

Time resolution of chirped lattice vibrations in a mixed-valence metal-halogen complex system

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A quasi-one-dimensional metal-halogen complex, $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2](\text{ClO}_4)_4$, has been investigated by a pump-probe measurement using sub-5-fs ultrashort white light pulses. The signal as a difference absorption was highly resolved both in time and frequency domains. By means of linear prediction-singular value decomposition calculation, four vibration modes, pairs of well-known and unknown modes, were retrieved, while almost no overtone was retrieved. Our analysis based on the dynamical matrix well explained the origin of one of the unknown modes. In addition, we found one more chirped low-frequency modulation in the slow-varying component of the signal, which is the first observation of a cluster motion of many lattice points and energy dissipation along the one-dimensional chain in this system.

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I. INTRODUCTION

During the last decade, investigations of ultrafast processes on the femtosecond time scale have significantly advanced, owing to the development of coherent light sources with ultrashort pulse durations. Such investigations involve nonlinear spectroscopy for bond-breaking¹ or electron-transferring reactions,² phase relaxation processes,^{3,4} inter- and intramolecular dynamic motions,⁵⁻⁷ dynamic mode coupling,⁸⁻¹⁰ dynamic intensity borrowing,¹¹⁻¹³ and photoisomerization processes.^{14,15} Especially, molecular vibration is time resolvable only by light pulses with substantially shorter durations than the vibrational period. Such short pulses can impulsively create coherent oscillations of wave packets (WPs) on potential energy surfaces (PESs) of electronic states. This WP motion modulates optical responses, such as ground-state absorption and induced emission and absorption in electronic transition processes.

Halogen-bridged mixed-valence metal complexes (MXs) are the simplest prototypes of the quasi-one-dimensional system, in which one-dimensional (1D) chains consist of alternating metal and halogen ions.¹⁶ Figure 1(a) depicts the ground state of one of the typical MXs, $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2](\text{ClO}_4)_4$ (so-called PtBr, where en = ethylenediamine), which has a charge-density wave (CDW) along the 1D chain as a consequence of Peierls' instability. This state is quite interesting and important to know the behavior of WPs due to the possibility of the coupling between CDW and a lattice distortion such as polarons, charged solitons, and self-trapped excitons (STEs) [see Fig. 1(b)]. The photoexcitation-relaxation process commonly considered for PtBr is illustrated in Fig. 1(c). When PtBr in the ground state is excited by a light with a proper photon energy, the charge transfer (CT) takes place along the 1D chain,¹⁶⁻¹⁸ and a strong charge-lattice coupling distorting the lattice induces a

free-exciton (FE) state. Afterward, a rapid relaxation to the STE occurs because no potential barrier exists between the FE and STE states as generally known in 1D systems. To date, there have been several investigations on transient processes of MX systems through the photoexcitation phenomena such as induced luminescence,¹⁹⁻²⁴ absorption change,²⁵⁻²⁹ and reflection change.³⁰ However, these reports merely show measurements only for a few probe conditions, which are insufficient to study spectroscopic features. In this paper, we will demonstrate a sub-5-fs time-resolved spectroscopic study on a PtBr thin film for the visible region.

II. EXPERIMENT

A sub-5-fs ultrashort pulse train at a repetition rate of 5 kHz from a noncollinear optical parametric amplifier (NOPA) system pumped up by a regenerative amplifier (Spitfire, Spectra Physics) was used for the pump-probe measurement to probe the ultrafast dynamics. Details of the NOPA system can be found elsewhere.^{31,32} As shown in Fig. 1(d), the generated photon energy range of 1.65–2.3 eV from the NOPA covers the broad stationary absorption band of PtBr extending broad around 2 eV, originating from the CT transition along the 1D-chain axis. The output beam from the NOPA was split into two: one was a pump beam optically exciting the sample and the other a probe beam probing the optical response induced by the pump one. The probe beam with a certain delay from the pump was focused onto the sample and collected by an optical fiber in the transmitting direction to be lead into a monochromator with a multichannel detector of an avalanche photodiode array. The converted electric signal was analyzed by a 128-channel dual phase lock-in amplifier system and recorded as a spectrum of difference absorption ΔA . A measured sample was a thin film of the crystalline PtBr fabricated by casting a solution of PtBr

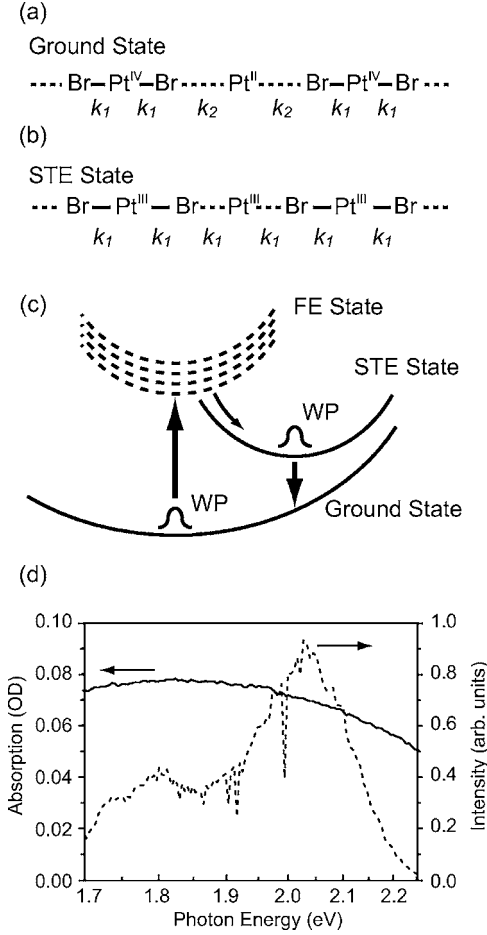


FIG. 1. 1D structures of PtBr (a) in the ground state and (b) in the STE state, (c) the excitation-relaxation scheme of its photoexcitation, and (d) spectra of the sample absorption (solid line) and the pump-probe light source (dashed line).

dissolved in water on an optical grade glass plate, having enough good quality as far as confirmed by a texture observation of the sample sandwiched with two crossed polarizers.

III. RESULT AND DISCUSSION

Figure 2 shows a result of the pump-probe measurement obtained as delay-time variation traces of ΔA . Here, “delay time” is defined as that of the probe pulse to the pump pulse at the sample position. Each ΔA trace shows an obvious modulation created by the coherent WPs relating to the structural vibrations in the PtBr lattice. The fast Fourier transform (FFT) spectrum of delay-time traces (between 100 and 5000 fs) against probe photon energy is two-dimensionally plotted in Fig. 3(a), which shows a strong modulation mode at about 170–180 cm^{-1} in wave number as well as several weak modulation modes. To determine exact modulation frequencies, a linear prediction-singular value decomposition (LPSVD) calculation after applying a high-pass filter were performed for the data points from 100 to 5000 fs. The retrieved frequencies by LPSVD are plotted in Fig. 3(b). The dominant mode in this system is a well-known symmetric vibration mode of Br-Pt^{IV}-Br at 170–180 cm^{-1} (denoted as

ν_1), which was observed also by a resonant Raman scattering (r-RS) measurement for the sample used in the present study. Another mode at 91–107 cm^{-1} (ν_2), undetectable in the r-RS measurement, has been controversially argued in the previous papers; Suemoto and co-workers considered the mode as a main vibration mode of Br-Pt^{III}-Br in the STE state,^{23,24} while Dexheimer *et al.* had suggested a lattice vibration preceding the formation of STE.^{26,27} In our experimental result, the decay time of ν_2 mode is almost on the same order as the one by Suemoto and co-workers but ~ 20 times longer than the one reported by Dexheimer *et al.*, so that our result supports the former. In addition to them, unknown Raman-inactive modes at 60–70 cm^{-1} (ν_3) and $\sim 250 \text{ cm}^{-1}$ (ν_4) were retrieved. They have not either been mentioned in the previous literature or could not be identified in the figures shown in them. Furthermore, there is another outstanding feature that overtones expected from the r-RS almost vanished in the real-time vibrational FFT spectrum.

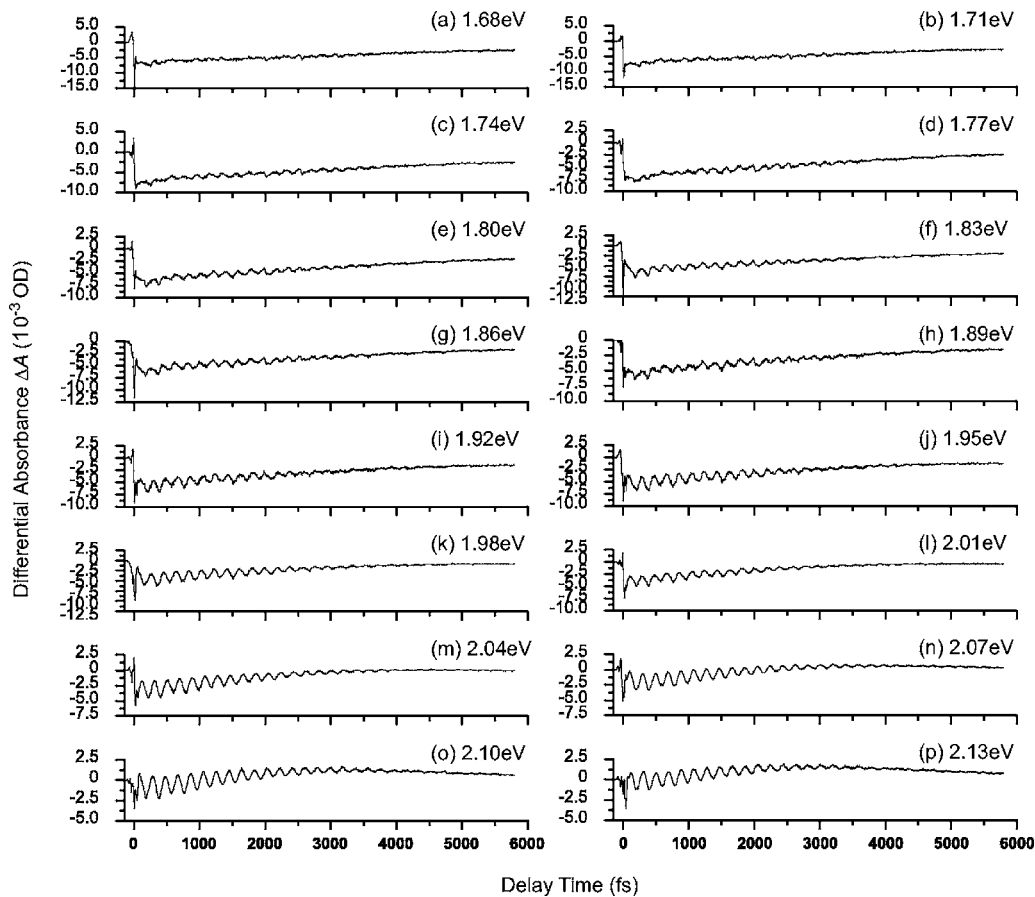
To discuss these unknown modes, a simple classical vibration model based on the dynamical matrix³³ was carried out. Assuming two force constants, k_1 and k_2 [see Figs. 1(a) and 1(b), where $k_1 \geq k_2$] for two bonds, Pt^{II}-Br and Pt^{IV}-Br in the main chain, and the first-nearest-neighbor approximation for the dynamical matrix, we can describe one Raman-active symmetric (ν_s) and two Raman-inactive asymmetric ($\nu_{a,low}$ and $\nu_{a,high}$) vibration modes as

$$\nu_s^2 = \left(\frac{\omega_s}{2\pi c} \right)^2 = \frac{k_1 + k_2}{m}, \quad (1)$$

$$\nu_{a,low}^2 = \left(\frac{\omega_{a,low}}{2\pi c} \right)^2 = (k_1 + k_2) \left(\frac{1}{M} + \frac{1}{2m} \right) (1 + \sqrt{1 - \alpha}), \quad (2)$$

$$\nu_{a,high}^2 = \left(\frac{\omega_{a,high}}{2\pi c} \right)^2 = (k_1 + k_2) \left(\frac{1}{M} + \frac{1}{2m} \right) (1 - \sqrt{1 - \alpha}), \quad (3)$$

where M and m are the masses of Pt and Br atoms, respectively, and $\alpha = 16[k_1 k_2 / (k_1 + k_2)^2][m(M + m) / (M + 2m)^2]$. Using these equations, we can estimate Raman-inactive mode frequencies, $\nu_{a,low}$ and $\nu_{a,high}$, as functions of k_2/k_1 by inputting the experimentally obtained frequency of the symmetric vibration mode into ν_s . In the present case, ν_2 mode is considered as the main vibration mode of the STE state, i.e., the symmetric stretching mode of Br-Pt^{III}-Br. Therefore, here we adopted $\nu_s = 99 \text{ cm}^{-1}$ which is an average frequency obtained by LPSVD. The frequencies, $\nu_{a,low}$ and $\nu_{a,high}$, calculated in this way are plotted as functions of k_2/k_1 in Fig. 4. In the STE state, each pair of adjacent Pt^{III} ions are connected with a Br ion, so that two force constants, k_1 and k_2 , are degenerate, and hence k_2/k_1 are expected to be very close to 1. As seen from the plot in the region of $k_2/k_1 \sim 1$ in Fig. 4, the calculated value of $\nu_{a,low}$ is in a range of 60–70 cm^{-1} , which agrees well with ν_3 in Fig. 3(b). Therefore, it is quite natural to consider that ν_3 is attributed to one of the Raman-inactive asymmetric vibration modes of the STE state. The reason why we observe the Raman-inactive mode can be explained


 FIG. 2. Probe delay-time traces of ΔA for several photon energies.

by peculiarities in excitation mechanism and/or degree of symmetry breaking in case of impulsive excitation by ultrashort pulses. On the other hand, ν_4 mode could not be identified even by this calculation. This mode may be corresponding to the ligand motions, since the mass of a ligand is on the same order as that of the Br ion. Another possibility is some kind of peculiarity in the impulsive excitation by ultrashort pulses. This peculiarity is not physically clarified but may also be one of the reasons why the modulation corresponding to $\nu_{a,high}$ is not observed in our experimental result.

Since the relaxation from the FE state to the STE state is generally expected to proceed very rapidly (within several tens of femtoseconds³⁴) because of no potential barrier,³⁵ it would be unresolvable in such a pump-probe experiment. Therefore, the three-level model depicted in Fig. 1(c) can be regarded equivalent to the two-level model to simplify the analysis. In this case, the observed temporal change of ΔA can be described in the general form including modulations discussed above,

$$\Delta A(E_p, t) = a_e(E_p) \exp(-t/\tau_e) + \sum_{i=1}^4 a_{\nu_i}(E_p) \exp(-t/\tau_{\nu_i}) \cos(\omega_{\nu_i} t + \phi_{\nu_i}), \quad (4)$$

where E_p and τ_e are the probe photon energy and the decay time of the STE state. The second term in the right side of Eq. (4) represents the sum of the sinusoidal modulations over

the four modes, $\nu_1 - \nu_4$. In fact, however, Eq. (4) does not fit the experimental result. For example, in both Figs. 2(o) and 2(p), the slowly varying component of ΔA increases between 0 and 3000 fs but obviously decreases after 3500 fs, which implies the existence of a component with a slower modulation frequency than 10 cm^{-1} . To explain this feature, we introduced one more vibration mode ν_5 which has a much longer decay time than the probing time range, $\sim 2 \text{ ps}$, and a very long period on the order of several picoseconds. Here, we also introduced a linear chirp as a manifestation of temporal change of PES because there seems to exist some kind of frequency change which makes it impossible to retrieve this mode by the LPSVD method. Now, the function of ΔA for the slowly varying component is^{14,36-39}

$$[\Delta A(E_p)]_{slow} = \exp\left(-\frac{t}{\tau_e}\right) \left[a_1(E_p) + a_2(E_p) \cos\left(\frac{2\pi t}{T_{\nu_5} + kt} + \phi_{\nu_5}\right) \right], \quad (5)$$

where T_{ν_5} and k , respectively, represent an initial modulation period and a chirp rate defined as an increase of the modulation period per unit time. The quasilinear chirp is expected when the low-frequency mode energy dissipates into even lower-frequency modes with time-independent mode coupling constants between the former and the latter. These are

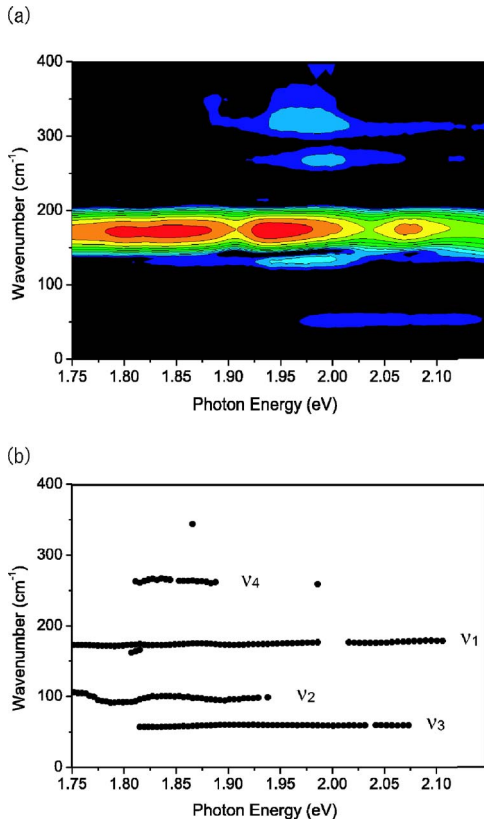


FIG. 3. (Color online) (a) 2D map of the FFT spectrum and (b) retrieved modulation frequencies by the LPSVD method applied for the experimental result.

global parameters common through the measured photon energy range, while a_1 and a_2 are local parameters depending on the probe photon energy. A comparison of the fitting using only Eq. (5) with the experimental result is presented in Fig. 5. A map of ΔA after removing the fast-varying components using a low-pass filter [Fig. 5(a)] is excellently reproduced in Fig. 5(b). The best-fit global parameters were $\tau_e = 4600.2$ fs, $T_{\nu_5} = 5969.4$ fs, and $k = 0.6235$. τ_e is on the same order but shorter than that of 5500 fs reported in the previous paper.²² This is probably because the slowly varying component was not taken into account in the latter. Obtained spectra of a_1 and a_2 by this fitting are shown together in Fig. 5(c). The

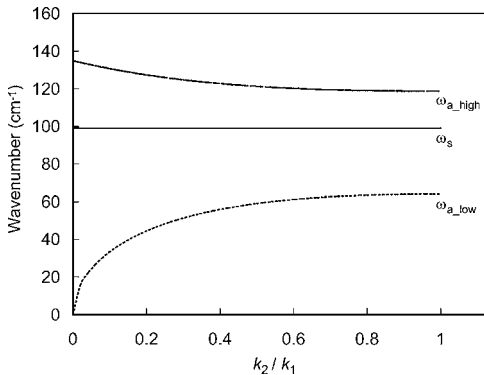


FIG. 4. Mode frequencies estimated by substituting 99 cm^{-1} for ν_5 in Eq. (3) based on the classical dynamical matrix.

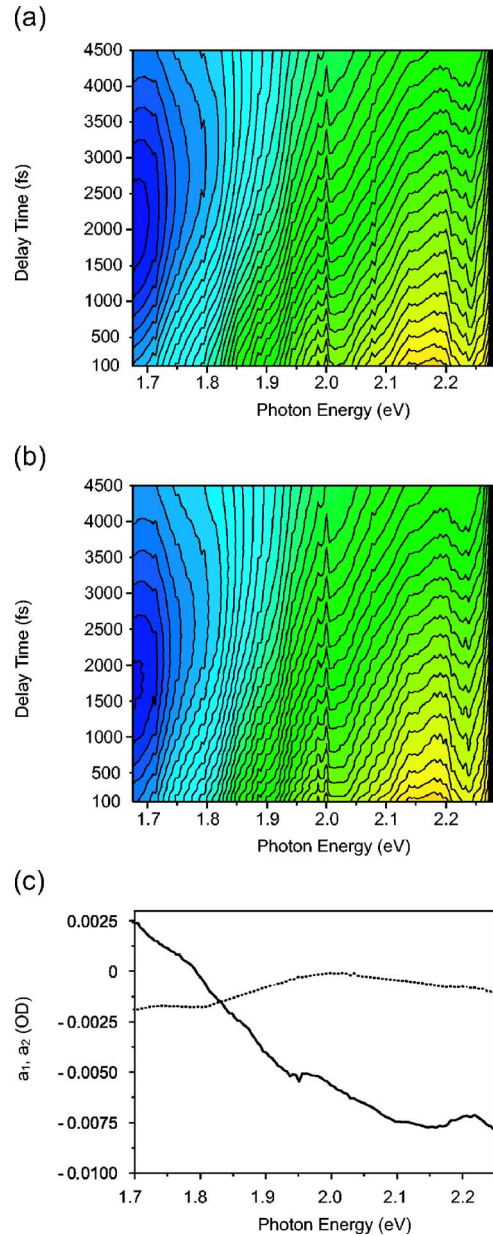


FIG. 5. (Color online) Fitting result of a spectrum of the slowly decaying component in the ΔA traces using Eq. (5). (a) Experimental data after removing fast-varying components using a low-pass filter, (b) fit to the above data using Eq. (5), and (c) obtained spectra of a_1 (solid line) and a_2 (dashed line) given by the fit.

negative a_1 around the photon energy near the peak of the stationary absorption can reasonably be attributed to the bleaching due to the ground-state depletion and some contribution of the stimulated emission. In addition, the positive value of a_1 in the lower photon energy region is also reasonable, since the induced absorption of PtBr by a polaron band has been reported previously in this region.^{25,26} These facts support the validity of our model and fitting.

Before discussing the origin of this chirped modulation expressed by the second term in the parentheses of Eq. (5), ν_5 mode, initial phases of the modulation components, ϕ_{ν_i} 's given in the above discussions, should be mentioned. A gen-

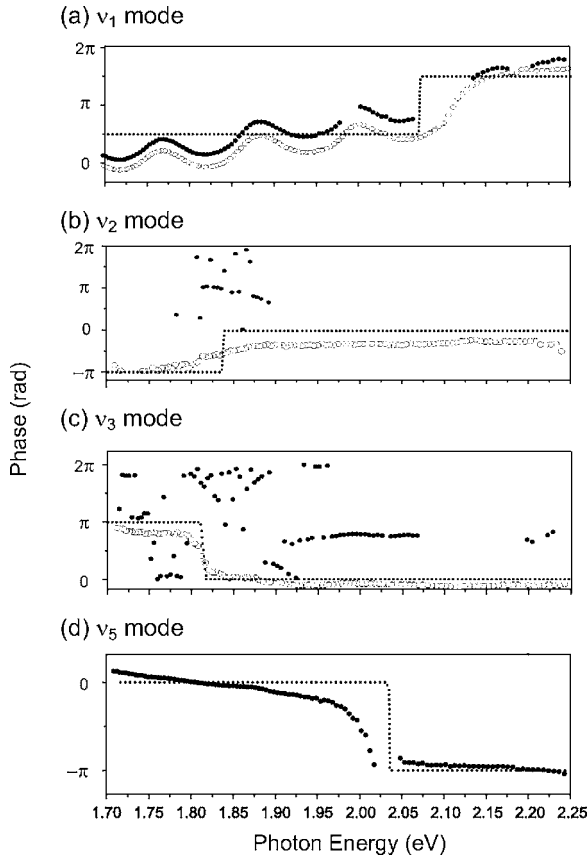


FIG. 6. Initial cosine phases of the modulation modes: (a) ν_1 , (b) ν_2 , (c) ν_3 , and (d) ν_5 . For (a), (b), and (c), open and closed circles represent the initial phases obtained by FFT and LPSVD, respectively. For (d), the initial phase was obtained from the fitting result shown in Fig. 5. Dotted lines are eye guides indicating ideal π jumps.

eral behavior of initial phases of such modulation components has been studied in terms of WP motion on PES in the previous literature.^{40,41} Generally, an induced WP on the ground-state PES creates a sinusoidal modulation on the ΔA and hence its initial phase with respect to the cosine function is expected to be $\pm\frac{\pi}{2}$ rad. On the other hand, a WP on the excited-state PES creates a cosinusoidal modulation on the ΔA , and its initial cosine phase will be 0 or $\pm\pi$ rad. It can be expected in both cases to exhibit a π jump around the peak of the stationary absorption. Note that the case of the excited state is limited only for the condition that the ΔA signal is contributed from the stimulated emission.

Figure 6 shows the photon energy dependence of the initial cosine phase of each modulation component. First, for ν_1 mode, both of the initial cosine phases given by FFT and LPSVD provide about $\frac{\pi}{2}$ rad or equivalently disregarding the sign of the amplitude $\frac{3\pi}{2}$ rad, which show π jumps around 2 eV near the CT transition band of PtBr. Therefore, it is reasonably concluded that ν_1 mode is mainly attributed to the WP motion on the ground state, same as mentioned in the previous reports.^{26,27} The initial phases of ν_2 and ν_3 modes obtained by FFT also show clear π jumps with the phase of about 0 or $\pm\pi$ rad which means a cosinusoidal modulation. This fact suggests that ν_2 and ν_3 modes are dominated by the

stimulated emission modulated by the WP motion on the excited state, that is, the STE state. For these modes, LPSVD was not available to obtain the phase behavior as shown in the plots, since the modulation amplitudes are too small to be detected with enough high signal-to-noise ratio. The initial cosine phase of ν_5 mode was obtained from the above fitting to Eq. (5) because neither FFT nor LPSVD could be used for such a chirped modulation. However, even in this case, we could obtain a clear π jump and cosinusoidal phase values. Therefore, similarly to ν_2 and ν_3 modes, ν_5 mode is reasonably identified as the WP motion on the STE state PES. This is consistent with that seen in the spectrum of a_2 , where ν_5 mode appears mainly in the induced absorption region of a_1 .

One of the explanations about the most likely origin of ν_5 mode is a cluster motion of many lattice points on the 1D chain. Assuming that (1) this cluster is considered to vibrate symmetrically in such a way that a single ion connected with a force constant of the STE state, $K=k_1+k_2$, to the 1D chain, and that (2) potential energy is negative constant inside the cluster but is 0 outside it, we can estimate how many ions are involved in this cluster motion at the initial time ($t=0$) by using Eq. (1) again. Since ν_5 mode is due to the WP motion on the STE state PES, $K=47.2$ N/m is obtained as a force constant of the STE state by introducing the frequency of ν_2 mode into Eq. (1). By substituting this value of K and introducing the initial frequency of ν_5 again into Eq. (1), the initial number of repeating units is estimated to be about 50. This size of the cluster may be corresponding to the extension of a single exciton on the 1D chain. Some of the previous theoretical works have already predicted the size of the exciton of the MX system to be about ten repeating units.^{42,43} The difference between these values may be due to approximations taken both in our analysis and the previous works such as neglect of interactions among the excitons and/or the chains, an assumption of the constant potential energy and/or inevitable experimental difficulties such as detection errors, and imperfectness of the microscopic structure in the sample.

Finally, the origin of the chirp of ν_5 mode is to be mentioned. In the present case, the vibrational frequency decreases as time evolves. Equation (1) simply suggests that the lower the vibrational frequency goes, the greater the relative masses become. Therefore, decrease of the vibrational frequency means increase of the size of the vibrating cluster. This may be explained by energy dissipation along the 1D chain. When the vibration energy dissipates along the 1D chain, adjacent ions are successively involved into the cluster. Thus, the total mass of the cluster increases and changes the curvature of the PES, on which the WP is oscillating, and eventually the vibration frequency decreases.

IV. CONCLUSION

In conclusion, a pump-probe measurement for a quasi-one-dimensional metal-halogen complex, PtBr, using a sub-5-fs ultrashort pulse train has been conducted. An LPSVD calculation revealed an existence of four dominant vibration modes. As a result, pairs of well-known and unknown modes, while expected overtones, which are clearly

observable in the conventional r-RS spectrum, appear only very weakly. These vibration modes were analyzed by the model based on the dynamical matrix; one of the unknown modes was identified. In addition, we found one more component of a chirped modulation with a very slow frequency. Our model including such a chirped modulation well fitted the experimental result, which confirms our proposed mechanism: existence of a cluster motion of many lattice points and an energy dissipation process along the 1D chain. The number of repeating units in the cluster was estimated to be about 50.

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