

Two-dimensional localized vibrational modes of $trans\text{-(CH)}_x$ around a polaron

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We assess the influence of a polyacetylene configuration on the localized vibrational modes around a polaron and find that the vibrations of carbon atoms normal to the chain is comparable to that along the chain for most of the modes. Ten localized modes have been found, compared with seven in the previous results.

A striking phenomenon, which has been observed in experiments on a number of conjugated polymers, is that the existence of nonlinear excitations either by doping^{1,2} or photoexcitation^{3,4} induces new features in the infrared-absorption spectra. These features are believed to result from localized vibrations of the polymers around the defects.⁵ Theoretical analyses of the phenomenon have mainly focused on polyacetylene as a simple prototypical system. The simple Su-Schrieffer-Heeger⁶ (SSH) model and the continuum-version Takayama-Lin-Liu-Maki (TLM) model⁷ have been very successful in explaining many experimental results. Of these efforts in explaining infrared-absorption spectra of polyacetylene, the most successful one is the Alexander-McTague (AM) formalism, which describes these vibrations as elementary excitations of the static distortion of the bond-alternating amplitude.⁸ Theoretical research has been carried out both on the basis of the discrete SSH model and the continuum TLM model. Three localized vibrational modes around a soliton^{5,8-11} and five modes around a polaron⁹⁻¹¹ have been found with the coupling constant $\lambda=0.19$ on the basis of the continuum models. These three ir-active modes for the soliton have been confirmed by experiment.¹² As some authors have pointed out, the calculations based on the continuum models will smear out additional ir-active modes, which are rapidly varying modes in configuration, called "staggered modes."¹³⁻¹⁶ One staggered mode has been found for a soliton and two for a polaron with the same coupling constant as given above, based on the SSH model. Thus, a total of four localized vibrational modes for a soliton and seven for a polaron have been obtained. Recently some authors considered the vibrational problem including electron interactions within the one-dimensional models.¹⁷⁻¹⁹ The results show that the electron correlation does not change the number of localized modes but causes shifts of the frequencies.

As we know, the SSH model assumes that atoms only move along the chain, neglecting the planar configuration of polyacetylene shown in Fig. 1. One will naturally ask

whether atomic motion normal to the chain (y direction) is negligible to that along the chain (x direction), and if not what will happen? The argument seems irrelevant to the static solution but relevant to the vibrational problem as we will show later. In this paper our interest will concentrate on the theoretical aspects of the lattice vibration around a polaron.

We start with the generalized SSH Hamiltonian:

$$H = - \sum_{n,s} (t_0 - \alpha \delta r_{n,n+1}) (c_{n+1,s}^\dagger c_{n,s} + \text{H.c.}) + \frac{k}{2} \sum_n (\delta r_{n,n+1})^2 + \frac{k'}{2} \sum_n (\delta \theta_n)^2 + \frac{M}{2} \sum_n (\dot{\mathbf{r}}_n)^2, \quad (1)$$

where t_0, α, k, M have the conventional meanings as they have in the SSH model. k' is the spring constant of the bond-bending term. $\delta r_{n,n+1}$ denotes the change of bond length from the equilibrium position between the n th and $(n+1)$ th site. Introducing a dimensionless order parameter $\delta U_{n,n+1}$, coupling constant λ , spring constant \tilde{k} , and time τ ,

$$\delta U_{n,n+1} = \frac{\alpha}{t_0} \delta r_{n,n+1}, \quad \lambda = \frac{2\alpha^2}{\pi k t_0}, \quad (2)$$

$$\tau = \omega_0 t, \quad \tilde{k} = k'/t_0,$$

where $\omega_0 = (4k/M)^{1/2}$ is the bare frequency, Eq. (1) can be rewritten as

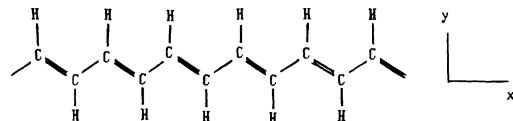


FIG. 1. Configuration of $trans\text{-(CH)}_x$. Bond lengths approximately equal 1.47 and 1.33 Å, alternatively, and bond angles equal 120°, which change little in the case of dimerization and undimerization.

$$\begin{aligned}
H/t_0 = & - \sum_{n,s} (1 - \delta U_{n,n+1}) (c_{n+1,s}^\dagger c_{n,s} + \text{H.c.}) \\
& + \frac{1}{\pi\lambda} \sum_n (\delta U_{n,n+1})^2 \\
& + \frac{4}{\pi\lambda} \sum_n (\dot{U}_n)^2 + \frac{\bar{k}}{2} \sum_n (\delta\theta_n)^2, \quad (3)
\end{aligned}$$

where $\dot{U}_n = (dU_n/d\tau)$. This shows that if the energy is measured with t_0 and the frequency with ω_Q , then the properties of the system will only depend on λ and \bar{k} . We first consider the case $\bar{k} \ll 1$ and neglect the bond-bending term, since the value of \bar{k} is unclear at present.

A static solution for a polaron, which is irrelevant to the bond-bending term and quite similar to previous results,^{6,20} can be determined by the following self-consistent equations:

$$\begin{aligned}
\varepsilon_i \phi_i(n) = & -(1 - \delta U_{n,n+1}) \phi_i(n+1) \\
& -(1 - \delta U_{n,n-1}) \phi_i(n-1), \\
\delta U_{n,n+1} = & -\pi\lambda \sum_i \phi_i(n) \phi_i(n+1) \\
& + \frac{\pi\lambda}{N} \sum_{i,n} \phi_i(n) \phi_i(n+1), \quad (4)
\end{aligned}$$

where periodic boundary conditions have been used. ε_i is the eigenvalue of the electron and $\phi_i(n)$ denotes the n th component of the electron eigenfunction. Apparently all previous static solutions can be preserved from Eq. (4).²⁰ To reproduce the results of the SSH model,⁶ we choose the parameters as follows:

$$t_0 = 2.5 \text{ eV}, \quad \alpha = 4.73 \text{ eV \AA}^{-1}, \quad k = 28 \text{ eV \AA}^{-2},$$

which correspond to an energy gap $2\Delta = 1.35 \text{ eV}$, dimerization $\delta\gamma = 0.07 \text{ \AA}$, and coupling constant $\lambda = 0.19$. We perform the calculation with 100 atoms, using the following trial function to iterate:

$$\begin{aligned}
\delta U_{n,n+1} = & (-1)^n \frac{\alpha}{t_0} \left\{ \frac{\delta r}{2} - \frac{\delta r}{2\sqrt{2}} \left[\tanh \left[\frac{n-50+m}{L} \right] - \tanh \left[\frac{n-51-m}{L} \right] \right] \right\} \\
& + (-1)^n \frac{\alpha}{t_0} \left\{ \frac{\delta r}{2} - \frac{\delta r}{2\sqrt{2}} \left[\tanh \left[\frac{n-49+m}{L} \right] - \tanh \left[\frac{n-50+m}{L} \right] \right] \right\}, \quad (5)
\end{aligned}$$

where $\delta r = 0.07$, $L = 7$, and $m = 4$. Finally one will obtain a set of $\{\delta U_{n,n+1}^p\}$, which determine the polaron configuration located in the center of the chain.

To consider the small lattice vibrations around a polaron, we expand $\delta U_{n,n+1}$ near the equilibrium configuration $\{\delta U_{n,n+1}^p\}$:

$$\delta U_{n,n+1} = \sin\theta(x_{n+1} - x_n) + (-1)^{n+1} \cos\theta(y_{n+1} - y_n) + \delta U_{n,n+1}^p, \quad (6)$$

where θ is the bond angle, and the coordinate system is chosen as shown in Fig. 1. Thus, the Hamiltonian (3) can be written as

$$H = H^p + H' + \frac{1}{\pi\lambda} \sum_n (\delta U_{n,n+1} - \delta U_{n,n+1}^p)^2 + \frac{4}{\pi\lambda} \sum_n (\dot{U}_n)^2, \quad (7)$$

where H^p is the Hamiltonian of a polaron, and H' is the perturbative term resulting from small vibrations,

$$H' = \sum_{n,s} \mathbf{q}_{n+1} \cdot (\mathbf{U}_{n+1} - \mathbf{U}_n) (c_{n+1,s}^\dagger c_{n,s} + \text{H.c.}), \quad (8)$$

TABLE I. Localized vibrational modes around a polaron for $\lambda = 0.19$. X'_m and Y'_m denote maximum amplitude of the i th mode in the x and y directions, respectively.

Localized mode	Frequency Ω_i^2/ω_Q^2	Parity	X'_m	Y'_m
G_1	0.000	odd	0.218	0.026
G_2	0.122	even	0.313	0.039
G_3	0.196	even	0.189	0.098
G_4	0.220	odd	0.122	0.133
G_5	0.279	odd	0.129	0.138
G_6	0.301	even	0.139	0.090
G_7	0.425	even	0.222	0.138
G_8	0.470	odd	0.249	0.133
G_9	0.573	odd	0.168	0.110
G_{10}	0.480	even	0.215	0.103

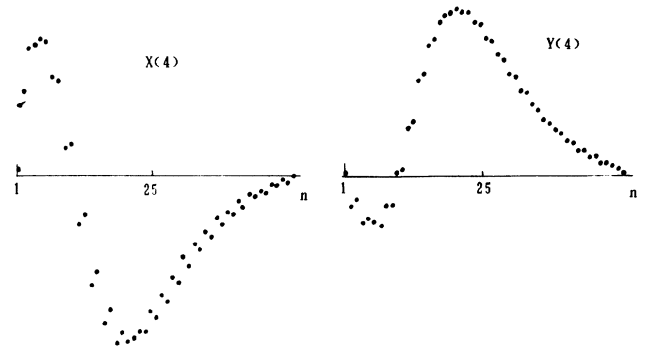


FIG. 2. Shape of the localized mode G_4 . The unit of abscissa is site number n , and the ordinate is in an arbitrary unit.

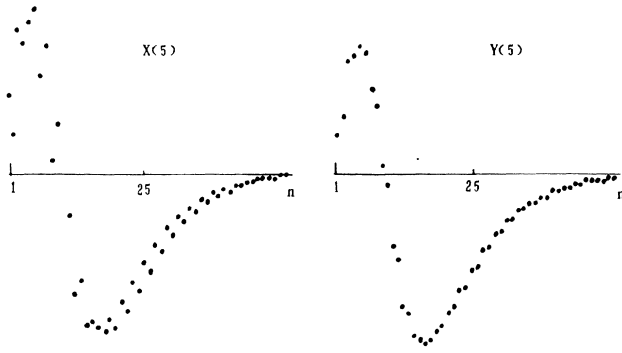


FIG. 3. Shape of the localized mode G_5 . The units of both axes are the same as in Fig. 2.

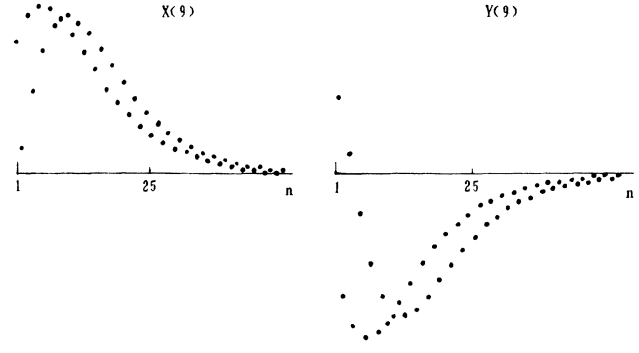


FIG. 4. Shape of the localized mode G_9 . The units of both axes are the same as in Fig. 1. The modes are plotted with $G_i(2m+l) = (-1)^m G_i(2m+l)$ where $l=0,1$, $m=1,2,\dots,25$ for $l=0$ and $m=0,1,\dots,24$ for $l=1$.

in which $\mathbf{U}_n = x_n \hat{\mathbf{i}} + y_n \hat{\mathbf{j}}$, and $\hat{\mathbf{q}}_{n+1}$ is the unit vector pointing from the n th to the $(n+1)$ th site. By calculating the energy of the system to the second order of H' , we obtain the total energy of the system:

$$E = E_p + \frac{1}{2} \sum_{m,n} V_{mn}^{\alpha\beta} \eta_m^\alpha \eta_n^\beta + \frac{4}{\pi\lambda} \sum_n (\dot{\mathbf{U}}_n)^2, \tag{9}$$

where $\alpha, \beta = 1, 2$ denote the x and y directions, respectively, and E_p is the energy of a polaron:

$$\eta_m' = x_m, \quad \eta_m^2 = y_m, \tag{10}$$

$$V_{mn}^{\alpha\beta} = 2 \left[\sum_{i(\text{opp})} \sum_{j \neq i} \frac{D_{ij}^{n\alpha} D_{ij}^{m\beta}}{\epsilon_i - \epsilon_j} + M_{mn}^{\alpha\beta} \right], \tag{11}$$

$$D_{ij}^{n\alpha} = C_{ij}^n q_n^\alpha - C_{ij}^{n+1} q_{n+1}^\alpha, \tag{12}$$

$$c_{ij}^n = \phi_i(n) \phi_j(n-1) + \phi_j(n) \phi_i(n-1), \tag{13}$$

$$\begin{aligned} M_{mn}^{\alpha\beta} = & \frac{2}{\lambda\pi} [\sin^2\theta \delta_{m,n} \delta_{\alpha,1} \delta_{\beta,1} + \cos^2\theta \delta_{m,n} \delta_{\alpha,2} \delta_{\beta,2}] \\ & - \frac{1}{\lambda\pi} [\sin^2\theta \delta_{m,n+1} \delta_{\alpha,1} \delta_{\beta,1} + \sin^2\theta \delta_{m,n-1} \delta_{\alpha,1} \delta_{\beta,1}] \\ & - \frac{1}{\lambda\pi} [\cos^2\theta \delta_{m,n+1} \delta_{\alpha,2} \delta_{\beta,2} + \cos^2\theta \delta_{m,n-1} \delta_{\alpha,2} \delta_{\beta,2}] \\ & - \frac{1}{\lambda\pi} [\sin\theta \cos\theta (-1)^{n+1} \delta_{m,n+1} \delta_{\alpha,2} \delta_{\beta,1} + \sin\theta \cos\theta (-1)^n \delta_{m,n-1} \delta_{\alpha,1} \delta_{\beta,2}] \\ & - \frac{1}{\lambda\pi} [\sin\theta \cos\theta (-1)^{n+1} \delta_{m,n+1} \delta_{\alpha,1} \delta_{\beta,2} + \sin\theta \cos\theta (-1)^n \delta_{m,n-1} \delta_{\alpha,2} \delta_{\beta,1}]. \end{aligned} \tag{14}$$

One obtains all vibrational modes by diagonalizing the matrix V_{mn} . We arrange the sites of the atoms along the chain in order $\{-50, -49, \dots, -1, 1, \dots, 49, 50\}$; thus the vibrational amplitude G_i corresponding to the frequency Ω_i , can be expressed as

$$G_i \equiv [X(i), Y(i)] = (X_{-50}^i \cdots X_{+50}^i, Y_{-50}^i \cdots Y_{+50}^i), \tag{15}$$

where X^i and Y^i stand for vibrational amplitudes in the x and y directions, respectively. Because of the conservation of parity in V_{mn} , the modes can be plotted as

$$G_i = (X_1^i \cdots X_{50}^i, Y_1^i \cdots Y_{50}^i) \tag{16}$$

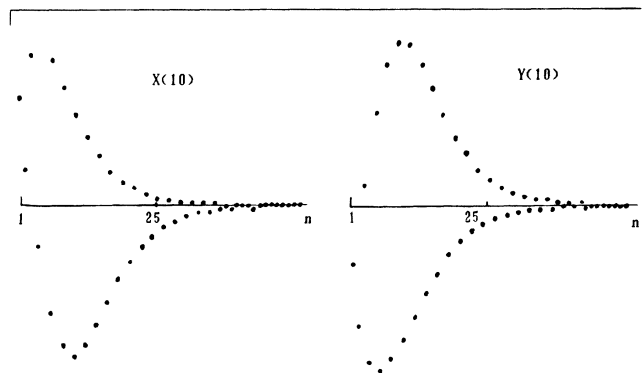


FIG. 5. Shape of the localized mode G_{10} . The modes are plotted as in Fig. 4.

by specifying the symmetry of the modes. Our calculation shows that among 200 modes, 101 modes have zero frequency, one of which corresponds to a Goldstone mode. Ten localized vibrational modes have been found, and their main features can be summarized in Table I.

It is worth noting from Table I that the amplitudes of both directions for a given mode are comparable except for the modes G_1 (Goldstone mode) and G_2 . The corresponding modes for G_1 to G_8 can be found in the one-dimensional case.¹⁴⁻¹⁶ By the corresponding modes, we mean that the mode in the one-dimensional case and the mode in the two-dimensional case have the same symmetry and similar amplitude shapes in the x direction. An interesting result is that G_4 and G_5 have similar amplitudes in the x direction and the same symmetry, but different amplitudes in the y direction and frequency (shown in Figs. 2 and 3). Hence, G_4 and G_5 correspond

to one mode in the one-dimensional case. G_9 and G_{10} do not exist in the previous results (shown in Figs. 4 and 5).

When the bond angles approach π , amplitudes in the y direction of all the modes will go to zero. G_4 and G_5 will be merged into one mode and G_9 and G_{10} will disappear. Thus only seven localized modes are found in the one-dimensional case, which just reduces to the previous result.

One can expect that the bond-bending term for large K will change the result to some extent. We plan to investigate the in problem in another paper.

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