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1995 J. Phys.: Condens. Matter 7 L7

(http://iopscience.iop.org/0953-8984/7/2/001)

J. Phys.: Condens. Matter 7 (1995) L7–L11. Printed in the UK

LETTER TO THE EDITOR

Local vibration around a ring-torsional soliton in polyaniline

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Received 5 September 1994

Abstract. This letter investigates ring-rotational vibration of a one-band model with electron–libron coupling and a steric potential suggested by Ginders and Epstein for the leucoemeraldine-base (LB) form of polyaniline. Five local modes around a hole soliton are found, and this number if consistent with infrared and Raman lines.

Polyaniline is a class of ring-containing conducting polymer. It has attracted much interest both experimentally and theoretically [1–7]. It is reported that rotational degrees of freedom (librons) of phenyl rings play an important role in the physics of the polymer, especially to support defects—the soliton and the polaron [2–5]. Infrared (IR) and Raman data have been collected as signatures of the existence of defect states, which relate to local modes of lattice vibration around the defect. The situation is well known for another conducting polymer, polyacetylene [7–9]. This letter investigates how the mechanism works in the case of polyaniline.

Ginder and Epstein (GE) proposed a tight-binding model to describe the LB form of polyaniline [2]. Mackenzie [3] and GE have a tanh soliton in the continuum limit. In this letter, we investigate the rotational vibration of phenyl rings in a chain containing a soliton, and try to understand the IR and Raman spectra.

We start from GE's effective one-band Hamiltonian [2, 3]

$$H = H_{\text{kin}} + H_{\text{el}} + V_{\text{s}} \tag{1}$$

where

$$H_{\text{kin}} = \sum_j \frac{1}{2} I \left(\frac{\alpha \phi_j}{\mathrm{d}t} \right)^2 \tag{1a}$$

represents the rotational kinetic energy of the constituent phenyl rings of the lattice, I is the moment of inertia and

$$H_{\text{el}} = \sum_{j,s} \left(\frac{\alpha_N}{2} + \frac{\mathrm{d}}{2} \cos \phi_j^2 \right) \left(C_{j,s}^{\dagger} C_{j,s} + C_{j+1,s}^{\dagger} C_{j+1,s} \right) - t_0 \sum_{j,s} \cos^2 \phi_j \left(C_{j+1,s}^{\dagger} C_{j,s} + \text{HC} \right) \tag{1b}$$

represents the energy of electrons. Here $C_{j,s}^{\dagger}$ ($C_{j,s}$) denotes creation (annihilation) of an electron with spin s at nitrogen site j.

$$V_{\text{s}} = V_{2,0} \sum_j \sin^2 \phi_j + V_{4,0} \sum_j \sin^4 \phi_j + V_{1,1} \sum_j \left(\sin \phi_j - \sin \phi_{j-1} \right)^2 \tag{1c}$$

0953-8984/95/020007+05$19.50

represents the steric potential.

The nitrogen atoms form a zig-zag lattice defining a plane. The angle ϕ_j measures the rotation of the phenyl ring between nitrogen site j and $j+1$ out of this plane. These angles ϕ_j are bosonic degrees of freedom, which are treated in the adiabatic approximation. GE used a hole version of this model. They employed the following set of parameters: $I = 89$ amu Å^2, $\alpha_N = -2$ eV, $\alpha = 2.76$ eV, $t_0 = 1.81$ eV, $V_{2,0} = 2$ eV, $V_{4,0} = 1.45$ eV, $V_{1,1} = 0.2$ eV.

We will find the lowest energy state self-consistently for a chain with an odd number of sites and periodic boundary conditions for the angles ϕ_j, the filled valence band with a hole; such a system must contain a soliton. Then we find the matrix of lattice dynamics based on the second-order perturbation theory. We measure energy in units t_0; all parameters of the model are dimensionless except I.

The electron eigenequation is

$$\epsilon_\mu \psi_\mu(j) = \left[\alpha_N + \frac{\alpha}{2}\left(\cos^2\phi_{j-1} + \cos^2\phi_{j+1}\right)\right]\psi_\mu(j) - \cos^2\phi_{j-1}\psi_\mu(j-1) - \cos^2\phi_{j+1}\psi_\mu(j+1). \tag{2}$$

Here ϵ_μ is the eigenenergy and ψ_μ the related wavefunction.

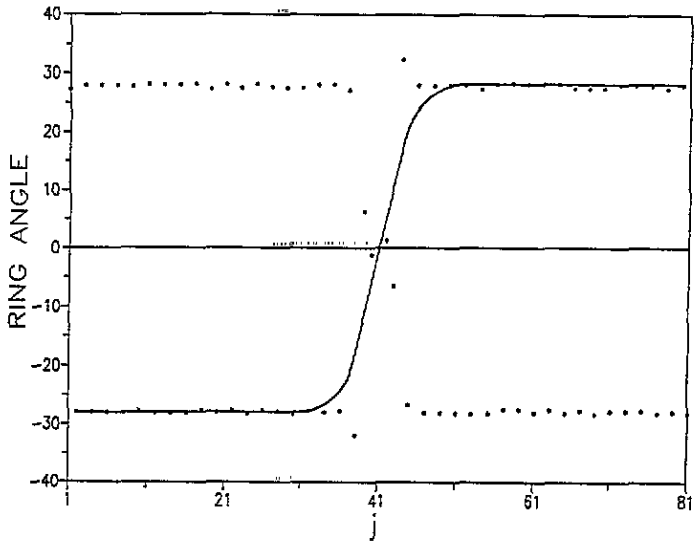

Figure 1. Ring-angle pattern for a hole soliton in chain with 81 sites. The centre of the soliton is at site 41. The tanh line marks odd-site rings.

Supposing a small deviation $\{\delta\phi_j\}$ from its ring-angle pattern $\{\phi_j\}$, the total energy of the system can be written as

$$E_{\text{total}} = E_0 + \sum_n A_n \delta\phi_n + \frac{1}{2}\sum_{m,n} B_{m,n}\delta\phi_m\delta\phi_n + \ldots. \tag{3}$$

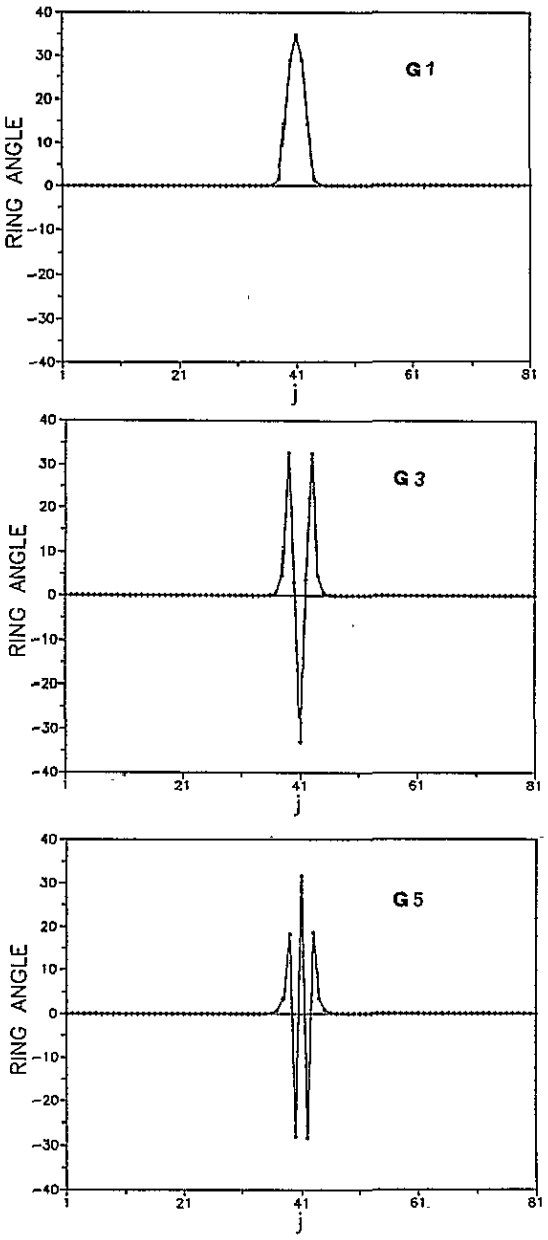

Figure 2. Local modes (with odd parity) of ring-rotational vibration around the soliton.

Here,

$$A_n = 2V_{4,0}\sin^3\phi_n + \left[\sum_{\mu(\mathrm{occ})} F^s_{\mu\mu}(n) + 2V_{1,1} - V_{2,0}\right]\sin\phi_n - V_{1,1}\left(\sin\phi_{n+1} + \sin\phi_{n-1}\right). \quad (4)$$

Here $F^s_{\mu\nu}(j)$ is defined by

$$F^s_{\mu\nu}(j) = \left\langle \mu \middle| \left(C^\dagger_{j+1,s}C_{j,s} + \mathrm{HC}\right) \middle| \nu \right\rangle - \frac{\alpha}{2}\left\langle \mu \middle| \left(C^\dagger_{j,s}C_{j,s} + C^\dagger_{j+1,s}C_{j+1,s}\right) \middle| \nu \right\rangle. \quad (5)$$

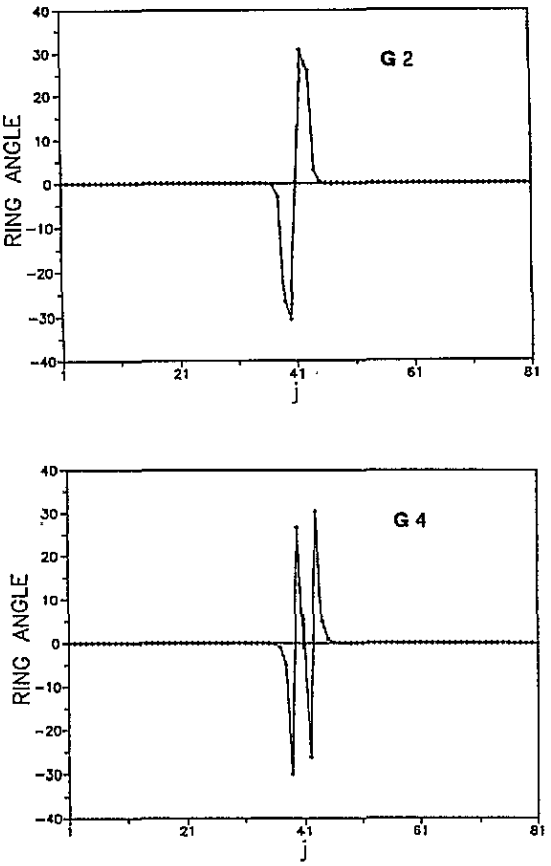

Figure 3. Local modes (with even parity) of ring-rotational vibration around the soliton.

The minimum energy needs $A_n = 0$. Solving simultaneous equations (2) and (4) by iterations, we get the electronic states and the static ring-angle pattern. The ring-angle pattern of the soliton is plotted in figure 1. Then the dynamics matrix can be expressed as

$$B_{m,n} = 2\sin\phi_m\cos\phi_m\sin\phi_n\cos\phi_n \sum_{\mu(\mathrm{occ})}\sum_{\gamma(\mathrm{unocc})}\sum_{s}\frac{F^s_{\mu\gamma}(m)F^s_{\mu\gamma}(n)}{\epsilon_\mu-\epsilon_\gamma}$$
$$+\Big[\big(2V_{1,1}-V_{2,0}\big)\big(1-2\sin^2\phi_n\big)+2V_{4,0}\sin^2\phi_n\big(3-4\sin^2\phi_n\big)$$
$$+V_{1,1}\sin\phi_n\big(\sin\phi_{n-1}+\sin\phi_{n+1}\big)\Big]\delta_{m,n}-V_{1,1}\cos\phi_n\big(\cos\phi_{n-1}\delta_{m,n-1}$$
$$+\cos\phi_{n+1}\delta_{m,n+1}\big). \tag{6}$$

Here $\mu(\mathrm{occ})$ and $\gamma(\mathrm{unocc})$ means the summation over all occupied and unoccupied states respectively. Diagonalizing matrix B, we get all modes of ring-rotational vibration. Of them, five are local around the soliton. Their frequencies are expressed as

$$\omega_1^2 = 0 \qquad \omega_2^2 = 1.95\omega_0^2 \qquad \omega_3^2 = 4.32\omega_0^2 \qquad \omega_4^2 = 6.49\omega_0^2 \qquad \omega_5^2 = 7.94\omega_0^2.$$

Here $\omega_0^2 = t_0/I$. With frequency, G1 is the so-called Goldstone mode. G1, G3 and G5 are of even parity, as shown in figure 2. This is infrared active vibration (IRAV). G2 and G4 are of odd parity, as shown in figure 3. They are Raman active.

Experimentally, two Raman lines [6] and two IRAV modes [1] have been observed in photo-induced LB; they are at 1188 cm, 1632 cm and 1144 cm, 1574 cm respectively. The number of lines is consistent with the present theory.

On the other hand, Harada *et al* [6] have observed four Raman lines in pernigraniline, the fully oxidized form of polyaniline. After being photo-induced, four IRAV modes appear. Some authors [5] tentatively assumed that the IRAV modes arise from the formerly Raman active modes. The number of local modes in the present work is consistent with the sum number of the IR and Raman lines.

There is some deviation in detail between the present theory and the experimental data. Further calculations may vary the model parameters and the filling extent of the valence band.

In conclusion, we have calculated ring-rotation–vibrational modes of LB, the reduced form of polyaniline. Five local modes around a ring-torsional soliton are found. The number is consistent with the IR and Raman spectra.

The author is indebted to J Voit for stimulating correspondence.

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