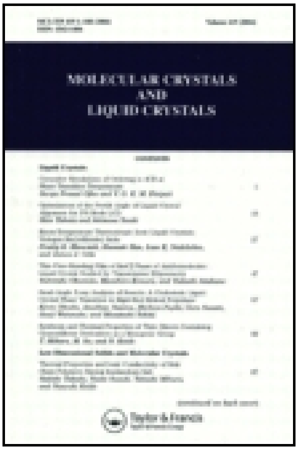

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Molecular Vibrations and Dynamics of Soliton Lattice for Trans-Polyacetylene

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MOLECULAR VIBRATIONS AND DYNAMICS OF SOLITON LATTICE FOR TRANS-POLYACETYLENE

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Abstract A semi-empirical MNDO method has been used to study soliton behaviours in trans-polyacetylene. The optimized structure shows a soliton lattice. The vibrational modes for the lattice structure have been calculated. One of the C-C stretching modes is a soliton lattice sliding mode. In putting some initial kinetic energy into this mode, molecular dynamics simulations have been carried out. The charged soliton lattice can slide along the polymer chain. On applying an electric field, the automatic sliding of the soliton lattice has been observed. The sliding motion couples strongly with one of the C-C stretching modes. This coupling is found to help to stabilize the lattice sliding speed.

INTRODUCTION

Heavily doped trans-polyacetylene which shows high conductivity has been studied by various methods for more than ten years. However, the question as to whether the structure is metallic, a soliton lattice or otherwise is still under discussion. Some work using spectroscopic data[1,2] and thermoelectric power[3] has insisted that the experimentally observed behaviour can be better explained by a soliton lattice than by a metallic structure, and some theoretical work[4,5] has shown the stability of the soliton lattice structure.

In this work, we study the structure and migration mechanisms of solitons in heavily doped trans-polyacetylene. We have calculated the vibrational modes and the molecular dynamics of a charged soliton lattice and have clarified some of the behaviour of the lattice in this polymer.

STRUCTURE AND VIBRATIONS OF THE SOLITON LATTICE

In our model molecule of heavily doped trans-polyacetylene, we have put one positive charge for some CH units, $(C_nH_n)^+$ (n = 4 - 10), and have made a periodic boundary condition where each periodic unit includes an even number of charges and carbons, *i.e.* unit = $(C_nH_n)_m{}^{m+}$ (m : even). The calculation is based on a semi-empirical molecular orbital MNDO method. First, we have optimized the geometry. The optimized structure shows that the solitons in the chain form a soliton lattice, *i.e.* the periodic repetition of a soliton and an anti-soliton. This is consistent with some previously published works[4,5] and discussion of these systems[1-3].

The vibrational modes have been calculated by solving the force constant matrix for the charged soliton lattice. For some of the modes, the displacements are distributed at and around the solitons. One of them has a low frequency (220 cm^{-1} for $(C_6H_6{}^+)_x$) and a strong I.R. absorption despite being a C-C stretching mode. This mode is shown in Figure 1. The displacement vectors shown there indicate that double and single bonds interchange on the right side of each soliton. This makes each soliton translate together to the right. This mode can therefore be called a soliton lattice sliding mode. The charge density of the carbon atoms is shown in Figure 1.

FIGURE 1 The displacement vectors of the soliton lattice sliding mode and the charge density distribution of the optimized structure.

A comparison of the charge density and the displacement vectors reveals that the positively charged carbons move to the right while the negatively charged ones move to the left. This causes a strong infrared absorption intensity. In previous work[6,7], the low lying broad I.R. peak $0<v<900$ cm^{-1} has been assigned to the single soliton sliding mode which corresponds to lightly doped polyacetylene. In the heavily doped system, this peak can be assigned to the soliton lattice sliding mode. As for the other modes in the present calculation, there are some C-C stretching modes which indicate soliton translation but not lattice sliding; those include solitons approaching and repelling each other.

SOLITON LATTICE SLIDING

A molecular dynamics simulations have been carried out in which some initial kinetic energy has been applied according to the displacement vectors of the soliton lattice sliding mode. The electronic state and the forces on the atoms are calculated at each time step of the molecular dynamics, and the atoms are moved. Our results show that the charged soliton lattice can slide along the polymer chain. For example, in Figure 2, we present results for which the initial kinetic energy is 20 kcal/mol-soliton. In this figure, there are solitons where the lines cross zero, and these solitons slide to the right along the chain. In this process, if the carbon atoms at a soliton are accelerated too much, the excess kinetic energy becomes the potential energy of the C-C bonds on the same carbon atoms after the soliton has gone away. This has occured at position A in Figure 2(a) as the marks are raised at 5.0 fs. After that, the carbon atoms release the potential energy as at point A in Figure 2(b) and let another soliton pass from the left to the right. This phenomenon implies that the period of the C-C stretching vibration becomes the same as the period of passing solitons .

We have also applied an electric field to polyacetylene with the soliton lattice. In this calculation, we have approximated that an atom will respond to the field according to the total charge of the atom at each time step of the molecular dynamics. In this simulation, the soliton lattice has begun to slide automatically. One of the results is shown in Figures 3-5, where an electric field of 0.2V/A is applied. Figure 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 goes on, and finally the period settles down to a roughly constant value (16 fs). The motions of C-C bonds at the beginning are shown in Figure 4, and those when the final speed is attained are shown in Figure 5. In these figures a soliton passes when the line crosses zero. In Figure 4, the vibration of C-C bond stretching is observed, which is independent of the soliton sliding. But in Figure 5, the vibration of the C-C stretching is synchronized with the soliton passing. This means that the sliding speed of the soliton lattice finally becomes stable as determined by the coupling between the sliding and the C-C stretching motion.

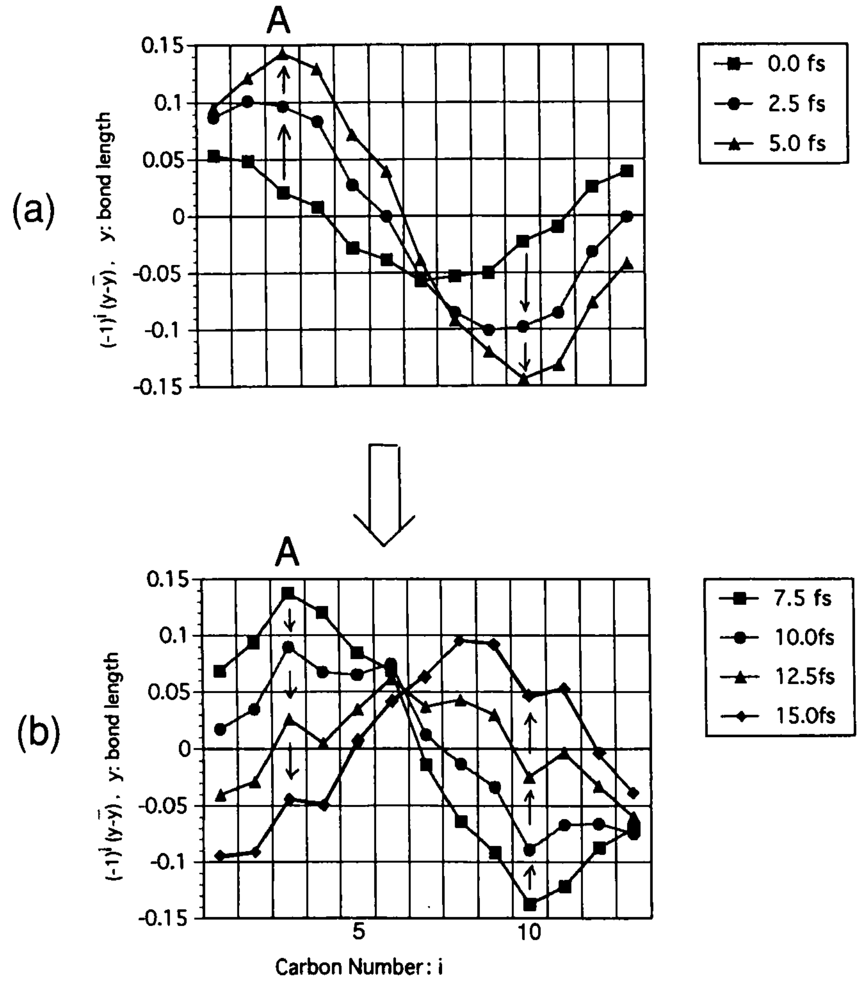

FIGURE 2 The behaviour of the poyacetylene chain $(C_7H_7^+)_x$ after initial kinetic energy is applied.

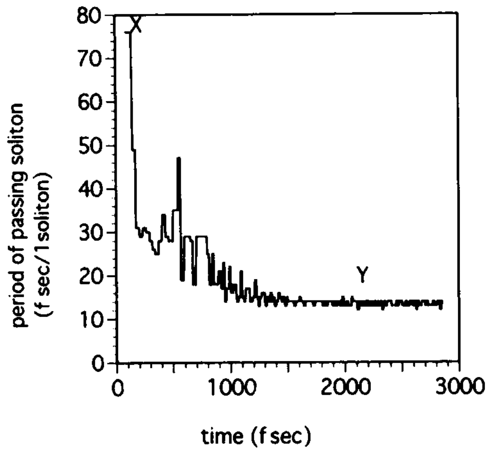

FIGURE 3 The period for solitons passing one after another observed at one point on the chain, $(C_6H_6^+)_x$.

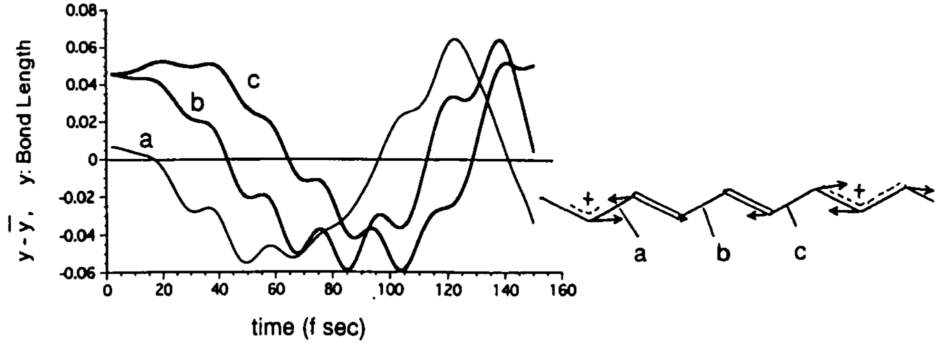

FIGURE 4 The change in bond length at X in Figure 3. The bonds are shown on the right.

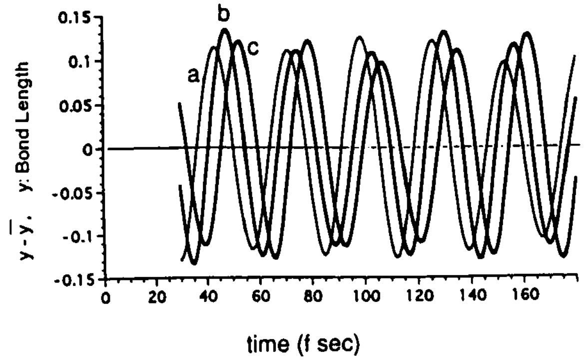

FIGURE 5 The change in bond length at Y in Figure 3. The bonds are the same as in Figure 4.

CONCLUSIONS

As a result of the calculation of the structure and molecular dynamics for trans-polyacetylene, the following conclusions may be made.

(1) The optimized structure according to this calculation is a soliton lattice, in agreement with previous work.

(2) The vibrational mode calculation reveals that one of the C-C stretching modes exhibits a soliton lattice sliding motion.

(3) By applying some initial kinetic energy corresponding to the sliding mode in the molecular dynamics calculation, the charged soliton lattice can slide along the polymer chain. Moreover, on applying an electric field, the automatic soliton lattice sliding has been observed.

(4) The sliding motion couples strongly with one of the C-C stretching modes. This coupling helps to stabilize the sliding speed.

In the present work, we have shown that (1)-(4) occur in one infinite trans-polyacetylene chain. We expect that (3) and (4) above can explain the conduction mechanism of heavily doped polyacetylene. Our calculations, however, do not yet include dopants or various kinks, which cause charged solitons to be pinned. Calculations which include such effects remain for future study.

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