Localized phonons in a pristine polyacene chain

**LETTER TO THE EDITOR**

# Localized phonons in a pristine polyacene chain

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**Abstract**
Within an extended Su–Schrieffer–Heeger model, we investigate the localized
phonons in a pristine polyacene chain, in which there is an interchain-coupled
neutral soliton of $D_{2h}$ symmetry. In addition to three pairs of twofold-degenerate
edge modes (three infrared active and three Raman active), we found in total
nine localized modes, among which four (three $B_{2u}$ and one $B_{3u}$) modes are
infrared active and the others (two $A_g$ and three $B_{1g}$) modes are Raman active.

Recently, there has been great progress as regards organic materials, such as organic super-
conductors [1], organic photovoltaic diodes [2], and organic solid-state injection lasers [3]; all
of these are based on the crystals of short acenes and have renewed interest in the electronic
properties of polyacene chains. Indeed, the properties of polyacene, as a novel conducting
polymer, have long been the focus of theoretical studies [4–11], though a long polyacene chain
has not been synthesized yet. A polyacene chain can be considered as two polyacetylene
chains coupled by cross-alternate interactions. Much theoretical work has been devoted to
the ground state of an infinite polyacene chain [4–9]. By means of a tight-binding study, a
polyacene chain composed of a finite number of aromatic rings has been studied [12] and its
elementary excitations and optical properties have been given. An interchain-coupled neutral
soliton was observed in a pristine polyacene chain [12]. In this letter, we would like to report
a primary investigation on localized phonons in a polyacene chain. In addition to the edge
modes, nine localized modes are found in a pristine polyacene chain. Among these modes,
four are infrared active while the others are Raman active.

Since a polyacene chain can be considered as two polyacetylene chains with alternate
interchain coupling, we use the following extended Su–Schrieffer–Heeger model [11–13]:

$$H = H_0 + H_1 + H_2, \tag{1}$$

where

$$H_0 = - \sum_{j,n,\sigma} [t_0 + \alpha(u_{j,n} - u_{j,n+1})](c_{j,n,\sigma}^\dagger c_{j,n+1,\sigma} + c_{j,n+1,\sigma}^\dagger c_{j,n,\sigma}) \tag{2}$$

describes the intrachain interactions,

$$H_1 = - \sum_{n,\sigma} [t_1 - (-1)^n t_2](c_{1,n,\sigma}^\dagger c_{2,n,\sigma} + c_{2,n,\sigma}^\dagger c_{1,n,\sigma}) \tag{3}$$

describes the alternate interchain interactions, and

$$H_2 = \tfrac{1}{2} K \sum_{j,n} (u_{j,n} - u_{j,n+1})^2 \tag{4}$$

is the lattice elastic energy; $j = 1, 2$ denotes the chain index, the site index $n$ runs from 1 to $2m + 1$ for a polyacene chain composed of $m$ aromatic rings, the quantity $t_0$ is the transfer integral for $\pi$-electrons in a regular lattice, $\alpha$ is the electron–lattice coupling constant, and $u_{j,n}$ is the lattice displacement of the $n$th site on chain $j$ from its equidistant position. The operator $c^+_{j,n,\sigma}$ ($c_{j,n,\sigma}$) creates (annihilates) a $\pi$-electron with spin $\sigma$ at the $n$th site on chain $j$, $K$ is the elastic constant due to the $\sigma$-bonds, and $t_1 = t_2$ corresponds to the case of polyacene. *Ab initio* calculations on short polyacene chains have shown that the bonds between the two chains are slightly longer than the single bond in the chain, so we would like to use $2t_1 = 0.864t_0$ in our calculations. The other quantities are taken as follows: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV Å$^{-1}$, $K = 15.5$ eV Å$^{-2}$; then the dimensionless electron–lattice coupling constant $\lambda$ ($\equiv 2\alpha^2/\pi t_0 K$) $= 0.276$ [11, 12], which is larger than that for polyacetylene [13].

It is easy to show [12] that *cis*-phases ($u_{1,n} \equiv u_{2,n}$) and *trans*-phases ($u_{1,n} \equiv -u_{2,n}$) are degenerate for an infinite polyacene, but for a finite polyacene chain, the bond configuration will always be in the *cis*-phase since the edge bonds should be short in a single polyacetylene chain as well as in a polyacene chain. So we should have $u_{j,n} \equiv u_n$ ($j = 1, 2$) for the bond configuration in the ground state of a polyacene chain, and the electronic wavefunctions must be symmetric ($\phi(1, n) = \phi(2, n) \equiv \phi^{(s)}(n)$) or anti-symmetric ($\phi(1, n) = -\phi(2, n) \equiv \phi^{(a)}(n)$). The bond order parameter is defined as $\delta_l = (-1)^l (u_{l+1} - u_l)$; the bond index $l$ runs from 1 to $2m$.

Then the Hamiltonian can be solved self-consistently using the following coupled equations:

$$\varepsilon^{(\kappa)}_\mu \phi^{(\kappa)}_\mu(n) = -[t_0 - (-1)^n \alpha \delta_n]\phi^{(\kappa)}_\mu(n+1) - [t_0 + (-1)^n \alpha \delta_{n-1}]\phi^{(\kappa)}_\mu(n-1)$$
$$- \eta_\kappa [t_1 - (-1)^n t_2]\phi^{(\kappa)}_\mu(n), \tag{5}$$

$$\delta_l = -(-1)^l \frac{2\alpha}{K} \sum_{\mu\,(occ.)} \left[ \phi^{(\kappa)}_\mu(l)\phi^{(\kappa)}_\mu(l+1) - \frac{1}{2m}\sum_l \phi^{(\kappa)}_\mu(l)\phi^{(\kappa)}_\mu(l+1) \right], \tag{6}$$

where $\kappa = s, a$, and $\eta_s = 1$ for symmetric states $\phi^{(s)}_\mu$ and $\eta_a = -1$ for anti-symmetric states $\phi^{(a)}_\mu$; the summation over occupied states is for both symmetric and anti-symmetric states; the last term in equation (6) comes from the Lagrange multiplier which is introduced to keep the total chain length unchanged—that is, $\sum_l (-1)^l \delta_l = 0$, and the wavefunction $\phi^{(\kappa)}_\mu(n)$ has the following properties:

$$\sum_n \phi^{(\kappa)}_\mu(n)\phi^{(\kappa)}_\nu(n) = \delta_{\mu\nu}/2 \qquad \sum_\mu \phi^{(\kappa)}_\mu(m)\phi^{(\kappa)}_\mu(n) = \delta_{mn}/2. \tag{7}$$

The ground state is

$$|G\rangle = \prod_{\mu,\sigma\,(occ.)} a^{(\kappa)\dagger}_{\mu,\sigma}|0\rangle, \tag{8}$$

where

$$a^{(\kappa)\dagger}_{\mu,\sigma} = \sum_n \phi^{(\kappa)}_\mu(n)(c^\dagger_{1,n,\sigma} + \eta_\kappa c^\dagger_{2,n,\sigma}), \tag{9}$$

$$c^\dagger_{j,n,\sigma} = \sum_\mu [\phi^{(s)}_\mu(n)a^{(s)\dagger}_{\mu,\sigma} + (3 - 2j)\phi^{(a)}_\mu(n)a^{(a)\dagger}_{\mu,\sigma}]. \tag{10}$$

Figure 1 shows the bond configuration $\{\delta_l\}$, with the schematic representation of the energy spectrum given as the inset, for a pristine polyacene chain composed of $m = 100$ aromatic rings, obtained by solving numerically the self-consistent equations (5) and (6). It is clear
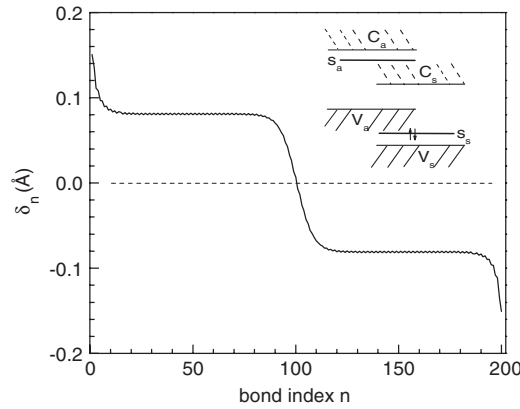
**Figure 1.** Bond alternation parameters $\delta_n$ of the ground state in a pristine polyacene chain. The inset shows a schematic representation of the electronic energy spectrum.

that the bond configuration has the symmetry $D_{2h}$, but there are only four one-dimensional irreducible representations $A_g$, $B_{1g}$, $B_{2u}$, and $B_{3u}$ for the model that we are considering for a polyacene chain, and the phonon modes corresponding to $B_{2u}$ and $B_{3u}$ are infrared active while the modes corresponding to $A_g$ and $B_{1g}$ are Raman active. Due to the interchain coupling [12], a pair of localized electronic levels originally at the mid-gap are down-shifted ($S_s$) and up-shifted ($S_a$) respectively, as shown in the inset of figure 1.

Now we consider a small departure $d_{j,n}$ of atoms from the self-consistent bond configuration $\{\delta_n\}$—that is, $u_{j,n} = u_n + (-1)^n d_{j,n}$; the perturbed electronic Hamiltonian due to the departure $\{d_{j,n}\}$ is

$$H'_e = -\alpha \sum_{j,n,\sigma} (-1)^n (d_{j,n} + d_{j,n+1})(c^\dagger_{j,n,\sigma} c_{j,n+1,\sigma} + c^\dagger_{j,n+1,\sigma} c_{j,n,\sigma}), \tag{11}$$

and the total energy of the system is expanded

$$E_t = E_0 + E_1 + E_2 + \cdots \tag{12}$$

in orders of the small quantities $d_{j,n}$, by perturbation theory. The vanishing of the first-order term $E_1$ in the total energy gives the self-consistent equations (5) and (6). The second-order term of the total energy is given by

$$E_2 = \sum_e \frac{|\langle e|H'_e|G\rangle|^2}{E_g^{(0)} - E_e^{(0)}} + \frac{1}{2}K \sum_{j,n}(d_{j,n} + d_{j,n+1})^2. \tag{13}$$

Defining the symmetric and anti-symmetric vibrational variables

$$d_n^{(s)} = \frac{1}{\sqrt{2}}(d_{1,n} + d_{2,n}), \qquad d_n^{(a)} = \frac{1}{\sqrt{2}}(d_{1,n} - d_{2,n}), \tag{14}$$

the vibrational Hamiltonian can be written as

$$H_{vib} = 2K \sum_{\kappa=s,a} \sum_{n,n'} A_{n,n'}^{(\kappa)} d_n^{(\kappa)} d_{n'}^{(\kappa)} + \frac{1}{2}M \sum_{\kappa=s,a} \sum_n (\dot{d}_n^{(\kappa)})^2, \tag{15}$$

where the elements of the vibrational matrices are as follows:

$$A_{n,n'}^{(\kappa)} = \frac{1}{4}(\zeta_n \delta_{n,n'} + \delta_{n,n'\pm1}) + \frac{1}{2}\lambda\pi t_0(-1)^{n+n'}(\Xi_{n,n'}^{(\kappa)} - \Xi_{n,n'-1}^{(\kappa)} - \Xi_{n-1,n'}^{(\kappa)} + \Xi_{n-1,n'-1}^{(\kappa)}), \tag{16}$$

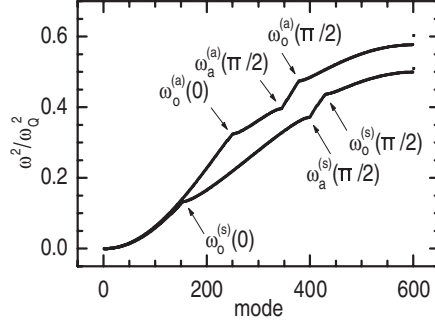where $\zeta_n = 1$ for $n = 1$ and $n = 2m + 1$, $\zeta_n = 2$ for all other $n$, and

**Figure 2.** Energies of phonon modes. The phonon energies corresponding the modes at $q = 0$ and $\pi/2$ in a uniform dimerized polyacene are indicated by arrows.
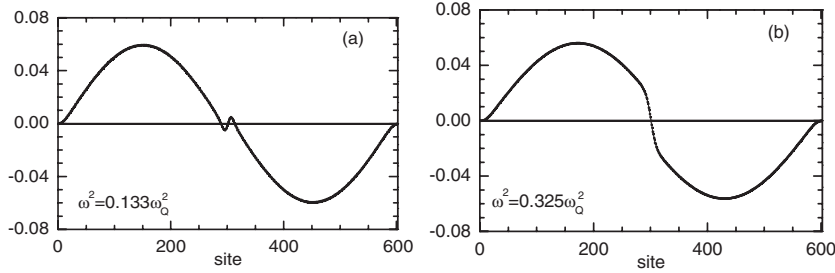


**Figure 3.** The optical phonon modes corresponding to (a) $\omega_o^{(s)}(0)$ and (b) $\omega_o^{(a)}(0)$ in a uniform dimerized polyacene.

$$\Xi_{n,n'}^{(s)} = \sum_{\mu\,(occ.),\nu\,(unocc.)} \sum_{\kappa=s,a} \frac{\chi_{\mu\nu}^{\kappa\kappa}(n)\chi_{\mu\nu}^{\kappa\kappa}(n')}{\varepsilon_\mu^{(\kappa)} - \varepsilon_\nu^{(\kappa)}}, \tag{17}$$

$$\Xi_{n,n'}^{(a)} = \sum_{\mu\,(occ.),\nu\,(unocc.)} \sum_{\kappa=s,a} \frac{\chi_{\mu\nu}^{\kappa\overline{\kappa}}(n)\chi_{\mu\nu}^{\kappa\overline{\kappa}}(n')}{\varepsilon_\mu^{(\kappa)} - \varepsilon_\nu^{(\overline{\kappa})}}, \tag{18}$$

where $\kappa = s, \overline{\kappa} = a$ and $\kappa = a, \overline{\kappa} = s$, and

$$\chi_{\mu\nu}^{\kappa\kappa'}(n) \equiv \phi_\nu^{(\kappa')}(n)\phi_\mu^{(\kappa)}(n+1) + \phi_\nu^{(\kappa')}(n+1)\phi_\mu^{(\kappa)}(n). \tag{19}$$

So we have the phonon frequency $\omega^{(\kappa)}$ from $(\omega^{(\kappa)})^2 = \omega_Q^2\lambda^{(\kappa)}$, where $\lambda^{(\kappa)}$ are the eigenvalues of the vibrational matrix $\{A_{n,n'}^{(\kappa)}\}$ given in equation (16) and the bare phonon frequency $\omega_Q \equiv \sqrt{4K/M}$, which is about 1900 cm$^{-1}$ for polyacene.

The diagonalization of the vibrational matrix $\{A_{n,n'}^{(\kappa)}\}$ gives both the eigenvalue $\lambda^{(\kappa)}$ and the vibrational eigenwavefunction $d^{(\kappa)}(n)$. To identify the localized modes, we define the localization factor $\gamma = \sum_n |d(n)|^4 / \sum_n |d(n)|^2$, which will decay as $1/m$ for an extended vibrational mode when the size $m$ becomes larger and larger, while it will approach a nonzero constant for a localized vibrational mode. We have done the calculations from $m = 100$–300, and a very good convergence for the localization factor is reached for a polyacene chain composed of $m = 300$ aromatic rings, for which all results presented below are obtained.

Figure 2 shows the energies of all vibrational modes. The energy positions of the vibrations corresponding to the modes at $q = 0$ and $\pi/2$ in a uniform dimerized polyacene are indicated by arrows. The two lowest optical modes corresponding to $\omega_o^{(s)}(0)$ and $\omega_o^{(a)}(0)$ are shown in figure 3; the energies are $\omega^2/\omega_Q^2 = 0.133$ and 0.325, respectively. In the weak-coupling model
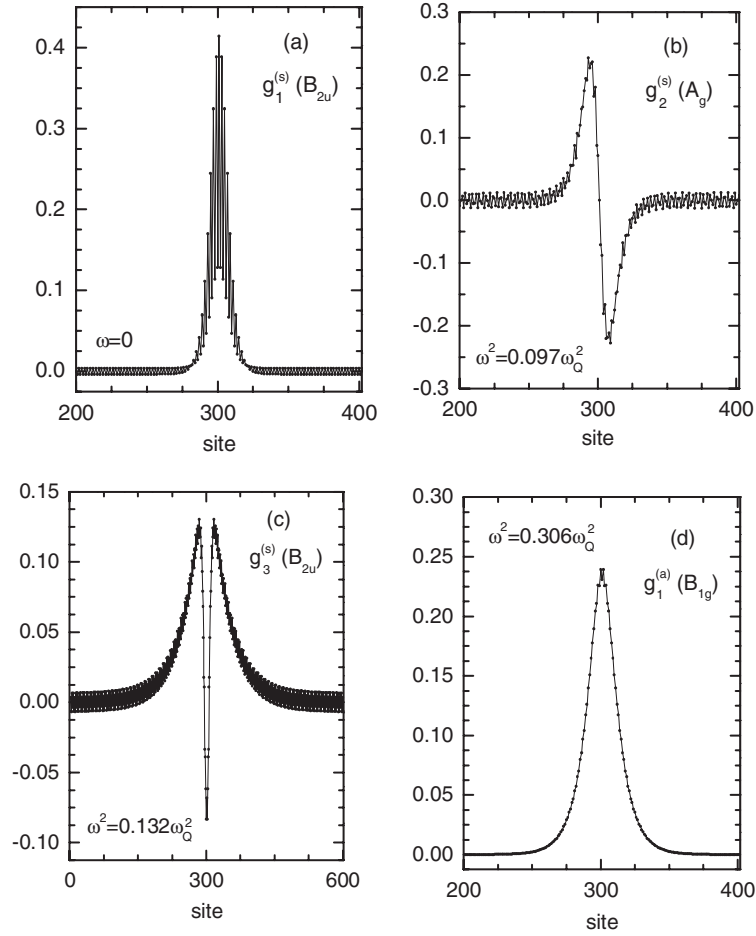
**Figure 4.** Localized slowly varying phonon modes ($q = 0$).

of polyacetylene, $\omega_o^2/\omega_Q^2 = 2\lambda$, which has a value of 0.552 for polyacene. Our results are much smaller than that value; this is clearly a result of the reduction of the dimerization due to the interchain coupling [14]. Furthermore, it can be seen that there are three nodes corresponding to a phase shift of $3\pi$ in the mode $\omega_o^{(s)}(0)$ and one node corresponding to a phase shift of $\pi$ in the mode $\omega_o^{(a)}(0)$, which indicate there are three symmetric ($g_1^{(s)}$, $g_2^{(s)}$, and $g_3^{(s)}$) localized modes and one anti-symmetric ($g_1^{(a)}$) localized mode at $q = 0$ according to Levinson's theorem [15]. Our calculation gives these four localized slowly varying modes as shown in figure 4; the corresponding representations of the group $D_{2h}$ are $B_{2u}$, $A_g$, $B_{2u}$, and $B_{1g}$, respectively. The first mode $g_1^{(s)}$ (the Goldstone mode corresponding the translation of the neutral soliton), the second mode $g_2^{(s)}$ (the amplitude mode corresponding to the amplitude vibration of the neutral soliton), and the third mode $g_3^{(s)}$ are the same as those found in polyacetylene [16]; the energies are $\omega^2/\omega_Q^2 = 0$, 0.097, and 0.132, respectively. The anti-symmetric mode $g_1^{(a)}$ is the relative vibration of the soliton structures in the two chains of polyacene; its energy $\omega^2/\omega_Q^2 = 0.306$ depends sensitively on the interchain coupling $t_\perp$. Similar modes ($g_2^{(a)}$ and $g_3^{(a)}$) are not found, due to the strong interchain coupling, and may appear in the system with
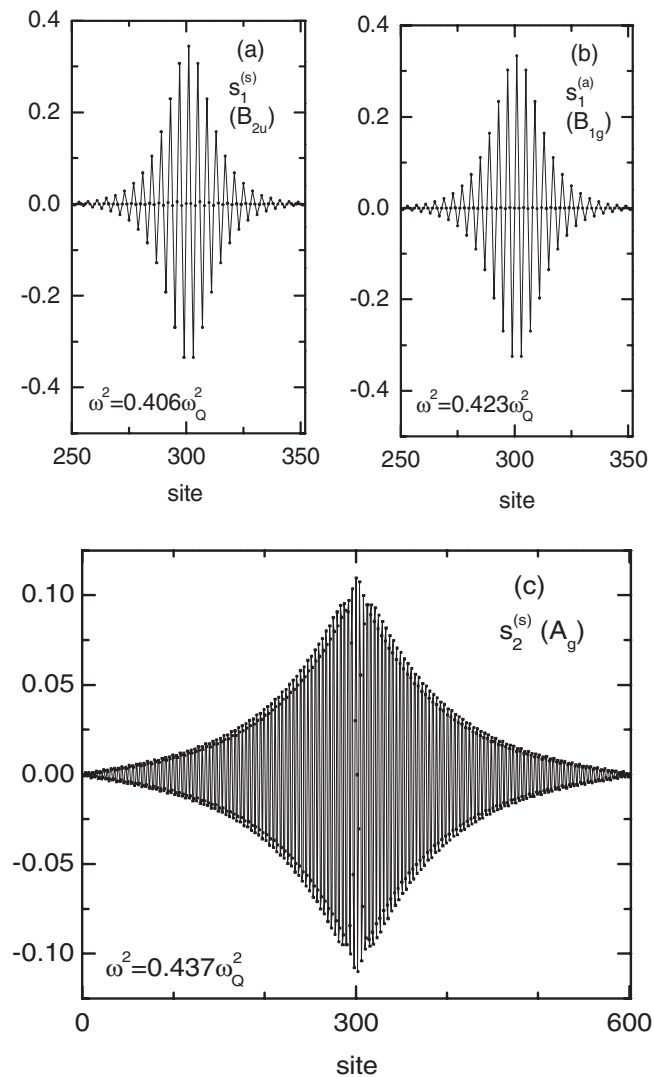
**Figure 5.** Localized quickly varying phonon modes ($q = \pi/2$).

a weak interchain coupling. In addition to the above four slowly varying modes, we found three quickly varying modes: two symmetric modes ($s_1^{(s)}$ and $s_2^{(s)}$) and one anti-symmetric mode ($s_1^{(a)}$). All of these modes, shown in figure 5, have a quasi-period of four sites, and can be regarded as modes at $q = \pi/2$. The mode $s_1^{(s)}$ ($\omega^2/\omega_Q^2 = 0.406$) shown in figure 5(a) is sited at the middle of the phonon gap ($\omega^2/\omega_Q^2 = 0.372$ for $\omega_a^{(s)}(\pi/2)$ and $\omega^2/\omega_Q^2 = 0.438$ for $\omega_o^{(s)}(\pi/2)$) at $q = \pi/2$ and has the peculiar property that all even atoms are fixed while odd atoms oscillate in alternate directions. This mode is nothing but the staggered mode found in polyacetylene [16]. The similar staggered mode $s_1^{(a)}$ ($\omega^2/\omega_Q^2 = 0.423$) shown in figure 5(b) is located below the middle of the phonon gap ($\omega^2/\omega_Q^2 = 0.396$ for $\omega_a^{(a)}(\pi/2)$ and $\omega^2/\omega_Q^2 = 0.474$ for $\omega_o^{(a)}(\pi/2)$); this should be caused by the different interchain coupling effects for localized and extended phonons. The last quickly varying mode ($s_2^{(s)}$) shown in
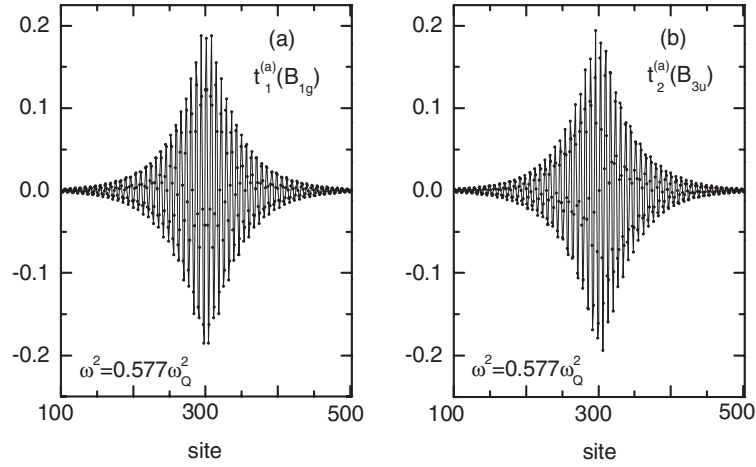
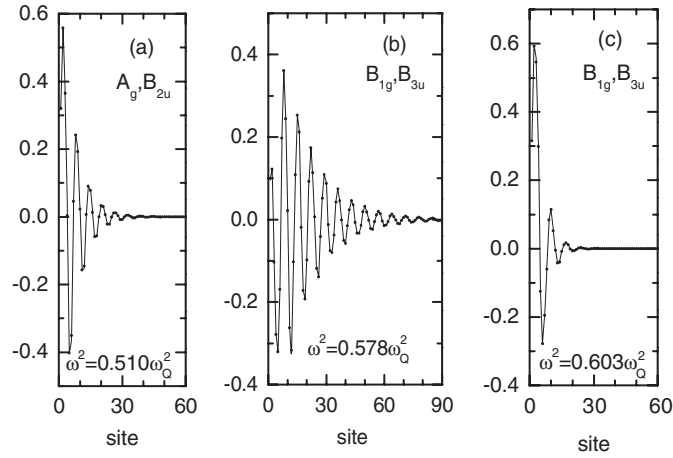**Figure 6.** Localized phonon modes ($q \approx 2\pi/7$).



**Figure 7.** Three pairs of edge phonon modes. Each pair contains one mode around the left end (shown here) and one around the right end (not shown). (a) is for $A_g$ or $B_{2u}$ symmetry and (b) and (c) are for $B_{1g}$ or $B_{3u}$ symmetry.

figure 5(c) is the second staggered one; its energy is $\omega^2/\omega_Q^2 = 0.437$ just below $\omega_o^{(s)}(\pi/2)$, the edge of optical phonon at $q = \pi/2$. The anti-symmetric counterpart of the second staggered mode is not be found, like that for slowly varying modes. The group representations for these localized quickly varying phonon modes have been indicated in figure 5; $s_1^{(s)}$ is infrared active and the other two are Raman active. In figure 6, we show two degenerate localized phonon modes $t_1^{(a)}$ and $t_2^{(a)}$ ($\omega^2/\omega_Q^2 = 0.577$) located on the top of the optical phonon continuum band, which are new findings for a polyacene chain. These two modes have a quasi-period of seven sites, corresponding to the wavevector $q \approx 2\pi/7$, which is exactly the wavevector of the phonon with the top energy at the optical phonon continuum band [14]. Finally, we point out that there have been found three pairs of edge phonon modes, shown in figure 7; since we are considering a finite-length polymer chain, all these edge modes are located above the optical phonon continuum bands and each pair contains one mode around the left end and its

counterpart around the right end. A recombination of these degenerate modes gives one pair ($\omega^2/\omega_Q^2 = 0.510$) with $A_g$ and $B_{2u}$ symmetries and the other two pairs ($\omega^2/\omega_Q^2 = 0.578$ and 0.603) have $B_{1g}$ and $B_{2u}$ symmetries. In total, three edge modes are infrared active and the other three are Raman active.

In summary, the localized phonon modes in a pristine polyacene are investigated. We find that there are nine localized phonon modes around the interchain-coupled neutral soliton; four modes are infrared active with the energies $\omega^2/\omega_Q^2 = 0, 0.132, 0.406$, and 0.577, and the other five modes are Raman active with the energies $\omega^2/\omega_Q^2 = 0.097, 0.306, 0.423, 0.437$, and 0.577. And there are three pairs of edge phonon modes; all are quickly varying modes with energies $\omega^2/\omega_Q^2 = 0.510, 0.578$, and 0.603, and both infrared and Raman active. The localized phonon modes can be considered the fingerprint [17] of localized excitations in polymers.

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