Nonlinear lattice relaxation of photogenerated charge-transfer excitation in halogen-bridged mixed-valence metal complexes. II. Polaron channel

A. Mishima
Kanazawa Institute of Technology, Ohgigaoka, Nonoichi, Ishikawa 921, Japan

K. Nasu
Institute for Molecular Science, 38 Nishigonaka, Myodaiji, Okazaki 444, Japan

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The one-dimensional extended Peierls-Hubbard model with half-filled-band electrons is studied in order to clarify the lattice relaxation path of the photogenerated charge-transfer excitation in halogen-bridged mixed-valence metal complexes. The ground and excited states are calculated within mean-field theory for electrons and the adiabatic approximation for phonons. It is concluded that the main origin of the photoinduced absorption is a distant pair of the hole-polaron and the electron-polaron. This distant pair is created not from the ground state of the self-trapped exciton (STE), but from the excited states of the STE through their autodissociation. This is consistent with the experiment on the excitation energy dependence of the photoinduced absorption yield.

I. INTRODUCTION

Optical properties of the halogen-bridged mixed-valence metal complexes (HMMC's) are of considerable interest in recent years, particularly as a typical example for the one-dimensional charge-density-wave (CDW) state.[1-6] This material has a strong-light-absorption band in the visible region,[1,2,5] and it is called the charge-transfer (CT) excitation band. When this CT band is excited by an intense light, two new light-absorption bands appear, as shown by Kurita *et al.*[4] These photoinduced absorption bands are named A and B, and their energies are about 70% and 80% of the energy gap of the CDW, respectively. In connection with this photoinduced absorption phenomenon, we have very recently studied the ground and the excited states of one-dimensional extended Peierls-Hubbard model with half-filled-band electrons, so as to clarify the lattice relaxation paths of the CT excitation in HMMC's. In this study, we have already clarified the photogeneration path of the self-trapped exciton (STE) and the soliton pairs, as well as the relative stabilities between them.[7] However, in that paper, we have not been fully concerned with the main origin of the A and B bands. Kuroda *et al.*[3] attributed the A band to the excitation from the soliton, while, Kurita *et al.*[4] suggested that the appearance of the A and B bands can be explained by a polaron picture.

Our aim of this paper is to clarify the lattice relaxation paths of the photogenerated CT excitation and the main origin of this photoinduced absorption bands. Since the relaxation to the soliton pair has been already studied in detail, in this paper we focus our attention to the relaxation process related with the polaron pair formation.

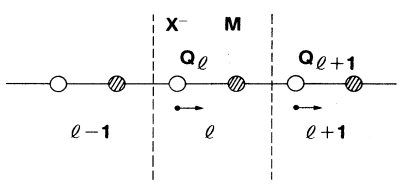

FIG. 1. Schematic structure of the HMMC; X^- and the open circles denote the halogen ions, while M and the shaded circles denote the metal.

II. EXTENDED PEIERLS-HUBBARD MODEL

Let us start from the following Hamiltonian H:

$$H=-T\sum_{l,\sigma}(a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.})+\omega\sum_{l}q_l^2/2 +\sqrt{S\omega}\sum_{l,\sigma}(q_l-q_{l+1})n_{l\sigma} +U\sum_{l}n_{l\alpha}n_{l\beta}+V\sum_{l,\sigma,\sigma'}n_{l\sigma}n_{l+1,\sigma'},\quad n_{l\sigma}\equiv a_{l\sigma}^{\dagger}a_{l\sigma}\ , \tag{2.1}$$

where $a_{l\sigma}^{\dagger}$ ($a_{l\sigma}$) denotes the creation (annihilation) operator of the electron with spin σ ($=\alpha,\beta$) at the site l ($-\infty\le l\le+\infty$). The total number of the sites is equal to the total number of electrons. T is the transfer energy of an electron between two neighboring metallic sites, denoted by M or shaded circles in Fig. 1. ω is the phonon energy of a halogen ion, denoted by X^- or open circles in Fig. 1. q_l is its dimensionless coordinate. It describes the motion of X^- along the direction parallel to the chain, and its kinetic energy is neglected according to the adiabatic approximation. S is the electron-phonon (e-ph) coupling energy, while U and V denote the intrasite and intersite Coulombic repulsions, respectively.

Introducing Q_l ($\equiv\sqrt{\omega/S}\,q_l$), h ($\equiv H/T$), s ($\equiv S/T$), u ($\equiv U/T$), and v ($\equiv V/T$), we rewrite Eq. (1) into a dimensionless form as

$$h=-\sum_{l,\sigma}(a_{l\sigma}^{\dagger}a_{l+1,\sigma}+\text{H.c.})+s\sum_{l}Q_l^2/2 +s\sum_{l,\sigma}(Q_l-Q_{l+1})n_{l\sigma}+u\sum_{l}n_{l\alpha}n_{l\beta} +v\sum_{l,\sigma,\sigma'}n_{l\sigma}n_{l+1,\sigma'}\ . \tag{2.2}$$

Within the mean-field theory, we approximate h by h_{HF} wherein $n_{l\sigma}$ and $(a_{l+1,\sigma}^{\dagger}a_{l\sigma})$ in the fourth and fifth terms of h are replaced by their averages as

$$n_{l\sigma}\rightarrow\langle n_{l\sigma}\rangle,\quad (a^{\dagger}_{l+1,\sigma}a_{l\sigma})\rightarrow m_{l\sigma}\ ,$$

$$h\rightarrow h_{\rm HF}=-\sum_{l,\sigma}[(1+vm_{l\sigma})a^{\dagger}_{l\sigma}a_{l+1,\sigma}+{\rm H.c.}]+\sum_{l,\sigma}[s(Q_l-Q_{l+1})+u\langle n_{l,-\sigma}\rangle+v(\langle n_{l+1}\rangle+\langle n_{l-1}\rangle)]a^{\dagger}_{l\sigma}a_{l\sigma}$$
$$+s\sum_l Q_l^2/2-u\sum_l\langle n_{l\alpha}\rangle\langle n_{l\beta}\rangle-v\sum_l\langle n_l\rangle\langle n_{l+1}\rangle+v\sum_{l,\sigma}m^{*}_{l\sigma}m_{l\sigma}\ , \tag{2.3}$$

where

$$\langle n_l\rangle\equiv\sum_{\sigma}\langle n_{l\sigma}\rangle\ . \tag{2.4}$$

$\langle n_{l\sigma}\rangle$ and $m_{l\sigma}$ are unknown, and must be determined self-consistently.

As mentioned in the preceding section, our main purpose is to clarify the nonlinear relaxation process of the CT excitation involving the polaron pair formation. For this aim, we introduce Q_l of the following form:

$$Q_l=(-1)^lQ\{1+[\Delta Q+{\rm sgn}(l)\Delta Q_-]$$
$$\times[\tanh\theta(|\,|l|-l_0/2|)-1]\}\ . \tag{2.5}$$

$(-1)^lQ$ denotes the Peierls distortion of the ground state of CDW, and this Q must be determined beforehand. The second term of the curly brackets denotes the local displacement of Q_l from this ground state. $(\Delta Q\pm\Delta Q_-)$ gives the amplitude of this local displacement in the right-half ($l>0$), or in the left-half ($l<0$) of the chain. The factor [ ] determines the spatial pattern of this local displacement centered at $\pm l_0/2$, and θ corresponds to the reciprocal width of the polaron. When $l_0=0$ and $\Delta Q_-=0$, it gives the STE-type symmetric local displacement. On the other hand, when $l_0\gg1$ and $\Delta Q_-=0$, it gives a symmetric displacement due to a distant pair of polarons centered at $\pm l_0/2$. If we make $\Delta Q_-\neq0$, these displacements in the left- and the right-hand sides become asymmetric and when $\Delta Q=\pm\Delta Q_-$ one of them disappears. Thus, this pattern of Q_l can describe almost all possibilities of the lattice relaxation related with the polaron pair formation.

Using this Q_l, we can determine the energies of the ground state E_G and that of the excited states E'_{x_n} ($n=1,2,3,\ldots$) as well as their wave functions $|E_G\rangle$ and $|E_{x_n}\rangle$, which are numbered according to their energies from lower ones to upper ones. As for the excited states, we take into account the first-order correction $\Delta E_{nn'}$ coming from the difference between h and $h_{\rm HF}$. It is given as

$$\Delta E_{nn'}=\langle E_{x_n}|(h-h_{\rm HF})|E_{x_{n'}}\rangle\ . \tag{2.6}$$

When there is no serious degeneracy between lower excited states, we determine their new energies E_{x_n} taking only the diagonal part of the correction as

$$E_{x_n}=E'_{x_n}+\Delta E_{nn}\ . \tag{2.7}$$

If there is a degeneracy between lower excited states, we diagonalize $\Delta E_{nn'}$ between these degenerate states and can obtain new diagonal correction terms $\Delta E'_{nn}$. From this we get the new energies as

$$E_{x_n}=E'_{x_n}+\Delta E'_{nn}\ . \tag{2.8}$$

III. NUMERICAL RESULTS

As shown in our previous papers,[6,7] the CDW state of HMMC is brought about through the delicate balance between the three main factors: the itineracy of an electron T, the e-ph coupling S and the Coulombic repulsion U. For this reason, we are interested neither in the strong limit nor in the weak limit of the e-ph coupling, but only in the intermediate case, wherein T and $2S$ is of the same order, and even U is only a little smaller than $2S$. Therefore, we will be concerned hereafter with the following case: $2S\approx T\geq U\gg V$, and perform numerical calculations.

Figure 2 shows adiabatic energies as a function of ΔQ, when $l_0=0$ and $\Delta Q_-=0$. θ is determined to minimize E_{x_1}. This figure just corresponds to the photogeneration of the CT excitation and its self-trapping process. The local minimum of E_{x_1} corresponds to the STE. Figure 3 shows the adiabatic energies as a function of l_0. In this calculation, ΔQ_- is fixed to zero, while θ and ΔQ are determined to minimize E_{x_1}. This figure just corresponds to the autodissociation process of the CT excitation into a distant pair of the hole-polaron and the electron-polaron.

When $l_0\approx6$, the two local displacements centered in the left-half and the right-half of the chain overlap with each other, resulting in two localized states of electron. As schematically shown in Fig. 4, we denote these two

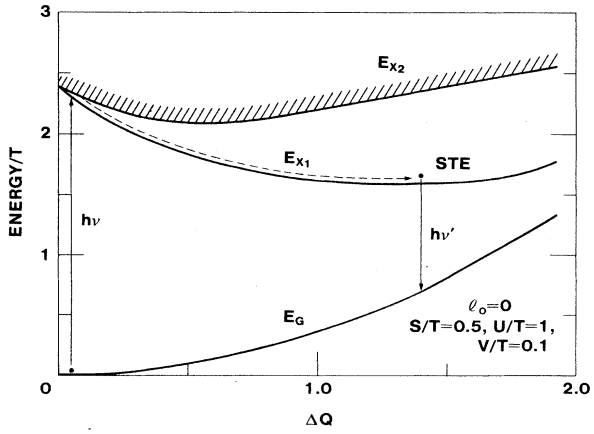

FIG. 2. Adiabatic energies as a function of ΔQ at $l_0=0$ and $\Delta Q_-=0$. θ is determined to minimize E_{x_1}.

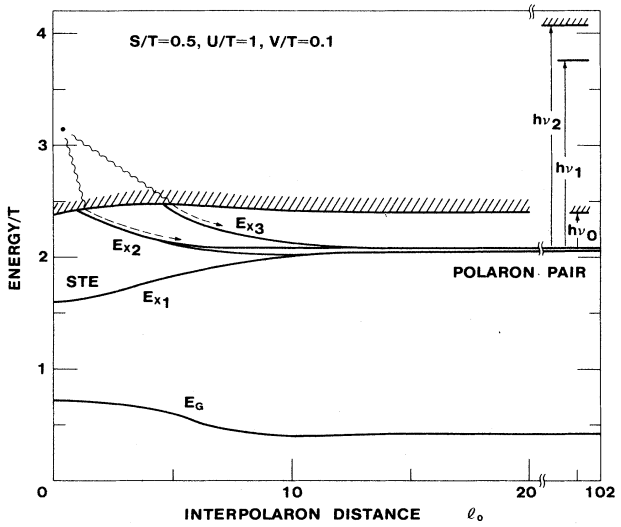

FIG. 3. Adiabatic energies as a function of l_0. ΔQ and θ are determined to minimize E_{x_1}. $\Delta Q_- = 0$.

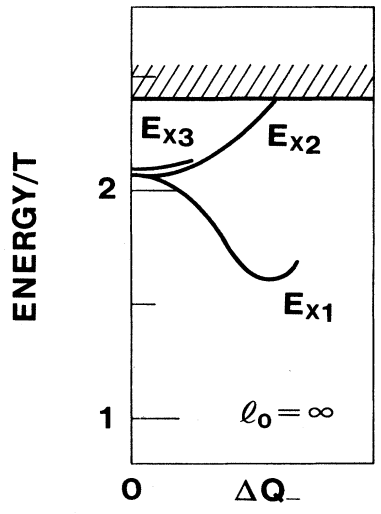

FIG. 5. Schematic nature of the adiabatic energies as a function of ΔQ_-. $l_0 = \infty$.

states $|P_B^-\rangle$ and $|P_A^-\rangle$. As for the hole, we also get two localized states denoted as $|P_B^+\rangle$ and $|P_A^+\rangle$. In this notation, subscripts $-$ and $+$ of P denote the electron and the hole, while B and A denote the bonding and antibonding states. In the ground state of the STE, an electron is in the state $|P_B^-\rangle$ and a hole is in the state $|P_B^+\rangle$. Thus, this ground state can be denoted $|P_B^- P_B^+\rangle$ and its energy is E_{x_1} in Fig. 3. As easily seen from Fig. 4, however, we have three excited states of the STE. Two of them are degenerate, and they are $|P_A^- P_B^+\rangle$ and $|P_B^- P_A^+\rangle$ with the energy E_{x_2}, while the energy of the state $|P_A^- P_A^+\rangle$ is E_{x_3}. Since the states $|P_A^-\rangle$ and $|P_A^+\rangle$ are antibonding states, these excited states can split off from the continuum only from finite values of l_0 as seen from Fig. 3, and when $l_0 = 0$ they are absent.

When $l_0 \gg 1$, the two local displacements centered in the left and the right of the chain have no overlap, resulting in two independent localized states of electron. We denote these state $|P_L^-\rangle$ and $|P_R^-\rangle$, respectively, and they are degenerate with each other as shown in Fig. 4. In this notation, the subscripts L and R mean the left and the right. In the case of hole, we also get two states $|P_L^+\rangle$ and $|P_R^+\rangle$. By combining these states we get four degenerate states $|P_L^- P_L^+\rangle$, $|P_R^- P_R^+\rangle$, $|P_L^- P_R^+\rangle$, and $|P_R^- P_L^+\rangle$. This degeneracy is removed by the electron-hole attraction coming from V through the correction term Eqs. (2.6)–(2.8). That is, the states $|P_L^- P_L^+\rangle$ and $|P_R^- P_R^+\rangle$ become lower than the states $|P_L^- P_R^+\rangle$ and $|P_R^- P_L^+\rangle$ because of the attraction as shown in Fig. 3. The latter two states correspond to the distant pair of the electron-polaron and the hole-polaron, while the former two states correspond to the STE only in the left and only in the right. Such asymmetric states are unstable for the asymmetric distortion ΔQ_-, as very schematically shown in Fig. 5. When $\Delta Q_- = \Delta Q$, the local distortion in the left disappears, while that in the right is doubled as explained before. Therefore, $|P_R^- P_R^+\rangle$ becomes equal to the STE, and $|P_L^- P_L^+\rangle$ returns back into the continuum, as shown

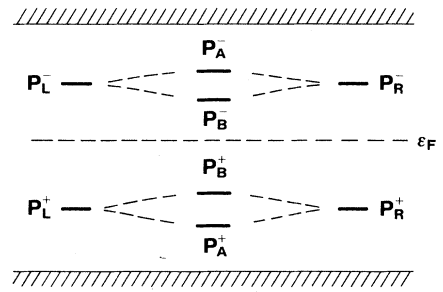

FIG. 4. Schematic nature of one-body energy levels that appeared within the gap. Upper (lower) shaded region corresponds to the electron (hole) continuum. Subscripts $-$ and $+$ of P correspond to the electron and the hole. L and R correspond to the left and the right when $l_0 = \infty$. B and A correspond to the bonding and antibonding states when $l_0 \approx 6$.

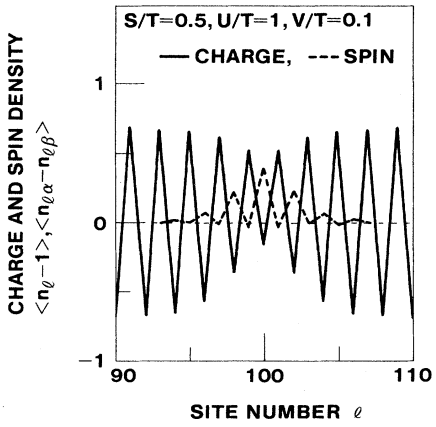

FIG. 6. Charge- and spin-density profiles of P_R^-. $\bar{n} = 1$.

by E_{x_1} and E_{x_2} in Fig. 5. Consequently, the lower two states are unstable, while, the states $|P_R^- P_L^+\rangle$ and $|P_L^- P_R^+\rangle$ state stable against ΔQ_-, as shown by E_{x_3} in Fig. 5, because in these states one of two polarons is in the right and the rest is in the left.

From these results it has become clear that the distant pair of the hole-polaron and the electron-polaron is one of local minima in the adiabatic potential-energy surface of the lattice. Such a state, if it is once created, can have an infinitely long lifetime within the adiabatic approximation at absolute zero temperature, although its energy is higher than other excited states.

Keeping these results in mind, let us consider the relaxation paths of the CT excitation. There may be two cases according to the exciting photon energy. When the CT excitation is created just by its threshold energy, the relaxation path will be such as described in our previous paper.[7] On the other hand, when the CT excitation is created by much higher energies than its threshold energy, it will relax first, not to the ground state of the STE, but to its excited states. Since these excited states have repulsive potential surfaces, in contrast to the attractive one of the ground state, they will dissociate automatically, and result in a distant pair of the electron-polaron and the hole-polaron. This distant pair is expected to have a long lifetime at low temperatures, because, as shown in Figs. 3 and 5, it is a local minimum in the adiabatic potential-energy surface of the lattice.

As seen from Figs. 3 and 4, there are three kinds of excitations from this distant pair. The first is the transition from $|P_{L(R)}^-\rangle$ to the electron continuum denoted by the energy $h\nu_0$. The second is the transition from $|P_{L(R)}^+\rangle$ to $|P_{L(R)}^-\rangle$ with the energy $h\nu_1$. The last is from $|P_{L(R)}^+\rangle$ to the electron continuum with the energy $h\nu_2$. As seen from Fig. 3, latter two energies are about 70% and 80% of the gap. From these results we can conclude that the A and B bands, observed by Kurita *et al.*, come from these origins, although the lower-energy band $h\nu_0$ has not been found yet because it is in the infrared region. This autodissociation mechanism from the excited state of the STE is also consistent with the observed excitation energy dependence of the photoinduced absorption yield. As shown by Kurita *et al.*,[4] the yield becomes greater as the exciting photon-energy exceeds the threshold energy.

Figure 6 shows the charge- and the spin-density profiles of $|P_R^-\rangle$, and we can see the polaron width is about 6 in the unit of the lattice constant. It is the characteristic of the intermediate coupling.

IV. CONCLUSIONS

We have thus studied the ground and the excited states of the one-dimensional extended Peierls-Hubbard model with half-filled-band electrons, so as to clarify the origin of the photoinduced absorption in HMMC's. When the CT excitation is created by the lights with higher energies than its threshold energy, a distant pair of polarons is created, not from the ground state of the STE, but from its excited states through their autodissociation. The observed photoinduced absorption bands are assigned to the excitations from this distant pair. This autodissociation mechanism is consistent with the observed excitation-energy dependence of the photoinduced-absorption yield.

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