Effect of quantum lattice fluctuations on the optical-absorption spectra of halogen-bridged mixed-valence transition-metal complexes

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Abstract

The effect of quantum lattice fluctuations on the optical-absorption spectra in the ground state of halogen-bridged mixed-valence transition-metal linear-chain complexes is studied by using a one-dimensional extended Peierls-Hubbard model. The nonadiabatic effects due to finite phonon frequency $\omega_\pi > 0$ are treated through an energy-dependent electron-phonon scattering function $\delta(k', k)$ introduced by means of an unitary transformation. The calculated optical-absorption spectra do not have the inverse-square-root singularity, but they have a peak above the gap edge and there exists a significant tail below the peak, which are consistent with the optical-absorption coefficient or the optical conductivity measurements of this material.

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1 Introduction

Halogen-bridged mixed-valence transition-metal complexes (HMMC’s or MX chain), as one of typical materials with a quasi-one-dimensional charge-density-wave (CDW) state, have been the subject of intense studies in recent years for both theoretists and experimentalists, because of the intrinsically interesting properties and the important technological applications of the materials [1, 2, 3]. Each chain of the materials is composed of transition-metal ions $M^{+3}$ (=Pt$^{+3}$, Pd$^{+3}$, Ni$^{+3}$) bridged by halogen ions $X^-$ (=Cl$^-$, Br$^-$, I$^-$), with ligands attached to the metals and in some cases counterions between the chains to maintain charge neutrality. $M^{+3}$ has an unpaired electron in its $d_{z^2}$ orbital ($\hat{z}$ is parallel to the chain), and this orbital makes an energy band through the supertransfer between neighbouring two $d_{z^2}$ orbitals. This supertransfer comes from the hybridization between the $d_{z^2}$ orbital and the $p_z$ orbital of $X$. Because of the electron-phonon (e-ph) coupling, the charge transfer occurs between neighbouring two $M'$s so as to give the mixed-valence state. This is nothing but the CDW state with twice the period of the original lattice. The MX chain materials constitute a rapidly expending class of near single-crystal quasi-one-dimensional systems with phases of ground states ranging from strong CDW to spin-density-wave or spin-Peierls [4].

Many previous investigations of MX chain materials used the adiabatic approximation for the phonons. The adiabatic approximation means neglect of the dynamic energy of halogen ions, that is, neglect of the effect of lattice vibration. In nonadiabatic case, the phonon frequency $\omega_\pi$ is finite. Generally speaking, the nonadiabatic effect will suppress the state order parameters of the system [5, 6]. As far as the optical-absorption coefficient is concerned, the results of adiabatic approximation methods have inverse-square-root singularity at the gap edge. By considering the nonadiabatic effect, the inverse-square-root singularity at the gap edge may disappear [7]. The relationship between the change of optic-absorption shape and the phonon frequency in the range from $\omega_\pi = 0$ to $\omega_\pi \to \infty$ should be studied for understanding the physical properties of e-ph interactions of MX chain in nonadiabatic case.
The one-dimensional one-band model for MX chain complexes can be written as

\[ H = \sum_l \left( \frac{1}{2M} P_l^2 + \frac{K}{2} u_l^2 \right) - \sum_{l,s} t_0 (c_{l,s}^\dagger c_{l+1,s} + c_{l+1,s}^\dagger c_{l,s}) + \sum_{l,s} \alpha (u_l - u_{l+1}) c_{l,s}^\dagger c_{l,s} + H_c, \]

where

\[ H_c = U \sum_l n_{l,\uparrow} n_{l,\downarrow} + V \sum_{l,s,s'} n_{l,s} n_{l+1,s'}. \]

Here \( c_{l,s}^\dagger \) and \( c_{l,s} \) are the creation and annihilation operators of electrons sitting at site \( l \) with spin \( s \), \( u_l \) (it’s conjugated momentum is \( p_l \)) is the displacement of the \( l \)th ion, \( t_0 \) is the supertransfer energy of electrons between neighbouring two orbitals, \( \alpha \) is the e-ph coupling constant, \( K \) is the elastic constant and \( M \) the mass of ions. \( U \) and \( V \) correspond to the on-site and the nearest-neighbour Coulomb energies, respectively (throughout this paper, we set \( \hbar = k_B = 1 \)).

2 Theoretical analysis

In the Hamiltonian (1), the operators of lattice modes, \( u_l \) and \( p_l \), can be expanded by the phonon creation and annihilation operators \( b_q^\dagger \) and \( b_q \), and after Fourier transformation, the \( H \) reads

\[ H = H^0 + H_{ep} + H_c, \]

where

\[ H^0 = \sum_q \omega_q \left( b_q^\dagger b_q + \frac{1}{2} \right) + \sum_{k,s} \epsilon_k c_{k,s}^\dagger c_{k,s}, \]

\[ H_{ep} = \sum_{q,k,s} \frac{1}{\sqrt{N}} g(q) (b_q + b_{-q}^\dagger) c_{k+q,s}^\dagger c_{k,s}. \]

Here, \( \epsilon_k = -2t_0 \cos k \) is the bare band function, and \( N \) is the total number of sites. The coupling function \( g(q) = \alpha \sqrt{1/(2M\omega_q)} [1 - \exp(iq)] \) and the dispersionless phonon frequency \( \omega_q = \sqrt{K/M} \).

In order to take into account the fermion-phonon correlation, an unitary transformation is applied to \( H \),

\[ H' = \exp(S) H \exp(-S), \]
where the generator $S$ is
\begin{equation}
S = \frac{1}{\sqrt{N}} \sum_{q,k,s} \frac{g(q)}{\omega_{\pi}} (b_{-q}^\dagger - b_q) \delta(k + q, k) c_{k+q,s}^\dagger c_{k,s}.
\end{equation}

Here we introduce a function $\delta(k', k)$ which is a function of the energies of the incoming and outgoing fermions in the fermion-phonon scattering process and will be determined later.

The unitary transformation can proceed order by order,
\begin{equation}
H' = H^0 + H_{ep} + H_c + [S, H^0] + [S, H_{ep}] + [S, H_c] + \frac{1}{2}[S, [S, H^0]] + \frac{1}{2}[S, [S, H_c]] + O(\alpha^3).
\end{equation}

The first-order terms in $H'$ are
\begin{align}
H_{ep} + [S, H^0] &= \frac{1}{\sqrt{N}} \sum_{q,k,s} g(q)(b_{-q}^\dagger + b_q) c_{k+q,s}^\dagger c_{k,s} \\
&\quad - \frac{1}{\sqrt{N}} \sum_{q,k,s} g(q) \delta(k + q, k) (b_{-q}^\dagger + b_q) c_{k+q,s}^\dagger c_{k,s} \\
&\quad + \frac{1}{\sqrt{N}} \sum_{q,k,s} \frac{g(q)}{\omega_{\pi}} \delta(k + q, k) (b_{-q}^\dagger - b_q) (\epsilon_k - \epsilon_{k+q}) c_{k+q,s}^\dagger c_{k,s}.
\end{align}

Note that the ground state $|g_0\rangle$ of $H^0$, the non-interacting system, is a direct product of a filled fermi-sea $|FS\rangle$ and a phonon vacuum state $|ph, 0\rangle$:
\begin{equation}
|g_0\rangle = |FS\rangle |ph, 0\rangle.
\end{equation}

Applying the first-order terms on $|g_0\rangle$ we get
\begin{equation}
(H_{ep} + [S, H^0]|g_0\rangle = \frac{1}{\sqrt{N}} \sum_{q,k,s} g(q)b_{-q}^\dagger c_{k+q,s}^\dagger c_{k,s} \left[ 1 - \delta(k + q, k) \left( 1 - \frac{\epsilon_k - \epsilon_{k+q}}{\omega_{\pi}} \right) \right] |g_0\rangle,
\end{equation}

since $b_q|ph, 0\rangle = 0$. As the band is half-filled, the Fermi energy $\epsilon_F = 0$. Thus $c_{k+q,s}^\dagger c_k|FS\rangle \neq 0$ only if $\epsilon_{k+q} \geq 0$ and $\epsilon_k \leq 0$. So, we have
\begin{equation}
(H_{ep} + [S, H^0]|g_0\rangle = 0,
\end{equation}

if we choose
\begin{equation}
\delta(k + q, k) = 1/(1 + |\epsilon_{k+q} - \epsilon_k|/\omega_{\pi}).
\end{equation}

This is nothing but making the matrix element of $H_{ep} + [S, H^0]$ between $|g_0\rangle$ and the lowest-lying excited states vanishing. Thus the first-order terms, which are not exactly
canceled after the transformation, are related to the higher-lying excited states and should be irrelevant under renormalization [13]. The second-order terms in \( H' \) can be collected as follows:

\[
[S, H_{ep}] + \frac{1}{2} [S, [S, H^0]] \\
= \frac{1}{2N} \sum_{q,k,s} \sum_{q',k'} \frac{g(q)g(q')}{\omega} \delta(k + q, k)[2 - \delta(k' + q', k')](b^\dagger_{-q'} + b_{q'})(b^\dagger_{-q} - b_{q}) \\
\times (c^\dagger_{k+q,s}c_{k',s}\delta_{k,k'+q'} - c^\dagger_{k'+q',s}c_{k,s}\delta_{k',k+q}) \\
+ \frac{1}{2N} \sum_{q,k,s} \sum_{q',k'} \frac{g(q)g(q')}{\omega^2} \delta(k + q, k)[2 - \delta(k' + q', k')](b^\dagger_{-q'} - b_{q'})(b^\dagger_{-q} - b_{q}) \\
\times (c^\dagger_{k+q,s}c_{k',s}\delta_{k,k'+q'} - c^\dagger_{k'+q',s}c_{k,s}\delta_{k',k+q}) \\
- \frac{1}{2N} \sum_{q,k,s} \sum_{q',k',s'} \frac{g(q)g(-q)}{\omega} \delta(k + q, k)[2 - \delta(k' + q, k')](b^\dagger_{-q} - b_{q}) \\
\times (c^\dagger_{k+q,s}c_{k',s}\delta_{k,k'+q'} - c^\dagger_{k'+q',s}c_{k,s}\delta_{k',k+q}).
\]  

(14)

\( \delta_{k',k+q} \) is the Kronecker \( \delta \) symbol. All terms of higher order than \( \alpha^2 \) will be omitted in the following treatment. Note that the first order terms of transformed \( H_c \) have not been included in the process of determining function \( \delta(k', k) \) (from Eq. (9) to Eq. (13)) and the second order terms of that have not been included in Eq. (14). The reason for doing so will be discussed later.

Then we make a displacement transformation to \( H' \) to take into account the static phonon-staggered ordering [4],

\[
\tilde{H} = \exp(R)H' \exp(-R).
\]

(15)

Here,

\[
R = -\sum_i (-1)^i u_0 \sqrt{\frac{M \omega_\pi}{2}} (b^\dagger_i - b_i),
\]

(16)

and \( \exp(R) \) is a displacement operator.

If the ground state of \( H \) is \( |g\rangle \), then the ground state of \( \tilde{H} \) is \( |g'\rangle \): \( |g\rangle = \exp(-S) \exp(-R) |g'\rangle \).

We assume that for \( |g'\rangle \), the fermions and phonons can be decoupled: \( |g'\rangle \approx |fe\rangle |ph, 0\rangle \), where \( |fe\rangle \) is the ground state for fermions. After averaging \( \tilde{H} \) over the phonon vacuum state, we get an effective Hamiltonian for the fermions,

\[
H_{\text{eff}} = \langle ph, 0 | \tilde{H} | ph, 0 \rangle
\]
\begin{align}
E_0(k) &= \epsilon_k - \frac{1}{N} \sum_{k'} \frac{g(k'-k)g(k-k')}{\omega^2_\pi} \delta(k',k) \delta(k,k')(\epsilon_k - \epsilon_{k'}), \\
\Delta_0(k) &= 2\alpha u_0[1 - \delta(k - \pi, k)], \\
V_0 &= \frac{1}{N^3} \sum_{k,k',q} \frac{g(q)g(-q)}{\omega_\pi} \delta(k+q,k)[2 - \delta(k'-q,k')].
\end{align}

Now, the total Hamiltonian can be divided as \( \tilde{H} = \tilde{H}_0 + \tilde{H}_1 \), where \( \tilde{H}_1 \) includes the terms that are zero after being averaged over the phonon vacuum state, and

\[ \tilde{H}_0 = \sum_q \omega_\pi \left( b_q^\dagger b_q + \frac{1}{2} \right) + H_{\text{eff}}. \]

After the unitary transformations, the Coulomb interaction \( H_c \) becomes \( H_c + \) higher order terms. The contributions of these higher order terms to \( \tilde{H}_0 \) are zero under the mean-field approximation. So, in the process of determining function \( \delta(k',k) \), which only concerns the first order terms of transformed Hamiltonian, and also in Eq. (14) and Eq. (17), we have not written out the higher order terms of transformed \( H_c \). By using the mean-field approximation to the terms of four-fermion interaction in \( H_{\text{eff}} \), we have

\[ \tilde{H}_0 = \frac{1}{2} K N u_0^2 + \sum_q \omega_\pi \left( b_q^\dagger b_q + \frac{1}{2} \right) + \sum_{k,s} E_k c_{k,s}^\dagger c_{k,s} + \sum_{k>0,s} \Delta_k (c_{k-\pi,s}^\dagger c_{k,s} + c_{k,s}^\dagger c_{k-\pi,s}). \]

In the theoretical analysis, we have distinguished different physical processes and taken into account the fact that only the Umklapp scattering terms affect the gap, and the forward and backward scattering terms contribute nothing to the ”charge” gap [14, 15]. The renormalized band function and the gap function are

\[ E_k = E_0(k) - \frac{2}{N} \sum_{k'} \left( \frac{\alpha^2}{K} \sin^2\left( \frac{k'-k}{2} \right) \delta(k',k)[2 - \delta(k',k)] - V \cos(k' - k) \right) \frac{E_{k'}}{W_{k'}}; \]

\[ \Delta_k = 2\alpha u_0[c - \frac{1}{2} \delta(k - \pi, k)]. \]
Where
\[ c = 1 + \frac{1}{N} \sum_{k > 0} \left[ 2V - \frac{1}{2}U - V_0 + \frac{4\alpha^2}{K}\delta(k - \pi, k) \right] \frac{\Delta_k}{2\alpha u_0 W_k}, \] (25)
and \( W_k = \sqrt{E_k^2 + \Delta_k^2} \) is the fermionic spectrum of elementary excitations in the dimerized state.

We find by means of the variational principle that the equation to determine dimerized lattice displacement ordering parameter \( u_0 \) is
\[ 1 = 4\frac{\alpha^2}{KN} \sum_{k > 0, s} [1 - \delta(k - \pi, k)] \frac{\Delta_k}{2\alpha u_0 W_k}. \] (26)
If \( \omega_\pi = 0 \) we have \( \delta(k', k) = 0 \). Eq. (26) becomes the same as that in the adiabatic theory. In our theory \( \delta(k - \pi, k) \) has a sharp peak at the Fermi point and, since
\[ 1 - \delta(k - \pi, k) = \frac{4t_0|\cos k|}{\omega_\pi + 4t_0|\cos k|}, \] (27)
the logarithmic singularity in the integration of Eq. (26) in the adiabatic case is removed by the factor \( 1 - \delta(k - \pi, k) \) as long as the ratio \( \omega_\pi/t_0 \) is finite. For the gapped state (insulating state) we believe that the mean-field approximation is still an effective one. The reason is as follows: The quadratic part of \( H_{\text{eff}} \) (which can be exactly diagonalized) contains a gap term \( (\Delta_0(k) \neq 0) \) that is related to the Peierls dimerization and suppresses the quantum fluctuations. Furthermore, the logarithmic singularity (related to the infrared divergence of low dimensional system) has been removed by the factor \( 1 - \delta(k - \pi, k) = 4t_0|\cos k|/(\omega_\pi + 4t_0|\cos k|) \). Comparing Eq. (24) with that in the adiabatic case, \( \Delta = 2\alpha u_0 \), we have the gap in the nonadiabatic case, \( \Delta = \Delta(\pi/2) = 2\alpha u_0[c - 1/2] \), which is nonzero but smaller than the adiabatic gap. This is the true gap in the fermionic spectrum.

3 Optical absorption

The optical-absorption coefficient \( \alpha(\omega) \) can be expressed by the retarded Green’s function as follows:
\[ \alpha(\omega) = -\frac{2}{\pi\omega} \text{Im} K^R(\omega), \] (28)
where $K^R$ is defined as

$$K^R(\omega) = -i \int_{-\infty}^{0} e^{-i\omega t} dt \langle [j(0)j(t) - j(t)j(0)] | g \rangle.$$  \hfill (29)

Here, $j$ is the current operator \[3\],

$$j = -ie t_0 \sum_{l,s} (c^\dagger_{l,s} c_{l+1,s} - c^\dagger_{l+1,s} c_{l,s})
= J \sum_{k,s} \sin k c^\dagger_{k,s} c_{k,s},$$  \hfill (30)

where $J = 2e t_0$, and $j(t) = \exp(i H t) j \exp(-i H t)$ is the form of $j$ in the Heisenberg representation. As $R$ commutes with $j$, the unitary transformation of the current operator is

$$e^S je^{-S} = j + [S, j] + \frac{1}{2} [S, [S, j]] + O(\alpha^3)
= J \sum_{k>0,s} \sin k (c^\dagger_{k,s} c_{k,s} - c^\dagger_{k-\pi,s} c_{k-\pi,s})
+ J \sqrt{N} \sum_{k>0,q,s} \frac{g(q)}{\omega} (b^\dagger_q - b_q) \delta(k + q, k) [\sin k - \sin(k + q)]
\times (c^\dagger_{k+q,s} c_{k,s} - c^\dagger_{k+q-\pi,s} c_{k-\pi,s})
- \delta(k, k - q') (c^\dagger_{k+q,s} c_{k-q',s} - c^\dagger_{k+q-\pi,s} c_{k-q'-\pi,s}).$$  \hfill (31)

Because the averaging of $\tilde{H}_1$ over the phonon vacuum state is zero, in the ground state at zero temperature, $\tilde{H}_1$ can be neglected. By using the approximately decoupling $|g'| \approx |g_0\rangle$, the ground state of $\tilde{H}_0$, and $\tilde{H} \approx \tilde{H}_0$ \[3\] in the calculation

$$\langle g| j(0)j(t)|g \rangle = \langle g'| e^{(S+R)} j e^{-(S+R)} e^{i\tilde{H}_1 t} e^{(S+R)} j e^{-(S+R)} e^{-i\tilde{H}_1 t} |g'\rangle
\approx \langle g'_0| e^S j e^{-S} e^{i\tilde{H}_0 t} e^{S} j e^{-S} e^{-i\tilde{H}_0 t} |g'_0\rangle,$$  \hfill (32)

we can get

$$K^R(\omega) = J^2 \sum_{k>0,s} \left( \frac{1}{\omega - 2W_k + i0^+} - \frac{1}{\omega + 2W_k - i0^+} \right)
\times \left\{ \sin^2 k + \frac{2\alpha^2}{KN\omega_s} \sum_{k'} [1 - \cos(k' - k)] \delta^2(k', k) \sin k (\sin k' - \sin k) \right\} \frac{\Delta^2_k}{W_k^2}$$

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\[ \alpha^2 J^2 \frac{N^2}{\omega_\pi} \sum_{k>0,k'>0} \left( \frac{1}{\omega - \omega_\pi - W_k - W_{k'} + i0^+} - \frac{1}{\omega + \omega_\pi + W_k + W_{k'} - i0^+} \right) \times \left\{ [1 - \cos(k' - k)] \delta^2(k', k)(\sin k' - \sin k)^2(\alpha_k \beta_{k'} + \beta_k \alpha_{k'})^2 \right. \\
\left. + [1 + \cos(k' - k)] \delta^2(k' - \pi, k)(\sin k' + \sin k)^2(\alpha_k \alpha_{k'} + \beta_k \beta_{k'})^2 \right\}, \tag{33} \]

where \( \alpha_k = \sqrt{(1 + E_k/W_k)/2} \), and \( \beta_k = \sqrt{(1 - E_k/W_k)/2} \). Thus, we have the optical-absorption coefficient

\[ \alpha(\omega) = \frac{2J^2(2s + 1)}{\omega N} \sum_{k>0} \delta(\omega - 2W_k) \\
\times \left\{ \sin^2 k + \frac{2\alpha^2}{KN\omega_\pi} \sum_{k'} [1 - \cos(k' - k)] \delta^2(k', k) \sin k(\sin k' - \sin k) \right\} \frac{\Delta_k^2}{W_k^2} \\
+ \frac{2\alpha^2 J^2(2s + 1)}{\omega KN^2\omega_\pi} \sum_{k>0,k'>0} \delta(\omega - \omega_\pi - W_k - W_{k'}) \\
\times \left\{ [1 - \cos(k' - k)] \delta^2(k', k)(\sin k' - \sin k)^2(\alpha_k \beta_{k'} + \beta_k \alpha_{k'})^2 \right. \\
\left. + [1 + \cos(k' - k)] \delta^2(k' - \pi, k)(\sin k' + \sin k)^2(\alpha_k \alpha_{k'} + \beta_k \beta_{k'})^2 \right\}. \tag{34} \]

The relationships between the change of the optical-absorption shape and the different phonon frequencies are shown in Figure 1. The parameter values used are: \( \alpha^2/K = 0.5t_0 \), \( U = 1.0t_0 \) and \( V = 0.15t_0 \) with \( \omega_\pi = 0.004t_0, 0.008t_0 \), and \( 0.012t_0 \). One can see that the spectrum broadens but the peak height decreases as \( \omega_\pi \) increases. The inverse-square-root singularity at the gap edge in the adiabatic case \[16\] disappears because of the nonadiabatic effect. For comparison, the adiabatic \( (\omega_\pi = 0) \) result is also shown which has an inverse-square-root singularity at gap edge. For finite \( \omega_\pi \), the singularity is absent and there is a significant tail below the peak. We note that in our theory, in mathematical viewpoint, the difference between the \( \omega_\pi = 0 \) and \( \omega_\pi > 0 \) cases mainly comes from the functional form of the gap [see Eq. (24)]. Comparing it with that in the adiabatic limit, one can see that the subgap states come from the quantum lattice fluctuations, i.e., the second term in the square bracket of Eq. (24).

Figure 2 shows the calculated optical-absorption coefficients \( \alpha(\omega) \) versus the normalized photon frequency relations for \( \omega_\pi = 0.008t_0 \), \( U = 1.0t_0 \) and \( V = 0.15t_0 \) in the cases of \( \alpha^2/K = 0.3t_0, 0.4t_0, \) and \( 0.5t_0 \). One can see that as the e-ph coupling constant \( \alpha^2/K \) increases, the peak of optical-absorption spectrum moves to higher photon energy and the
The dimerization gap becomes wider.

Figure 3 (a) and Figure 3 (b) show the calculated optical-absorption coefficients $\alpha(\omega)$ versus the normalized photon frequency relations for $\omega_\pi = 0.008t_0$ and $\alpha^2/K = 0.5t_0$ in the cases of different $U$ and $V$ values, respectively. One can see that the spectra are generally the same, except that the peak height decreases and shifts to higher photon energy when $U$ decreases or $V$ increases. The on-site and the nearest-neighbour Coulomb repulsions are to weaken and strengthen the lattice dimerization, respectively. In the $MX$ chain, a charge-transfer (CT) excitation originates in the electron excitation over the CDW gap. If no definite fine structure can be observed in the absorption band, it cannot be clarified, only from the line shape of optical-absorption, whether this band is due to the CT exciton or the interband transition. Wada et al. [17] claimed that because of the electric field dependence of the modulation signal observed in the measurement of the electroreflectance spectra of the $MX$ chain, it can be excluded that the CT excitation absorption band is an interband absorption. However, K. Iwano et al. [18] indicated that in the case of weak electron-hole binding, i.e., small $V$, the spectrum becomes the mixture of the exciton absorption and the interband ones. If the value of $V$ is reduced toward zero, the exciton contribution then becomes more and more small and, finally, the exciton disappears and the spectrum is now given completely by the interband transitions. Our calculated result of the $V = 0$ case is also shown in Fig. 3 (b) and this is the optical-absorption spectrum of the interband transitions.

In Figure 4, we compare our calculation (solid line) with the observed optical absorption (solid circles) of $MX$ chain complexes [19]. Here we use the same input parameters (without adjusting them) $U = 1.0t_0$ and $V = 0.3t_0$, as those of K. Iwano and K. Nasu [18]. Other input parameters used are $\omega_\pi = 0.01t_0$ and $\alpha^2/K = 0.2t_0$. One can see that the agreement between the experiment result and our calculation is quite good. In experiments, the measurement of optical-absorption spectrum could be affected by various factors, such as the impurity in samples, the finite measurement temperature, and the finite measurement resolution (about $\pm5\%$ accuracy of the reflectivity measurement [19]). These made the measured absorption spectrum to be broadened and led to the slight discrepancy between the experiment result and our calculation.
In Figure 5, we plot the calculated optical-absorption coefficients versus the rescaled photon frequency relations with $U = 1.0t_0$ and $V = 0.15t_0$ for different $\omega_\pi$ and $\alpha^2/K$. Quite remarkably, when we scale the optical-absorption coefficient by the peak value, and scale the photon frequency by $\Gamma$, the half-width for the low photon frequency side of the peak, we find that the scaled curves for various $\omega_\pi$ and $\alpha^2/K$ values have an universal form below the peak photon frequency. In their studies of temperature dependence of subgap optical conductivity for KCP(Br) and trans-polyacetylene, J.W. Wilkins et al. [20] discovered that the strong subgap tail of the conductivity had an universal scaling form. We use the same scaling method as that of J.W. Wilkins et al., but to study the $\omega_\pi$ and $\alpha^2/K$ dependence of optical-absorption coefficient. Our universal form is similar to that of J.W. Wilkins et al., which implies that the temperature effect and nonadiabatic effect on quasi-one-dimensional Peierls systems have similar characteristic properties.

4 Conclusions

The effects of quantum lattice fluctuations on the optical-absorption coefficient in the ground state of $MX$ chain are studied by introducing an energy-dependent e-ph scattering function $\delta(k', k)$ via an unitary transformation. The functional dependence of $\delta(k', k)$ on $k'$ and $k$ is determined by the vanishing of the second-order perturbation of first-order terms in the transformed Hamiltonian. By using the retarded Green’s-function method we have shown that our theory gives a good description of the effects of quantum lattice fluctuations and change of various parameters on the optical-absorption. The inverse-square-root singularity of optical-absorption spectrum at the gap edge in the adiabatic case disappears because of the nonadiabatic effect. The calculated optical-absorption coefficient is consistent well with the experiment observation of optical conductivity measurements. The curve of subgap optical-absorption coefficient has an universal scaling form.

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Figure Caption

**Fig. 1.** The relationships between the change of optical-absorption shape and the different phonon frequencies in the cases of $\alpha^2/K = 0.5t_0$, $U = 1.0t_0$ and $V = 0.15t_0$ with $\omega_\pi = 0.004t_0, 0.008t_0$, and $0.012t_0$. For comparison, the adiabatic ($\omega_\pi = 0$) result is also shown which has an inverse-square-root singularity at gap edge.

**Fig. 2.** The calculated optical-absorption coefficients $\alpha(\omega)$ versus the normalized photon frequency relations for $\omega_\pi = 0.008t_0$, $U = 1.0t_0$ and $V = 0.15t_0$ in the cases of $\alpha^2/K = 0.3t_0$, $0.4t_0$, and $0.5t_0$.

**Fig. 3 (a).** The calculated optical-absorption coefficients $\alpha(\omega)$ versus the normalized photon frequency relations for $\omega_\pi = 0.008t_0$, $\alpha^2/K = 0.5t_0$ and $V = 0.15t_0$ in the cases of $U = 0.6t_0, 0.8t_0$, and $1.0t_0$.

**Fig. 3 (b).** The calculated optical-absorption coefficients $\alpha(\omega)$ versus the normalized photon frequency relations for $\omega_\pi = 0.008t_0$, $\alpha^2/K = 0.5t_0$ and $U = 1.0t_0$ in the cases of $V = 0, 0.15t_0, 0.25t_0$, and $0.35t_0$.

**Fig. 4.** The rescaled optical-absorption coefficient $\alpha(\omega)/\alpha_{\text{peak}}$ versus the normalized photon energy $\omega/\omega_{\text{peak}}$ relations, where $\alpha_{\text{peak}}$ and $\omega_{\text{peak}}$ are the optical-absorption coefficient and the photon energy at the peak, respectively. The solid circles are the result of experiment observation for [Pt(en)$_2$][PtX$_2$(en)$_2$](ClO$_4$)$_4$ (Ref.[13], Fig.6). The solid line is our result by using $\omega_\pi = 0.01t_0$, $U = 1.0t_0$, $V = 0.3t_0$, and $\alpha^2/K = 0.2t_0$.

**Fig. 5.** Scaling plot of the calculated optical-absorption coefficients $\alpha(\omega)/\alpha_{\text{peak}}$, where the photon energy is scaled by $\Gamma$, the half-width for the low photon energy side of the peak. Note we claim only that the subgap($\omega < \omega_{\text{peak}}$) optical-absorption coefficients scale.