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# THE INFRARED ACTIVE LOCALIZED MODES OF SOLITON IN TRANS-$(CH)_x^*$

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Five localized vibrational modes have been found for the soliton in a finite ring of *trans*-$(CH)_x$ from the SSH model, among them three are infrared active, i.e. Goldstone, third and staggered mode, and they can be used to interpret the three observed infrared absorption lines at 900, 1260 and 1370 $cm^{-1}$.

IN RECENT YEARS, three infrared absorption lines have been observed in *trans*-$(CH)_x$, i.e. 900, 1260, 1370 $cm^{-1}$ for doping induced absorption [1], and 500, 1260, 1370 $cm^{-1}$ for photoinduced [2]. While 900 $cm^{-1}$ being considered as a pinning Goldstone mode [2, 3], 1260 and 1370 $cm^{-1}$ are intrinsic feature of soliton. By using a force field model Mele and Rice [4] got several localized vibrational modes or resonances, among which the first two modes were used to interpret the absorption lines at 900 and 1370 $cm^{-1}$. Then other authors investigated this problem based on the TLM model [5]. Nakahara and Maki found two localized modes for soliton by variational method [6], Hicks and Blaisdell got the same modes by Green function [7], and Ito, Terai, Ono and Wada established an integral equation and found one more localized mode, the third mode in the soliton case, which is infrared active and accords with the 1370 $cm^{-1}$ line [8]. However, both in doping induced and photoinduced absorption, there are two lines at 1260 and 1370 $cm^{-1}$, none of the above theories could give these two close standing lines. Besides, since the TLM model is a continuum approximation of SSH model [9], the rapidly varying configurations should be smeared out, and some localized modes could be lost in TLM model.

Instead of TLM model we start from SSH model with a finite length of ring and investigate the small oscillation around the soliton. The SSH Hamiltonian reads

$$H = -\sum_{n,s} [t_0 - \alpha(u_{n+1} - u_n)](C^+_{n+1,s}C_{n,s} + h.c.) + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 + \sum_n \frac{M}{2}\dot{u}_n^2, \quad (1)$$

and

$$u_n = (-1)^n(\psi_n + \delta\psi_n), \quad (2)$$

where $\psi_n = -u_0 \,\mathrm{th}(n/\xi)$ is the static soliton configuration and $\delta\psi_n$ is the small displacement from the equilibrium position. In the adiabatic process and small deviation limit,

$$H = E_0 + E_s + \sum_n \frac{M}{2}(\delta\dot{\psi}_n)^2 + \frac{1}{2}\sum_{m,n} U_{mn}\delta\psi_n\delta\psi_m, \quad (3)$$

where $E_0$ is the ground state energy and $E_s$ the soliton energy,

$$U_{mn} = K(\delta_{m,n+1} + \delta_{m,n-1} + 2\delta_{m,n}) + 2\alpha^2(-1)^{m+n}\sum_{\mu(\mathrm{occ})}\sum_{\nu\neq\mu}\frac{C^m_{\mu\nu}C^n_{\mu\nu}}{\epsilon_\mu - \epsilon_\nu}, \quad (4)$$

$$C^m_{\mu\nu} = Z_{m,\mu}(Z_{m+1,\nu} - Z_{m-1,\nu}) + Z_{m,\nu}(Z_{m+1,\mu} - Z_{m-1,\mu}). \quad (5)$$

$\epsilon_\mu$ and $Z_{n,\mu}$ are the eigenvalue and eigenvector of electron in eigenstate $\mu$.

By diagonizing $U_{mn}$ we can get all phonon modes. In our preliminary work [10] we found indication that 5 localized modes may exist. To confirm these results with better accuracy and explore the connection between these localized modes and observed infrared absorption, in this paper we take a ring of 101 atoms with parameters $t_0 = 2.5$ eV, $\alpha = 7.3$ eV Å$^{-1}$ and $K = 52$ eV Å$^{-2}$. The

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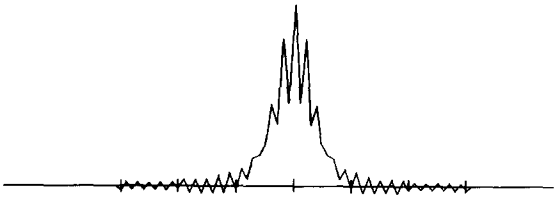

Fig. 1. Goldstone mode $g_1$.

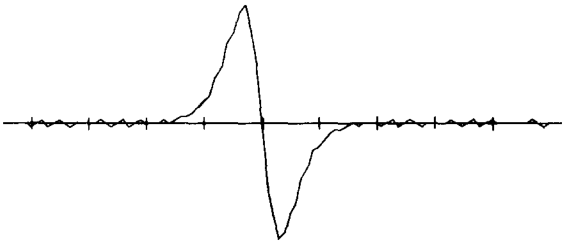

Fig. 2. Amplitude mode $g_2$.

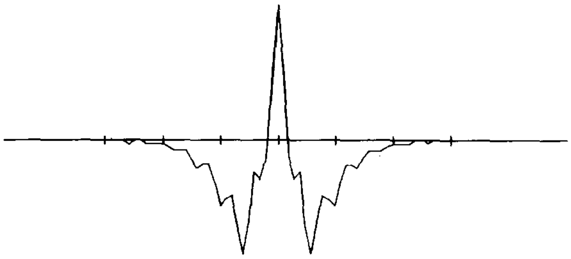

Fig. 3. Third mode $g_3$.

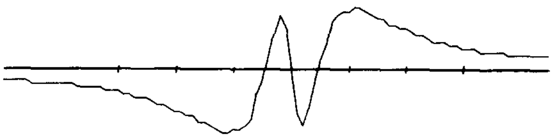

Fig. 4. Fourth mode $g_4$.

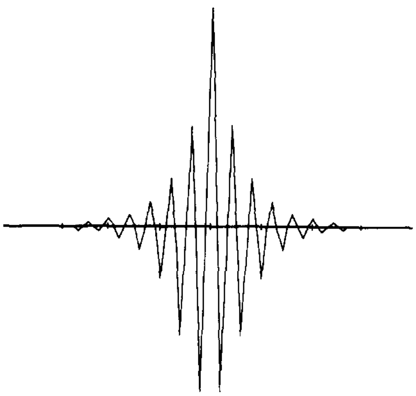

Fig. 5. Staggered mode $g_s$.

result shows that five localized modes emerged very distinctly from the extended modes, which form the acoustic and optical branches. The shapes of these localized modes are shown in Figs. 1–5, and their properties are listed in Table 1.

*Table 1. The properties of localized modes*

| Mode | Parity | Number of nodes | Frequency $(\Omega/\omega_0)^2$ |
|---|---|---|---|
| $g_1$ | even | 0 | $\approx 0$ |
| $g_2$ | odd | 1 | 0.68 |
| $g_3$ | even | 2 | 0.90 |
| $g_4$ | odd | 3 | 0.99 |
| $g_s$ | even | staggered | 0.93 |

It is easy to identify our $g_1$, $g_2$ and $g_3$ with those obtained in work [8]. The fourth mode $g_4$ and the staggered mode $g_s$ are new findings. As is expected, following $g_1$, $g_2$ and $g_3$, $g_4$ should have 3 nodes with odd parity. For mode $g_s$, the odd atoms are fixed whereas the even atoms oscillate in alternate direction one by one, obviously it comes from the optical mode in Brillouin zone boundary ($k = 1/4a$), and that is the reason for this mode to be called as staggered mode. Since $g_s$ is even, it is infrared active. Therefore among these five localized modes, three are infrared active, i.e. Goldstone, third and staggered.

Due to the existence of soliton the extended phonon will have phase shift in their asymptotic behavior. According to the Levinson theorem, the optical phonon mode with $k = 0$, which frequency is $\omega_0$, should have the phase shift $\delta = N_L \pi$, where $N_L$ is the number of localized modes. By examining our first optical phonon mode ($k = 0$) shown in Fig. 6, it does have phase shift $5\pi$, which confirms the fact that there exist a total of five localized modes.

The remarkable feature is that it happens to be three infrared active modes in our calculation, while the Goldstone mode corresponding to $900\,\mathrm{cm}^{-1}$, the third mode is such close to the staggered mode as the two close standing absorption lines 1260 and $1370\,\mathrm{cm}^{-1}$. Therefore these three infrared active modes can be used to interpret three observed infrared absorption.

Finally we should mention that the parameters taken in the present calculation are somewhat artificial for saving the computer time. In order to get quantitative comparison with the observations we are going to make a further computation with real parameters and longer ring.

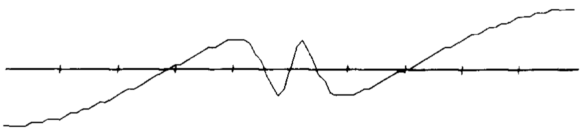

Fig. 6. Optical phonon mode with $k = 0$.

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## REFERENCES


1. T. Tanaka *et al.*, *Mol. Cryst. Liq. Cryst.* **83**, 75 (1982).
2. G. Blanchet *et al.*, *Phys. Rev. Lett.* **50**, 1938 (1983); Z. Vardeny, J. Orenstein & G. Baker, *Phys. Rev. Lett.* **50**, 2032 (1983).
3. B. Horovitz, *Solid State Commun.* **41**, 729 (1982).
4. E. Mele & M. Rice, *Phys. Rev. Lett.* **45**, 926 (1980).
5. H. Takayama, Y.R. Lin-liu & K. Maki, *Phys. Rev.* **B21**, 2388 (1980).
6. M. Nakahara & K. Maki, *Phys. Rev.* **B25**, 7789 (1982).
7. J. Hicks & G. Blaisdell, *Phys. Rev.* **B31**, 919 (1985).
8. H. Ito, A. Terai, Y. Ono & Y. Wada, *J. Phys. Soc. Japan.* **53**, 3519 (1984); H. Ito & Y. Ono, *J. Phys. Soc. Japan.* **54**, 1194 (1985).
9. W. Su, J. Schrieffer & A. Heeger, *Phys. Rev.* **B22**, 2099 (1980).
10. C. Wu, X. Sun & L. Fu, *Chinese Phys. Lett.* (to be published).