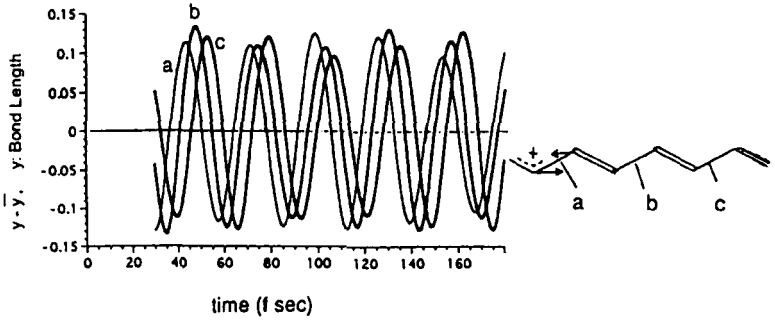

FIGURE 4 The change in bond length at A in FIGURE 3. The bonds are shown on the right.

SOLITON LATTICE SLIDING AND FINAL SPEED

Sliding simulations are carried out by applying an electric field to polyacetylene. It is approximated that an atom will respond to the field according to the total charge of the atom in the molecular dynamics. At each time step, the electronic state and the forces on the atoms are calculated by the MNDO method and the atoms are moved. In this process, the soliton lattice has begun to slide automatically. The results for $(C_7H_7)^+_x$ and $(C_{15}H_{15})^+_x$ are shown in Fig. 3, where an electric field of 0.2~0.4 V/Å is applied. Fig. 3 shows a time period which is the time interval between one soliton passing and another arriving at the same point. In this figure, the sliding speed is slow at the beginning and accelerates as time proceeds, and finally the period settles down to a roughly constant value (16 fs). The saturated speed does not depend on the strength of the electric field in this condition. And both $(C_7H_7)^+_x$ and $(C_{15}H_{15})^+_x$ have the same final period. The motions of C-C bonds at the saturated speed are shown in Fig. 4, In the figure, the C-C stretching vibration is synchronized with the soliton passing. The sliding speed of the soliton lattice finally becomes stable as determined by the coupling which is explained above and in Fig. 2.

SOME OTHER SATURATED SPEEDS

If the neighbouring solitons are not close enough or if the kinetic energy is not strong enough, the next soliton in Fig. 2 cannot catch up with the time when the atoms release their potential energy. The periods of passing solitons for $(C_{18}H_{18})^+_x$ and $(C_{24}H_{24})^+_x$ are shown in Fig. 5, where the soliton density is lower than in Fig. 3. The period settles down to about 32 fs in Fig. 5(a), and to about 47 fs in Fig. 5(b). These are two or three times as long as the above mentioned final period. This means that the period of the passing solitons is synchronized with two or three times the period of the C-C stretching vibration. The distributions of the bond length, y, are shown in Figs. 6 and 7 by the parameter $(-1)^i(y-\bar{y})$, where it is about 1000 fs after the electric field is applied. The distribution of the C-C bond implies that the C-C bond vibrates twice between the passing solitons in Fig. 6 and three times in Fig. 7.

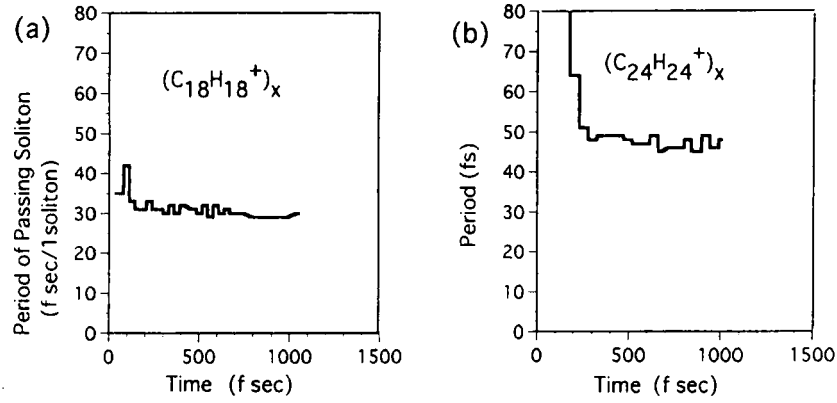

FIGURE 5 The period for solitons passing one after another at one point on the chain. (a) $(C_{18}H_{18})^{+}_{x}$ and (b) $(C_{24}H_{24})^{+}_{x}$.

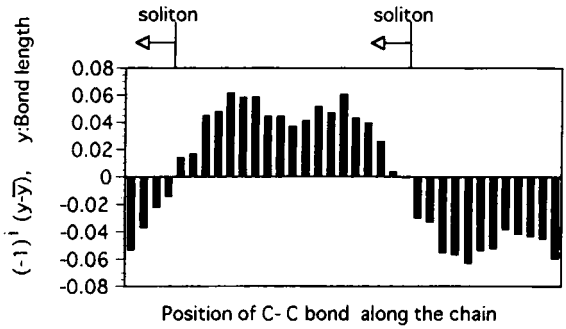

FIGURE 6 The distribution of the bond length y by $(-1)^{i}(y-y)$ for $(C_{18}H_{18})^{+}_{x}$; 1070 fs after the electric field is applied.

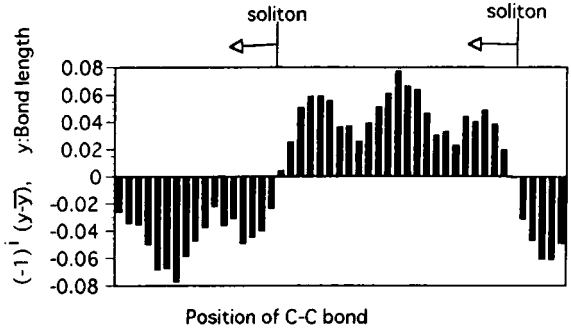

FIGURE 7 The distribution of the bond length y by $(-1)^{i}(y-y)$ for $(C_{24}H_{24})^{+}_{x}$; 960 fs after the electric field is applied.

CONCLUSIONS

A study of the behaviour of the soliton lattice for trans-polyacetylene, using the semi-empirical MNDO method with molecular dynamics and normal mode calculation, has revealed the following.

(1) A vibrational mode calculation has shown that one of the modes is a soliton lattice sliding mode.

(2) A molecular dynamics calculation showed that the soliton lattice begins to slide automatically and the sliding speed finally becomes stable as determined by the following coupling.

(3) On considering the displacement vectors of the soliton lattice sliding mode, coupling is found to occur where the vibration of the C-C stretching is synchronized with the soliton passing.

(4) If the neighbouring solitons are not close enough to catch up with the above coupling, the period of the passing solitons can be synchronized with two or three times the period of the C-C stretching vibration.

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