Soliton-induced optical absorption of halogen-bridged mixed-valence binuclear metal complexes

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Employing the one-dimensional single-band extended Peierls-Hubbard model, we investigate optical conductivity for solitonic excitations in halogen-bridged binuclear metal (MMX) complexes. Photoinduced soliton absorption spectra for MMX chains possibly split into two bands, forming a striking contrast to those for conventional mononuclear metal (MX) analogs, due to the broken electron-hole symmetry combined with relevant Coulomb and/or electron-phonon interactions.

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I. INTRODUCTION

Halogen (X)-bridged mixed-valence metal (M) complexes [1,2] such as [Pt(en)2X](ClO4)2 (X = Cl, Br, I; en = ethylenediamine = C2H8N2), which are referred to as MX chains, have been playing a prominent role in understanding the electronic properties of one-dimensional Peierls-Hubbard systems. The competing electron-electron and electron-phonon interactions yield various ground states [3,4], which can be tuned by chemical substitution [5] and pressure [6]. Solitonic excitations inherent in charge-density-wave (CDW) ground states stimulate further interest in MX complexes. In this context, we may be reminded of polyacetylene, the trans isomer of which exhibits topological solitons [7,8]. Several authors [9–11] had an idea of similar defect states of MX complexes, which are referred to as MMX complexes, as recently investigated both analytically and numerically [22]. The direct M–M overlap contributes to the reduction of the effective on-site Coulomb repulsion and therefore electrons can be more itinerant in MMX chains. Hence we take more and more interest in solitons as charge or spin carriers.

The ground-state properties of MMX complexes were well revealed by means of X-ray diffraction [23], nuclear magnetic resonance [24], and the Raman and Mössbauer spectroscopy [16], while very little [25,26] is known about their excitation mechanism. Photoinduced absorption spectra, which served as prominent probes for nonlinear excitations in MX complexes [12,13], have, to our knowledge, not yet measured on MMX complexes probably due to the lack of a guiding theory. Thus motivated, we study optical conductivity for MMX solitons with particular emphasis on a contrast between topical MMX and conventional MX complexes. Photoexcited MMX chains may yield distinct spectral shapes due to the definite breakdown of the electron-hole symmetry.

II. MODEL HAMILTONIANS AND THEIR GROUND-STATE PROPERTIES

We describe MX and MMX chains by the one-dimensional $\frac{1}{2}$ and $\frac{3}{4}$-filled single-band Peierls-Hubbard Hamiltonians

$$H_{MX} = \hbar^{(1,1)}_{MXM} + \hbar^{(1,1)}_M + \hbar_{MX},$$

$$H_{MMX} = \hbar^{(1,2)}_{MMM} + \hbar^{(1,2)}_M + \hbar_{MX},$$

respectively, where

$$h^{(\mu,\nu)}_{MM} = -t_{MM} \sum_{n,s}(a_{\mu;n,s}^\dagger a_{\nu;n,s} + a_{\mu;n,s}^\dagger a_{\nu;n,s})$$

$$+ V_{MM} \sum_{n,s,s'} n_{\mu;n,s} n_{\nu;n,s'},$$

$$h^{(\mu,\nu)}_{MMX} = -\sum_{n,s} [t_{MMX} - \alpha (\langle l_n^- \rangle + \langle l_n^+ \rangle)] (a_{\mu;n+1,s}^\dagger a_{\nu;n,s})$$

$$+ \alpha_{\mu;n,s} a_{\mu;n+1,s} + V_{MMX} \sum_{n,s,s'} n_{\mu;n+1,s} n_{\nu;n,s'},$$

$$h_M^{(\mu,\nu)} = -\beta \sum_{n,s} (\langle l_n^- \rangle n_{\mu;n,s} + \langle l_n^+ \rangle n_{\nu;n,s})$$

$$+ \frac{\nu U_M}{2} \sum_n (n_{\mu;n,+} n_{\mu;n,-} + n_{\nu;n,+} n_{\nu;n,-}),$$

$$h_{MX} = K_{MX} \sum_n [\langle l_n^- \rangle^2 + \langle l_n^+ \rangle^2].$$

Here, $n_{\mu;n,s} = a_{\mu;n,s}^\dagger a_{\mu;n,s}$ with $a_{\mu;n,s}^\dagger$ being the creation operator of an electron with spin $s = \frac{1}{2}$ (up and down) for the $M d_{\pm,\pm}$ orbital labeled as $\mu = 1, 2$ in the $n$th MX or MMX unit, $t_{MM} = \hbar^{(1,1)}_{MMM}$ and $t_{MMX} = \hbar^{(1,2)}_{MMM}$ describe the intra- and
interunit electron hoppings, respectively, $\alpha$ and $\beta$ are the site-off-diagonal and site-diagonal electron-lattice coupling constants, respectively, $t_n^{(-)} = v_n - u_{n-1}$ and $t_n^{(+)} = u_n - v_n$ with $u_n$ and $v_n$ being, respectively, the chain-direction displacements of the halogen and metal in the $n$th unit from their equilibrium position, and $K_{MX}$ is the metal-halogen spring constant. We assume, based on the thus-far reported experimental observations, that every $M_2$ moiety is not deformed. The notation is further explained in Fig. 1. We set $t_{MMX}$ and $K_{MX}$ both equal to unity in the following.

The existent MMX complexes consist of two families: $R_4[Pt_2(pop)\cdot X]_2$-nH$_2$O ($X$ = Cl, Br, I; $R$ = Li, K, Cs, ...; pop = diphosphonate = $P_2O_6H_2^{2-}$) and $M_2$[dta]_4$I$ ($M$ = Pt, Ni; dta = dithioacetate = $CH_2CS_2^-$), which are referred to as pop and dta complexes. The pop complexes possess the mixed-valence ground state illustrated in Fig. 1(b) [24,27], while the dta complexes exhibit distinct types of ground states [14–16,28] due to the predominant site-off-diagonal electron-phonon coupling [29] or metal-on-site Coulomb repulsion [30]. Conventional MX complexes structurally resemble MMX complexes of the pop type and have the mixed-valence ground state illustrated in Fig. 1(a) [2], which is symmetrically equivalent to that in Fig. 1(b) [15,31]. Hence we study the pop complexes in our first attempt to compare the photo-products in MMX and MX chains. While the dta complexes behave as $d$-$p$-hybridized two-band materials in general, the pop complexes are well describable within $d$-$z$-single-band Hamiltonians [15]. Since the site-off-diagonal electron-phonon coupling is of little significance with the CDW backgrounds of the Fig. 1 type, we set $\alpha$ equal to zero. The rest of parameters are, unless otherwise noted, taken as $U_M = 1.2$, $V_{MMX} = 0.3$, and $\beta = 0.7$ for MX chains [1,32,33], while $U_M = 1.0$, $V_{MMX} = 0.5$, $V_{MMX} = 0.3$, and $\beta = 1.4$ for MMX chains [19,26].

III. CALCULATIONAL PROCEDURE

We treat the Hamiltonians (1) within the Hartree-Fock approximation. The lattice distortion is adiabatically determined and can therefore be expressed in terms of the electronic density matrices $\langle n_{\mu;n,s}\rangle_{HF}$, where $\langle \cdot \rangle_{HF}$ denotes the thermal average over the Hartree-Fock eigenstates. Since no spontaneous deformation of the metal sublattice has been observed in any MX and MMX pop complexes, we enforce the constraint $t_n^{(-)} + t_n^{(+)} = 0$ on every $M-X-M$ bond. Then the force equilibrium conditions

$$\frac{\partial \langle H_{MX} \rangle_{HF}}{\partial t_n^{(\pm)}} = 0, \quad \frac{\partial \langle H_{MMX} \rangle_{HF}}{\partial t_n^{(\pm)}} = 0,$$

yield

$$2K_{MX}t_n^{(-)} = \beta \sum_s \langle n_{\mu;n,s}\rangle_{HF} - \langle n_{\nu;n-1,s}\rangle_{HF},$$
$$2K_{MX}t_n^{(+)} = \beta \sum_s \langle n_{\nu;n,s}\rangle_{HF} - \langle n_{\mu;n+1,s}\rangle_{HF},$$

where $\mu = \nu = 1$ for MX chains, while $\mu = 1$, $\nu = 2$ for MMX chains.

The real part of the optical conductivity is given by

$$\sigma(\omega) = \frac{\pi}{N\omega} \sum_{\epsilon,\epsilon'} f(\epsilon) [1 - f(\epsilon')] |\langle \epsilon'|J|\epsilon \rangle|^2 \delta(\epsilon' - \epsilon - \hbar\omega),$$

where $f(\epsilon) = (e^{\epsilon/k_BT} + 1)^{-1}$ and $\langle \epsilon'|J|\epsilon \rangle$ is the matrix element of the current density operator $J$ between the eigenstates of energy $\epsilon$ and $\epsilon'$. $J$ is defined as

$$J_{MX} = J_{MMX}, \quad J_{MMX} = J_{MM} + J_{MMX},$$

for MX and MMX chains, respectively, with

$$J_{MM}^{(\mu,\nu)} = \frac{i\epsilon}{\hbar} c_{MM} t_{MM} \sum_{n,s} (a_{\nu;n,s}^\dagger a_{\mu;n,s} - a_{\mu;n,s}^\dagger a_{\nu;n,s}),$$
$$J_{MMX}^{(\mu,\nu)} = \frac{i\epsilon}{\hbar} c_{MMX} \sum_{n,s} [t_{MMX} - \alpha(t_n^{(-)} + t_n^{(+))}]$$
$$\times (a_{\mu;n+1,s}^\dagger a_{\nu;n,s} - a_{\mu;n,s}^\dagger a_{\nu;n+1,s}),$$

where $c_{MM}$ and $c_{MMX}$ are the average $M-M$ and $M-X-M$ distances, respectively, and are set for $c_{MM} = 2c_{MMX}$ [34,35].

In order to elucidate the intrinsic excitation mechanism, solitons are calculated at a sufficiently low temperature without any assumption on their spatial configurations. Charged solitons ($S^\pm$; $\sigma = \pm$) are obtained by setting the numbers of up- and down-spin electrons, $N_+$ and $N_-$, both equal to $(p - 1/2)N - \sigma/2$, while spin-$s$ neutral solitons ($S^0$; $s = \pm 1/2$) with $N_\pm = (p - 1/2)N \pm s$, where $N$, taken to be 401 in our calculation, is the number of unit cells and $p$ is the number of metal sites in the unit cell.
FIG. 2. Spatial configurations of the optimum solitons in $MX$ and $MMX$ chains.

FIG. 3. The formation energies of the stably located solitons as functions of the Coulomb interaction, where $\beta = 0.7$ and $U_M$ varies keeping the relation $U_M = V_{MMX}/0.25$ for $MX$ chains, while $\beta = 1.4$ and $U_M$ varies keeping the relation $U_M = V_{MMX}/0.5 = V_{MMX}/0.3$ for $MMX$ chains.

IV. RESULTS

We show the spatial configurations of the optimum solitons in Fig. 2 and plot their formation energies $\Delta E_S$ in Fig. 3. In $MX$ chains, charged solitons are stable laying their centers on halogen sites, while neutral solitons on metal sites. In $MMX$ chains, all the optimum solitons are halogen-centered. As the Peierls gap $E_{\text{gap}}$ increases, solitons generally possess increasing energies and decreasing extents, and end up with immobile defects. $U_M$ and $V_{MMX}$ reduce $E_{\text{gap}}$ and thus enhance the mobility of solitons, while $V_{MMX}$ has an opposite effect. Without any Coulomb interaction, the soliton formation energies are all degenerate and scaled by the Peierls gap as $\Delta E_S = E_{\text{gap}}/\pi$ in the weak-coupling region $E_{\text{gap}} \lesssim \frac{1}{2} V_{MMX}$ [36], whereas their degeneracy is lifted and neutral solitons have higher energies than charged solitons with further increasing gap. Since $E_{\text{gap}}$ decreases with increasing $U_M$, $\Delta E_S$ is a decreasing function of $U_M$. Neutral solitons are more sensitive to the Coulomb interaction and thus their formation energy turns smaller than that of charged solitons with increasing $U_M$. Considering that $E_{\text{gap}}$ is a linear function of $U_M$, we learn that neutral solitons well keep the scaling relation $\Delta E_S \propto E_{\text{gap}}$ against the Coulomb interaction.

Figure 2 suggests that an $MX$ soliton of charge $\sigma$ and spin $s$, $S^{\sigma s}$, described in terms of electrons is equivalent to its counterpart $S^{-\sigma-s}$ described in terms of holes. Such a symmetry is more directly observed through the energy structures shown in Fig. 4. Solitons generally exhibit an additional level within the gap. There appear further soliton-related levels in the strong-coupling region [37].

FIG. 4. Density of states for the optimum soliton solutions.

FIG. 5. (Color online) Energy shifts of the localized soliton levels from the gap center scaled by the Peierls gap as functions of the Coulomb interaction. The parametrization is the same as that in Fig. 3. The level structures of up- and down-spin electrons are plotted by solid (broken) and broken (solid) lines, respectively, for $S^\text{or}_{\sigma}$ ($S^\text{ol}$), while they are degenerate for charged solitons.
The intragap soliton levels are analyzed in more detail in Fig. 5. When the coupling strength increases without any Coulomb interaction, the mid-gap level due to a neutral soliton keeps still, while the charged-soliton levels deviate from the gap center. symmetry. Once the Coulomb interaction is switched on, the neutral-soliton level also begins to move away from the gap center breaking the spin up-down asymmetry between the two $S^\pm$ bands is in proportion to the on-site Coulomb repulsion and may therefore be reduced with pressure applied, whereas the asymmetry between the two $S^\pm$ bands is sensitive to the electron-lattice coupling and may thus be enhanced by the halogen replacement Cl → Br → I. Photoinduced absorption measurements on MMX complexes may not only reveal the novel doublet structures of soliton-induced spectra but also give a key to the unsettled problem in MX complexes—the shoulder structure of the $S^0$ absorption spectrum. Let us make a close collaboration between experimental and theoretical investigations of dynamic properties of MMX complexes.

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