

Photoinduced electronic ferroelectric phase in a metal-organic framework

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We investigate the physical properties and lattice relaxation of important photoexcited states in a charge-transfer-type metal-organic framework $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$. We construct the one-dimensional spinless fermion model for the material and numerically calculate the photoexcited states and the lattice-relaxed states from them. The ground state is a charge-ordered (CO) state with a uniform lattice. The dominant peak in the light absorption spectrum corresponds to an optically allowed bond order wave (BOW) state with charge disproportionation (CD). This Franck-Condon BOW state forms as a linear combination of two degenerate inversion-symmetry-broken BOW states, which have different phases of bond order alternation, combined with the CD, and the inversion symmetry is restored in the state. The Franck-Condon BOW state is strongly coupled to the lattice deformation of bond length alternation, and lattice relaxation can occur even in this rigid material. The lattice-relaxed state originating from the Franck-Condon state is a BOW state with CD, where inversion symmetry is broken due to bond length alternation, making it an electronic ferroelectric state. The largest peak in the induced light absorption spectrum from this lattice-relaxed BOW state results from excitation to another BOW state with CD, which has the opposite phase of bond order alternation. This state is also an electronic ferroelectric, with its polarization opposite to that of the lattice-relaxed BOW state from the Franck-Condon state. This shows that polarization can be reversed instantly through resonant photoexcitation from the lattice-relaxed state.

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I. INTRODUCTION

Metal-organic frameworks (MOFs) [1–4] are composed of metal ions and organic molecules bonded in a network. With their large surface areas from nanometer-scale voids, MOFs are promising for gas storage [5], gas separation [6,7], and catalysis [8–10]. They are also used for x-ray analysis of nanogram- to microgram-scale samples [11]. The flexibility in choosing metals and organic molecules enables the design of MOFs with interesting properties [12–19]. In particular, stimuli-responsive MOFs have attracted attention; donor (D)-acceptor (A)-type MOFs with charge-transfer phase transitions [20–23] are one example.

Recently, a charge-transfer-type phase transition has been reported in a D-A-type MOF $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$ (NPr_4 = tetra-*n*-propylammonium; Cl_2An = 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) [24,25]. The structure of $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$ is a D_{2A_3} -type two-dimensional honeycomb layer, where D and A correspond to the Fe and Cl_2An , respectively, as shown in Fig. 1. The NPr_4^+ cations sit between the honeycomb layers. This compound shows a two-step charge-transfer phase transition at 317 and 354 K

[25]. The electronic and lattice structures of each phase were determined by magnetic measurements, x-ray diffraction, and Mössbauer spectroscopy [25]. The low-temperature (LT) phase for $T < 317$ K consists of quasi-one-dimensional (1D) chains of Fe^{3+} ($S = 5/2$) and $\text{Cl}_2\text{An}^{3-}$ ($S = 1/2$), joined by $\text{Cl}_2\text{An}^{2-}$ ($S = 0$), as in Fig. 1. Spins of Fe^{3+} and those of $\text{Cl}_2\text{An}^{3-}$ are antiferromagnetically coupled along the chain. The high-temperature (HT) phase for $T > 354$ K contains quasi-1D chains of Fe^{2+} ($S = 2$) and $\text{Cl}_2\text{An}^{2-}$ ($S = 0$), joined by $\text{Cl}_2\text{An}^{2-}$ ($S = 0$), as in Fig. 1. The intermediate (IM) phase for $317 \text{ K} < T < 354 \text{ K}$ consists of spatially disordered quasi-1D chains formed by Fe^{3+} and $\text{Cl}_2\text{An}^{3-}$, as well as Fe^{2+} and $\text{Cl}_2\text{An}^{2-}$, in a 1:1 ratio. Although the electronic structure changes, the space group ($P2_1/n$) remains unchanged during the transitions. Charge transfer between Fe and Cl_2An occurs within each chain during both the LT-IM and IM-HT phase transitions. Magnetic susceptibility indicates that spin interactions are much stronger within a chain than between chains [25]. Additionally, the charge-transfer peak in the reflectivity spectrum is present only when the electric field of light aligns with the chain [26]. Together, these findings demonstrate that the low-energy properties throughout all three phases can be effectively described by considering a single chain.

Given these properties, charge-transfer phase transitions in such materials suggest that photoexcitation-induced charge transfer may also trigger similar transitions. This motivates exploration of light-driven phenomena in MOFs. A tetrathiafulvalene *p*-chloranil compound (TTF-CA) is a typical example of a compound exhibiting a transition between neutral (N) and ionic (I) phases, which is a type of

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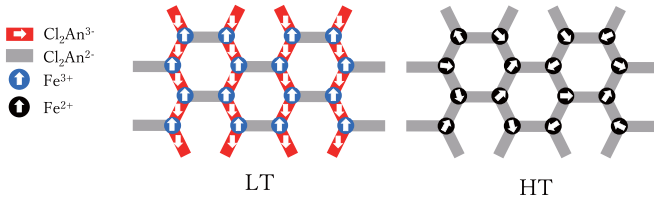


FIG. 1. Schematic representations of the LT and HT phases with spin directions indicated by arrows.

charge-transfer phase transition. Actually, TTF-CA exhibits highly efficient photoinduced N-I phase conversions [27–33], which can be regarded as photoinduced phase transitions [34–40].

Recently, ultrafast dynamics induced by photoexcitation have been investigated in $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$, and a charge-transfer-type ultrafast photoinduced phase transition is reported in the LT phase [26,41]. The ultrafast, efficient transition of the photoexcited state suggests that it involves more than a simple charge transfer between a single D-A pair. It indicates a collective charge-transfer process involving many electrons. New spectral features in the charge-transfer transition and mid-IR ranges point to a structural change in the photoinduced phase. This transition involves local inversion symmetry breaking, and the photoinduced phase differs from both the HT and IM phases. This phase is the photoinduced hidden (PH) state, which is not accessible in thermal equilibrium [40,42].

Photoinduced phase transitions [34–40] have been observed in various materials. If the photoinduced phase is a nonequilibrium state that cannot be realized in thermal equilibrium, it reveals new aspects of the material that differ significantly from those in the ground state. Analysis of these photogenerated phases provides a better understanding of the material from new and general perspectives. In addition to revealing new material properties, we also observe the ultrafast dynamics of quantum order formation during the photoinduced phase transition. By analyzing these dynamics, we can understand the origin of this order from a perspective distinct from the analysis of equilibrium phases. Furthermore, this research connects directly to the challenge of achieving light-controlled functionality in solid-state systems. This expands the relevance and scope of photoinduced phase investigations in MOFs.

However, despite these advances, the electronic and lattice structures of the photoinduced phase remain unclear. In particular, the structural change is unexpected, given the typically robust, covalently bonded structure of MOFs. The origin of the strong electron-lattice coupling remains unresolved. This issue highlights a central challenge in elucidating the mechanisms underlying photoinduced phenomena in these systems. To clarify these points, we have investigated the photoexcited states and their lattice relaxation using the spinless fermion model for $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$. The dominant peak in the light absorption spectrum $\alpha(\omega)$ is due to the excitation to the bond order wave (BOW) state with charge disproportionation (CD) from the charge-ordered (CO) ground state. The Franck-Condon BOW state is given by the linear combination of two degenerate BOW states with different phases of bond order

alternation, and therefore, the state has inversion symmetry. The Franck-Condon BOW state is strongly coupled to the lattice deformation of bond length alternation, which is the origin of the lattice relaxation of the photoinduced phase. In the lattice relaxation process, the inversion symmetry is broken, and the lattice-relaxed state from the Franck-Condon BOW state is an electronic ferroelectric state, which can be described by the Rice-Mele model [43]. The lattice relaxation process of the photoexcited state demonstrates the polarization formation described by this representative model of electronic ferroelectrics in real materials. Part of this paper's content has already been submitted in a joint paper with the experimental group [41].

II. MODEL

In $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$, six oxygen ligand atoms surrounding a central Fe ion interact with the d orbitals of the Fe ion, causing them to split into the t_{2g} and e_g energy levels. As mentioned in Sec. I, it has been experimentally shown that the LT phase can be described by quasi-1D chains of Fe^{3+} ($S = 5/2$) and $\text{Cl}_2\text{An}^{3-}$ ($S = 1/2$), which are antiferromagnetically coupled [25]. The d orbitals are occupied by five electrons with the same spin in Fe^{3+} , which is because the Hund's rule coupling is much larger than the crystal field splitting. We assume that five up-spin electrons occupy the five d orbitals in all the Fe^{3+} ions without loss of generality, and the electron configuration of Fe^{3+} (Fe^{2+}) is $t_{2g}^3 e_g^2$ ($t_{2g}^3 t_{2g}^1 e_g^2$). The HT phase can be described as quasi-1D chains of Fe^{2+} ($S = 2$) and $\text{Cl}_2\text{An}^{2-}$ ($S = 0$). The down-spin electron that occupies the highest occupied molecular orbital (HOMO) of $\text{Cl}_2\text{An}^{3-}$ is transferred to Fe^{3+} in the transition from the LT to HT phases. These experimental results show that the Hund's rule coupling is so strong that only down-spin electrons are relevant when considering the charge transfer in the LT phase. Therefore, we employ the spinless fermion model [44–46], where the transfer of only down-spin electrons is considered, and down-spin electrons are treated as spinless fermions, to describe the low-energy properties of the LT phase.

Since the on-site $d-d$ Coulomb interaction is sufficiently large, it can be assumed that the maximum number of down-spin electrons that can exist in an Fe site is one, which allows us to neglect the orbital degeneracy of the $t_{2g\downarrow}$ level. The main effect of orbital degeneracy can be incorporated by increasing the magnitude of the transfer integral. The Hamiltonian for the LT phase is given by

$$\begin{aligned}
 H = & \frac{\Delta}{2} \sum_{i=1}^N (-1)^{i-1} \hat{n}_i - t_0 \sum_{i=1}^{N/2} [(1 - \alpha x_{2i})(c_{2i}^\dagger c_{2i-1} + c_{2i-1}^\dagger c_{2i}) \\
 & + (1 + \alpha x_{2i})(c_{2i+1}^\dagger c_{2i} + c_{2i}^\dagger c_{2i+1})] \\
 & + \sum_{i,j}^{1 \leq i < j \leq N} V_{i,j} \hat{n}_i \hat{n}_j + K \sum_{i=1}^{N/2} x_{2i}^2.
 \end{aligned} \quad (1)$$

The first term describes the difference in energy (Δ) between the $t_{2g\downarrow}$ energy level and the HOMO of $\text{Cl}_2\text{An}^{3-}$, where N is the system size, $c_i^\dagger$ (c_i) is the creation (annihilation) operator for spinless fermion (down-spin electron), $\hat{n}_i = c_i^\dagger c_i$ is the spinless fermion density operator at the site i , and Fe and

Cl_2An are placed at odd-numbered and even-numbered sites, respectively. The second term describes the transfer of spinless fermions, and the electron-lattice coupling is introduced in this term, where $-t_0$ is the transfer integral between the neighboring sites for the uniform lattice. Since the quasi-1D chains are bridged by Cl_2An that is covalently bonded to Fe (see Fig. 1), only the deviation of Cl_2An is considered. We take account of the dependence of the transfer integral between the neighboring sites on x_{2i} only to first order, where x_{2i} is the deviation of Cl_2An from the position of the uniform lattice along the chain direction at the site $2i$, and α is the electron-lattice coupling constant. The third term describes the Coulomb interaction between the different sites, where the Coulomb interaction energy $V_{i,j}$ between the spinless fermions at the sites i and j is given by

$$V_{i,j} = \frac{V}{r_{i,j}} \exp[-\kappa(r_{i,j} - 1)], \quad (2)$$

V is the Coulomb interaction energy between the spinless fermions at the neighboring sites, $r_{i,j}$ is the distance between the sites i and j , κ is the screening constant, and we set the unit of length so that the lattice spacing for the uniform lattice is 1. The interactions $V_{i,j}$ for $r_{i,j} \geq 2$ are important. As described below, CO states and BOW states play crucial roles in the optical properties of this system. Coulomb interactions between sites at even distances stabilize the BOW states relative to the CO state. The CO state becomes excessively stabilized when we consider only the Coulomb interaction between the nearest-neighbor sites. The fourth term describes the lattice deformation energy, where K is the elastic coefficient. Periodic boundary condition is used.

We calculate the adiabatic potentials for the important energy eigenstates that can be excited by light. We consider the lattice deformation of uniform bond length alternation, where the lattice displacement is given by $\alpha x_{2i} = u$, and u is the adiabatic parameter. There are two phases of bond length alternation. In the A-phase (B-phase) bond length alternation, $u > 0$ ($u < 0$) holds, and odd-numbered (even-numbered) bonds are longer, where the bond connecting site i and site $i + 1$ is designated as bond i . The absolute value $|u|$ is proportional to the difference in length between the shorter and longer bonds.

In the following, we use the unit of energy in which $t_0 = 1$ and consider the dimensionless adiabatic Hamiltonian $H(u)$. It is given by the sum of the electronic part $H_e(u)$ and the lattice deformation energy as

$$H(u) = H_e(u) + \frac{N\tilde{K}}{2}u^2, \quad (3)$$

$$\begin{aligned} H_e(u) = & \frac{\tilde{\Delta}}{2} \sum_{i=1}^N (-1)^{i-1} \hat{n}_i - \sum_{i=1}^{N/2} [(1-u)(c_{2i}^\dagger c_{2i-1} + c_{2i-1}^\dagger c_{2i}) \\ & + (1+u)(c_{2i+1}^\dagger c_{2i} + c_{2i}^\dagger c_{2i+1})] \\ & + \sum_{1 \leq i < j \leq N} \tilde{V}_{i,j} \hat{n}_i \hat{n}_j, \end{aligned} \quad (4)$$

where $\tilde{\Delta} = \Delta/t_0$, $\tilde{V}_{i,j} = V_{i,j}/t_0$, $\tilde{V} = V/t_0$, and $\tilde{K} = K/(t_0\alpha^2)$. The absolute value $2|u|$ shows the difference in the magnitude

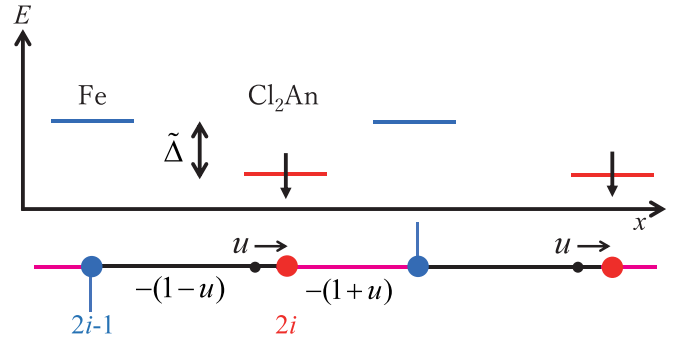


FIG. 2. Schematic representation of the dimensionless adiabatic Hamiltonian. $\tilde{\Delta}$ shows the difference in energy between the t_{2g} energy level and the HOMO of $\text{Cl}_2\text{An}^{3-}$, and $2|u|$ shows the difference in the magnitude of the transfer integral between the shorter and longer bonds.

of the transfer integral between the shorter and longer bonds in this dimensionless Hamiltonian as seen in Fig. 2.

We numerically calculate the energy eigenstates $|\phi_n(u)\rangle$ with the energy eigenvalue $E_n(u)$ of $H_e(u)$ that contribute to the photoinduced dynamics by the following method [47]. We numerically solve the time-dependent Schrödinger equation when the ground state is excited by light. From the solution, we obtain the coefficient matrix, the $i - l$ element of which is the coefficient of the l th basis state in the solution at the i th discretized time. By performing a randomized singular value decomposition of the coefficient matrix, a practically exact solution is obtained using a linear combination of the important energy eigenstates, the number of which is much smaller than the dimensions of the Hilbert space in most cases. The electron-field coupling is introduced into the transfer integral as a Peierls phase as

$$\begin{aligned} & \sum_{i=1}^{N/2} [(1-u)(e^{-iA(t)} c_{2i}^\dagger c_{2i-1} + e^{iA(t)} c_{2i-1}^\dagger c_{2i}) \\ & + (1+u)(e^{-iA(t)} c_{2i+1}^\dagger c_{2i} + e^{iA(t)} c_{2i}^\dagger c_{2i+1})]. \end{aligned} \quad (5)$$

We consider the dynamics induced by the light pulse given by the vector potential

$$A(t) = A \exp \left[-\left(\frac{t}{D} \right)^2 \right] \cos(\omega t), \quad (6)$$

where A is the maximum amplitude, D is the pulse duration, and ω is the optical frequency. The values of $D = 0.1$ and $\omega = 2$ are determined so that the Fourier components of $A(t)$ sufficiently cover the region where peaks exist in the light absorption spectrum. The value of $A = 0.5$ is in the strong excitation region where the multiphoton excitation effect cannot be neglected. We calculate the nine photoexcited energy eigenstates with the largest quantum weights in the solution of the time-dependent Schrödinger equation. The sum of the quantum weights of these nine photoexcited energy eigenstates and the ground state is 0.997 for $u = 0$. A linear combination of these, as few as ten important energy eigenstates, can represent the solution almost exactly. These important energy eigenstates $|\phi_n(u)\rangle$ are numbered in order of increasing energy, and

$|\phi_0(u)\rangle$ is the ground state. The energy eigenvalues of these states for $u = 0$ are as follows: $E_n(0) - E_0(0) = 2.366, 2.380, 3.168, 3.966, 4.636, 5.233, 5.847, 6.410,$ and 7.541 for $1 \leq n \leq 9$.

The energy level crossing does not occur between these important energy eigenstates when u is changed from 0 to 0.01. The adiabatic potential for $|\phi_n(u)\rangle$ is given by

$$U_n(u) = E_n(u) - E_n(0) + \frac{N\tilde{K}}{2}u^2. \quad (7)$$

III. RESULTS

We consider a chain with a system size of $N = 18$, and the number of spinless fermions, n_{SLF} , is $N/2$. We adopt the following parameters: $\tilde{\Delta} = 0.4$, $\tilde{V} = 7.6$, $\kappa = 0.1$. This set of parameters reasonably reproduces experimental results. We will discuss later how the results shown below depend on the parameters. To investigate the physical properties of $|\phi_n(u)\rangle$, we calculate charge density n_i at the site i , bond order p_i at the bond i , charge density correlation $\xi_{i,j}$ between the sites i and j , and bond order correlation $\kappa_{i,j}$ between the bonds i and j :

$$n_i = \langle \phi_n(u) | \hat{n}_i | \phi_n(u) \rangle, \quad (8)$$

$$p_i = \langle \phi_n(u) | \hat{p}_i | \phi_n(u) \rangle, \quad (9)$$

$$\xi_{i,j} = \langle \phi_n(u) | \hat{n}_i \hat{n}_j | \phi_n(u) \rangle - \bar{n}^2, \quad (10)$$

$$\kappa_{i,j} = \frac{1}{2} \langle \phi_n(u) | \hat{p}_i \hat{p}_j + \hat{p}_j \hat{p}_i | \phi_n(u) \rangle - \bar{p}^2, \quad (11)$$

where $\hat{p}_i = c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i$ is the bond order operator at the bond i , $\bar{n} = 0.5$ is the average charge density, and $\bar{p} = (p_{2i-1} + p_{2i})/2$ is the average bond order.

We first consider the ground state $|\phi_0(0)\rangle$ of $H_e(0)$ in the case of a uniform lattice. The state $|\phi_0(0)\rangle$ is stable against the lattice deformation in the realistic parameter region as will be mentioned in detail, and $|\phi_0(0)\rangle$ with the uniform lattice of $u = 0$ is the lowest-energy electron-lattice state. The Hamiltonian $H_e(0)$ exhibits both inversion symmetry with the center of inversion at a site and translation symmetry by two sites. Therefore, all the odd-numbered (even-numbered) sites are equivalent, and all the bonds are equivalent in $|\phi_n(0)\rangle$. In the ground state $|\phi_0(0)\rangle$, $n_{2i-1} = 0.118$ and $n_{2i} = 0.882$ hold. The charge density of transferable electrons alternates every two sites, and they exist mainly at Cl_2An sites as schematically shown in Fig. 3(a). This charge density alternation is consistent with the electronic structure of the LT phase, which can be described by the 1D chain of Fe^{3+} ($S = 5/2$) and $\text{Cl}_2\text{An}^{3-}$ ($S = 1/2$). We show the charge density correlation for $|\phi_0(0)\rangle$ in Fig. 4. The charge density correlation with the charge-rich site 2, $\xi_{2,2+r}$, is negative (positive) when r is odd (even), and the decay of $\xi_{2,2+r}$ is too slow to be confirmed by calculations on the present finite-size system, showing that charge order exists in $|\phi_0(0)\rangle$. Both the Coulomb interaction and the site energy terms contribute to the charge structure. However, the charge structure factor $S(\pi) = (1/N) \sum_{i=1}^N \xi_{2,i} (-1)^{i-2}$, which shows the magnitude of charge order, at $\tilde{V} = 7.6$, is approximately four times greater than $S(\pi)$ at $\tilde{V} = 0$. Thus, $|\phi_0(0)\rangle$ can be regarded as a CO state, which results from the

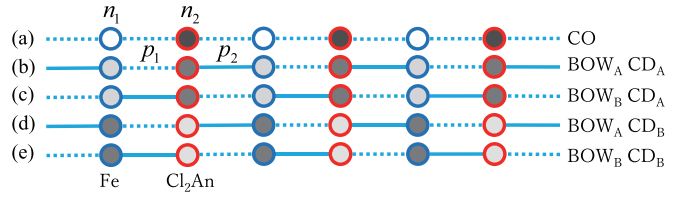


FIG. 3. Schematic representation of charge and bond structures of (a) the CO state, (b) A-phase BOW state with A-phase CD, (c) B-phase BOW state with A-phase CD, (d) A-phase BOW state with B-phase CD, and (e) B-phase BOW state with B-phase CD. Fe (Cl_2An) sites are represented by circles with blue (red) circumferences, with higher-charge-density sites shown in darker colors. Each bond is represented by a line, with strong bonds shown as thick solid lines and weak bonds as thin dashed lines.

Coulomb interaction. The LT phase corresponds to the CO state in the spinless fermion model.

We show the light absorption spectrum $\alpha(\omega)$ in Fig. 5. The lowest-energy peak is the largest, which agrees reasonably with the experimentally obtained one, and the absorption gap is reproduced for $t_0 = 0.338$ eV [26,41]. This characteristic $\alpha(\omega)$ can be reproduced except for the region $\tilde{\Delta} \leq 0.06$.

In Fig. 6(a), we show the change in electronic energy $E_n(u) - E_n(0)$ induced by the bond length alternation in $|\phi_n(u)\rangle$ with $n = 0, 1$, and 2 . The lowest-energy and dominant peak in $\alpha(\omega)$ is due to the excitation from the ground state $|\phi_0(0)\rangle$ to the Franck-Condon state $|\phi_1(0)\rangle$. Since $E_n(u)$ is an even function of u , the lowest-order term is the second-order one in the Taylor expansion of $E_n(u) - E_n(0)$ with respect to u . We see from numerical results that the second-order term is dominant in $E_1(u) - E_1(0)$ for $u \leq 0.002$, and $E_1^{(2)}(0) = 84E_0^{(2)}(0)$ holds, where $E_n^{(2)}(0)$ is the second-order differential coefficient of $E_n(u) - E_n(0)$. The energy gain due to bond length alternation of $|\phi_1(u)\rangle$ is much larger than that of

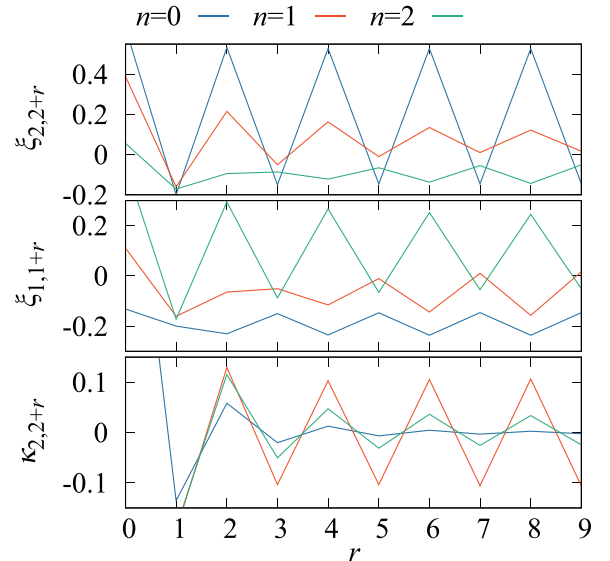


FIG. 4. The charge density correlations $\xi_{2,2+r}$ and $\xi_{1,1+r}$, and the bond order correlation $\kappa_{2,2+r}$ for $|\phi_n(0)\rangle$ with $n = 0, 1$, and 2 .

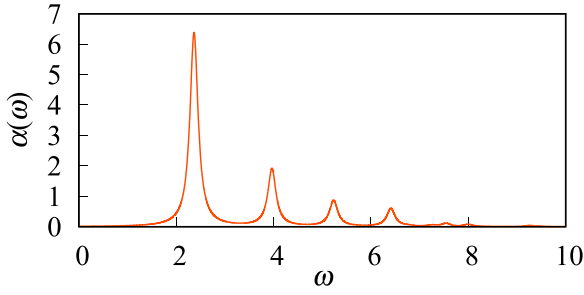


FIG. 5. Light absorption spectrum $\alpha(\omega)$ for $u = 0$. The broadening of 0.1 is used.

$|\phi_0(u)\rangle$, showing that $|\phi_1(u)\rangle$ is strongly coupled to the lattice deformation of bond length alternation.

We show the adiabatic potential $U_1(u)$ for various values of $\tilde{K}$ in Fig. 7. For $\tilde{K} < 65$, $U_1(u_{\min}) < U_1(0)$, where $U_1(u)$ has a local minimum value at $u = u_{\min} > 0$, and lattice relaxation occurs from the Franck-Condon state $|\phi_1(0)\rangle$ to the relaxed state $|\phi_1(u_{\min})\rangle$ with bond length alternation. The adiabatic potential $U_1(u)$ is an even function of u . Therefore, $U_1(u)$ has a local minimum value also at $u = -u_{\min}$. There are two degenerate lattice-relaxed states $|\phi_1(u_{\min})\rangle$ and $|\phi_1(-u_{\min})\rangle$ with the opposite phases of bond length alternation.

The phase transition between the N and I phases can also be regarded as a charge-transfer phase transition. TTF-CA is a typical example of a compound exhibiting an N-I phase

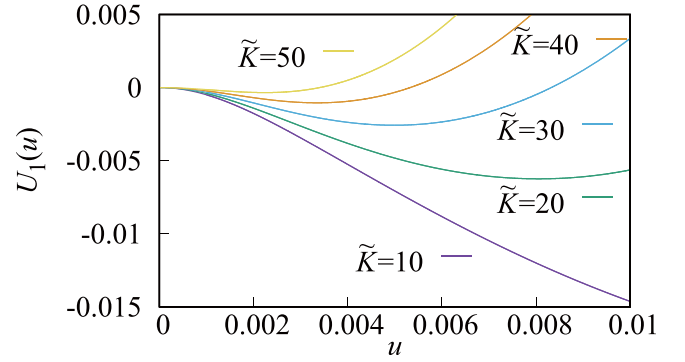


FIG. 7. The adiabatic potential $U_1(u)$ for various values of $\tilde{K}$.

transition, and bond length alternation occurs in the I phase [48]. Fe ions and Cl_2An molecules are bonded by covalent bonds in the present system, but TTF and Cl_2An molecules are bound by π stacking in TTF-CA. As a result, the elastic coefficient K in the present system is considered to be much larger than that in TTF-CA. The value of $\tilde{K}$ for TTF-CA is estimated to be 2.97 [49] from the length difference between the longer and shorter bonds in the I phase [48], and the THz-pulse induced coherent oscillation in reflectivity change (54 cm^{-1}), which is associated with the bond length alternation mode [50]. In the present system, the corresponding Fe-O stretching mode is about 650 cm^{-1} [51–53], indicating that K is about 100 times as large as that in TTF-CA. It is difficult to estimate the electron-lattice coupling constant α in the present system because the lattice structure of the relaxed photoexcited state remains unclear. If α in the present system is 1.4 times larger than that in TTF-CA, then $\tilde{K} < 65$ and the lattice relaxation of bond length alternation occurs from the dominant photoexcited state $|\phi_1(0)\rangle$. It is natural to assume a much larger value of α in the present system than that in TTF-CA because the d orbitals are localized. The lattice relaxation of the bond length alternation does not occur in the ground state except in unrealistic cases where α in the present system is more than 13 times larger than that in TTF-CA, which is consistent with the uniform lattice in the LT phase.

To understand the origin of strong electron-lattice coupling in $|\phi_1(0)\rangle$, we show the charge density correlation with the charge-rich site $\xi_{2,2+r}$ and the bond order correlation $\kappa_{2,2+r}$ for $|\phi_1(0)\rangle$ in Fig. 4. Note that all the bonds are equivalent in $|\phi_1(0)\rangle$. In $|\phi_1(0)\rangle$, charge density at the Cl_2An sites ($n_{2i} = 0.64$) is larger than that at the Fe sites ($n_{2i-1} = 0.36$), but the difference $n_{2i} - n_{2i-1}$ between them is much smaller than that for $|\phi_0(0)\rangle$. Despite the CD, $|\xi_{2,2+r}|$ decreases with increasing r . Furthermore, in $|\phi_1(0)\rangle$, $\kappa_{2,2+r} < 0$ ($\kappa_{2,2+r} > 0$) holds when r is odd (even), and the decay of $\kappa_{2,2+r}$ is too slow to be confirmed by the present calculations on a finite-size cluster. This shows that $|\phi_1(0)\rangle$ is the BOW state, where the bond order p_i alternates every two bonds, with CD. A large number of electrons move collectively in the excitation from the CO ground state to the Franck-Condon state $|\phi_1(0)\rangle$. This is consistent with the experimentally observed ultrafast and efficient transition [26,41].

There are two BOW states with different phases. In the A-phase BOW (BOW_A) state and the B-phase BOW (BOW_B) state, $p_{2i} > p_{2i-1}$ and $p_{2i} < p_{2i-1}$ hold, respectively.

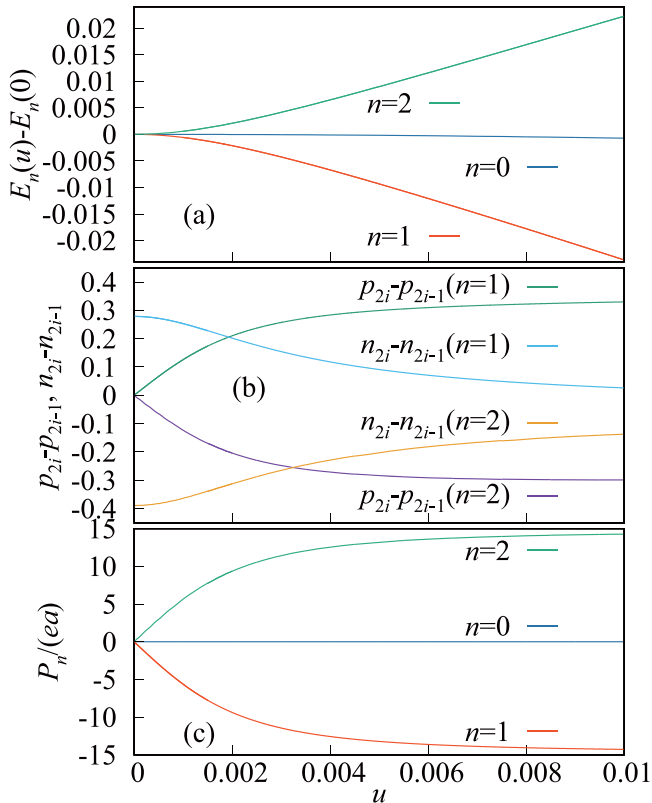


FIG. 6. (a) The u dependence of $E_n(u) - E_n(0)$ for $n = 0, 1$, and 2 . (b) The u dependence of $n_{2i} - n_{2i-1}$ and $p_{2i} - p_{2i-1}$ for $|\phi_n(u)\rangle$ with $n = 1$ and 2 . (c) The u dependence of $P_n(u)$ for $n = 0, 1$, and 2 .

There are two CD patterns. The CD where $n_{2i} > n_{2i-1}$ holds and the CD where $n_{2i} < n_{2i-1}$ holds are denoted as the A-phase CD (CD_A) and the B-phase CD (CD_B), respectively. Therefore, there are four BOW states with CD: the BOW_A state with CD_A ($|\psi_{BOW_A+CD_A}\rangle$), the BOW_B state with CD_A ($|\psi_{BOW_B+CD_A}\rangle$), the BOW_A state with CD_B ($|\psi_{BOW_A+CD_B}\rangle$), and the BOW_B state with CD_B ($|\psi_{BOW_B+CD_B}\rangle$), the charge and bond structures of which are schematically shown in Figs. 3(b), 3(c), 3(d), and 3(e), respectively.

The adiabatic Hamiltonian $H_c(0)$ for $u = 0$ exhibits inversion symmetry with the center of inversion at a site. The CO ground state $|\phi_0(0)\rangle$ has the symmetry, but the symmetry is broken in these four BOW states with CD. If the charge density is uniform, the BOW states exhibit inversion symmetry, with the bond center as the center of inversion. Since Fe and Cl_2An sites are not equivalent in the present model, and CD exists in the four BOW states, they have no inversion symmetry. The inversion symmetry is restored in $|\phi_1(0)\rangle$ by making the linear combination of these symmetry-broken BOW states.

To clarify the phases of the symmetry-broken BOW states in the linear combination, we define the phase of $|\psi_{BOW_B+CD_X}\rangle$ by $|\psi_{BOW_B+CD_X}\rangle = U_I |\psi_{BOW_A+CD_X}\rangle$, where U_I is the inversion operator with the center of inversion of a site, and $X = A$ or B . There are four BOW states with the restored inversion symmetry:

$$|\psi_{S-BOW+CD_X}\rangle = \frac{1}{\sqrt{2}}(|\psi_{BOW_A+CD_X}\rangle + |\psi_{BOW_B+CD_X}\rangle), \quad (12)$$

$$|\psi_{AS-BOW+CD_X}\rangle = \frac{1}{\sqrt{2}}(|\psi_{BOW_A+CD_X}\rangle - |\psi_{BOW_B+CD_X}\rangle). \quad (13)$$

The state $|\psi_{AS-BOW+CD_X}\rangle$ ($|\psi_{S-BOW+CD_X}\rangle$) is antisymmetric (symmetric) with respect to inversion symmetry. Therefore, $|\psi_{AS-BOW+CD_X}\rangle$ ($|\psi_{S-BOW+CD_X}\rangle$) is optically allowed (forbidden) from the symmetric ground state $|\phi_0(0)\rangle$. Furthermore, since $|\phi_1(0)\rangle$ has the CD_A , where $n_{2i} > n_{2i-1}$ holds, $|\phi_1(0)\rangle = |\psi_{AS-BOW+CD_A}\rangle$ holds.

This can be confirmed from the overlap between $|\phi_1(0)\rangle$ and $|\Psi_{BOW_A+CD_X}\rangle$ ($|\Psi_{BOW_B+CD_X}\rangle$), which is the BOW_A (BOW_B) state with CD_X when we neglect the quantum fluctuations. The state $|\Psi_{BOW_A+CD_X}\rangle$ is given by

$$|\Psi_{BOW_A+CD_X}\rangle = b_2^\dagger b_4^\dagger \cdots b_N^\dagger |\text{vac}\rangle, \quad (14)$$

where $|\text{vac}\rangle$ is the vacuum state. The bond connecting the sites i and $i + 1$ with CD_X is created by $b_i^\dagger$, and it is given by

$$b_{2i-1}^\dagger = C c_{2i-1}^\dagger + \sqrt{1 - C^2} c_{2i}^\dagger, \\ b_{2i}^\dagger = \sqrt{1 - C^2} c_{2i}^\dagger + C c_{2i+1}^\dagger, \quad (15)$$

where C is a real and positive number. The BOW_B state with CD_X is defined by $|\Psi_{BOW_B+CD_X}\rangle = U_I |\Psi_{BOW_A+CD_X}\rangle$, and it is given by

$$|\Psi_{BOW_B+CD_X}\rangle = (-1)^Q b_1^\dagger b_3^\dagger \cdots b_{N-1}^\dagger |\text{vac}\rangle, \quad (16)$$

where $Q = n_{SLF}(n_{SLF} - 1)/2$. CD is determined by C , and $n_{2i-1} = C^2$ and $n_{2i} = 1 - C^2$ hold for $|\Psi_{BOW_A+CD_X}\rangle$ and $|\Psi_{BOW_B+CD_X}\rangle$, and $p_{2i} = 2C\sqrt{1 - C^2}$ and $p_{2i-1} = 0$ ($p_{2i} = 0$ and $p_{2i-1} = 2C\sqrt{1 - C^2}$) hold for $|\Psi_{BOW_A+CD_X}\rangle$

($|\Psi_{BOW_B+CD_X}\rangle$). It is noted that the bond order of the stronger bond decreases as $|n_{2i} - n_{2i-1}|$ increases.

We numerically identify the significant overlaps: $|\langle \Psi_{BOW_A+CD_A} | \phi_1(0) \rangle|^2 = |\langle \Psi_{BOW_B+CD_A} | \phi_1(0) \rangle|^2 = 0.336$, and find that the relation $\langle \Psi_{BOW_A+CD_A} | \phi_1(0) \rangle = -\langle \Psi_{BOW_B+CD_A} | \phi_1(0) \rangle$ holds. This confirms that $|\phi_1(0)\rangle = |\psi_{AS-BOW+CD_A}\rangle$ holds.

There is an energy eigenstate $|\phi_2(0)\rangle$ at $E_2(0) - E_0(0) = 2.380$ slightly above $|\phi_1(0)\rangle$ at $E_1(0) - E_0(0) = 2.366$. The state $|\phi_2(0)\rangle$ cannot be excited by a one-photon from the ground state. However, by performing singular value decomposition of the coefficient matrix [47] in the strong excitation case, we numerically obtain $|\phi_2(0)\rangle$.

As seen in Fig. 6(b), $n_{2i} < n_{2i-1}$ holds in $|\phi_2(0)\rangle$. We show the charge density correlation with the charge-rich site $\xi_{1,1+r}$ and the bond order correlation $\kappa_{2,2+r}$ for $|\phi_2(0)\rangle$ in Fig. 4. In $|\phi_2(0)\rangle$, the decay of $\xi_{1,1+r}$ is slow, but the decay of $\kappa_{2,2+r}$ is slower than that of $\xi_{1,1+r}$. Therefore, we can conclude that $|\phi_2(0)\rangle$ is also a BOW state with CD_B . Since $|\phi_2(0)\rangle$ is symmetric with respect to inversion symmetry, $|\phi_2(0)\rangle = |\psi_{S-BOW+CD_B}\rangle$ holds. This can be confirmed from the large overlaps $|\langle \Psi_{BOW_A+CD_B} | \phi_1(0) \rangle|^2 = |\langle \Psi_{BOW_B+CD_B} | \phi_1(0) \rangle|^2 = 0.314$ and the fact that $\langle \Psi_{BOW_A+CD_B} | \phi_2(0) \rangle = \langle \Psi_{BOW_B+CD_B} | \phi_2(0) \rangle$ holds.

Next, we consider the lattice relaxation of the Franck-Condon state $|\phi_1(0)\rangle$ by investigating how $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$ change when u is changed. It is shown from numerical calculations that both $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$ exhibit the characteristic charge density and bond order correlations of the BOW states, and $n_{2i} > n_{2i-1}$ ($n_{2i} < n_{2i-1}$) holds in $|\phi_1(u)\rangle$ ($|\phi_2(u)\rangle$) as seen in Fig. 6(b), showing that $|\phi_1(u)\rangle$ ($|\phi_2(u)\rangle$) is given by the linear combination of two BOW states $|\psi_{BOW_A+CD_A}\rangle$ and $|\psi_{BOW_B+CD_A}\rangle$ ($|\psi_{BOW_A+CD_B}\rangle$ and $|\psi_{BOW_B+CD_B}\rangle$) in the considered region $u \leq 0.01$.

We first consider the u dependence of $|\phi_1(u)\rangle$. We show the u dependence of $n_{2i} - n_{2i-1}$ and $p_{2i} - p_{2i-1}$ for $|\phi_1(u)\rangle$ in Fig. 6(b). The difference in bond order $p_{2i} - p_{2i-1}$ between the even-numbered and odd-numbered bonds increases rapidly with increasing u , but the CD $n_{2i} - n_{2i-1}$ between charge-rich and charge-poor sites is nearly constant with u for $0 < u < 0.001$. These characteristic u dependence of $n_{2i} - n_{2i-1}$ and $p_{2i} - p_{2i-1}$ can be explained by the transfer of weight between $|\psi_{BOW_A+CD_A}\rangle$ and $|\psi_{BOW_B+CD_A}\rangle$ because $p_{2i} - p_{2i-1}$ increases as the weight of $|\psi_{BOW_A+CD_A}\rangle$ increases, but $n_{2i} - n_{2i-1}$ is not altered by the transfer of the weight. Since the magnitude of the transfer integral is larger (smaller) at the even-numbered (odd-numbered) bonds for $u > 0$, $|\psi_{BOW_A+CD_A}\rangle$ ($|\psi_{BOW_B+CD_A}\rangle$) is stabilized (destabilized) by the bond length alternation. The increases (decreases) in the weight of the $|\psi_{BOW_A+CD_A}\rangle$ ($|\psi_{BOW_B+CD_A}\rangle$) with increasing u can be attributed to the stabilization (destabilization). The inversion symmetry is broken in $|\phi_1(u > 0)\rangle$ by the transfer of the weight. It is noted that a change of only 0.1% in the transfer integral ($u = 0.001$) results in a change of several tens of percent in the bond order. This rapid and significant change of the bond orders is the origin of the strong electron-lattice coupling in $|\phi_1(0)\rangle$. The Franck-Condon state $|\phi_1(0)\rangle$ is stabilized by hybridization of $|\psi_{BOW_A+CD_A}\rangle$ and $|\psi_{BOW_B+CD_A}\rangle$. The rapid change results from the fact that the energy gain due

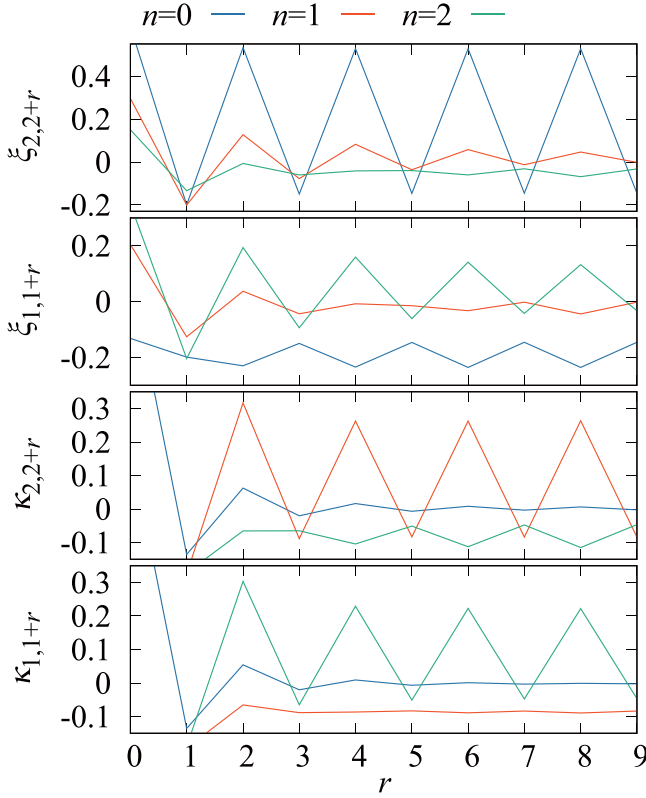


FIG. 8. The charge density correlations $\xi_{2,2+r}$ and $\xi_{1,1+r}$, and the bond order correlations $\kappa_{2,2+r}$ and $\kappa_{1,1+r}$ for $|\phi_n(u)\rangle$ with $n = 0, 1$, and 2 at $u = 0.005$.

to the bond length alternation in $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ is comparable to the energy gain due to the hybridization even in the small magnitude region $0 < u < 0.001$ of bond length alternation.

The CD $n_{2i} - n_{2i-1}$ for $|\phi_1(u)\rangle$ decreases significantly with increasing u for $u > 0.001$. This cannot be attributed to the transfer of the weight. As u increases, p_{2i} for $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ increases to gain the transfer energy at the even-numbered bonds with transfer integrals of larger absolute value. Since the large bond order p_{2i} is incompatible with large CD between the sites $2i$ and $2i + 1$ as mentioned before, $n_{2i} - n_{2i+1}$ for $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ decreases with increasing u . This is the primary cause of the decrease in $n_{2i} - n_{2i+1}$ with increasing u . As u increases, not only the weight but also the BOW state $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ changes significantly in the region. We show $\xi_{2,2+r}$, $\xi_{1,1+r}$, $\kappa_{2,2+r}$, and $\kappa_{1,1+r}$ for $|\phi_1(u)\rangle$ at $u = 0.005$ in Fig. 8. The bond order correlations between the even-numbered bonds are much larger than those between the other bond pairs, and the decay of $\kappa_{2,2+r}$ for even r is much slower than the other correlations. This shows that $|\phi_1(u)\rangle$ is roughly approximated by $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ at $u = 0.005$. This can be confirmed from the numerically calculated overlaps; $|\langle \psi_{\text{BOW}_A+\text{CD}_A} | \phi_1(u) \rangle|^2 = 0.443$ is much larger than $|\langle \psi_{\text{BOW}_B+\text{CD}_A} | \phi_1(u) \rangle|^2 = 0.070$. The relation $|\phi_1(u)\rangle \simeq |\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ holds true for $u > 0.002$. When u is decreased from zero, the weight of $|\psi_{\text{BOW}_B+\text{CD}_A}\rangle$ increases, and the relation $|\phi_1(u)\rangle \simeq |\psi_{\text{BOW}_B+\text{CD}_A}\rangle$ holds true for $u < -0.002$.

We also calculate the electronic polarization $P_n(u)$ per unit cell for $|\phi_n(u)\rangle$. The electronic polarization cannot be

determined from the charge distribution in the unit cell, but it is obtained from the integral of the Berry connection over the Brillouin zone in the noninteracting electron model [54–64]. Several methods to calculate the electronic polarization in the interacting electron models have been proposed [62,65–72]. We here calculate it by integrating numerically obtained current over time when adiabatic parameter u is changed [49,73] because no approximations need to be imposed. We solve the time-dependent Schrödinger equation.

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = H_e(u(t)) |\psi(t)\rangle, \quad (17)$$

when the adiabatic parameter is changed slowly according to the equation $u(t) = 0.1(t/T)$, where T is a constant, and we adopt $T = 400\,000$ for the following calculations, with the initial condition $|\psi(0)\rangle = |\phi_n(0)\rangle$. When T is large enough, $|\psi(t)\rangle = |\phi_n(u(t))\rangle$ holds. We numerically confirmed this by comparing the energy eigenstates obtained by the singular value decomposition of the coefficient matrix [47] and those obtained by solving Eq. (17). By integrating $i_i(t) = \langle \psi(t) | \hat{i}_i(t) | \psi(t) \rangle$ over time, where $\hat{i}_i(t) = ie a(1 + (-1)^i u(t))(c_i^\dagger c_{i+1} - c_{i+1}^\dagger c_i)$ is the current operator for the bond i , a is the average lattice spacing along the 1D direction, and e is the elementary charge, we obtain $P_n(u)$ as

$$P_n(u(t)) = \int_0^t i_1(s) ds + \int_0^t i_2(s) ds, \quad (18)$$

where we used the fact that $P_n(0) = 0$ because $|\phi_n(0)\rangle$ is either symmetric or antisymmetric under inversion.

We show the u dependence of $P_1(u)$ in Fig. 6(c). The magnitude of electronic polarization $|P_1(u)|$ for $|\phi_1(u)\rangle$ increases significantly with increasing u , and the lattice-relaxed state $|\phi_1(u_{\min})\rangle$ is an electronic ferroelectric state. This is in contrast to electronic polarization for the CO ground state $|\phi_0(u)\rangle$; $|P_0(u)|$ is effectively zero and much smaller than $|P_1(u)|$. Furthermore, the relation $P_1(-u) = -P_1(u)$ holds, and both the two degenerate lattice-relaxed states $|\phi_1(u_{\min})\rangle$ and $|\phi_1(-u_{\min})\rangle$ are electronic ferroelectric states with opposite directions of polarization. It is noted that the current generating polarization is spin-polarized.

The present adiabatic Hamiltonian is an extension of the Rice-Mele Hamiltonian [43], which describes electronic ferroelectricity arising from topological properties. The primary difference between these models is that the Rice-Mele model incorporates both up-spin and down-spin electrons, whereas the present model includes the Coulomb interaction. In the noninteracting Rice-Mele model, it has been shown that the ground state has electronic polarization or boundary charge of topological origin when $\Delta \neq 0$ and $u \neq 0$ hold [67,68]. In this case, both the bond order and charge density alternate every two bonds and sites, respectively, in the ground state. Inversion symmetry breaking due to the charge and bond structure results in electronic ferroelectricity. It has been further shown that this property remains unchanged even when Coulomb interactions are introduced [67–70]. Therefore, the origin of electronic polarization of the lattice-relaxed photoexcited state in the present Hamiltonian is the same as that of the ground state in the Rice-Mele model. The polarization generation due to CD and bond length alternation has been demonstrated in related models [62,65,71,72], and electronic

ferroelectricity in the I phase of TTF-CA [74] can also be considered an example of this phenomenon.

In previous investigations, the crossover from the symmetric CO state to the symmetry-broken state, characterized by both CD and bond order alternation, has been discussed. The symmetric state is different in the crossover of $|\phi_1(u)\rangle$ investigated in this paper; the symmetric state $|\phi_1(0)\rangle$ is the BOW state with CD, where the inversion symmetry is restored by making the linear combination of two BOW states $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ and $|\psi_{\text{BOW}_B+\text{CD}_A}\rangle$ with opposite phases of bond order alternation. The states $|\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ and $|\psi_{\text{BOW}_B+\text{CD}_A}\rangle$ have electronic polarizations with opposite directions. Since they have equal weight in $|\phi_1(0)\rangle$, the electronic polarization of the symmetric state is zero. The increase in $|P_1(u)|$ with increasing u is mainly due to the transfer of the weights of these two symmetry-broken BOW states.

The ground state phase diagram has been investigated in the spinless fermion model with $\tilde{\Delta} = 0$, and it is shown that the BOW state becomes the ground state in a very small parameter region [46]. However, charge density is uniform in the BOW states, and they have inversion symmetry in this case. Electronic ferroelectricity cannot be described by the model.

We next consider the u dependence of $|\phi_2(u)\rangle$. Since $|\phi_2(u)\rangle$, which is given by the linear combination of $|\psi_{\text{BOW}_A+\text{CD}_B}\rangle$ and $|\psi_{\text{BOW}_B+\text{CD}_B}\rangle$, is orthogonal to $|\phi_1(u)\rangle$, the weight of $|\psi_{\text{BOW}_B+\text{CD}_B}\rangle$ increases in $|\phi_2(u)\rangle$ as u increases. As a result, $p_{2i} - p_{2i-1}$ is negative and $|p_{2i} - p_{2i-1}|$ increases rapidly with increasing u as seen in Fig. 6(b). Since the BOW_B state is destabilized by bond length alternation for $u > 0$, $E_2(u)$ increases rapidly with increasing u . The state $|\phi_2(u)\rangle$ is also strongly coupled to the lattice deformation of bond length alternation. We show $\xi_{2,2+r}$, $\xi_{1,1+r}$, $\kappa_{2,2+r}$, and $\kappa_{1,1+r}$ for $|\phi_2(u)\rangle$ at $u = 0.005$ in Fig. 8. The bond order correlations between the odd-numbered bonds are much larger than those between the other bond pairs, and the decay of $\kappa_{1,1+r}$ for even r is much slower than the other correlations. This shows that $|\phi_2(u)\rangle$ is roughly approximated by $|\psi_{\text{BOW}_B+\text{CD}_B}\rangle$ at $u = 0.005$. This can be confirmed from the numerically calculated overlaps; $|\langle\psi_{\text{BOW}_B+\text{CD}_B}|\phi_2(u)\rangle|^2 = 0.422$ is much larger than $|\langle\psi_{\text{BOW}_A+\text{CD}_B}|\phi_2(u)\rangle|^2 = 0.037$. The relation $|\phi_2(u)\rangle \simeq |\psi_{\text{BOW}_B+\text{CD}_B}\rangle$ holds true for $u > 0.002$. The electronic polarization $P_2(u)$ for $|\phi_2(0)\rangle$ increases significantly with increasing u as seen from Fig. 6(c), and $|\phi_2(u)\rangle$ with $u \neq 0$ is also an electronic ferroelectric state. The electric polarizations of $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$ have opposite signs, while the absolute values are nearly identical but not exactly the same. A noticeable difference is observed in the absolute values for $\tilde{V} \leq 6$.

We show the induced light absorption spectrum $\alpha_1(\omega)$ from $|\phi_1(u)\rangle$ when the bond length is uniform ($u = 0$) and when bond length alternation occurs ($u = 0.005$) in Fig. 9. As mentioned before, $|\phi_2(u)\rangle$ cannot be excited by a one-photon from the ground state $|\phi_0(u)\rangle$. However, the largest peak near $\omega = 0$ in $\alpha_1(\omega)$ is due to the excitation from $|\phi_1(u)\rangle$ to $|\phi_2(u)\rangle$. The pump-probe reflectivity spectrum $\Delta R(\omega)$ was measured across the energy range $\omega > 100$ meV [26,41]; therefore, this characteristic low-energy peak around a few meV in $\alpha_1(\omega)$ has not been observed experimentally. In pump-probe spectroscopy experiments, a peak that increases over time after

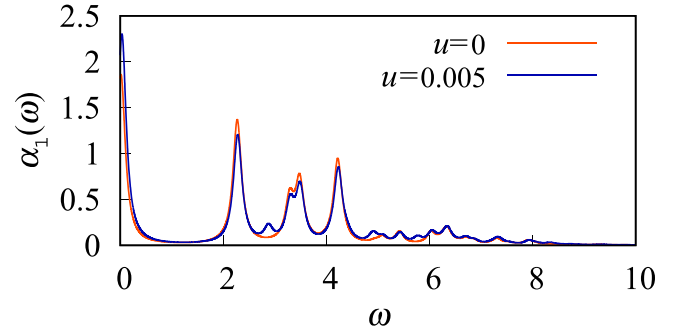


FIG. 9. Induced light absorption spectrum $\alpha_1(\omega)$ from $|\phi_1(u)\rangle$ for $u = 0$ and $u = 0.005$. The broadening of 0.1 is used.

pump excitation has been reported near $\omega = 1$ eV [41]. The peak at $\omega = 2.878$ in $\alpha_1(\omega)$ for $u = 0.005$ does not appear at $u = 0$ and grows larger as u increases. Moreover, the peak energy corresponds to 0.973 eV with the parameter $t_0 = 0.338$ eV used in this study, which closely matches the energy of the peak that increases over time observed in pump-probe spectroscopy experiments. Considering that lattice relaxation involving bond length alternation occurs after photoexcitation, these results provide a consistent explanation for the time-dependent changes in $\Delta R(\omega)$ observed experimentally, thereby confirming the findings of this paper.

In the lattice relaxation process of $|\phi_1(u)\rangle$, $|\phi_2(u)\rangle$ can be resonantly excited, and the polarization is reversed instantaneously by the light with photon energy of $\omega = E_2(u) - E_1(u)$. The instantaneous reversal is due to the shift current [70,75–84]. For $u > 0.002$, $|\phi_1(u)\rangle \simeq |\psi_{\text{BOW}_A+\text{CD}_A}\rangle$ and $|\phi_2(u)\rangle \simeq |\psi_{\text{BOW}_B+\text{CD}_B}\rangle$ hold. By photoexcitation, the BOW_A state, where spinless fermions are located mainly at the even-numbered bond, is excited to the BOW_B state, where spinless fermions are located mainly at the odd-numbered bond. A large number of spinless fermions are transferred to neighboring bonds collectively in the photoexcitation process. This collective nature of photoexcited states is the origin of the large shift current.

Since $E_2(u)$ is a monotonically increasing function of u for $u > 0$, u decreases over time after excitation from $|\phi_1(u)\rangle$ to $|\phi_2(u)\rangle$, causing the polarization to disappear. The lifetime of the reverse polarization state is roughly equal to the time it takes for the lattice to relax and form the bond-length-alternating state, estimated at about 30 fs [41].

As mentioned earlier, the solution to the time-dependent Schrödinger equation when the ground state is excited by light is nearly exactly represented by a linear combination of nine key photoexcited energy eigenstates and the ground state. The excited states associated with all peaks in $\alpha(\omega)$ shown in Fig. 5 are included in these nine photoexcited energy eigenstates. We also examine the physical properties of these important photoexcited energy eigenstates beyond $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$. In these seven photoexcited energy eigenstates, neither bond order nor charge density correlations that exhibit extremely slow spatial decay are observed. These features indicate that these states are neither BOW nor CO states. Furthermore, the electronic polarizations of these states are effectively zero, indicating they are not electronic ferroelectric states. Only the electronic ferroelectric states $|\phi_1(u)\rangle$

and $|\phi_2(u)\rangle$ are exceptional among these photoexcited energy eigenstates. This also agrees with the finding that these important photoexcited states other than $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$ are not BOW states.

As seen from Eqs. (14) to (16), the four BOW states $|\Psi_{\text{BOW}_A+\text{CD}_A}\rangle$, $|\Psi_{\text{BOW}_A+\text{CD}_B}\rangle$, $|\Psi_{\text{BOW}_B+\text{CD}_A}\rangle$, and $|\Psi_{\text{BOW}_B+\text{CD}_B}\rangle$ are not mutually orthogonal. We used these nonorthogonal states to represent $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$ for clarity of physical properties. Among these important photoexcited energy eigenstates other than $|\phi_1(u)\rangle$ and $|\phi_2(u)\rangle$, neither $|\psi_{\text{AS-BOW}+\text{CD}_B}\rangle$ nor $|\psi_{\text{S-BOW}+\text{CD}_A}\rangle$ are found, which can be attributed to the nonorthogonality.

So far, we have shown the results for the specific set of parameters: $\tilde{\Delta} = 0.4$, $\tilde{V} = 7.6$, and $\kappa = 0.1$. We examine how the results mentioned above depend on the parameters within the ranges where the light absorption spectrum is reasonably reproduced: $0.06 \leq \tilde{\Delta} \leq 2$ at $\tilde{V} = 7.6$ and $\kappa = 0.1$, $3 \leq \tilde{V} \leq 10$ at $\tilde{\Delta} = 0.4$ and $\kappa = 0.1$, and $0.1 \leq \kappa \leq 0.5$ at $\tilde{\Delta} = 0.4$ and $\tilde{V} = 7.6$. In these parameter regions, the following conclusions hold. For $u = 0$, the lowest energy peak in $\alpha(\omega)$ is the largest, and this peak is due to the excitation to the optically allowed antisymmetric BOW state with CD from the CO ground state. Furthermore, there is an optically forbidden symmetric BOW energy eigenstate with CD for $u = 0$, and these two BOW energy eigenstates are electronic ferroelectric states when bond length alternation occurs. However, there are two distinct parameter regions, I and II, in which lattice relaxation behaves very differently. In the region I, qualitatively the same results as those for $\tilde{\Delta} = 0.4$, $\tilde{V} = 7.6$, and $\kappa = 0.1$ are obtained. In the region II, the energy eigenvalue of the optically forbidden BOW state is slightly smaller than that of the optically allowed BOW state, and the lower-energy (higher-energy) BOW energy eigenstate $|\phi_1(0)\rangle$ ($|\phi_2(0)\rangle$) has the CD_B (CD_A). That is, $|\phi_1(0)\rangle = |\psi_{\text{S-BOW}+\text{CD}_B}\rangle$ and $|\phi_2(0)\rangle = |\psi_{\text{AS-BOW}+\text{CD}_A}\rangle$ hold. Furthermore, $E_1(u)$ significantly decreases and $E_2(u)$ significantly increases with increasing u . Since the one-photon active state $|\phi_2(0)\rangle$ blue shifts as u increases from 0, the lattice relaxation of one-photon excited states does not occur, and the lattice relaxation to the electronic ferroelectric state can be induced by two-photon excitation to $|\phi_1(0)\rangle$. The following regions belong to the region II: $\tilde{V} \geq 7.74$ when $\tilde{\Delta}$ and κ are fixed at 0.4 and 0.1, respectively, $\tilde{\Delta} \leq 0.36$ when $\tilde{V}$ and κ are fixed at 7.6 and 0.1, respectively, and $\kappa \geq 0.2$ when $\tilde{\Delta}$ and $\tilde{V}$ are fixed at 0.4 and 7.6, respectively. All through the region, the second-order differential coefficients $|E_1^{(2)}(0)|$ and $|E_2^{(2)}(0)|$ are much larger than those of the ground state, and electron-lattice coupling with the bond length alternation is very large in the BOW states. The second-order differential coefficient $E_1^{(2)}(0)$ generally becomes large near the boundary between regions I and II. For example, $E_1^{(2)}(0)$ decreases as $\tilde{V}$ is lowered from 7.6, and $E_1^{(2)}(0)$ at $\tilde{V} = 7$ is 22% of that at $\tilde{V} = 7.6$.

IV. SUMMARY AND DISCUSSIONS

We construct the spinless fermion model for charge-transfer-type MOF $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$, and investigate the physical properties and lattice relaxation of important

photoexcited states. The dominant peak in the light absorption spectrum is due to the excitation to an optically allowed BOW state $|\phi_1(0)\rangle$ with CD. The Franck-Condon BOW state is given by the linear combination of the inversion-symmetry broken BOW_A and BOW_B states with CD_A with equal weights and opposite phases, and the inversion-symmetry is restored in $|\phi_1(0)\rangle$. The state $|\phi_1(0)\rangle$ is strongly coupled to the lattice deformation of bond length alternation, and the lattice relaxation can occur even in this rigid material. As the lattice relaxation proceeds and the magnitude $|u|$ of bond length alternation increases, the weight shifts from one inversion-symmetry broken BOW state to the other one with opposite phase of bond order alternation. As a result, the inversion symmetry is broken in the lattice-relaxed state $|\phi_1(u)\rangle$ from $|\phi_1(0)\rangle$, and the state becomes an electronic ferroelectric state. Furthermore, another energy eigenstate $|\phi_2(u)\rangle$ is also a BOW state with CD, which is also an electronic ferroelectric state with the opposite sign of polarization to that of $|\phi_1(u)\rangle$. The largest peak in the induced light absorption spectrum $\alpha_1(\omega)$ from $|\phi_1(u)\rangle$ is due to the excitation to $|\phi_2(u)\rangle$, and polarization can be reversed instantaneously by resonant photoexcitation from $|\phi_1(u)\rangle$. This finding is significant because it suggests the potential for rapid, reversible polarization control in MOFs, opening new possibilities for picosecond polarization control in rigid materials. This could lead to innovative advancements in electronic and photonic devices.

The BOW state has the largest transition dipole moment from the CO ground state in the present finite-cluster calculation. However, since they are asymptotically orthogonal, a domain of BOW will be generated by photoexcitation in the real infinite system. As mentioned in the previous section, the bond-order correlation $\kappa_{2,2+r}$ for $|\phi_1(0)\rangle$ is almost constant for even r as r increases to the maximum $N/2$, which shows that uniform BOW order is generated in $|\phi_1(0)\rangle$. We have also considered lattice relaxation, in which bond length alternation occurs within a domain. However, the energy of the relaxed state with uniform bond length alternation is always lower. These results show that the size of the photogenerated BOW domain exceeds the present system size, $N = 18$.

In the excitation from the CO ground state to the BOW or BOW domain state, a large number of electrons move collectively. This collective nature of the photoexcited state is unique even in the correlated electron systems. For example, in the Mott insulators, photoexcitation can be described by the generation of a holon-doublon pair, and in charge-transfer solids, the dominant photoexcitation can be described by local electron transfer from one D-site to one A-site, which can be regarded as an exciton. The bound states of more than two excitons (exciton strings) have been found in some quasi-1D organic charge-transfer solids [85–91], and the extended Hubbard model for the Mott insulators [92–94]. However, the domain sizes photogenerated in these cases are much smaller than those of the present system. The difference can be attributed to large quantum fluctuations in the present spinless fermion model.

We have shown that a ferroelectric phase is photogenerated in the 1D chain. The adiabatic potential $U_1(u)$ of $|\phi_1(u)\rangle$ has a local maximum at $u = 0$ and two local minima at $u = u_{\min}$ and $u = -u_{\min}$, meaning the polarization direction of the relaxed

state, influenced by the relaxation direction of u , is determined by small disorder or fluctuation in the ground state lattice. However, bulk polarization is generated when polarization directions of 1D chains are aligned in $(\text{NPr}_4)_2[\text{Fe}_2(\text{Cl}_2\text{An})_3]$. By simultaneously exciting the ground state with a light pulse and irradiating it with a THz pulse, it may be possible to control the relaxation direction and the polarization directions in all chains. Since polarization direction and the phase of bond length alternation are strongly correlated, the lattice structure can be controlled by the THz pulse. Furthermore, polarization is instantaneously reversed by excitation from $|\phi_1(u)\rangle$ to $|\phi_2(u)\rangle$ in the relaxation process or in the relaxed state. To verify these findings, experimental tests could focus on observing light and THz double-pump and second harmonic generation-probe experiments. Clear identification

of these signatures would strongly support the theoretical framework presented and possibly inspire collaborative efforts. These dynamics-related problems will be investigated elsewhere.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [95].

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