Photogenerated polaronic state in a one-dimensional dimerized Mott insulator K-TCNQ

Nobuya Maeshima1, Kenji Yonemitsu2,3 and Ken-ichi Hino1

1 Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573, Japan
2 Institute for Molecular Science, Okazaki 444-8585, Japan
3 Graduate University for Advanced Studies, Okazaki 444-8585, Japan

maeshima@vivaldi.bk.tsukuba.ac.jp

Abstract. We discuss photogenerated midgap states of a one-dimensional dimerized Mott insulator potassium-tetracyanoquinodimethane (K-TCNQ). We take account of two types of phonons, the intermolecular and the intramolecular vibrations. We treat these phonon modes adiabatically and analyse a theoretical model by using the density matrix renormalization group (DMRG). Our numerical results demonstrate that the midgap state of K-TCNQ can be reproduced by the intermolecular lattice distortion.

1. Introduction

The mechanism of polaronic states appearing in quasi one-dimensional (1D) organic insulators has been investigated intensively because of the strong connection with photoinduced phenomena [1,2]. In particular, macroscopic photoinduced phenomena, called photoinduced phase transitions, may accompany formation of polaronic states, which can be observed as appearance of midgap peaks in the optical conductivity spectrum.

An organic quasi 1D Mott insulator, potassium-tetracyanoquinodimethane (K-TCNQ) is a good example that shows the polaronic state and the following photoinduced phase transition. This material shows a spin-Peierls transition at 395 K [3]. In 1991, Koshihara et al. have shown that an irradiation of a laser pulse decreased the lattice dimerization of K-TCNQ in the dimerized phase [4]. This phenomenon is regarded as a photoinduced inverse spin-Peierls transition. Recently, a high-resolution experiment has demonstrated that a midgap peak appears in photoinduced reflectivity changes spectra before the dimerization starts to decrease [5]. Thus the polaronic state is considered to be the starting point of the photoinduced inverse spin-Peierls transition, and the nature of the polaronic state is a key to understand the mechanism of this photoinduced phase transition.

We study the nature of the polaronic states of K-TCNQ by using numerical methods, exact diagonalization and the density matrix renormalization group (DMRG) [6]. Our results demonstrate that the midgap state in K-TCNQ can be reproduced by polaronic lattice configurations with the relaxed inter-molecular vibration mode [7].

2. 1D Peierls-Hubbard model

In this work, we use the 1D extended Hubbard model with Peierls and Holstein types of electron-phonon (e-ph) couplings. The Hamiltonian is given by...
\[
H = -\sum_{l=0}^{N-2} (t_0 - \alpha u_l) \hat{t}_{l,l+1} + U \sum_{l=0}^{N-1} n_{l\uparrow} n_{l\downarrow} + V \sum_{l=0}^{N-2} n_{l\downarrow} n_{l+1\uparrow} - \beta \sum_{l=0}^{N-1} v_l (n_l - 1) + \frac{K_\alpha}{2} \sum_{l=0}^{N-2} u_l^2
\]

where
\[
\hat{t}_{l,l+1} = \sum_\sigma (c_{l+1,l,\sigma}^\dagger c_{l,\sigma} + c_{l,\sigma}^\dagger c_{l+1,l,\sigma})
\]

and \(c_{l,\sigma}^\dagger\) is the creation (annihilation) operator of an electron with spin \(\sigma\) in the LUMO of a TCNQ molecule on site \(l\), \(n_{l,\sigma} = c_{l,\sigma}^\dagger c_{l,\sigma}\), \(n_l = \sum_\sigma n_{l,\sigma}\), \(u_l\) denotes the distortion of the \(l\)-th bond and \(v_l\) gives the molecular deformation. Other physical parameters are introduced in Ref. [7].

To obtain the stable (i.e., fully relaxed) lattice configuration, we use the Hellmann-Feynman theorem;
\[
\frac{\partial \langle H \rangle}{\partial u_l} = 0, \quad \text{and} \quad \frac{\partial \langle H \rangle}{\partial v_l} = 0,
\]

where \(\langle \ldots \rangle\) denotes the expectation value for the ground state. To keep the fixed chain length, \(\Gamma\) is introduced, and it satisfies the following relation;
\[
\Gamma = -\sum_{l=0}^{N-2} \frac{\langle \hat{t}_{l,l+1} \rangle}{N - 1}.
\]

We iteratively update \(u\) and \(v\) as shown in Ref. [7] and finally reach the stable lattice configuration. We obtain almost all physical quantities in this study by using DMRG calculations on \(N=40\) systems with retained bases \(m=80\).

To deal with the polaronic states, we consider systems where one electron is introduced in the half-filled systems. We consider the following cases for lattice configuration: (case 1) \(u\)-relaxed and \(v\)-fixed, (case 2) \(u\)- and \(v\)-relaxed, and (case 3) \(u\)-fixed and \(v\)-relaxed, where \(u\) (\(v\))-relaxed means that the intermolecular (intramolecular) distortion \(u\) (\(v\)) is relaxed to the stable configuration, and the \(u\) (\(v\))-fixed denotes that the lattice configuration is fixed to the homogeneous one at half filling.

**Figure 1.** Spectral function \(\omega \sigma(\omega)\) for the half filling and several polaronic states. In cases 2 and 3 \(K_\beta\) is set to 1.0. The inset shows \(\omega \sigma(\omega)\) for the midgap region. The symbols show experimental results of photoinduced reflectivity changes spectra in Ref. [5].
3. Results

3.1. Spectral functions for the polaronic states

Figure 1 shows a spectral function $\omega \sigma(\omega)$ of the polaronic states for these three lattice configurations. We also note that the most plausible values of $U$, $V$, and $K/\omega a$ are obtained by comparing the calculated data with the experimental result of Ref. [8], and the estimated values are $U/t_0 = 5$, $V/t_0 = 1.7$, $K/\omega a = 1.6/t_0$, and $t_0 = 0.291eV$. It is found that case 1 and case 2 well reproduce the midgap peak of photoinduced reflectivity changes ($\Delta R$) spectra around 0.3 eV[5]. It should be noted that, however, a small difference exists between the two cases. The result for the former case shows a shoulder on the lower energy side of the main midgap peak at 0.3 eV. By contrast, case 2 seems to have a single peak at 0.3 eV. The result of case 3, which has a midgap state above 0.5 eV, seems to be inconsistent with the experimental result. These observations suggest that the lattice configurations with relaxed $u$ reproduce the experimental result.

4. Conclusion

We have investigated polaronic midgap states in the 1D extended Hubbard model with Peierls and Holstein types of e-ph couplings to clarify the origin of the photoinduced midgap peak in K-TCNQ. Our conclusion is that the polaronic states with the relaxed intermolecular lattice distortion can cause the midgap peak around 0.3 eV. Although polaronic states with only the intramolecular vibration mode relaxed are found to make midgap peaks, their locations are not coincident with the experimental results.
5. Acknowledgments
The authors are grateful to Professor H. Okamoto for enlightening discussions. Some of numerical calculations were carried out on Altix3700 BX2 at YITP in Kyoto University, and on TX-7 and PRIMEQUEST at Research Center for Computational Science, Okazaki, Japan.

References
[1] Heeger A J, Kivelson S, Schrieffer J R, and Su W-P 1988 Rev. Mod. Phys. 60 781
[2] Okamoto H and Yamashita M 1998 Bull. Chem. Soc. Jpn. 71 2023
[3] Vegter J G, Hibma H, and Kommandeur 1969 J. Chem. Phys. Lett. 3 427
[4] Koshihara S, Tokura Y, Iwasa Y, and Koda T 1991 Phys. Rev. B 44 431
[5] Okamoto H, Ikegami K, Wakabayashi T, Ishige Y, Togo J, Kishida H, and Matsuzaki H 2006 Phys. Rev. Lett. 96 037405
[6] White S R 1992 Phys. Rev. Lett. 66 2863
[7] Maeshima M and Yonemitsu K 2008 J. Phys. Soc. Jpn. 77 074713
[8] Yakushi K, Kusaka T, and Kuroda H 1979 Chem. Phys. Lett. 68 139