Layer-Dependent Coherent Acoustic Phonons in Two-Dimensional Ruddlesden-Popper Perovskite Crystals

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ABSTRACT

By combining femtosecond transient reflectance (TR) spectroscopy and density functional theory (DFT) calculations, we reveal the impact of the length of the organic linkers ($\text{HOC}_2\text{H}_4\text{NH}_3^+$ and $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+$) and the number of inorganic layers ($n = 1$ to 3) on the hot carrier relaxation dynamics and coherent acoustic phonons in 2D Ruddlesden-Popper (RP) perovskites. We find that the interplay between the hot-carriers and the coherent longitudinal acoustic phonons (CLAPs) can extend the oscillation of the TR kinetics to nanoseconds, which could lead to the higher thermal conductivities of 2D RP perovskites. Moreover, we find that the frequency of the acoustic phonon oscillation and phonon velocity decreases with the increasing number of layers due to the increased mass of the inorganic layers and reduced electron-phonon coupling. This finding provides new physical insights into how the organic spacers and number of inorganic layers control the overall carrier dynamics of 2D perovskite materials.

TOC Graphic

Two-dimensional (2D) Ruddlesden-Popper (RP) perovskites have recently attracted considerable attention in the field of optoelectronic devices owing to their improved thermal stability and moisture sustainability (versus their conventional three-dimensional, 3D, perovskite counterparts),¹⁻⁸ as well as their facile synthesis either by solution processing or vapor deposition,^{4, 9-11}. 2D RP hybrid perovskites consist of corner-sharing inorganic layers separated by the organic linkers, which achieves a hierarchical configuration with the chemical formula of $L_2A_{n-1}B_nX_{3n+1}$, where L is the organic linker, A is the organic cation, B is the metal cation, X is the halide, and n is the number of inorganic layers.¹²⁻¹⁴ Recently, theoretical and experimental studies have suggested that the photophysical and optoelectronic properties of 2D RP hybrid perovskites can be controlled by varying the number of cation units.¹⁵⁻¹⁸ Although many theoretical and experimental studies have been conducted to understand photophysical processes, such as free charge carriers and large polaron generation as well as carrier separation and diffusion, the hot carrier relaxation processes associated with longitudinal acoustic phonons in 2D RP perovskites still need to be understood. In particular, due to the repetition of the soft organic and hard inorganic intercalation in the 2D RP perovskites, the hot carriers generated upon band-edge excitation can relax through nonradiative phonon emission (vibration) in the form of heat, resulting in the oscillation of coherent acoustic phonons.

Low-energy coherent acoustic phonons have been experimentally observed in inorganic superlattice structures, including Si-Ge¹⁹⁻²⁰ and metal nanocrystals²¹, due to the structural arrangement, which favors wave propagation in the form of phonon emission via vibration. Despite the presence of the organic moieties in 2D RP hybrid perovskites, the crystal structure has the features of the superlattice that can transport thermal energy by carrying the phonons along the cross plane direction ([110] for tetragonal phases and [100] for cubic phases).²²⁻²³ Notably, the 2D

RP hybrid perovskite structure connects through a single [100] unit between the alkylammonium cation units, which are held together through van der Waals interactions and π - π connections in the case of the aryl chain.²⁴ Therefore, the hot carrier relaxation in 2D RP perovskites is coupled with phonon emission because of the crystal's inherent structural configuration. The oscillation of the acoustic phonon transport in a 2D RP hybrid perovskite was experimentally explored by Guo *et al.*²⁵ In this careful study, the generation and propagation of the low energy, heat carrying longitudinal acoustic phonons along the cross-plane direction of the 2D crystals were experimentally observed in the near-infrared (NIR) spectral region.²⁵ However, the study on the generation and propagation of the acoustic phonons that are coupled with the hot carrier relaxation in the 2D RP hybrid perovskites, especially analyzed by the optical response in the visible spectral region, is missing in the literature. In this case, the significant impact of the number of layers and the nature of the organic spacer on the CLAPs generation and propagation in the 2D RP hybrid perovskites are crucial not only for the fundamental understanding of their thermal dissipation properties but also for developing 2D hybrid perovskite materials with higher thermal conductivities for device applications.

In this Letter, we explore and decipher the photogeneration and propagation of the coherent longitudinal acoustic phonons during the hot carrier cooling processes in 2D RP hybrid perovskite crystals using a combination of femtosecond transient reflectance (TR) spectroscopy measurements and density functional theory (DFT) calculations. We uncover the effects of organic linkers and the number of inorganic layers on the propagation periodicity and group velocity of the coherent acoustic phonon of 2D RP hybrid perovskite crystals. More specifically, we find that a slower hot carrier cooling and a longer coherent acoustic phonon oscillation period time can be

achieved by increasing the layer number from $n = 1$ to 3 as well as changing the dielectric constant of the organic linkers.

Figure 1. (a, b) Two-dimensional color plots of the transient reflectance (TR) spectra; (c, d) normalized TR spectra at early delays of EA ($n = 1$) and PEA ($n = 1$) single crystal at the excitation wavelength of 330 nm; and (e, f) the hot carrier temperature (T_c , in K) as a function of delay times for EA ($n = 1$) and PEA ($n = 1-3$) perovskite single crystals.

We first study the charge carrier dynamics of 2D RP perovskite single crystals to elucidate the impact of the organic linkers and the number of layers on the hot carrier relaxations. The details of the synthesis methods and characterizations of these perovskite crystals can be found in our previous studies.^{16, 26} The TR spectroscopy measurements were performed using ultrafast transient absorption (TA) spectroscopy.²⁷⁻²⁸ Here, the negative TR signal (*i.e.*, $-\frac{R(t_i)-R(t_0)}{R(t_0)} = -\frac{\Delta R}{R(t_0)} < 0$)

and positive TR signal (*i.e.*, $-\frac{R(t_i)-R(t_0)}{R(t_0)} = -\frac{\Delta R}{R(t_0)} > 0$) are assigned to the photobleaching (PB) and photoinduced absorption (PIA), respectively, where $R(t_0)$ and $R(t_i)$ are the reflectance signals without and with pumping at the delay time t_i . Figures 1a and 1b show the 2D color plot of the transient reflection spectra of (EA)₂PbI₄ and (PEA)₂PbI₄ single crystals within a 1-ns time window above the bandgap excitation (*i.e.*, 330 nm). We find that *i*) a strong photobleaching signal (in blue) appears at 505 nm for (EA)₂PbI₄ and 500 nm for (PEA)₂PbI₄, which could be attributed to band filling effect;²⁹ *ii*) a strong photoinduced absorption signal (in red) appears at 534 nm for (EA)₂PbI₄ and 520 nm for (PEA)₂PbI₄; and *iii*) a weak broad photoinduced absorption is observed above 550 nm in both single crystals. From the normalized TR spectra of both crystals, as shown in Figures 1c and 1d, the photobleaching signal in the high-energy region (*i.e.*, below the band-edge region) is broad at early delays after photoexcitation, which is attributed to the thermal quasi-equilibrium distribution of the hot electrons (holes).³⁰⁻³² As a result, the hot electrons (holes) exhibit a carrier temperature (T_C) larger than the lattice temperature.^{30, 32-33} The weak broad photoinduced absorption beyond the bandgap can be assigned to the generation of free carriers.³³ The TR spectra of the other two PEA-linked 2D perovskite crystals ($n = 2$ and $n = 3$) are shown in Figure S1 of the Supporting Information. Similar to the case of $n = 1$, the TR spectra consist of band-edge photobleaching signals together with the broad photoinduced absorption of the hot and free charge carriers.

In the perovskite crystal lattice, the quasi-equilibrium distribution of the hot charge carriers follows the cooling distribution according to the Boltzmann distribution equation of $\Delta R/R[E] \propto e^{-(E-E_f)/(k_B T_C)}$, which can be used to estimate the T_C of the hot carriers in the hybrid perovskites. Through fitting the broadening of the high-energy tail of the ground-state bleaching, the hot carrier temperature of single-layer perovskite crystals are extracted and compared in Figures 1e,1f. We

find that the initial hot carrier temperature of (EA)₂PbI₄ is much higher than that of (PEA)₂PbI₄ because of the lower exciton binding energy of (EA)₂PbI₄ (13 meV) compared to (PEA)₂PbI₄ (330 meV)¹⁶. Moreover, we find that the decay of the hot carrier temperature in (EA)₂PbI₄ is much slower than that in (PEA)₂PbI₄ due to the larger dielectric constant of the organic cation: $\epsilon_{EA}=37$ for (EA)₂PbI₄ vs. $\epsilon_{PEA}=3.3$ for (PEA)₂PbI₄,¹⁶ as well as the smaller nonadiabatic couplings between the high-energy states that can prolong the hot carrier thermalization. However, the broadening of the high-energy tail is almost negligible following the band-edge excitation (*i.e.*, 480 nm, see Figures S2-S3 of the Supporting Information). On the other hand, for PEA-linked perovskites with different numbers of layers ($n = 1$ to 3), the initial carrier temperature decays slowly by increasing the number of inorganic layers because of the large density of states as well as the couplings between the inorganic layers and organic cations.

Figure 2. Transient reflectance kinetics probe at 680 nm (the photoinduced absorption signal) of 2D perovskite single crystals at the excitation wavelength of 330 nm for (a) the EA ($n = 1$) and PEA ($n = 1$) and (b) PEA ($n = 1-3$). The dotted lines represent the fit of the experimental data. The initial decay and the oscillation of the TR signal are fitted using exponential and Sine functions, respectively.

Similar to the inorganic semiconductor superlattice, the hot carriers in 2D RP perovskites can relax through phonon emission, resulting in a gradual decrease in the TR signal with the delay time. Upon photoexcitation with excess energy, the charge carriers populate the hot electronic states, and then the excited charge carriers release the excess energy into the crystal lattice through the phonon emission. As demonstrated by Wright and coworkers, the carrier relaxation in halide perovskite occurs mainly through longitudinal optical phonons via the Fröhlich interactions at room temperature.³⁴ To gain insights into the hot carrier relaxations, we compare the TR kinetics traces as a function of organic spacers and the number of inorganic layers. As shown in Figures 2a and 2b, the TR kinetics in the entire spectral region consist of a fast subpicosecond decay followed by a periodic TR oscillation by comparing the kinetics probe at 680 nm of all studied crystals. Note that the oscillation of the TR spectra retains the same feature in the entire probed region (see Figures S4-S7 of the Supporting Information). At very early delays, the photoinduced TR signal of the 2D RP perovskite crystals decays with an average time of 1.5-8 ps, which can be attributed to the relaxation of the hot carriers associated with longitudinal optical (LO) phonons. The TR signal of (PEA)₂PbI₄ decays faster than that of (EA)₂PbI₄ (1.5 ps vs. 5.5 ps) since the larger exciton binding energy of the PEA-linked 2D crystal promotes the release of the LO at a faster rate.³⁵⁻³⁶ Therefore, the slower LO phonon emission rate with increasing number of inorganic layers is due to decreased exciton binding energy.^{37,38} The observed TR oscillation can be attributed to the propagation of the coherent longitudinal acoustic phonons (CLAPs) inside the crystal lattice.^{21, 25, 39-40} The amplitude difference of the TR signal is due to the relative contribution of the thermoelastic properties and the deformation potential values of the perovskite crystals.³⁹

The oscillation of the CLAPs was fitted by the Sine function, and the propagation velocity of the phonon was calculated based on the period (T) of the probe oscillation. The value of the

oscillation period can be directly obtained from the difference of the highest TR signal intensity (see two vertical dotted lines in Figure 2). Interestingly, the T value gradually increases with the increasing number of inorganic layers from $n = 1$ to 3 (61, 65, and 83 ps for $n = 1, 2$, and 3, respectively). On the other hand, almost the same period of oscillation for CLAPs can be found in $(\text{EA})_2\text{PbI}_4$ and $(\text{PEA})_2\text{PbI}_4$ crystals for $n = 1$ (61 vs. 62 ps). However, at band-edge excitation as a control experiment, the oscillation of the acoustic phonons was not observed since it lacks the excess energy to create the hot carriers (see Figures S8 of the Supporting Information). Thus, we can conclude that oscillation of the acoustic phonons is layer dependent (interaction among the hard inorganic part), while the role of the organic spacer on the periodicity of the oscillation can be neglected.

Figure 3. (a) Schematic illustration of the coupling interaction among the layers; (b) propagation of the acoustic phonon periodicity and velocity; and (c) calculated deformation potential (DP) and bandgap DP of the 2D RP hybrid perovskites.

As shown in Figures 3a and 3b, the velocity (v) of the CLAPs was calculated using the equation of $T[\lambda] = \frac{\lambda}{2 v n(\lambda)}$, where λ is the probe wavelength, $n(\lambda)$ is the refractive index at λ .^{25, 41-43} The calculated velocity of the CLAPs varies from 1540 to 2100 m/s, which are lower than that of the 3D counterpart.^{25, 44} The deformation potential (DP) constant can be used to characterize the coupling strength of the electron or hole to the acoustic phonon and understand the different values of the CLAP velocity. The DP constant is defined as $E_{DP} = \Delta E / (\Delta l / l_0)$, where ΔE is the band edge energy change with respect to the lattice dilation $\Delta l / l_0$ within the inorganic-plane (xy-axis) and out-inorganic-plane (z-axis) directions. Since the charge carriers appear at the band edge with the low concentration, we took the energy change in the valence band maximum (VBM) for holes and the change in the conduction band minimum (CBM) for electrons. Figure 3c shows the DP constants for both the holes and electrons of 2D hybrid perovskites obtained from density functional theory (DFT) calculations. We find that (i) the electron-phonon couplings of 2D hybrid perovskites are relatively stronger compared to 3D MAPbI₃ with the largest DP constant of ~ 5 eV⁴⁵; (ii) the DP constants for holes are larger than for electrons within the inorganic plane, indicating that the holes are more scattered by the acoustic phonon than the electrons in the inorganic layers; and (iii) the DP constants of the out-inorganic plane for holes and electrons are similar. In addition, we have calculated the bandgap DP constant (defined as $\alpha = \frac{\partial E}{\partial \ln V}$)⁴⁶⁻⁴⁷ of these 2D RP perovskites (lower panel in Figure 3c) and find that the bandgap DP constants of the inorganic plane are much larger than those of out-inorganic-plane. The bandgap DP constants of EA ($n = 1$) and PEA ($n = 1$) are very close and smaller than those of PEA ($n = 2$) and PEA ($n = 3$). This finding indicates that the dielectric confinement (*i.e.*, organic space) has a negligible effect on the electron-acoustic phonon coupling, while a stronger quantum confinement, especially n

= 1 perovskite crystals, can lead to the large scattering of the electrons or holes with the acoustic phonon and reduce the coherence time.

Figure 4: Schematic illustration of carrier relaxation processes in 2D RP hybrid perovskites upon (a) the band-edge (480 nm) and (b) above the bandgap (330 nm) excitation and (c) optical and acoustic phonon vibration coupled with hot carrier relaxation. The vertical dotted lines represent the equilibrium position of the atoms in the perovskite crystal lattice.

To understand the effects of LO and acoustic phonons on the charge carrier dynamics, we illustrate the charge carrier relaxation processes of 2D RP perovskites in Figure 4. At band-edge excitation, the excited state decay is mainly driven by direct electron-hole recombination (Figure 4a). Interestingly, upon perturbing the system with excess energy, the charge carriers are populated at the higher electronic states (the carriers with energy larger than k_{BT} are known as hot carriers, as shown in Figure 4b) and then quickly thermalize through a nonradiative phonon emission process. Both LO and CLAPs are associated during hot charge carrier relaxation. Moreover, the average time for the LO-assisted phonon emission occurs on a subpicosecond time scale and varies by

changing both the dielectric confinement of the organic spacer and the number of layers. On the other hand, the CLAP emission due to the oscillation of the lattice vibration is prolonged up to the nanosecond time scale (see Figure S9), which is independent of the dielectric confinement of the organic linkers but highly dependent on the number of inorganic layers (*i.e.*, the mass of the inorganic part). The light-induced lattice vibrations in the perovskite crystals are illustrated in Figure 4c. The LO phonons are associated when the consecutive lattice points are vibrated in the same (compression) or opposite direction (stretching) (upper panel of Figure 4c). On the other hand, the acoustic phonons (sinusoidal wave) are propagated with a combination of compression and rarefaction vibration motions (lower panel of Figure 4c). Therefore, the motion of the acoustic phonon is attenuated by the medium (mass of the crystal lattice), while the LO phonon is independent of the entire mass of the crystal. Likewise, in this study, we experimentally identified the two phonon motions in the 2D RP hybrid perovskite crystals during the relaxation of hot electrons (holes). The confined-LO phonons are detected by identifying the fast decay component in the photoinduced TR signal that varies with the dielectric and quantum confinement of the 2D perovskite. The scheme shows that the entire medium vibrates with the combination of compression and rarefaction during the propagation of the acoustic phonon, which directly reflects the oscillation of the TR signals.

In summary, we have studied the effects of the organic spacer and the number of layers on the photogeneration and propagation of CLAPs in 2D RP hybrid perovskites using a combination of femtosecond TR measurements and DFT calculations. Our time-resolved results demonstrate that the thermalization of the hot carriers is associated with longitudinal optical and acoustic phonons, which are observed in the TR spectrum in the visible region upon above band-gap excitation. The time scale of the optical phonons varies at the subpicoseconds level, while the oscillation of the

acoustic phonons can extend up to nanoseconds. Interestingly, the slow relaxation of the hot carrier is achieved by increasing the dielectric constant of the organic linker in single layer perovskite and by increasing the number of inorganic layers. We also conclude that the CLAPs associated during the thermalization of the hot relaxation and frequency of the acoustic phonon oscillation and phonon velocity can be reduced with an increasing number of inorganic layers due to strong electron–phonon coupling within the inorganic layers. Our findings provide insights into hot carrier cooling processes and the propagation of acoustic phonons in 2D RP hybrid perovskite crystals.

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ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental and computational methods, TR spectra of PEA ($n = 2$ and $n = 3$), TR spectra of EA ($n = 1$) and PEA ($n = 1$) single crystals at band edge excitation, and TR kinetics probed at different wavelengths.

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