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Influence of dielectric confinement on excitonic nonlinearity in inorganic-organic layered semiconductors

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We have investigated photoinduced spectral changes of excitons in inorganic-organic layered semiconductors, $(C_6H_5C_2H_4NH_3)_2PbI_4$ (PhE-PbI_4) and $(C_6H_{13}NH_3)_2PbI_4$ (C6-PbI_4), by means of the subpicosecond pump-probe spectroscopy. The two semiconductors consist of the same inorganic layers and different organic layers. In the two substances, the blueshift and the bleaching of the exciton are observed. It is found that both of the blueshift and the bleaching are considerably stronger in C6-PbI_4 than in PhE-PbI_4. The weight of the blueshift relative to the bleaching is larger in PhE-PbI_4 than in C6-PbI_4. These differences are qualitatively explained in terms of the stronger dielectric confinement in C6-PbI_4 than in PhE-PbI_4 due to the lower dielectric constant of the organic layers in C6-PbI_4 than in PhE-PbI_4. Delay time dependences of the blueshift and the bleaching and their polarization dependences are understood as being due to the exciton relaxation in the angular momentum space with rates of 2.7 and 4.1 ps^{-1} for PhE-PbI_4 and C6-PbI_4, respectively.

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I. INTRODUCTION

For tailoring electronic properties of semiconductors, the hybridization of essentially different sorts of substances is a possible strategy. While attempts for artificially realizing such hybrid structures by mean of various surface deposition techniques are still in preliminary stages, there are a series of inorganic-organic hybrid perovskite compounds[1] whose structures are realized by self-organization, i.e., crystallization from mixed solutions of constituents.

Among such hybrid compounds, the PbI-based perovskites are one of the most studied semiconductors up to now.[2,3] Zero-, one-, two-, and three-dimensional networks of $[PbI_6]^{4-}$ octahedra are realized in crystals, where low-dimensional networks are separated each other by organic parts. Linear optical properties have been systematically investigated.[4–6] Since the band gap energies of organic parts (typically 6 eV) are much larger than that of the inorganic part (1.68 eV),[7] carriers and low-energy excitations are confined in the inorganic part. Thus, it is possible to understand their electronic properties in analogy with quantum dots, wires, wells, and the bulk of conventional semiconductors. According to the tight binding calculation,[6] the valence band top consists of Pb(6*s*) and I(5*p*) orbitals, while the conduction band bottom mainly consists of Pb(6*p*) orbitals, regardless of the dimensionality. Excitons are understood consistently from viewpoints of the *potential confinement* and the *dielectric confinement*. The potential confinement is brought about by the larger band gap energy of the organic part. The potential confinement enhances both the kinetic energy and the exciton Rydberg. The dielectric confinement effect, which we refer here separately from the simple potential confinement effect, is brought about by a considerably smaller dielectric constant of the organic part. The dielectric confinement results in the enhancement of the exciton Rydberg, because the effective dielectric constant which carriers experience in the inorganic part is lowered due to the organic parts. In fact, the dielectric confinement effect is significant.[8]

The dielectric confinement, as a concept, was theoretically examined by Rytova[9] and Keldish.[10] Its influence on the exciton Rydberg in semiconductor quantum wells was calculated by Hanamura *et al.*[11] Ishihara *et al.*[12,13] applied it to the inorganic-organic layered perovskites. A practical model to deal with excitons in the perovskite compounds, which includes not only the potential confinement but also the dielectric confinement effect, was proposed by Muljarov *et al.*,[14] and the model has been further verified in detail by means of two-photon and the electroabsorption spectroscopies by Tanaka *et al.*[15] By these efforts, it seems to be established that the excitons in two-dimensional perovskites are elucidated quite well as two-dimensional Wannier excitons, although their in-plane exciton Bohr radii are no more than several times as large as the unit cell. Hereafter in this paper, unless otherwise noted, we shall limit our discussion to the two-dimensional perovskites, which we call the inorganic-organic layered semiconductors.

Excitonic nonlinearity in these layered semiconductors has been reported in several papers up to now. The excitonic molecule with a binding energy of 50 meV was observed in PhE-PbI_4 $[(C_6H_5C_2H_4NH_3)_2PbI_4]$ by the photoluminescence measurement by Ishihara *et al.*[16,17] The large modulus of $\chi^{(3)}$ at the exciton resonance was observed in C6-PbI_4 $[(C_6H_{13}NH_3)_2PbI_4]$ by Kondo *et al.*[18] A nondegenerate four-wave-mixing measurement was carried out for C6-PbI_4 by Ishi *et al.*,[19] to demonstrate biexcitonic contributions. The result was analyzed with a few-level model which includes biexcitons. Detuning dependence of the ac Stark shift in PhE-PbI_4 was studied by Shimizu *et al.*,[20] to show the bound and unbound biexcitonic contributions. It was also suggested that the giant oscillator strength model for the excitonic molecule may not be applicable due to the extremely large exciton oscillator strength.[21] Namely, the exciton-related optical nonlinearities observed in the layered semiconductors are characterized by the strong exciton-exciton interaction and the strong light-exciton interaction. Nevertheless, the detail of the exciton-exciton interaction has not been

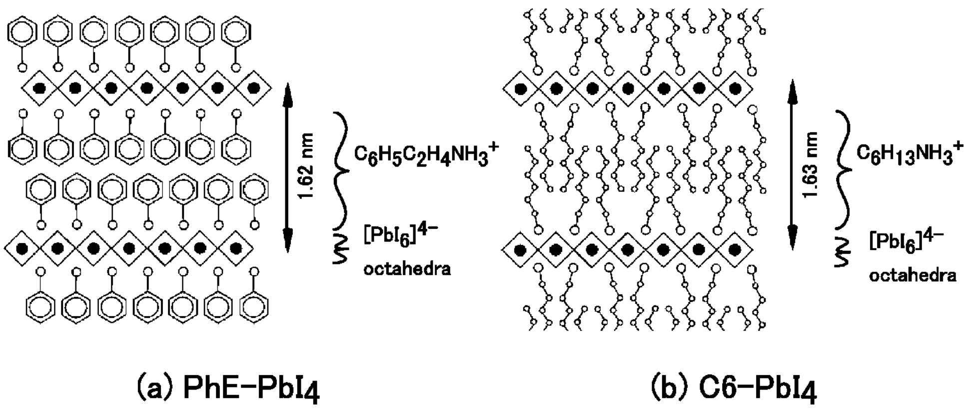

FIG. 1. Schematic drawing of crystal structures of PhE-PbI$_4$ (a) and C6-PbI$_4$ (b). Cross sections are perpendicular to layers.

examined. In order to understand it, it is necessary to consider the two factors, the potential confinement and the dielectric confinement, which are known to dominate the excitonic properties in the layered semiconductor.

The influence of the potential confinement on the excitonic nonlinearity has been studied in the conventional semiconductor quantum wells extensively for two decades.[22,23] The strong bleaching[24,25] and the blueshift[26,27] of excitons have been observed, depending on experimental conditions. Plenty of works on this issue have been reported up to now, and it seems to be established that the reduced dimensionality realized by the potential confinement enhances the importance of the Pauli exclusion principle, while decreases the contribution of the long-range Coulomb interaction.[28,29]

The influence of the dielectric confinement on the excitonic nonlinearity, on the other hand, has not been studied up to now. There are two possibilities. The first is that the interaction between excitons may be weakened, because the charge neutrality of an exciton is enhanced due to the smaller exciton Bohr radius. The second possibility is the enhancement of the interaction expected from the logarithmic Coulomb potential.[10] As Keldish pointed out, the the Coulomb interaction between confined carriers are less screened at larger distance, because carriers mainly experience small dielectric constant of the organic part at large distance relative to the width of a well layer. Thus, the exciton-exciton interaction, which consists of the Coulomb interaction between constituent carriers, is expected to be strengthened or different qualitatively.

In this paper, the authors report the subpicosecond pump-probe study of the excitonic nonlinearity in inorganic-organic layered semiconductors. Two similar substances, PhE-PbI$_4$ and C6-PbI$_4$ are adopted as samples for comparison, in order to investigate the influence of the dielectric confinement. The two substances consist of almost the same inorganic parts and different organic parts. Hence, difference in degrees of the dielectric confinement is expected. From amplitudes of spectral changes, dependences on angular momenta, and dependences on the delay time, the authors try to understand the interaction between excitons in the basic level.

Crystal structures of the two substances are schematically drawn in Fig. 1.[15,30,31] Cross sections are perpendicular to the layers. In both substances, inorganic layers consist of $[PbI_6]^{4-}$ octahedra which share four vertices one another. Distances between neighboring inorganic layers are ~1.6 nm in both. In this distance, electronic interaction between nearest inorganic layers is expected to be negligibly small, because optical spectra of Cn-PbI$_4$ $[(C_nH_{2n+1}NH_3)_2PbI_4]$ with $n \geqslant 4$, whose interlayer distances depend on n, are very similar.[5,6,32] The high frequency dielectric constant of the inorganic part (ϵ_{PbI}) is considered to be 6.1,[33] while those of the organic parts (ϵ_{org}) in PhE-PbI$_4$ and C6-PbI$_4$ are estimated to be 3.32 and 2.44, respectively.[33] This difference is understood as being due to the higher electron density in the phenethyl group than in the alkyl group. Thus, the stronger influence of the dielectric confinement is expected for C6-PbI$_4$ than for PhE-PbI$_4$. Exciton Rydbergs (G_x) are estimated to be 250[13,14] and 300 meV,[14,15] respectively, for PhE-PbI$_4$ and C6-PbI$_4$. Excitons have two-dimensional envelopes within an inorganic layer with in-plane Bohr radii (a_B) of 14.2 and 13.1 Å in PhE-PbI$_4$ and C6-PbI$_4$, respectively.[14]

II. EXPERIMENT

Both of PhE-PbI$_4$ and C6-PbI$_4$ were prepared by chemical synthetic methods.[13,30,31] The samples for the measurement were polycrystalline films made by spin coating from solution. Layers in each polycrystalline domain are parallel to the substrate, and there is no polarization dependence in the linear optical response within the plane. Thicknesses of the samples were determined to be 9.8 and 41.0 nm for PhE-PbI$_4$ and C6-PbI$_4$, respectively, by means of a surface profiler (DEKTAK) and an atomic force microscope. The absorption coefficients at peaks of the lowest excitons were estimated to be 1.2×10^6 and 7.9×10^5 cm^{-1}, respectively, for PhE-PbI$_4$ and C6-PbI$_4$.[34] Peak optical densities were 0.67 and 1.3 in PhE-PbI$_4$ and C6-PbI$_4$, respectively, the latter of which was too thick to generate excitons homogeneously. Since it was very difficult to control qualities of thinner films, we compromised with this rather thick film of C6-PbI$_4$. In measurements, spin coated films were attached to a cold finger of a cryostat and cooled to ~10 K.

Pump-probe measurement was setup in the transmission geometry. A 1 kHz Ti:Al$_2$O$_3$ regenerative amplifier was used as the light source, the output of which was split off for generating pump and probe lights. The pump light was tuned to be resonant with the excitons. A prism pair was used for optimizing the pump pulse duration. The probe light was the white-light continuum generated in a water cell. Pump and

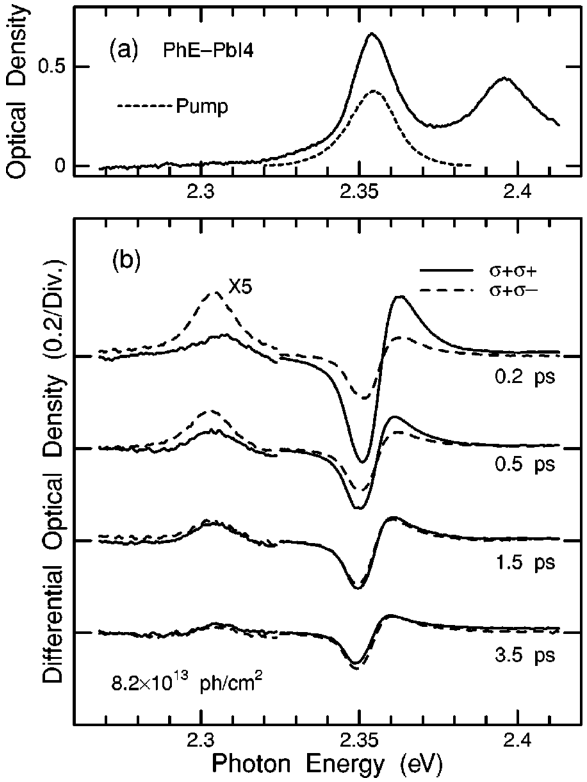

FIG. 2. Linear absorption spectrum (a) and the photoinduced absorption change (b) of PhE-PbI$_4$. In (a), the spectrum of the pump light is overdrawn with a dotted line. In (b), delay times are shown on the right-hand side of each spectrum. Solid and dashed curves show spectra observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$, respectively.

probe lights were same-circularly ($\sigma^+\sigma^+$) or opposite-circularly ($\sigma^+\sigma^-$) polarized with achromatic wavelength plates. The angle between pump and probe beams was 11°. The autocorrelation of the pump pulse and the crosscorrelation between pump and probe pulses were typically 150 and 100 fs, respectively, in the full width at half maximum. The overlap of the pump and probe beams on the sample was carefully controlled with a video telescope. Spot sizes of pump and probe beams on the samples were measured with a pinhole equipped with a micrometer stage and were estimated to be 60.5 and 4.53 μm, respectively, in diameters. Because the delay time (τ_d) of the probe pulse to the pump pulse depends on the wavelength, obtained spectra were numerically corrected after measurements. The pump light intensity was measured with a photodiode powermeter.

III. RESULTS

Figure 2(a) shows the linear absorption spectrum of PhE-PbI$_4$. Two peaks are observed. The peak at 2.355 eV is the lowest 1*s* exciton. The other peak at 2.395 eV is also assigned to a 1*s* exciton which is originated from another electronic band, which is splitted from the former because a unit cell consists of two formula units.[30] In this work, we investigated the shift and the bleaching of the exciton at 2.355 eV by exciting it resonantly. The spectrum of the pump light is overdrawn with the dotted line in the figure.

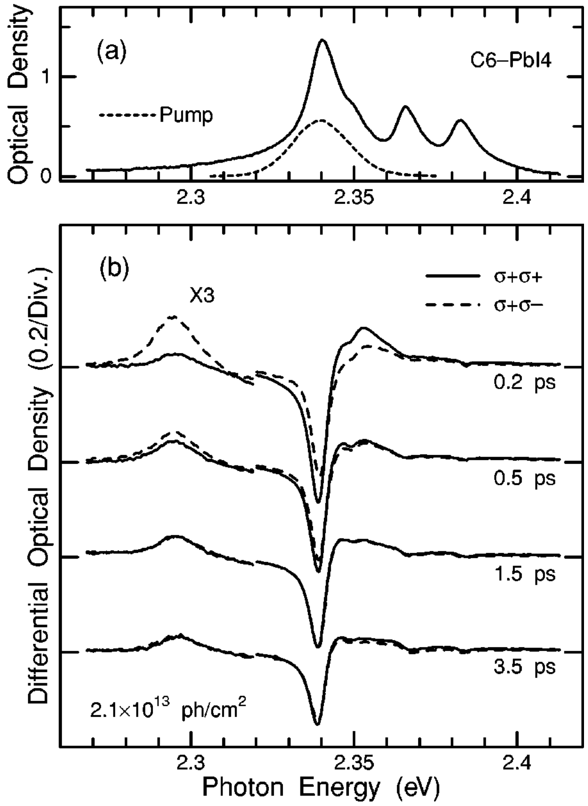

FIG. 3. Linear absorption spectrum (a) and the photoinduced absorption change (b) of C6-PbI$_4$. In (a), the spectrum of the pump light is overdrawn with a dotted line. In (b), delay times are shown on the right-hand side of each spectrum. Solid and dashed curves show spectra observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$, respectively.

The photoinduced spectral change is shown in Fig. 2(b). The pump intensity was 8.2×10^{13} photons cm^{-2}, spectral changes with which were almost proportional to the intensity. The generated exciton density is estimated to be 5.7×10^{19} cm^{-3}. The strong blueshift of the exciton band is observed as the derivative shape of differential spectra around 2.355 eV. The slight bleaching is suggested by the slightly larger decrease at the low-energy side than the increase at the high-energy side. Besides the exciton renormalization, an induced absorption is observed at 2.305 eV, which is below the exciton by 50 meV. This induced absorption is assigned to the excitation of the exciton to the excitonic molecule, as the energy separation from the exciton matches with that observed previously in photoluminescence.[13,17] At small delay time (τ_d=0.2 ps), the blueshift is stronger in $\sigma^+\sigma^+$ than in $\sigma^+\sigma^-$, while the induced absorption is much stronger in $\sigma^+\sigma^-$ than in $\sigma^+\sigma^+$. These polarization dependences almost disappear after 1.5 ps.

The linear absorption spectrum of C6-PbI$_4$ is shown in Fig. 3(a). Three peaks and a shoulder are observed. The peak at 2.340 eV is the lowest 1*s* exciton.[32] We assign the shoulder at 2.350 eV to a phonon sideband of the 2.340 eV band, because the photoinduced change shows the similar behavior to that of the main band, as is seen below. Peaks at 2.365 and 2.383 eV are most probably assigned to other 1*s* excitons related to other electronic bands, but have not been identified yet. The change of the exciton at 2.340 eV was investigated

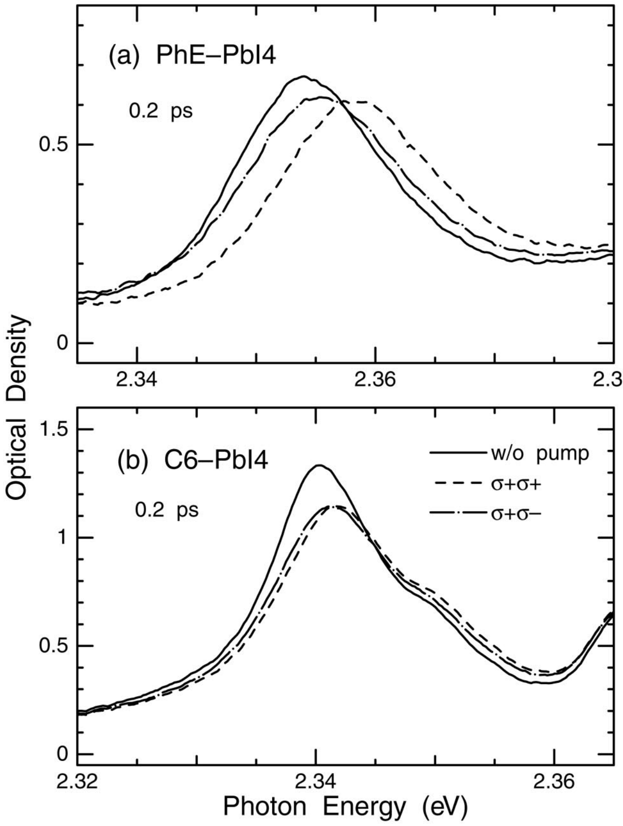

FIG. 4. Absorption spectra without and with irradiating the pump light, of PhE-PbI$_4$ (a) and of C6-PbI$_4$ (b). Exciton densities are estimated to be 5.7×10^{19} and 4.9×10^{18} cm^{-3}, respectively. Horizontal scales are the same in (a) and (b).

by pumping it resonantly. The spectrum of the pump light is shown with the dotted line.

Figure 3(b) shows the photoinduced change of C6-PbI$_4$. The pump intensity was 2.1×10^{13} photons cm^{-2}, with which the initial exciton concentration is estimated to be 4.9×10^{18} cm^{-3}. The blueshift and the bleaching of the exciton are observed, as are similarly observed in PhE-PbI$_4$. In contrast to PhE-PbI$_4$, however, the bleaching seems to be rather strong relative to the blueshift (this is seen as the much larger decrease at the low-energy side than the increase at the high-energy side of the peak, taking into account that the increase at the high-energy side is superimposed with the small derivative structure by the phonon side band). This difference is more clearly seen in Fig. 4, where optical density spectra with and without irradiating the pump light are plotted in the same horizontal scale. In PhE-PbI$_4$, the exciton peak is rather strongly shifted with slight bleaching, while in C6-PbI$_4$, the peak is only slightly shifted but is lowered significantly. In Fig. 3(b), an induced absorption due to the excitation of the exciton to the excitonic molecule is observed at 2.295 eV which is below the exciton by 45 meV. It will be worth noting that this observed binding energy of the excitonic molecule in C6-PbI$_4$ is slightly *smaller* than that in PhE-PbI$_4$ by 5 meV. Considering the *stronger* dielectric confinement in C6-PbI$_4$ than in PhE-PbI$_4$, this fact is quite interesting, but the authors have no reasonable account now.

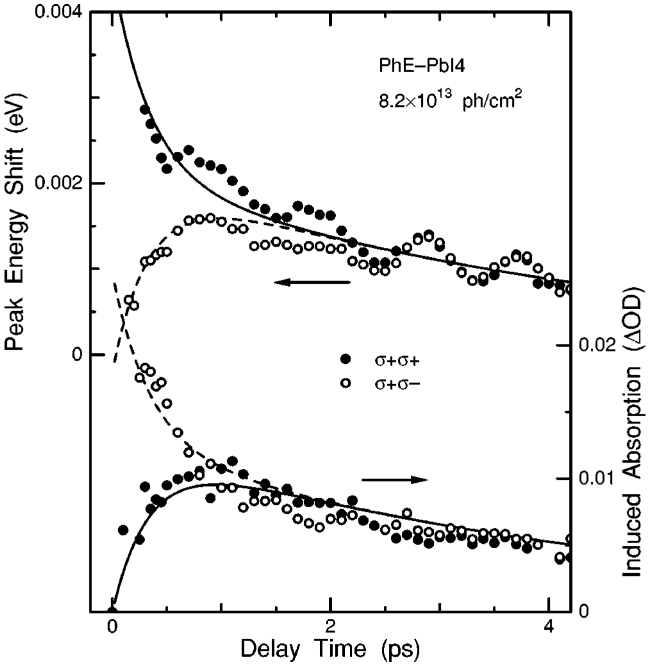

FIG. 5. Exciton peak energy shift (upper) and the induced absorption due to the generation of the excitonic molecule (bottom) as functions of the delay time in PhE-PbI$_4$. Data observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ are plotted with closed and open circles, respectively. Curves show the best fit with Eqs. (2a) and (2b) described in Sec. IV.

This fact had been implied in previous works,[16,17,19,35,36] but not clarified because values depends on reports. Here, the authors have clarified the fact by systematic measurements.

Delay time dependences of the exciton peak energies and the amplitudes of the induced absorption in PhE-PbI$_4$ and C6-PbI$_4$ are shown in Figs. 5 and 6, respectively. Closed and open circles show the experimental data observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$, respectively. Solid and dotted curves show the best fits to the data observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$, respectively, by the model discussed in the next section. Since the peak energies at less than $\tau_d=0.2$ ps are influenced by the ac Stark shift, they are eliminated from the target of the fit and thus also from the plot. The ac Stark shift was reported in detail elsewhere.[20] In this work, we confine ourselves into the population effect. Although the phase coherence of excitons should be partly conserved for hundreds femtoseconds and may bring about some minor effects, the difference between coherent and decohered excitons is neglected, as a first approximation.

In PhE-PbI$_4$, the exciton blueshift in $\sigma^+\sigma^+$ decays monotonously with a fast decay at $\tau_d<1$ ps and a slow decay later, although it is only concluded according to the rate equation analysis discussed below. In $\sigma^+\sigma^-$, the peak energy increases until ~1 ps and then decreases. The polarization dependence almost disappears within 2 ps. On the other hand, the induced absorption amplitude in $\sigma^+\sigma^+$ grows until ~1 ps and then decreases, and that in $\sigma^+\sigma^-$ decreases with a fast decay at $\tau_d<1$ ps, and a slow decay later. Changes in the peak energy and the induced absorption amplitude are synchronous, which is examined quantitatively in the next section. It is to be noted that the oscillation seen in the peak

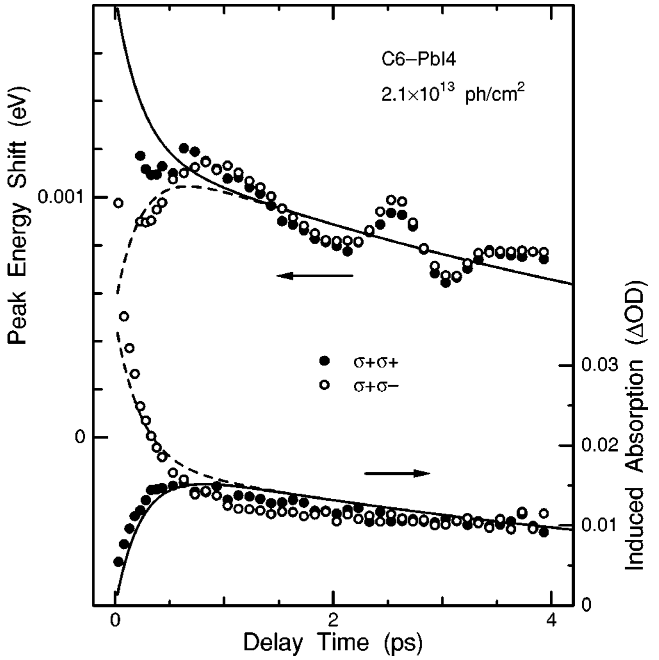

FIG. 6. Exciton peak energy shift (upper) and the induced absorption due to the generation of the excitonic molecule (bottom) as functions of the delay time in C6-PbI$_4$. Data observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ are plotted with closed and open circles, respectively. Curves show the best fit with Eqs. (2a) and (2b) described in Sec. IV.

energy shift is explained to be due to the excitation of coherent phonons and is not due to the quantum beat, because the oscillation amplitude was independent of the change of the pump photon energy. Two internal modes within a Pb-I plane are identified in the oscillation, according to the Fourier transform analysis.[37]

In C6-PbI$_4$, as is observed in PhE-PbI$_4$, exciton peak energies and induced absorption amplitudes show the synchronous change. However, the polarization anisotropy in C6-PbI$_4$ decays faster than that in PhE-PbI$_4$. The fast decay in $\sigma^+\sigma^-$ and the rise in $\sigma^+\sigma^+$ of the induced absorption occurs in the time scale of less than 1 ps. The fast decay of the exciton peak energy in $\sigma^+\sigma^+$ is not clearly resolved later than 0.2 ps, due to the fast depolarization and the coherent phonon oscillation.

Quantitative differences between two substances are summarized in Table I. The shift ($\Delta\omega_x$), the change of peak absorption coefficient of the exciton ($\Delta\alpha_x$), and the amplitude of the induced absorption by the excitonic molecule ($\Delta\alpha_m$) are listed, normalized by the in-plane exciton concentration ($n_x d$, where n_x and d denote three-dimensional density and the sum thickness of an inorganic layer and an organic layer). The quantities are estimated from mean values of what observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ at $\tau_d=0.2$ ps, assuming that the exciton density is equal to that generated initially by a pump pulse. It is clear that both of the blueshift and the bleaching are much stronger in C6-PbI$_4$ than in PhE-PbI$_4$. It is also seen, as is shown in Fig. 4, the amount of the blueshift divided by the amount of bleaching is larger in PhE-PbI$_4$ than in C6-PbI$_4$.

It is noted that, for estimating exciton densities, the in-depth nonuniformity was averaged out, although optical densities of the used samples were not really small. Estimates normalized by these averaged exciton densities are justified for two reasons. The one is that the observed spectral changes were almost proportional to the intensity.[38] The other is that the possible slight sublinearity at the incident surface of a sample will result in slight underestimate of a mean value which the proportionality is postulated for. This slight underestimate will be the case, if it is, rather for the thick C6-PbI$_4$ film than for the PhE-PbI$_4$ film. Thus, the comparison arguments in the above paragraph are valid, regardless of the nonuniformity.

TABLE I. Comparison between PhE-PbI$_4$ and C6-PbI$_4$ in terms of fundamental parameters and experimental results.

	PhE-PbI$_4$	C6-PbI$_4$
ϵ_{org}	3.32[a]	2.44[a]
G_x (meV)	250[b,c]	300[c,d]
a_B (Å)	14.2[c]	13.1[c]
G_m (meV)	50	45
$\Delta\omega_x/n_x d$ (eV cm^2)	2.4×10^{-16}	1.6×10^{-15}
$\Delta\alpha_x/n_x d$ (cm)	-3.5×10^{-22}	-3.5×10^{-21}
$\Delta\alpha_m/n_x d$ (cm)	8.1×10^{-23}	3.2×10^{-22}
$\Delta\omega_x/\Delta\alpha_x$ (eV cm)	6.7×10^{5}	4.5×10^{5}
$\Delta\omega_x/\Delta\alpha_m$ (eV cm)	2.9×10^{6}	4.8×10^{6}
$\Delta\alpha_x/\Delta\alpha_m$	−4.3	−11
γ_d (ps^{-1})	0.22	0.15
γ_s (ps^{-1})	1.4	2.1
I_{+-}/I_{++}	−0.05±0.05	0.3±0.2

[a] For derivation, see Ref. 33.
[b] Experimentally estimated to be 220±30 meV in Ref. 13.
[c] Theoretical estimates in Ref. 14.
[d] Experimentally estimated to be 360 meV in Ref. 15.

IV. DISCUSSION

A. Polarization and delay time dependences

In order to examine the polarization dependence of photoinduced spectral changes, we model the exciton relaxation dynamics and the exciton renormalization.

We assume the three level system, i.e., the ground state, the σ^+ exciton, and the σ^- exciton, as is schematically shown in Fig. 7. The influence of forming the excitonic molecule on the exciton renormalization is neglected as a minor factor and for simplification. The population dynamics is expressed by a set of rate equations as

$$\frac{dn_+}{dt} = g_0(t) - (\gamma_d + \gamma_s)n_+ + \gamma_s n_-, \tag{1a}$$

$$\frac{dn_-}{dt} = \gamma_s n_+ - (\gamma_d + \gamma_s)n_-, \tag{1b}$$

where $n_\pm$ represents the density of $\sigma^\pm$ excitons. $g_0(t)$, γ_d, and γ_s represent the exciton generation, the exciton decay rate,

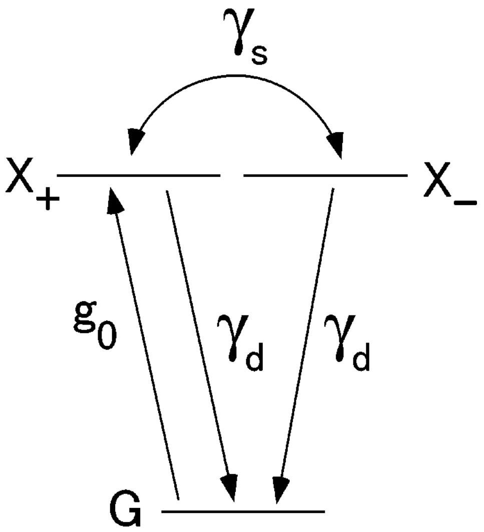

FIG. 7. Schematic diagram of the exciton relaxation. G, X_+, and X_- represent the ground, σ^+ exciton, and σ^- exciton states, respectively. g_0, γ_d, and γ_s express the exciton generation, the exciton decay rate, and the conversion rate between σ^+ and σ^- excitons, respectively.

and the conversion rate between σ^+ and σ^- excitons, respectively. The exciton generation is approximated as $g_0(t) = g_0\delta(t)$, which is reasonable because the other time constants are much slower than the pump pulse duration. Then, Eqs. (1a) and (1b) are analytically solved as

$$n_+ = \tfrac{1}{2}g_0\{\exp(-\gamma_d t) + \exp[-(\gamma_d + 2\gamma_s)t]\}, \tag{2a}$$

$$n_- = \tfrac{1}{2}g_0\{\exp(-\gamma_d t) - \exp[(\gamma_d + 2\gamma_s)t]\}. \tag{2b}$$

In this model, any other higher states are neglected, because the pump photons resonantly generate the lowest excitons. Since the exciton Rydberg is far larger than the temperature ($k_B T \approx 1$ meV), the thermal dissociation of excitons to charge carriers and the excitation of higher exciton states are hardly expected. The excitation of the other excitons which belong to other electronic bands is also negligible, because the obtained spectra show no considerable spectral change on these excitons.

The exciton renormalization due to the exciton-exciton interaction is given as[29]

$$\langle i|\Delta H|i\rangle = \sum_j V_x(ijji)n_j + \frac{1}{2}\sum_{jkl}\frac{|V_x(lkji)|^2}{E_l + E_k - E_j - E_i + i\epsilon}n_j, \tag{3}$$

where indices (i-l) specify angular and translation momenta. n_j represents the exciton number in the j state. $V_x(ijkl)$ represents the effective interaction between two excitons. The effective interaction includes electron-electron, electron-hole, hole-hole Coulomb interactions and the effect of Pauli exclusion principle as $V_x(ijkl) \equiv \langle ij|(1-P_e)(1-P_h)v|kl\rangle$, where $P_{e/h}$ and v represent the exchange of electrons/holes and the Coulomb interaction, respectively. First and second terms on the right-hand side of Eq. (3) are called the Hartree-Fock (HF) term and the correlation term, respectively. Not only the HF term but also the real part of the correlation term contribute to the energy shift.

For examining the polarization dependence, we express the angular momentum dependence of the exciton-exciton interaction more explicitly. On the assumption that the there is no spatial correlation between excitons, shifts of σ^+ and σ^- excitons are represented, respectively, as

$$\Delta\omega_+ = I_{++}n_+ + I_{+-}n_-, \tag{4a}$$

$$\Delta\omega_- = I_{+-}n_+ + I_{++}n_-, \tag{4b}$$

in which contributions of the interactions between two $\sigma^{+(-)}$ excitons and that between σ^+ and σ^- excitons are denoted as I_{++} and I_{+-}, respectively. Not only the first term but also the real part of the second term of Eq. (3) are included in I_{++} and I_{+-}.

The exciton density is related to the experimentally observed induced absorption. Since an excitonic molecule can be generated by combining σ^+ and σ^- excitons, the induced absorption amplitudes observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ polarizations should be proportional to the density of σ^- and σ^+ excitons, respectively. Accordingly, induced absorption amplitudes observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ are related to the exciton concentrations as $\Delta\alpha_{m\pm} = \gamma_m n_{\mp}$, respectively, where γ_m represents the quantity which includes the dipole matrices.

Combining Eqs. (2), (4), and the above relation, the delay time dependences of both the exciton shift and the amplitude of the induced absorption are simultaneously fit, as are shown in Figs. 5 and 6 for PhE-PbI_4 and C6-PbI_4, respectively. Solid and dotted curves represent the best fits for data observed in $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$, respectively. For PhE-PbI_4, the fit is good except for the oscillation due to the coherent phonon excitation. For C6-PbI_4, the fit is uncertain at short delay time; because of the oscillation and the fast relaxation in the angular momentum space, the rise and the fast decay of the blueshift are not well resolved.

Obtained parameters are listed in Table I. The exciton decay rate is larger in PhE-PbI_4 than in C6-PbI_4. These values are slightly larger than that reported elsewhere,[39] but the difference might be related to the quality of samples via nonradiative decay channels. The relaxation rate ($2\gamma_s$) in the angular momentum space is larger in C6-PbI_4 than in PhE-PbI_4. One might also attribute this difference to the quality of samples, considering that the polycrystalline domain possibly makes angular momenta less defined. Yet, the relaxation in the angular momentum space here is more reasonably ascribed to the exciton-phonon scattering, considering that the obtained value for C6-PbI_4 is close to the dephasing rate measured by the degenerate four-wave-mixing experiment under the weak excitation regime.[40] Unfortunately, a four-wave-mixing experiment has not been performed for PhE-PbI_4. On the assumption that a phonon scattering makes an exciton relax in the angular momentum space, we have no concrete explanation for the larger dephasing rate in C6-PbI_4 than that in PhE-PbI_4. On the nature of exciton-exciton interaction, $I_{+-}/I_{++} = -0.05 \pm 0.05$ and 0.3 ± 0.2 are obtained for PhE-PbI_4 and C6-PbI_4, respectively. The errors are estimated from degrees of the fit near the time origin. Thus, it is only roughly concluded that the I_{+-}/I_{++} is zero or slightly negative for PhE-PbI$_4$, while that is positive with a considerable value for C6-PbI$_4$. The source of this difference is discussed in the next section.

B. Influence of dielectric confinement

The excitonic blueshift has been observed in conventional quantum wells,[27] as a manifestation of the two dimensionality of the exciton envelope and the density of states. It is understood that, while HF and correlation terms in Eqs. (3) are well balanced and thus cancel out each other in bulk materials, the correlation term loses its relative weight in the quantum wells.[29] Three factors influence on the shift. The first is the two dimensionality of the exciton envelope, which creates nonzero quadrupole moment. The second factor is the exciton Bohr radius: The effective exciton-exciton interaction is diminished for the smaller radius because positive and negative Coulomb interactions cancel each other out. The third factor is the dimensionality of the density of states: With a reduced density of states, the scattering between excitons is less frequent, i.e., the correlation term, which is known to always give *negative* contribution, become less important. According to Manzke *et al.*,[29] the relative weight between HF and correlation contributions to the blueshift is estimated to be 4:−1, respectively, for the infinitely thin GaAs-AlGaAs quantum well.

Also in the inorganic-organic layered semiconductors, the observed blueshifts are understood as results of the two dimensionality, because excitons are confined in an inorganic monolayer and the dispersion along the direction perpendicular to layers are negligible.[6] Blueshifts normalized by the exciton density (see Table I) are smaller by some orders in the two substances than that ($\approx 10^{-12}$ eV cm^2) reported for the GaAs quantum well.[26] This difference is understood as being mainly due to the large difference in exciton Bohr radii ($\sim$ several nm in the GaAs quantum wells).

In comparison between PhE-PbI$_4$ and C6-PbI$_4$, the main difference is in the dielectric constants of the organic parts. We can samely assume the two dimensionality for both substances in terms of the potential confinement. Because of the smaller dielectric constant of the organic part in C6-PbI$_4$ than in PhE-PbI$_4$, both of HF and correlation terms in Eq. (3) are expected to be larger in C6-PbI$_4$ than in PhE-PbI$_4$. Accordingly, the larger blueshift in C6-PbI$_4$ than in PhE-PbI$_4$ is explained with the stronger interaction in C6-PbI$_4$. For the same reason, the stronger bleaching in C6-PbI$_4$ than in PhE-PbI$_4$ is explained: The renormalization of the exciton wave function, which results in the decrease of the oscillator strength, is believed to be stronger in C6-PbI$_4$ than in PhE-PbI$_4$ due to the stronger interaction. Also, the imaginary part of the correlation term gives scattering-induced broadening, which results in the lowering of the peak intensity.

The dependence of the exciton-exciton interaction potential upon their angular momenta is also related to dielectric constants of the organic parts. Since Pauli exclusion principle restricts only the interaction between excitons with the same angular momentum, I_{+-} is free from, whereas I_{++} is restricted by the exclusion principle. Considering the nature of the Coulomb potential under the dielectric confinement,[9,10] the effective Coulomb potential is longer-ranged, i.e., more logarithmic,[10] in C6-PbI$_4$ than in PhE-PbI$_4$. This effective potential is understood in the following way: electrons experience a high dielectric constant of the well layer when they are very close, but a low dielectric constant of the barrier layers when they are separated by a large distance relative to the well width. On the other hand, the exclusion principle plays a role only when envelopes of two excitons are spatially overlapped. Therefore, it is qualitatively understood that the larger I_{+-}/I_{++} in C6-PbI$_4$ than in PhE-PbI$_4$ is brought about by the lower dielectric constant of the organic part in C6-PbI$_4$ than in PhE-PbI$_4$ with the increase of the long-range part of the interaction.

To I_{++} and I_{+-}, various sorts of interaction are considered to contribute. Because of the two-dimensional envelope of excitons, the quadrupole-quadrupole interaction is of the lowest order, which is always positive (repulsive). The induced dipole-dipole interaction is negative (attractive). The Heitler-London type short-range interaction is negative between σ^+ and σ^- excitons, and positive between two $\sigma^{+(-)}$ excitons. The last two types of interaction are considered with the renormalization of the exciton wave function and thus are higher-order effects for the shift. Thus, we interpret the difference in I_{+-}/I_{++} as that the quadrupole-quadrupole interaction is rather enhanced in C6-PbI$_4$ than in PhE-PbI$_4$ due to relatively stronger dielectric confinement. It might be noteworthy that the importance of the quadrupole-quadrupole interaction between well-separated excitons has also been shown for GaAs quantum wells.[41]

The relative weights of the blueshift and the bleaching can be explained with the balance between HF and correlation terms. Because HF and correlation terms are proportional to the first power and the second power of the interaction, respectively, the stronger interaction in C6-PbI$_4$ than in PhE-PbI$_4$ will result in the increase of the relative importance of the correlation term for C6-PbI$_4$. The increase of the imaginary part of the correlation term causes the scattering-induced broadening to lower the peak intensity.

It is noted that the slight difference in the exciton Bohr radius may give an opposite contribution as mentioned in Sec. I: the smaller Bohr radius in C6-PbI$_4$ may result in weaker interaction between excitons. However, we consider this difference as a minor factor. In fact, the estimated Bohr radii are different only within 10%,[14] although these estimates may depend on theoretical assumptions and used parameters.[15]

The quantitative differences (in factors of 5–10) observed in both the blueshift and the bleaching are far larger than those (in a factor of ≈ 1.4) expected simply from the difference in the dielectric constants of the organic parts. The authors would suggest a possibility to explain this disagreement.

The possibility is that the assumption of the uniform exciton generation is not valid due to the low crystallinity of the C6-PbI$_4$ film. The C6-PbI$_4$ film may be only partly crystallized, considering two contradicting facts. The one is that the exciton oscillator strength per formula unit in C6-PbI$_4$ is estimated to be about 1.4 times as large as that in PhE-PbI$_4$

from the exciton Rydbergs determined experimentally.[14] The other is that the spectrally integrated exciton absorption coefficient is stronger in the PhE-PbI$_4$ film than in the C6-PbI$_4$ film.[42] In order to accept these facts, it is a probable interpretation that the exciton transition in the C6-PbI$_4$ film is only contributed from a part of the total film volume, and thus excitons are generated in some smaller volume than the total film volume. Thus, the real local exciton concentration may be larger than that expected, and accordingly $\Delta\omega_x/n_x d$ and $\Delta\alpha_x/n_x d$ for C6-PbI$_4$ listed in Table I may be overestimated. To be convinced quantitatively, it might be necessary to perform measurements with single crystals.

In order to circumvent the problem of crystallinity, it is practical to normalize the observed quantities by amplitudes of the induced absorption due to the excitation of excitonic molecules, on the assumption that the oscillator strengths for exciting an exciton to an excitonic molecule are not sizably different between two substances. Both $\Delta\omega_x/\Delta\alpha_m$ and $\Delta\alpha_x/\Delta\alpha_m$, as listed in Table I, are larger in C6-PbI$_4$ than in PhE-PbI$_4$ by factors of 1.7 and 2.6, respectively. These factors are enough larger than the factor (1.4) for the difference in the exciton oscillator strength between two substances, which gives the approximate difference in the oscillator strength for generating an excitonic molecule.[43] Therefore, regardless of the crystallinity, it is a qualitative conclusion that both the bleaching and the blueshift are stronger in C6-PbI$_4$ than in PhE-PbI$_4$, which is ascribed to the dielectric confinement effect.

V. CONCLUSION

We have investigated the blueshift and the bleaching of excitons in PhE-PbI$_4$ and C6-PbI$_4$ with pump lights resonant with their excitons. The following results were obtained: (1) Both of the blueshift and the bleaching normalized by the exciton density are larger in C6-PbI$_4$ than in PhE-PbI$_4$; (2) Bleaching relative to the blueshift is more prominent in C6-PbI$_4$ than in PhE-PbI$_4$; (3) The ratio of the effective interaction between σ^+ and σ^- excitons to that between excitons with the same angular momentum, I_{+-}/I_{++}, is larger in C6-PbI$_4$ than in PhE-PbI$_4$. These results are qualitatively understood as consequences of the lower dielectric constant of the organic part in C6-PbI$_4$ than in PhE-PbI$_4$.

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[8] The importance of the dielectric confinement is seen in comparison between the three-dimensional perovskite, C1-PbI$_3$, and the two-dimensional perovskites. According to the theory of semiconductor quantum well which does not include the dielectric confinement effect, the exciton Rydberg in the *ideal* two-dimensional system is four times as large as that in the three-dimensional system (see Ref. 47). However, the exciton Rydberg in C1-PbI$_3$ is estimated to be 40 meV (see Refs. 45 and 46), while those in two-dimensional perovskites are 200–400 meV, depending on organic parts. Thus, exciton Rydbergs in the two-dimensional perovskites are 5–10 times as large as that in C1-Pb$_4$. This disagreement is ascribed to the dielectric confinement effect. For further details, see also Refs. 11,13–15.

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[33] Here, the dielectric constants are supposed to be at the transparent frequencies, well below the fundamental absorption edges. The dielectric constant of the inorganic part is assumed to be the same as that of the bulk $\mathrm{PbI_2}$, as postulated in Ref. 13. Those in organic parts are estimated from the total values including both inorganic and organic parts assuming that the total values are mean values weighted by thicknesses of inorganic and organic layers (see Ref. 13). We note, one may also adopt the value (6.5) (see Ref. 46) of C1-$\mathrm{PbI_3}$ as that for the inorganic part.

[34] The peak absorption coefficient of the well-matured PhE-$\mathrm{PbI_4}$ film is about three times as large as that just after the spin coating. This fact may be related to the mean size of polycrystalline domains in PhE-$\mathrm{PbI_4}$ films. Thus, in order to stabilize and maximize the exciton absorption, every spin coated PhE-$\mathrm{PbI_4}$ films were annealed at 50 °C for 30–50 h in the dry nitrogen circumstance after the spin coating. For C6-$\mathrm{PbI_4}$, such the annealing was not performed, because the annealing rather causes degradation to lower the peak absorption coefficient. This fact might be related to the possibility that not all the part of C6-$\mathrm{PbI_4}$ film is crystallized well.

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[43] The oscillator strength for exciting an exciton to an excitonic molecule in C6-$\mathrm{PbI_4}$ is estimated to be about 1.4 times that in PhE-$\mathrm{PbI_4}$, from three factors. The first is the exciton oscillator strength per unit cell. The second factor is the volume of a molecule. The volume is expected to be slightly larger in C6-$\mathrm{PbI_4}$, considering the slight difference in binding energies of molecules, while it is expected to be larger in PhE-$\mathrm{PbI_4}$, considering the higher dielectric constant of organic part. The third is the polaritonic effect examined in Ref. 21, which is expected to be slightly stronger in C6-$\mathrm{PbI_4}$, due to the larger exciton oscillator strength. But, the last two factors are considered to be minor.

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