Ultrafast photomodulation spectroscopy of π -conjugated polymers, nanotubes and organometaltrihalide perovskites; a comparison

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Abstract:

We compare the ultrafast dynamics of the primary photoexcitations in various π -conjugated organic semiconductors, semiconducting single-walled carbon nanotubes (S-NTs) and organometaltrihalide perovskites including $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) and $\text{CH}_3\text{NH}_3\text{PbI}_{1.1}\text{Br}_{1.9}$ ($\text{MAPbI}_{1.1}\text{Br}_{1.9}$), using broadband pump-probe photomodulationspectroscopy in the spectral range of 0.2-2.7 eV with 300 fs time resolution. The primary photoexcitations in single polymer chains and isolated S-NTs have been found to be quasi-one-dimensional (q-1D) excitons, with characteristic photoinduced absorption (PA) band due to intra-band transitions. This conclusion is in agreement with the large exciton binding energy, E_b in polymers and S-NTs (where $E_b > 200$ meV), illustrating the universal optical characteristic features of q-1D excitons. In three dimensional (3D) semiconductors of organometaltrihalide perovskites such as MAPbI_3 we found that with above-gap excitation both photo-carriers and excitons are photogenerated; but only photocarriers are photogenerated with below-gap excitation. In contrast, mainly excitons are photogenerated in $\text{MAPbI}_{1.1}\text{Br}_{1.9}$. The contrast between MAPbI_3 and $\text{MAPbI}_{1.1}\text{Br}_{1.9}$ is ascribed to the difference of E_b , which is ~ 20 meV and ~ 110 meV, respectively. Our work shows that E_b is one of the crucial parameters that determine the

photophysics characteristic of semiconductors, that result in universal occurrence of an excitonPA band, regardless if the compound is 1D carbon based π -conjugated semiconductors, NTs, or 3D crystalline perovskite semiconductors. At the same time, our work also shows that the broadband ultrafast photomodulation spectroscopy is a powerful tool in analyzing the photophysics of semiconductors, and emphasizes the need for a broad probe spectral range in order to decipher the primary photoexcitation species.

1. Introduction

In solid-state physics the density of states (DOS) of a system describes the number of states per energy interval at a particular energy, E [1]. In a typical three dimensional (3D) inorganic semiconductor such as Gallium Arsenide (GaAs), the $DOS(E)$ function is proportional to the square root of the energy ($\sim E^{1/2}$) [2]. Optical excitation of semiconductors causes electron transitions from the valence band (VB) into the conduction band (CB), leaving behind a positively charged “hole” in VB. The description of a single electron-hole (e-h) pair in GaAs-like semiconductors has been borrowed from the ‘Bohr Hydrogen atom’ model, because the attractive Coulomb interaction between the electron and hole may be regarded as analog of the electron and proton in the Hydrogen atom. Such an e-h pair was dubbed Wannier exciton [2, 3]. However because of the smaller effective mass of the electrons and holes in 3D semiconductors compared to the electron and proton in Hydrogen atom, as well as the large background dielectric constant that reduces the Coulomb interaction, the exciton binding energy, E_b is typically in the range of a few meV. Thus the absorption band due to exciton can only be clearly observed at low temperature, where $k_B T < E_b$ [3].

In contrast the typical feature for quasi one-dimensional (q-1D) semiconductors is their $DOS(E)$ that is proportional to $E^{-1/2}$. Therefore unlike the DOS in 3D compounds, the peaks found in the DOS of q-1D materials are quite sharp, as shown in Fig 1(c) [4]. Strictly 1D materials, however may not be easy to find, because the competing 3D interaction. The π -conjugated polymers (PCP) as well as semiconducting single walled carbon nanotubes (S-NT) are considered to be q-1D semiconductors [5], because there is a small but not negligible interchain (or inter-tube) interaction. Both compounds have been proven to have strong exciton effect, because of the large exciton binding energy, E_b . Consequently most of the π - π^* oscillation strength goes to the exciton transition [6]. Under these conditions the absorption spectrum changes from a sharp singularity at the band edge to a symmetric shape [see Fig. 1(d)].

Two kinds of primary photoexcitation species should exist following photon absorption of a semiconductor. One species is photocarriers, which are typical in common inorganic semiconductors such as Si and GaAs. The photocarriers do not show structured photoinduced absorption (PA) bands in the mid-IR spectral range. Instead their optical signature is free carrier absorption (FCA), which is described by the Drude model. The FCA may be written as: $FCA \sim N/[1+(\omega\tau_s)^2]$ [1], where N is the photocarriers density, ω is the photon frequency, and τ_s is the momentum scattering time. Thus the FCA contribution is limited to ω in the spectral range $\omega\tau_s < 1$ (see Fig. 1(f)). For high mobility semiconductors such as GaAs and Si, strong FCA spectrum occurs in the THz range since τ_s is of the order ~ 1 ps. From the hole mobility, μ obtained in crystalline perovskites ($\mu \sim 100$ cm²/Vs) [7] we deduce $\tau_s \sim 10$ fs in these compounds, and consequently the FCA spectrum would be relevant in the spectral range of few tens of meV in these materials.

The second type of photoexcitation species in semiconductors are excitons. This species may have PA bands in the mid-IR spectral range that originate from intersub-band or/and interband transitions (Fig. 1(f)), as in semiconducting nanotubes [8] and π -conjugated polymers [9]; or transitions into the continuum band at energies that correspond to high DOS as in amorphous semiconductors [10]. The different PA bands for carriers and excitons may be thus used to separate their contributions in the PA spectrum and consequently thoroughly study their characteristic properties [8-15]; however, one needs to apply *broadband probe spectroscopy* in order to access their separate PA bands.

In this work we review our studies of ultrafast photoexcitations dynamics in various π -conjugated organic semiconductors, semiconducting single-walled carbon nanotubes (S-NTs) and organometal trihalide perovskites including CH₃NH₃PbI₃ (MAPbI₃) and CH₃NH₃PbI_{1.1}Br_{1.9} (MAPbI_{1.1}Br_{1.9}), using broadband pump-probe spectroscopy in the spectral range of 0.13-2.7 eV with 300 fs time resolution. We show that excitons are the primary photoexcitations in single polymer chains and in

isolated S-NTs, where the PA band due to excitonic transition is prominent in the PM spectra. In 3D organometal trihalide perovskites, we demonstrate the existence of *exciton/carrier duality* response. With above-gap pulse excitation we found in MAPbI₃ instantaneously generated carriers *and* excitons, but only carriers are photogenerated when excited below the gap (i.e. into the film's Urbach absorption tail). In MAPbI_{1.1}Br_{1.9}, however we detected mainly photogenerated excitons. Our results show that broadband ultrafast optical probe is *crucial* for revealing the characteristic perovskites photophysics properties, because photogenerated carriers and excitons in these materials contribute in different spectral ranges.

2. Experimental

For measuring the transient photoexcitation response in the sub-pstons time domain, we have used the broadband femtosecond pump-probe correlation technique. Two laser systems have been used; a high repetition rate, low power laser for the mid-IR spectral range [8]; and a high power low repetition rate laser system for the near-IR/visible spectral range [16].

The low power high repetition rate laser system is based on a Ti-sapphire 100 femtosecond oscillator operating at 80 MHz repetition rate (Tsunami, Spectral Physics). The pump beam was the second harmonic of the fundamental at 3.1 eV with energy/pulse of about 0.1 nJ. With this low intensity system that generates low-density photoexcitations, we have diminished the problem of exciton-exciton annihilation and processes based on two-photon-absorption. Sometimes we also used a pump beam from the fundamental at 1.55 eV. The probe beam spectrum was extended using an Optical Parameter Oscillator (OPO) (Opal, Spectral Physics) that covers the spectral range from 0.5 eV to 1 eV. To further extend the probe spectral range from 0.15 eV to 0.42 eV, the signal and idler beams of OPO have been made collinear and focused with a single lens onto a nonlinear crystal (AgGaS₂) to generate difference frequency; this configuration was used because of the higher efficiency and controllable output beam direction. Two suitable filters were used in the

measurements; one filter was placed before the sample to eliminate unwanted probe beam; the other filter was placed before the detector to eliminate scattered pump light. In the PM measurements we monitored the probe beam transmission that is modulated by the pump beam, where the time delay of the probe pulses are delayed vs. the pump pulses using a mechanically-controlled translation stage (1 ps = 300 μ m delay). In order to increase the signal/noise ratio, an acoustic-optical modulator (AOM) operating at 40 kHz was used to modulate the pump beam intensity. For our measurements, we used a nitrogen cooled Germanium (Ge) detector in the spectral range from 0.8 μ m to 1.8 μ m; and a nitrogen cooled Indium Antimonite (InSb) detector in the spectral range from 1 μ m to 5.5 μ m. For the spectral range from 5.5 μ m to 9.5 μ m, liquid N₂ cooled Mercury Cadmium Telluride (MCT) detectors were used.

For the near-IR/visible spectral range we used a high intensity laser system [16]. This laser system was based on a home-made Ti:sapphire regenerative amplifier that provides pulses of 100 fs duration at photon energy of 1.55 eV, with 400 μ J energy per pulse at a repetition rate of 1kHz. The second harmonic of the fundamental pulses at 3.1 eV was used as the pump beam. The probe beam was a white light super-continuum within the spectral range from 1.1 to 2.8 eV, which was generated using a portion of the Ti:sapphire amplifier output focused onto a 1-mm-thick sapphire plate. To improve the signal-to-noise ratio in our measurements, the pump beam was synchronously modulated by a mechanical chopper at exactly half the repetition rate of the Ti:sapphire laser system ($\cong$ 500 Hz). The probe beam was mechanically delayed with respect to the pump beam using a computerized translation stage in the time interval, t up to 2 ns.

The scheme of the PM experiments is the following: the sample is photoexcited with light pulses, and the changes in the optical absorption of the sample are probed in a broad spectral range from the mid-IR to visible spectra range. The PM spectrum is essentially a difference spectrum, i.e., the difference in the optical absorption ($\Delta\alpha$)

spectrum of the polymer when it contains a non-equilibrium photoexcitation species and that in the equilibrium ground state. Therefore the optical transitions of the various photoexcitations are revealed in the experiment. Transient photomodulation (PM) gives information complementary to that obtained by transient photoluminescence (PL), which is limited to radiative processes, or transient photoconductivity (PC), which is sensitive to high mobility photocarriers. The PM method, in contrast, is sensitive to non-equilibrium excitations that reside *all* states.

To achieve a transparent solid sample in the broadest spectrum possible that contains isolated nanotubes 0.005% HiPCOproduced SWCNTs were mixed with 0.610% sodium dodecyl sulfate (SDS) surfactant and 0.865% polyvinyl alcohol (PVA) in deionized water. Sonication for an hour before sample preparation resulted in relatively well-separated nanotubes. We then deposited a film of the solution onto CaF_2 by drop-casting at 80°C . The film consisted of mostly separated SWCNTs (with some bundling) embedded in an insulating matrix of PVA. Neither PVA nor SDS has absorption bands in the spectral range over which we measured the absorption and transient PM spectra. Resonant Raman scattering of the radial breathing mode was used to determine that the nanotubes in our sample have a diameter distribution around the mean diameter of ~ 0.8 nm, and contain about 1/3 metallic and 2/3 semiconducting SWCNTs [17].

The semiconducting π -conjugated polymers used in our studies included: (i) a polypara-phenylenevinylene (PPV) derivative: dioctyloxyPPV (namely DOO-PPV) that was synthesized in our laboratory [18]; (ii) a low band gap copolymer PTB7 $((\text{C}_{41}\text{H}_{53}\text{FO}_4\text{S}_4)_n)$ that was synthesized by researchers at the University of Chicago [19]; and (iii) 2-methoxy-5-2'-ethylhexyloxy PPV (MEH-PPV) that was purchased from ADS Inc. and used as received.

For the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films we mixed 159 mg $\text{CH}_3\text{NH}_3\text{I}$ and 461 mg PbI_2 (at mole ratio of 1:1) in anhydrous N,N-Dimethylformamide (DMF, 1.2 mL) solution, and stir it

overnight at 60°C. For the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films, $\text{CH}_3\text{NH}_3\text{Br}$ (112 mg) and PbBr_2 (367 mg) were dissolved in 2 mL DMF, and stirred overnight at room temperature. The obtained solution was then spin-coated on O_2 plasma treated sapphire substrate at 2000 RPM, and annealed at 100°C for 30 minutes. Finally, a uniform layer of $\text{CH}_3\text{NH}_3\text{PbI}(\text{Br})_3$ was obtained for the optical measurements. All processes were performed in a glovebox filled with nitrogen (O_2 and $\text{H}_2\text{O} < 1$ ppm).

3. Results and discussions

3.1 Ultrafast Spectroscopy of Excitons in carbon-based π -conjugated systems

π -conjugated polymers (PCPs) are characterized by the delocalization of π -electrons along the polymer backbone. PCPs have shown potential applications as the active layers in organic light-emitting diodes (OLEDs) [20-22], thin-film transistors [23, 24], organic photovoltaic (PV) solar cells [25, 26], and organic spin-valve devices [27, 28]. Therefore the properties of the photoexcitations in PCPs have attracted immense interest in order to achieve fundamental understanding of their characteristic properties, which are essential for designing better organic optoelectronic devices [29, 30].

Upon photon absorption in PCP an electron and hole pair with opposite spins are created. It is expected that the electron and hole would be tightly bound by their Coulomb attraction in a singlet exciton state. An important question is the binding energy (E_B) of the exciton. At present it is generally accepted that E_B in PCP is of the order of 0.5 eV [16, 17, 31], which is much larger than $k_B T$ at room temperature (~ 26 meV, k_B is the Boltzmann constant and T is the ambient temperature), as well as the most coupled vibration of ~ 0.2 eV [32-34]. It is worth noting, however that nevertheless the nature of photoexcitations in PCPs has been extensively debated for more than two decades [29, 30]. For example, E_B in PPV has been estimated to span a wide range: $E_B \sim k_B T$ (as inferred from nanosecond photoconductivity data) [35-36] to $E_B \sim 1$ eV based on analysis of the optical absorption spectra [31, 37].

Because of the large exciton binding energy in PCP, the 1D Van Hove singularities at the band edges do not show up in the absorption spectrum, and do not play a major role in determining the PL spectrum in these materials, since most of the oscillation strength in the interband transition are taken by the excitons [6]. Therefore an exciton is immediately generated following photon absorption, and consequently dominates feature in absorption and PL spectra. A typical transient PM spectrum measured in DOO-PPV film cast from Toluene solution at $t=0$ ps following photon absorption is shown in Fig. 2(a) [9]. In addition the absorption and PL spectra are both due to the singlet exciton transitions, as also shown in Fig. 2(a). Two prominent features are observed in the PM spectrum, namely PA_1 , and SE. The PA band was interpreted as transitions from the lowest excitonic state (E_1) to another excitonic state (E_2) at higher energies that is most strongly coupled to the lowest energy exciton, as shown in Fig. 1(f). SE is the ‘stimulated emission’ from the exciton, which shows the same spectral features as those of the PL spectrum (Fig. 2(a) inset). Fig. 2(b) compares the dynamics of PA_1 and SE; as is clearly seen they are identical and this is a strong evidence for our interpretation. It is known that DOO-PPV films have mainly isolated polymer chains that result in weak interchain interaction [38]. Frolov et al. [38, 39, 40] profoundly discussed the exciton photoexcitations in this polymer. We show here more clearly the lack of polaron bands and photoinduced infrared active vibrations (IRAV) modes [9] in transient PM spectra, which is in agreement with our interpretation that the neutral primary photoexcitations in DOO-PPV are strongly bound quasi-1D excitons.

Exciton-related PA bands (PA_1) were also observed in the mid-IR spectral range in three different π -conjugated semiconductors: (a) another PPV derivative, namely MEH-PPV solution (Fig. 3(a)) [9]; (b) low band gap copolymers, namely PTB7 (Fig. 3(b)) [19]; and (c) semiconducting carbon nanotubes film (Fig. 3(c)) [17]. In all of these materials $E_B > 200$ meV and therefore the primary photoexcitations are excitons that show strong optical transitions in both linear absorption and nonlinear transient PM spectroscopy.

In addition diverse PCPs have been introduced in the last three decades. In general the PCPs fall in one of two categories [41]; polymers having degenerate ground state (DGS) represented by trans-polyacetylene $[t-(CH)_x]$, and polymers having non-degenerate ground state (NDGS) such as polyfluorene (PFO). An alternative way to categorize these materials is related with their photoluminescence (PL) quantum efficiency (PLQE) [42, 43]; where polymers with high PLQE have been used as active materials for OLED applications. We have measured ultrafast dynamics of the primary photoexcitations in four typical polymers that represent both degenerate and non-degenerate ground state polymers. This includes trans-polyacetylene (DGS, low intrinsic PL efficiency) [44], polyfluorene (NDGS, high PL efficiency) [16], DPA (DGS, high PL efficiency) [45], and regio-random poly (thienylene-vinylene) (NDGS, low intrinsic PL efficiency) [46]. In all of these polymers, the exciton is the primary photoexcitation when the laser excitation photon energy is close to the absorption onset of polymers; in all cases an excitonic transition such as PA_1 is observed in the transient PM spectroscopy, having different dynamics.

3.2 Ultrafast Spectroscopy of Photoexcitations in Organometal Trihalide Perovskites

The photovoltaic (PV) solar cells based on the semiconductors methyl-ammonium (CH_3NH_3 ; MA) lead halide perovskites, $MAPbX_3$ (where X stands for halogen) have recently (and quite rapidly) emerged as one of the most promising class of contenders, with extraordinary power conversion efficiencies [47]. From 2009 to 2015, the efficiency of perovskite solar cells has increased from 3.8% to more than 20% [48-52]. In addition the hybrid perovskites have found other promising applications such as light emitting diodes [53], lasers [54], and field effect transistors [55]. The inorganic perovskite counterparts (ABX_3) have been extensively studied in the past 40 years. However, the replacement of the inorganic cation (A) by an isoelectronic organic moiety such as MA^+ provides a unique way of tuning the chemical bonding, and consequently also the optical and electronic response of these materials which are very different from those of the inorganic perovskites [56]. In particular, the exciton binding energy, E_B of typical hybrid perovskites such as $MAPbI_3$ and $MAPbBr_3$ has

been reported to be in the range of 10-150 meV [57-61]; of the order of the thermal energy at room temperature, RT ($k_B T = 26$ meV at $T = 300$ K). This is very different than conventional inorganic semiconductors, where for typical Wannier excitons $E_B \ll k_B T$ at RT, and consequently the role of excitons in conventional PV solar cells devices is trivial. Therefore the class of 3D hybrid perovskites is an ideal system for studying Wannier-type excitons, and perhaps also RT 'excitonic solar cell' [62, 63] without the complication of quantum confinement effect in other excitonic solar cell candidates, such as quantum dots and PCP. However this intermediate E_B value bears upon one of the fundamental questions of the perovskite photophysics, namely the branching ratio between the initial photogeneration of free carriers and excitons, which still remains unclear. Moreover a firm method to optically discern between these two kinds of photoexcitation species is also lacking. In addition, whether the PL in the perovskites occurs via direct photocarriers recombination, or is preceded by exciton formation, in particular at high pump intensity, is still debated [63, 64].

Fig. 4(a) shows the unit cell structure of the perovskite $\text{CH}_3\text{NHPbI}_3$, (MAPbI_3) where Iodine could be replaced by Chlorine (MAPbCl_3), Bromine (MAPbBr_3) or their mixtures ($\text{MAPbI}_{3-x}\text{Cl}_x$, $\text{MAPbI}_{3-x}\text{Br}_x$, or $\text{MAPbCl}_{3-x}\text{Br}_x$). The rest of Fig. 4 summarizes the ps transient PM spectroscopy results of MAPbI_3 film with above-gap excitation (~ 3.1 eV) at RT. At $t=0$ the PM spectrum contains three main spectral features (Fig. 4(b)). In the visible/near-IR range there is a large photo-bleaching, PB band at ~ 1.65 eV (PM_1), which is correlated with a neighboring PA band (PM_2) that extends to higher energies. PB and PA_2 bands have been recently observed in the ps and nanosecond time domains, as well as in continuous wave (cw) PM spectroscopy [11, 12, 65, 66]. Although the origin of these bands is still under debate, it has been widely accepted that PM_1 is due to PB caused by band-filling effect of the photocarriers [11, 12, 65, 66, 67]; the origin of PM_2 is still unknown. However, whether excitons may also cause the PM_1 - PM_2 spectral feature is unknown at the present time [11, 12, 67]. We have recently proposed an alternative explanation for

these two correlated bands, and other similar bands at energies above these two bands.

It is known from band structure calculation which includes e-h interaction, that there are two types of excitons in the perovskites, namely optically allowed excitons (having irreducible representation, IRR; Γ_4) and optically forbidden exciton (IRR; Γ_1) from the ground state (IRR; Γ_1); which are very close in energy [59] (E_1 in Fig. 4(b) inset). The pump excitation is not absorbed homogeneously in the film (especially true for the perovskites having large absorption coefficient (α), and thus it generates photoexcitations density that varies with z away from the film's surface, in the form of $\exp(-z/z_0)$, where z_0 is the pump laser penetration depth ($z_0 \sim 1/\alpha_L$ at the laser frequency). These photoexcitations create strain in the film due to the change in the deformation potential between the ground and excited states, which also varies with z following the same exponential form as that of the absorbed laser intensity. In turn, the photoinduced static strain associated with the photoexcitations, being spatially inhomogeneous, breaks the inversion symmetry in the illuminated sample, in the same way as an applied electric field [68], causing a PM spectrum that is similar to the electro-absorption in these materials, and hence the PM features close to the band edge.

The third feature in the transient PM spectrum of MAPbI₃ is a new PA band in the mid-IR range that peaks at ~0.8 eV (PA₁; Fig. 4(b)). PA₁ decay dynamics is shown in Fig. 4(c) in comparison to the decay dynamics of PM₁ in Fig. 4(d) at comparable pump intensity. It is clearly seen that the decay dynamics are very different for the PA₁ and PM₁ bands, indicating that they originate from two different photoexcitation species. We also see (Fig. 4(d)) a delay of ~1 ps at the onset of PB(t) transient, which is not seen in PA₁(t) dynamics. We therefore conclude that PA₁ is generated instantaneously within our time resolution (~ 300 fs), whereas PM₁ generation is delayed. Therefore PA₁ and PB originate from two different species, suggesting the coexistence of two types of primary photoexcitations in this perovskite.

Being a band-like transition, PA_1 cannot be explained as due to FCA of thermalized photocarriers since such spectrum does not contain a pronounced band (see Fig. 1b). In addition, the FCA of carriers in the perovskites should be mostly pronounced for probe energies below ~ 60 meV, which is outside the probe spectral range here. We therefore assign PA_1 as due to photogenerated excitons; *similar to the PA_1 band in the PM of PCP and SNT*. There are two clear exciton transitions in MAPbI₃ absorption spectrum, namely E_1 at 1.66 eV and E_2 at 2.48 eV (Fig. 4(b) inset) [59]. These two transitions are separated by ~ 0.8 eV that is the same as PA_1 peak, which strongly indicates that PA_1 may be an optical transition from the excitons at E_1 to E_2 , similar as for transient PA between two adjacent bands in nanotubes [8, 69] (Fig. 4(c)). In fact from band structure calculation that includes e-h interaction [59] the allowed high-energy exciton (IRR; Γ_4) is accompanied by a close forbidden exciton (IRR: Γ_3 and Γ_5) of which transitions from the lower lying exciton (IRR; Γ_4) are indeed allowed.

PA_1 appears to be instantaneously generated within the time resolution of the experiment (300 fs). This shows that the exciton excess energy thermalization rate, $R = \Delta E / \Delta t$ in the perovskite is large. The largest possible thermalization rate is: $R_{\max} = \hbar \nu^2$, where ν is the phonon frequency averaged over the phonon DOS in the material [70]. Since the hybrid perovskites also contain an organic moiety, namely the MA molecule, the available vibration frequencies may reach ~ 1500 cm⁻¹ (C-N stretching vibration) and even ~ 3200 cm⁻¹ (C-H and N-H stretching vibrations) [71]. If we take the average available phonon frequencies in the organic molecule at 2350 cm⁻¹, then $R_{\max}$ in perovskites may thus be as large as ~ 20 eV/ps, which is similar to that in PCP. The excess energy, ΔE of excitons due to the pump excitation at 3.1 eV is ~ 1.5 eV; thus the exciton thermalization time, $\tau = \Delta E / R_{\max} \approx 75$ fs. This is below our experimental time resolution that explains the instantaneous response of PA_1 .

It is interesting to compare the exciton thermalization time to that of photocarriers

which is revealed via PB formation time (Fig. 2(c)). Photocarriers first form hot charge plasma by e-e collision, which occurs much faster than their thermalization time. Subsequently the generated hot plasma cools to the lattice temperature by emitting LO phonons via the relatively weak Froehlich interaction [72]. This usually takes few ps time that is in agreement with PM_1 formation time (Fig. 4(d) inset). We thus conclude that the different thermalization times of excitons and photocarriers fit well the formation times of PA_1 and PM_1 , respectively and this unravels the photoexcitations duality of the perovskites.

Fig.4(c) (lower panel) shows that PA_1 decays as a power law, $(t/t_0)^{-\alpha}$, where $\alpha \sim 0.21$. This explains the relatively fast decay of PA_1 seen in the first few ps (Fig. 4(d)); this is a part of the power law decay, rather than photocarriers thermalization [12]. This non-exponential PA_1 decay may originate either from dispersive transport type process [73], where the exciton diffusion towards recombination centers is time dependent [74], or is due to a distribution $g(\tau)$ of lifetimes, τ having a tail towards longer lifetimes of the form $\tau^{-(1+\alpha)}$ with $\alpha \sim 0.21$ [75].

As a consequence of our PA_1 assignment as due to excitons, and based on the different decay dynamics of PA_1 and PM_1 , we thus assigned PM_1/PM_2 feature as due to symmetry breaking caused mainly by photogenerated free carriers in $MAPbI_3$. This assignment does not mean that the optical feature of PM_1/PM_2 is a signature of free carriers per se, since photogenerated excitons may also produce an optical modulation at the absorption edge (see below), based on the same process as that of free photocarriers, namely photoinduced spatially inhomogeneous strain. We thus conclude that the derivative-like feature at the band-edge may be produced by a symmetry breaking process, in addition to photo-bleaching caused by phase space filling [76, 77].

In Fig.5 we show the transient PM spectrum of $MAPbI_3$ with below-gap excitation, at $\omega_{pump} = 1.55$ eV, i.e. into the film's exponential Urbach edge [78]. One of the two

possibilities for the pump excitation in this case is an optical transition from the VB edge to the CB tail inside the gap, as schematically shown in Fig. 6(c) (the other possibility is VB tail to the CB edge). Under these conditions exciton photogeneration is impossible, since $\omega_{\text{pump}} < E_1 \sim 1.68$ eV. Indeed no PA band in the mid-IR is observed (Fig. 6(a)), and this justifies our assignment of PA₁ band as due to excitons. In contrast, the PM₁/PM₂ feature at the band edge is still clearly seen, and the overall PM spectrum shows the same dynamics across the entire measured spectral range (see Fig. 6(b) for the decay dynamics at 0.4 eV and 1.63 eV). This is consistent with our interpretation that the PM₁/PM₂ feature in MAPbI₃ is due to photogenerated carriers, since excitons are simply not generated here.

We extended our transient spectroscopy measurements to a mixed perovskite film, namely MAPbI_{3-x}Br_x. The MAPbI_{3-x}Br_x system might be important for tandem solar cells, because its optical gap can be tuned from 1.57 eV to 2.3 eV when the composition parameter, x changes from x=0 to 3. From the absorption edge of this film at ~ 2.1 eV (Fig. 6(a) inset), we estimate $x=1.9$ [79]. In this case we cannot excite the perovskite film with below-gap pump excitation at 1.55 eV, because the absorption Urbach tail of this film does not extend to such low energy. Fig. 6(a) presents the transient PM spectrum of the MAPbI_{1.1}Br_{1.9} film at $t = 0$ ps when exciting at 3.1 eV. Similar to the PM spectrum of MAPbI₃ shown in Fig. 4(a), the PM spectrum here also contains three features: PA₁ at ~ 0.5 eV, and PM₁ and PM₂ at ~ 2.1 eV and 2.3 eV, respectively. We attribute PA₁ to exciton transition between adjacent bands (interband), similar to the analysis of this PA band in MAPbI₃. PA₁ decay dynamics measured at 0.41 eV (broken line) plotted with false colors (lower panel) were shown in Fig. 6(b). The line through the data points in the upper panel is a fit using a single exponential decay with a lifetime $\tau=100$ ps. From the absorption spectrum (Fig. 6(a) inset) we identify two exciton transitions, E₁ at 2.1 eV and a broader transition, E₂ with a shoulder at 2.7 eV. Thus there is a possible interband exciton transition from E₁ to E₂ at similar energy as PA₁ in this perovskite. In contrast to MAPbI₃, however the dynamics of the PM bands up to 500 ps are the same

as that of PA_1 ; this also includes their formation dynamics near $t \sim 0$ (Fig. 6(c)). This shows that excitons also may induce symmetry breaking in the film via photoinduced static strain (same as photocarriers in MAPbI_3 discussed above), and generate PB due to phase space filling which modulate the film absorption edge in the form of the PM_1/PM_2 optical feature. We conclude that *excitons* are the primary photoexcitations in $\text{MAPbI}_{1.1}\text{Br}_{1.9}$; consistent with the larger exciton binding energy of this perovskite, which we estimate to be ~ 110 meV [80]. This is much larger than $k_B T$ at RT, thus preventing dissociation of excitons to free carriers in this perovskite in the ps time domain.

4. Conclusions

In this work we review and compare the studies of ultrafast photoexcitations in π -conjugated polymers and organic lead halide perovskites. Our work shows the universal existence of excitonic transitions in π -conjugated polymers as well as in perovskite in near IR and mid-IR spectra range. We conclude that the broadband ultrafast photomodulation spectroscopy is a powerful tool in analyzing the photophysics in semiconductor materials.

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Fig. 1. (a): The density of states (DOS) of typical inorganic three dimensional semiconductor such as GaAs. Without the ‘exciton effect’, the DOS increases as a square root of energy. (b) The DOS including the ‘exciton effect’. The exciton is Hydrogen atom like, where the binding energy, E_B is few meV. Since E_B is small compared to $k_B T$ at room temperature, its absorption feature can be clearly seen at low temperatures. (c) Typical DOS in one dimensional materials. VHS: Van Hove singularity. (d) DOS of quasi 1D systems such as PCP and SWNT with strong ‘exciton effect’. Here the 1D Van Hove singularity is negligibly small, since most of the interband transition oscillation strength go to the exciton. (e) and (f): Schematic presentation of typical photoinduced absorption (PA) bands in semiconductors for free carriers and excitons, respectively. The free carrier absorption (FCA) process is described by the Drude free carrier model. The exciton PA is due to a transition from the lowest-lying exciton state (E_1) to higher lying exciton state (E_2). GS: ground state.

Fig. 2. The transient PM spectrum of DOO-PPV at $t = 0$ ps (a) and dynamics at various probe energies (b). PA_1 and SE are assigned in (a). (Adapted from ref. 5).

Fig. 3. Exciton-related PA bands in the mid-IR spectral range in three different quasi-1D semiconductors: (a) dilute solution of π -conjugated polymer, namely MEH-PPV [9]; (b) thin film of π -conjugated copolymer, namely PTB7 [19]; and (c) carbon nanotubes film [8]. These PA bands are due to photogenerated excitons.

Fig. 4.(a)The unit cell structure of the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, where Iodine could be replaced by Cl or Br or their mixture. (b) Transient PM spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ measured at $t = 0$; various bands are assigned. The inset shows the film absorption spectrum, where two excitons, E_1 and E_2 and the interband PA_1 transition between them are assigned. (c) PA_1 decay dynamics plotted with false colors (upper panel) and at 0.6 eV on double logarithmic scale (lower panel) measured at 0.6 eV (the broken line in the upper panel). The line through the data points is a power law fitting $(t/t_0)^{-\alpha}$, with $\alpha = 0.21$. (d) and its inset: Decay dynamics of PB and PA_1 bands up to 500 ps and 10 ps, respectively, respectively. The red line through the data points are fitting using the power law decay described in (c).

Fig. 5.(a), PM spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ excited with below-gap pump at 1.55 eV at $t = 0$ ps; various bands are assigned. (b) Decay dynamics of PM₁ band at 1.63 eV and PB at 0.4 eV up to 500 ps. (c) Schematic energy diagram that explains the process of photogenerated free holes with below-gap excitation into the perovskite Urbach edge.

Fig.6.(a) PM spectrum of $\text{MAPbI}_{1.1}\text{Br}_{1.9}$ at $t=0$, where various bands are assigned. The inset shows the film absorption spectrum, where two excitons, E_1 and E_2 and the interband PA_1 transition between them are assigned. (b), PA_1 decay dynamics measured at 0.41 eV (broken line) plotted with false colors (lower panel), and on double logarithmic scale (upper panel). The line through the data points in the upper panel is a fit using a single exponential decay with a lifetime $\tau=100$ ps.(c), Decay dynamics of PM_1 and PA_1 bands up to 15 ps (inset) and 500 ps. The similar dynamics points to a common underlying photoexcitation species that we identify as due to excitons.