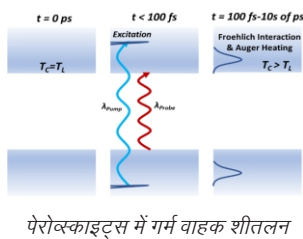# तप्त आवेश वाहक गतिशीलता

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हैलाइड पेरोव्स्काइट्स में तप्त वाहकों और हम फेमटोसेकंड क्षणिक अवशोषण स्पेक्ट्रमिकी के साथ उनका अनुसरण कैसे करते हैं?

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पेरोव्स्काइट्स में गर्म वाहक शीतलन

ABSTRACT

पेरोव्स्काइट्स के अद्वितीय गतिकी गुणधर्मों में से एक धीमी गति से तप्त वाहक का ठंडा होना है। वर्तमान लेख में, हमने चर्चा की है कि तप्त वाहक क्या है? और फेमटोसेकंड क्षणिक अवशोषण स्पेक्ट्रमिकी का उपयोग करके इस घटना का अध्ययन हम कैसे कर सकते हैं, को दर्शाया है। इसके अतिरिक्त हमने, तप्त वाहकों के ठंडा होने में शामिल तंत्रों और शीतलन गतिकी को नियंत्रित करने वाले कारकों पर चर्चा की है। हमने इसे लीड हैलाइड पेरोव्स्काइट्स कहे जाने वाले पदार्थ वर्ग के शीतलन को तप्त वाहकों के उदाहरण के साथ भी स्पष्ट किया है।

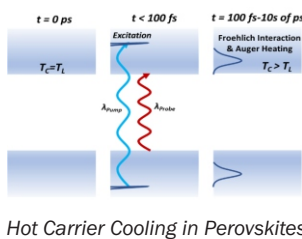मुख्य शब्द : *क्षणिक अवशोषण , नैनोकण , तप्त वाहक , पेरोव्स्काइट्स।*

Hot Charge Carrier Dynamics

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Hot Carriers in Halide Perovskites & How do we follow them with Femtosecond Transient Absorption Spectroscopy?

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Hot Carrier Cooling in Perovskites

ABSTRACT

One of the unique dynamics properties of perovskites is slow hot carrier cooling. In the present article, we discuss, what hot carriers are? and show how we can study this phenomenon using femtosecond transient absorption spectroscopy. We additionally discuss the mechanisms involved in cooling of hot carriers and factors governing the cooling dynamics. We also illustrate this with example of hot carriers cooling from class of materials called lead halide perovskites.

KEYWORDS: *Transient Absorption, Nanoparticle, Hot Carriers, Perovskites*

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Introduction

Lead Halide perovskites have shown immense potentials in thin film photovoltaics with high power conversion efficiency (PCE) of ~26% [1-2]. While Shockley Queisser (S-Q) limit sets a theoretical maximum for a single junction solar cell of 31%, there are avenues that one can explore to achieve a high PCE by mitigating carrier heat losses in photovoltaic devices. However, in a semiconductor extracting hot carriers (HC) before cooling is a futile exercise unless one can either extract carriers 'fast' or 'slowing' HC cooling. However, above mentioned approaches are easier said than done in a typical solar cell where cooling takes place in a time scale of <100 fs and extraction times in 10-100s of ps. The present article attempts to introduce the phenomena of HC cooling and is not an exhaustive report on the topic.

In the present article, we introduce what hot carriers are and discuss factors governing HC cooling and we attempt to show that HC in lead halide perovskites sustain for a longer period of time 10-100s of ps and possibility of extraction remains a distinct 'reality'. The HC cooling is followed by femtosecond Transient Absorption (fs-TA) Spectroscopy.

Carrier Cooling in Semiconductors

A semiconductor is defined by a forbidden gap between the Valence and Conduction Band also called as band gap as shown in Fig.1, with the band composed of energy levels spacing of less than thermal energy. Typical above band gap excitation leads to higher kinetic energy on carriers and non-equilibrium distribution of carriers. These carriers subsequently relax via intervalley scattering, carrier-carrier scattering etc. leading to establishment of quasi equilibrium. Since these energy levels are closely spaced in individual bands with energy separation < E_{Phonon} (Energy of phonons), interaction with phonons help release this energy in form of heat within the system. Typical cooling mechanism involving e-phonon interaction in a polar semiconductor is called Froehlich interaction or e$^-$-LO phonon interaction or polaron formation and takes place in a time scale of <100 fs [5-6]. Subsequent cooling in typical semiconductors happens by decay of optic phonons to acoustic phonons as shown in Fig.2. Therefore, the carrier temperature (TC) decays until it equals lattice temperature leading to a quasi-equilibrium. In case of a

confined semiconductor the cooling is hindered due to discreteness in energy levels of individual bands with energy spacing within individual bands > E_{Phonon}. This occurs due to quantum confinement effect and cooling takes place in a time scale of 100 fs-few ps. This is called phonon bottleneck. This is the typical cooling observed under low pump intensity, however under high pump intensity the rate of relaxation like phonon-phonon scattering rates, Auger heating, hot phonon bottleneck play a major role in HC cooling. The mechanisms involved in these HC cooling are described in Fig.1.

Carrier Cooling Mechanisms

Typical mechanisms involved in HC cooling are described below.

Hot Phonon Bottleneck

Most common mode of relaxation in a polar semiconductor, like lead halide perovskites, is Froehlich interaction which is essentially interaction between macroscopic electric field due to longitudinal optic (LO) phonon and electrons with subsequent decay of LO phonons into 2 longitudinal acoustic (LA) modes also called Klemens mode. However, under high pump intensity carrier reheating occurs due to competition between phonon decay rate and carrier density dependent e-LO scattering leading to a non-equilibrium phonon population and hindered cooling. This process is called hot phonon bottleneck. This HC cooling can be modelled based of Froehlich interaction with the energy loss rate as given below,

$$\left(\frac{dE}{dt}\right)_{Phonon} \approx -\frac{\hbar\omega_{LO}}{\tau_{LO}}\left\{\left(e^{-\frac{\hbar\omega_{LO}}{k_b T_C}}\right) - \left(e^{-\frac{\hbar\omega_{LO}}{k_b T_L}}\right)\right\} \quad (1)$$

where $\hbar\omega_{LO}$ is the phonon energy, τ_{LO} is the HC cooling time or LO phonon lifetime and T_c and T_L are the carrier and lattice temperatures respectively [4].

Modelling HC cooling in Halide perovskite under low carrier density <<10^{18}/cm^3 reveals a rate of <1 ps. However a typical Froehlich interaction times are of the order of lifetimes of LO phonons which is <100 fs. Therefore, the typical modelling based on the above energy loss rates indicate cooling time of ~300-1000 fs indicating hot phonon bottleneck at play.
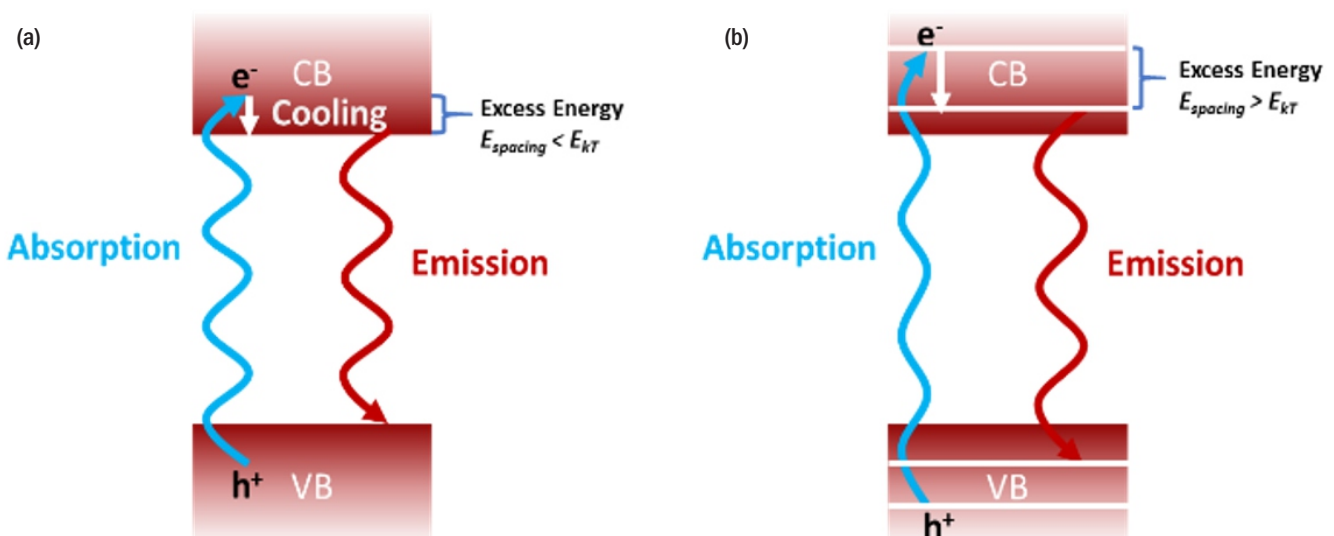

Fig.1: Typical carrier relaxation processes in semiconductors (a) Bulk semiconductor (b) Quantum Dot. Note: Carrier Trapping and other relaxation modes not shown.

Auger Heating

Under high pump intensities, $<N>=j\sigma$ where N is the average number of excitons/crystal, j is pump fluence and σ absorption cross section, is greater than 1, therefore possibility of single nanocrystal containing multiexciton increases. These carriers interact via coulomb interaction and undergo fast carrier-carrier scattering with scattering times, governed by size, shape, composition of etc. Therefore, if a particular nanocrystal harbors a biexciton, then energy associated with exciton recombination is transferred to the other exciton forming a hot exciton in the nanocrystal. These HC release the energy via carrier-LO phonon interaction subsequently heating the system. The Auger heating rates are therefore directly proportional to the number of particles within the system as given below in equation 2.

$$\left(\frac{dE}{dt}\right)_{Total} = \left(\frac{dE}{dt}\right)_{e-Phonon} + k_3(E_g + E)n^2 \quad (2)$$

where k_3 is the Auger recombination coefficient E_g is the band gap.

$\left(\frac{dE}{dt}\right)_{Total}$ and $\left(\frac{dE}{dt}\right)_{e-Phonon}$ are energy loss rates

Therefore, under heating due to Auger recombination, while the initial carrier cooling proceeds via Froehlich mode and hot phonon bottleneck, the energy loss rate decreases as cooling proceeds and eventually matched with Auger heating rate and this form a negative feedback leading to cooling rate governed by Auger process which had a ΔT^2 dependence [5-7].
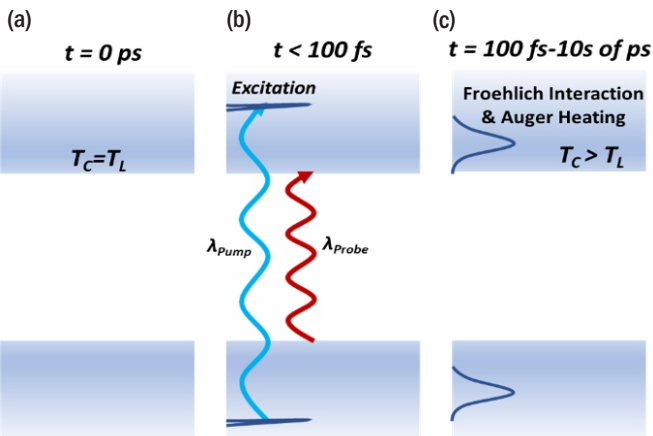
Acoustic-Optic Phonon Up-conversion

Fig.2: Schematic representation of HC cooling processes (a) Before excitation (b) On photoexcitation, electrons and holes in conduction and valence bands respectively with narrow energy distribution above the individual band minima (or maxima) from conduction (or valence) band are created (c) Subsequent cooling via Froehlich interaction Auger heating etc.

Under still higher carrier densities $>10^{18}/cm^3$, LO phonons decay to Acoustic modes and these Acoustic phonons propagate through the solid and dissipated heat. However, if a given material has a low thermal conductivity, propagation of the Acoustic modes is hindered. This in turn leads to localization and therefore longer lifetime for Acoustic phonons thereby increasing the probability of up-conversion of Acoustic phonons back to optic phonons by a process called Acoustic-Optic phonon up-conversion. The probability of up-conversion is also enhanced if there exists a significant overlap between low energy optic modes and acoustic modes. In a lead halide perovskite with organic a cation, a substantially low thermal conductivity accompanied by the strong overlap between low frequency modes of the organic cation with lead halide phonon modes lead to a high probability for an up-conversion to occur.

How to Monitor Carrier Cooling using fs-TA Spectroscopy?

Here we are interested in monitoring HC dynamics using femtosecond transient absorption spectroscopy (fs-TA). In a typical excitation, with a fs pulse the non-equilibrium distribution of carriers are generated by 400 nm pump pulse with pulse width of <100 fs. The carriers are monitored through visible wavelengths using a probe pulse spanning the entire visible region from 400-750 nm. The primary focus here is to monitor charge carrier dynamics. This is accomplished by tracking bleach of the ground state exciton after pump pulse excitation. The bleach is created due to depletion of the ground state and state filling. The schematic in Fig.2 represents the events with respect to time on photoexcitation. The initial state before excitation represents an equilibrium between the TC and the lattice temperature (T_L). On photoexcitation, a non-equilibrium carrier distributions is established which is pulse limited or instantaneous. Subsequently the system cools in the time scale of 100 fs-10 s of ps via Froehlich interaction and phonon-phonon interaction. The depletion in the ground state as monitored at bleach wavelength shows an asymmetry towards blue side due to HC as shown in the Fig.3. Since the bleach tracks the population of carriers, it can be used as index for TC. HC absorption is at blue side compared to ground state bleach position, leading to asymmetry of the bleach towards the higher energy region. Therefore, the HC population distribution can be fitted with a Maxwell Boltzmann distribution as given below to retrieve T_c.

$$\Delta A(E) = -A_0 e^{\frac{-E}{k_b T_c}} \quad (3)$$

ΔA is change in absorbance, T_c is the carrier temperature. TC for individual delay time is used to extract TC decay.

Below we illustrate how this is accomplished using fs-TA spectroscopy for Methylammonium lead bromide (MAPbBr$_3$) quantum dots (QD). Fig.3 gives the pseudo color TA spectra with respect to time. The Figure shows TA spectra with a bleach at 2.35eV and which could be assigned to first exciton transition based on comparison between ground state absorption of MAPbBr$_3$ QDs. As shown in the Fig.3 a, c and b, d for TA spectra for low and high intensities as labelled indicates considerable broadening towards the blue side of the bleach at high pump intensity. This bleach broadening decrease slower
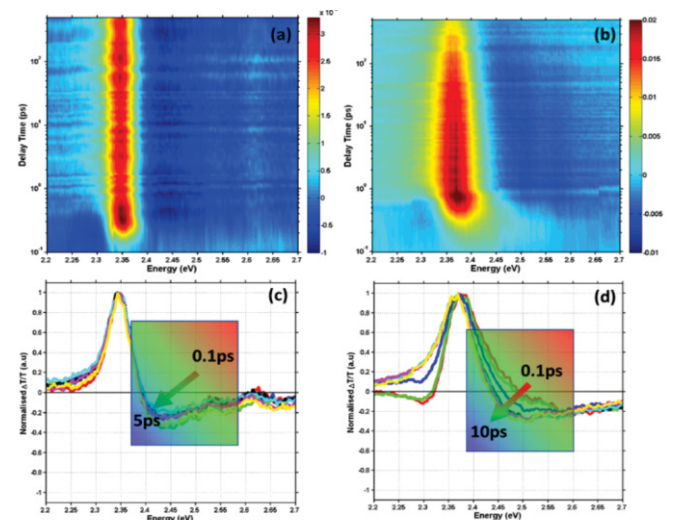

Fig.3: (a) & (c) Pseudocolor TA $\Delta T/T$ spectra, (b) & (d) Normalised $\Delta T/T$ spectra for MAPbBr$_3$ NCs at carrier density of $1.5\times10^{17}/cm^3$ and $10^{18}/cm^3$ respectively.
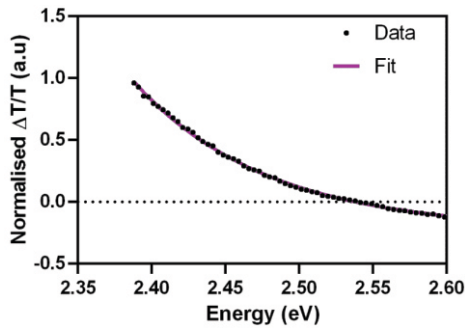
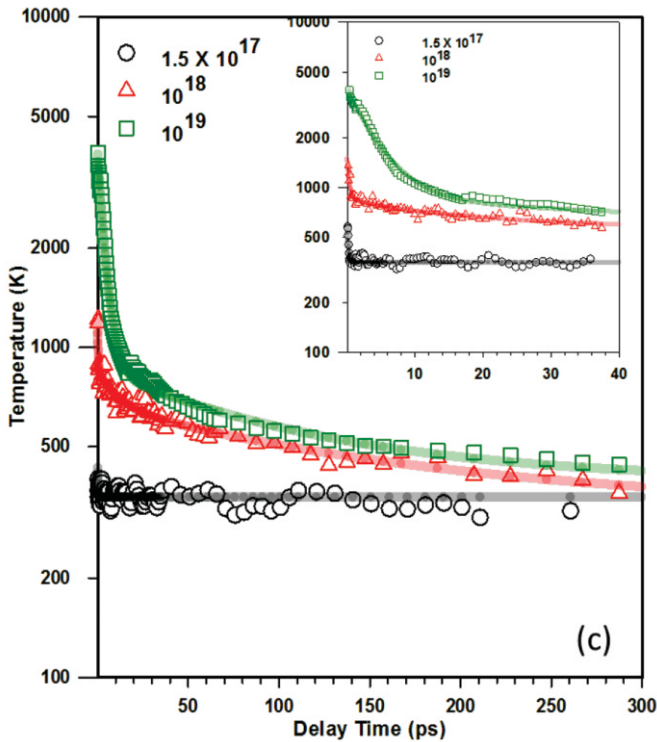*Fig.4: Data (open circles) & Exponential Fits (line) for a typical time delay.*

Fig.5: HC cooling dynamics at initial carrier densities 1.5×10¹⁷, 10¹⁸ & 10¹⁹/cm³.

at higher pump intensity. To quantitatively understand the above observation, we have fitted the wings of the bleach as described above using Maxwell Boltzmann statistics using expression 1. A typical fit is represented in Fig.4. The time slices of TA spectra are used to build T_c vs time curve which is shown in Fig.5. The T_c vs t shows that under low pump intensity the T_c decay is fast and cooling occurs < 1ps indicating role of Froehlich interaction and hot phonon bottleneck. However,

under higher intensity HC cooling is slow with times of 11 ps and ~100 ps, indicating different regimes of cooling operational. As mentioned earlier under high pump intensity the Auger heating could be one possible reason for slow HC cooling. We verified the same from measurement of biexciton Auger recombination time (τ_{Auger}) which was ~30 ps. The HC cooling times scaling is in accordance to Auger heating time with a ~τ_{Auger} / 3 scaling. The slowest component indicates that the cooling is hindered in this system with the slowest component of ~100 ps. In hybrid lead halide perovskite the thermal conductivity for these perovskites are low due to anharmonic phonon-phonon scattering leading to possibility of up-conversion of acoustic phonon to optic phonon leading to reheating of carriers. This up-conversion explain slow HC cooling in MAPbBr$_3$ [8-9].

Conclusion

Here we have attempted to show how a novel phenomenon like slow HC cooling in Lead halide perovskites can be followed using fs-TA spectroscopy. The possibility of slow HC cooling offers some hope towards achieving the goal of breaking S-Q limit. The study shown here is not extensive however some of our recent results indicate modulation of HC cooling using different variants of halide perovskite structure. Some of these works demonstrate immense potential of halide perovskites in HC solar cells.

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