Carrier Dynamics in Nanocrystals and Nanocrystal Solids: Experiment and Simulation
Carrier Dynamics in Nanocrystals and Nanocrystal Solids: Experiment and Simulation

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Abstract

Films of semiconductor nanocrystals (NC-solids) hold great promise as low-cost, solution-processable semiconductors with electronic and optical properties that can be tuned by varying the size and composition of the constituent nanocrystals (NCs), as well as their surface-terminating ligands. Further increase in the performance parameters of devices incorporating NC-solids will require a robust understanding of the effects of the composition, size, and surface termination of the individual NCs on the charge carrier dynamics resulting from their assembly into densely packed films.

Here we investigate the phononic structure of the NCs, the resulting electron-phonon interactions, and their influence on charge carrier transport in NC-solids. We choose lead sulfide (PbS) NCs as a model system, due to the extensive literature and their use in a wide range of applications from LEDs, photodetectors, solar cells, and thermoelectrics.

Knowledge of the phononic properties of NCs and how the phonons couple to the electronic states of the NCs is crucial for understanding energy gain, loss, and transport processes in NC-solids. Using inelastic neutron scattering measurements and Ab-Initio Molecular Dynamics (AIMD) simulations, we quantify the phonon density of states of nano-sized crystallites as a function of crystallite size. We demonstrate that the mechanical softening of the surface of nanocrystalline domains results in low and high energy phonon modes with reduced symmetry and large thermal displacements. Using simulation, we show that these modes couple strongly to the electronic states in NCs and cause strong thermal broadening of optical transitions and efficient phonon-mediated electronic transitions, effects which have
been observed experimentally. We study the impact of thiol versus halide terminations of the NC surface, and demonstrate that the electron-phonon coupling in the NCs can be tuned through the choice of surface termination.

To investigate charge carrier transport in NC solids, we perform Time of Flight (TOF) photocurrent transient measurements on PbS NC solids. The TOF technique provides a robust approach to probe carrier dynamics in disordered, low-mobility materials. We find that the carrier mobility extracted via TOF in NC solids is temperature activated, and that both the activation energy and temperature independent prefactor of the carrier mobility scale strongly with NC size. Our analysis indicates that the distribution of carrier hopping times is power-law distributed with divergent mean values. This is characteristic of disordered solids and explains our finding that the extracted carrier mobilities from TOF depend on the device thickness. Indeed, this implies that the series resistance will depend superlinearly on the device thickness.

Finally, we motivate a model for charge carrier transport in NC solids based on phonon-mediated electron transfer. Using AIMD, we calculate the wavefunction overlap between neighboring NC and the reorganization energies associated with charge transfer for a series of NC sizes. Our model explains the scaling of the temperature dependent mobility with NC size measured with TOF. We further demonstrate that the activation energy of the transport can additionally be associated with the size dispersion of the NCs.

Our work here on PbS NCs suggests a future path for systematically tuning charge carrier dynamics in arbitrary NC systems. Namely, NC size and surface chemistry can be selected to determine the electronic and phononic properties of NCs, electron-phonon interactions in them, and charge transfer rates between them.
Zusammenfassung

Kolloidal in Lösung synthetisierte Nanokristalle (NCs) sind vielversprechende Halbleitermaterialien deren elektrische und optische Eigenschaften durch Größe, atomarer Zusammensetzung und der Wahl der Oberflächenmoleküle definiert werden. Für eine Weiterentwicklung optoelektronischer Bauteile ist ein fundiertes Verständnis des Einflusses ebenjener Charakteristika auf die Ladungsträgerdynamik in zusammengesetzten Dünnschichten unabdinglich.

In der vorliegenden Arbeit untersuchen wir die Eigenschaften der quantisierten Gitterschwingungen in Nanokristallen, die Elektron-Phonon Interaktionen sowie deren Einfluss auf den Ladungstransport. Aufgrund ihres breiten Anwendungsspektrums in LEDs, Photodetektoren, Solarzellen bis hin zu thermoelektrischen Anwendungen betrachten wir Blei-Sulfid (PbS) NCs als ein Modellsystem.

Oberflächenterminierung und zeigen, dass die Wahl zwischen ihnen die Elektronen-Phononen Kopplung bestimmt.


Unsere Arbeit zeigt auf wie die Ladungsträgerdynamik in Nanopartikelsystemen gezielt modifiziert werden kann. Insbesonderen erörtern wir, dass Nanopartikelgröße und Oberflächenterminierung die elektronischen und phononischen Eigenschaften von Nanopartikeln, die Elektron-Phonon Interaktion in ihnen sowie die Ladungstransferraten zwischen ihnen definiert.
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Chapter 1

Introduction

At the heart of the rapid advancement of bulk semiconductor technologies over the past 50 years has been a robust fundamental understanding of the physical processes occurring in periodic atomic lattices [1–4]. Before production began on the world’s first commercial transistor in 1951, for example, the theory of phonon-mediated non-radiative electronic transitions in defected bulk semiconductors, still used to this day, was already firmly established [5].

Infinite bulk crystals can be described with a few key pieces of information, namely a small set of lattice vectors and the atomic basis. Closed form expressions derived from first principles for physical processes are thus in theory, mathematically tractable. When working with disordered systems, to which most nanoscale and amorphous semiconductor technologies belong, we are not afforded such luxury. Single atom bases are replaced by approximate atomistic models and lattice vectors are replaced with statistical distributions. The result is an increased complexity in both the experimental characterization, first principles modelling, and the interplay between them.

In this thesis, our goal is to gain a deeper insight into carrier dynamics in nanocrystals (NCs) and functional solids derived from them (NC-solids). In particular we investigate charge carrier transport, electron-phonon coupling, and the relation between them, through a combination of experiment and theory. Given the extensive work on
lead sulfide (PbS) NCs and NC-solids, we employ it as a model system for our investigations.

1.1 Nanocrystals: from Colloids to Functional Assemblies

One of the most instantly appealing features of semiconductor NCs is the tuning of their emission color through precise control of their size and composition (see Fig. 1.1). The backlight of many commercial LED TVs now use red- and green-emitting semiconductor NCs to achieve higher spectral purity and a larger range of achievable colors.

The color of a NC is given by the wavelength of the emitted photons, λ, which in depends on the bandgap of the NCs \( \lambda = h c / E_g \), where \( h \) is the Planck constant and \( c \) is the speed of light. The concept of a semiconductor with a tuneable bandgap also makes semiconductor NCs appealing for thin film semiconductor technologies, such as solar cells [8, 9], photodetectors [10, 11], transistors [12], LEDs [13], and thermoelectrics [14].

Here we provide a brief introduction to semiconductor NCs first providing a simple model for the dependence of their bandgap on their size, followed by a discussion of their synthesis and assembly into functional solids.
1.1.1 Effects of Quantum Confinement

In bulk semiconductors, electrons and holes attract each other and can form a bound state called an Wannier exciton (see Fig. 1.2). The characteristic radius of the exciton is given by the effective Bohr radius:

\[ r_{WE} = \frac{4\pi\epsilon h^2}{m^*e^2}, \]  

(1.1)

where \( h \) is the reduced Planck constant, \( e \) is the charge of the electron and hole, \( \epsilon \) is the dielectric constant of the semiconductor, and \( m^* \) is the reduced mass of the electron and hole, \( m^* = m_e m_h / (m_e + m_h) \), where \( m_e \) and \( m_h \) are the mass of the electron and hole respectively. \( r_{WE} \) is typically on the order of 1-10nm for most semiconductors. As the size of the crystallite is reduced, the discreteness of the density of electronic states will become increasingly apparent, but provided the crystallite radius is larger than \( r_{WE} \), the bandgap will remain relatively unchanged. As the radius of the crystallite is decreased further, below that of \( r_{WE} \), the carriers will become increasingly confined, raising their kinetic energies, and opening up the bandgap. We call this the regime of quantum confinement, and crystallites in this regime are referred to as “quantum dots”, or, as we will refer to them for the remainder of this thesis, semiconductor NCs.

Following Norris [15], we can approximate how the size of the NCs affects the bandgap by modelling the NCs as spherical potential wells of radius \( a \), corresponding to a potential \( V \):

\[ V = \begin{cases} 
0, & r < a, \\
\infty, & r > a,
\end{cases} \]  

(1.2)

The solution to the Schrödinger equation yields wavefunctions:

\[ \psi_{n,l,m}(r, \theta, \phi) = C j_l(k_{n,l}, r) Y^m_l(\theta, \phi)/r, \]  

(1.3)

where \( C \) is a normalisation constant, \( Y^m_l \) are the spherical harmonics, \( j_l \) is the \( l^{th} \) order spherical Bessel function and \( k_{n,l} = \alpha_{n,l}/a \), where \( \alpha_{n,l} \) is the \( n^{th} \) zero of \( j_l \). These wavefunctions are atomic-like orbitals,
and we can label them with their quantum numbers $n$, $l$, and $m$. The corresponding energies are:

$$E_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2ma^2},$$

where $m$ is the effective mass of the electron or hole. We can improve upon the energies in eq. 1.4 by invoking the effective mass approximation and replacing the electron and hole mass by their effective masses in the semiconductor, $m_{e,\text{eff}}$ and $m_{h,\text{eff}}$. The energy of an electron hole pair in a NC will then be given by:

$$E_{e,h}(n_h, L_h, n_e, L_e) = E_g + \frac{\hbar^2}{2a^2} \left( \frac{\alpha_{n_h,L_h}^2}{m_{h,\text{eff}}} + \frac{\alpha_{n_e,L_e}^2}{m_{e,\text{eff}}} \right) - E_c,$$

where $E_g$ is the bandgap of the bulk semiconductor, and $E_c$ is the Coulomb energy associated with the interaction between the electron and hole and can be approximated as $E_c = 1.8e^2/ea$. Within this model, the bandgap of the NC depends on the square of the inverse radius $a^{[15]}$. 

Figure 1.2: The effect of reducing crystallite radius below that of the Wannier exciton.
1.1.2 Colloidal Synthesis

Modern colloidal syntheses of semiconductor NCs are based on the hot-injection method introduced by Murray et al. [16], which enables control over NC size and shape, and is applicable to a broad range of materials [17,18].

For the synthesis of a binary NC, $AB$ (e.g., PbS), two molecular precursors are separately prepared in solution, $xA$ and $yB$ (e.g., (lead)oleate, and bis(trimethylsilyl)sulfide). One of the precursors (Pb) is heated to an elevated temperature (typically $\sim 400K$), and the other precursor (S) is swiftly injected. At these conditions, the precursors react rapidly and the reaction solution becomes supersaturated with $AB$ product. The supersaturation causes nucleation of $AB$ clusters, which lowers the concentration of the molecular precursors (see Fig. 1.3a). Once the molecular precursor concentrations fall below the nucleation threshold, nucleation of new clusters ceases. The remaining precursor molecules then contribute to the growth of the already nucleated clusters until the synthesis is terminated [19].

Figure 1.3: Precursor concentration versus time during a synthesis of colloidal NCs is shown in (a). The surface volume and free energy curves for the growth of colloidal NCs is shown in (b). Indicated in the figure is the critical radius, $r_c$, as discussed in the main text. Adapted from Murray [19], Kwon [20], et al.
CHAPTER 1. INTRODUCTION

The nucleation process is driven by the free energy of the nucleated clusters, which with a simple spherical model for the NCs can be expressed as,

$$\Delta G(r) = 4\pi r^2 \gamma_{SE} + \frac{4}{3} \pi r^3 \Delta G_V,$$

where \(r\) is the radius of the cluster, \(\gamma_{SE}\) is the surface free energy per unit area, and \(\Delta G_V\) is the unit energy per unit volume for the cluster and is negative. A example plot of eq. (1.6) is given in Figure 1.3b. Below a critical radius, \(r_c\), the nucleated clusters will redissolve into solution, while clusters which reach or exceed \(r_c\) will remain and continue to grow during the growth phase of the reaction [20]. Achieving monodisperse NCs requires fine tuning of the nucleation stage. If nucleation is too slow, clusters which form early in the solution will have more time to grow than the clusters which form later on. If the nucleation is too rapid, many small cluster will form, leaving no precursor molecules for the growth phase of the reaction.

During the growth phase, the growth of the NCs can be modelled by the kinetic equation [20],

$$\frac{dr}{dt} \propto \frac{D([AB]_{sol} - [AB]_{surf})}{r - D/k_r},$$

where \(D\) is the diffusion coefficient of the AB monomers, \([AB]_{sol}\) are the concentration of the monomers in solution and \([AB]_{surf}\) the concentration of monomers on the surface of the NC and \(k_r\) is the reaction rate constant for the attachement/deattachment of monomers to the NC surface. The growth phase can thus be either diffusion limited, or reaction rate limited. In practice, most syntheses are in the mixed regime.

The as synthesized colloidal NCs have their surfaces capped with ligands [21], which also play an important role in the synthesis. These ligands are typically mixed in with one of the molecular precursors prior to the hot-injection. Ligands can be used, for example, to modify the diffusion constant \(D\) of the monomers, influence the reaction rate constant \(k_r\), define the solubility of monomers and formed NCs and modify the surface free energies \(\gamma_{SE}\) of the NCs [17, 21]. As we will discuss in Chapter 2.1.2 the specific surface free energies of the possible NC facets influence, and in most cases determine, the shape
1.1. NCS: FROM COLLOIDS TO FUNCTIONAL ASSEMBLIES

Figure 1.4 displays Transmission Electron Microscope (TEM) images of various NC systems, displaying the broad range of morphologies achievable with colloidal synthesis.

Figure 1.4: Various morphologies of colloidally synthesized NCs
Adapted from Yarema [22]

1.1.3 Nanocrystal Solids

In order to utilize colloidal NCs in functional electronic devices, they must first be brought into a densely packed, conducting solid, as shown in Figure 1.5. To maintain a colloidal suspension of the NCs long insulating organic ligands (e.g., oleic acid (OA)) are often employed.
in the synthesis. Brought directly from solution into solid state, these native ligands result in an insulating NC thin-film. A major leap in the advancement of NC solids for electronics was the replacement of the native ligands with short organic [23–26], or inorganic ligands [27, 28]. The resulting films show resistivities many orders of magnitude smaller than from films made with the native ligands.

![Figure 1.5: Illustration of NC solid fabrication. The colloidal suspension is dropcast, spincast, or dipcoat onto the substrate, and the resulting thin film is thin immersed in the ligand exchange solution where the long initial ligand are replaced with short organic or inorganic ligands.](image)

1.2 Charge Transport in Nanocrystal Solids

Further improvement of devices utilizing semiconducting NC solids requires an understanding of the charge transport mechanisms, and how the material parameters effect them. Here we give an overview of the charge transport models commonly used to describe charge transport in NC solids, and various experiments which have been performed to test these models.
1.2. Models of Charge Transport

There are two important intrinsic sources of disorder in NC-solids, which lead to carrier localisation \[29\]. Variation in the size of the individual NCs results in energetic disorder of the superlattice. Furthermore, practical NC solid fabrication techniques employed for devices result in superlattices with significant spatial disorder (inter-NC distances) \[30, 31\]. Due to the high amount of disorder in these systems, charge transport in semiconducting NC solids occurs via non-resonant charge transfer between NCs, i.e. carrier hopping \[32,33\].

The most rigorous models for the description of non-resonant charge transfer are the electron-transfer (ET) models of Marcus, Dogonadze, Jortner, Bixon, Efirma, and Ulstrop \[36–44\], developed to describe oxidation/reduction reactions in solution and intra-molecular charge transfer processes. A detailed explanation of these models is given in Chapter 5. Here we discuss the main implications and commonly used approximations of the model. In its most basic form, the ET rate from NC \(i\) to NC \(i+1\) is given by \[2\]

\[
k_{ET} = \frac{2\pi}{\hbar} |V|^2 \sqrt{\frac{1}{4\pi \lambda k_B T}} \exp \left[ -\frac{(\lambda + \Delta E_{i,i+1})^2}{4\lambda k_B T} \right], \quad (1.8)
\]

where \(|V|^2\) is the electronic coupling between the NCs, which will in general depend on their center-to-center separation \(\vec{R}\). \(\lambda\) is the reorganisation energy associated with the ET and \(\Delta E_{i,i+1}\) is the change in the energy of the carrier upon transfer. If the transport states are assumed to derive from the quantum confined states of the NCs, we can write:

\[
\Delta E_{i,i+1} = \left( E_{g,i+1} - E_{g,i} \right) / \chi_b, \quad (1.9)
\]

where \(E_{g,i}\) is the bandgap of the \(i^{th}\) NC, \(\chi_b\) is a unitless empirical parameter that describes how the CB and VB levels align between neighboring NCs. The \(\chi_b\) satisfy \(\chi_b > 1\) and \(\chi^{-1}_{CB} + \chi^{-1}_{VB} = 1\). In most studies, \(\chi_b = 2\) is used.

\[1\] We do not discuss transport in annealed films where NCs are used as precursors. See for example \[34,35\].

\[2\] We assume here that the change in entropy associated with the hop of the charge is 0.
Studies which have employed the full ET model of eq. 1.8 have typically used the Coulomb charging energy as the reorganisation energy,

$$\lambda = \frac{e^2}{4\pi\epsilon_0 r} \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right),$$  
(1.10)

which corresponds to the energy required to bring a charge $e$ from vacuum to a metallic sphere of radius $r$ in a dielectric medium with optical and static permittivities $\epsilon_{op}$ and $\epsilon_s$ respectively [17, 45–47].

The incompleteness of this treatment will be the subject of Section 5.2.

In the limit that $\Delta E_{i,i+1} \gg \lambda$, and that there is a continuum of states above the conduction band minimum (CBM) and valence band maximum (VBM) of the NCs, the non-adiabatic ET rate of eq. 1.8 can be approximated by the Miller-Abrahams model [48],

$$k \propto k_0 \exp \left[ -\Delta E_{i,i+1} / k_B T \right] \quad \Delta E_{i,i+1} > 0$$  
(1.11)

$$k \propto k_0 \quad \Delta E_{i,i+1} \leq 0.$$  
(1.12)

The Miller-Abrahams model is one of the most commonly used models for charge transport in NC solids [47, 49–53]. While the assumption
1.2. CHARGE TRANSPORT IN NANOCRYSTAL SOLIDS

that the energetic disorder will outweigh the reorganisation energy may be reasonable, the approximation of the continuum of states is not necessarily reflective of the sparse density of electronic states for NCs in the strong confinement regime \[54\].

The other key parameter of eq. 1.8 is the electronic coupling, \(|V|^2\), given by

\[
|V|^2 = \langle \psi_{i,n}^* (\vec{r}) | H | \psi_{i+1,n'} (\vec{r} + \vec{R}) \rangle,
\]

(1.13)

where \(\psi_{i,n}^*\) is the wavefunction of the \(n^{th}\) level of the \(i^{th}\) NC and \(H\) is the Hamiltonian of the system comprised of both NCs. As transport is typically assumed to derive from the ground states of the VB and CB, eq. 1.13 is typically evaluated with \(n = n' = CBM\) or \(n = n' = VBM\). Modelled as spherical potential wells, the ground state wavefunctions will be spherically symmetric (S-type), and eq. 1.13 takes the simple form

\[
|V|^2 \propto \exp \left[-\kappa (2r - R)\right] = \exp \left[-\kappa \delta\right],
\]

(1.14)

where we have defined \(\delta\) as the edge to edge separation of the NCs. The ET rate thus exponentially depends on the inter NC separation, \(\delta\).

Combining eq. 1.11 and 1.14 gives

\[
k \propto \exp \left[-\kappa \delta - \Delta E_{i,i+1}/k_B T\right].
\]

(1.15)

Since the \(E_i\) belong to a statistical distribution so do the \(\Delta E_{i,i+1}\). As the temperature decreases, hops of the carrier to NCs where \(\Delta E_{i,i+1} > 0\) will become slower and slower. For a charge sitting on a NC with all the \(\Delta E_{i,i+1}\) to its nearest neighbours large, the rate to a more distant NC may become larger than all of the rates to its nearest neighbours. Mott showed that if the \(E_i\) are uniformly distributed within an energy range \(\Delta E\) about the Fermi-level, then, at low temperatures \[55\]

\[
k \propto \exp \left[-(T_0/T)^{1/4}\right],
\]

(1.16)

where \(T_0 \propto \Delta E \rho^{1/3}/k_B\), where \(\rho\) is the density of hopping sites. Efros and Shklovskii showed that in the limit of high carrier density, Coulomb interaction of the charge carriers leads to a reduction of the rate \[56\]

\[
k \propto \exp \left[-(T_0/T)^{1/2}\right].
\]

(1.17)
Several studies have confirmed the scaling in eq. 1.17 in the conductivity of NC solids at low temperatures \[50, 52, 57\].

### 1.2.2 Tuneability of Charge Transport

One of the most attractive features of semiconducting NC solids is their tunability. For a chosen NC material, the choice of NC size and ligand used in the NC solid fabrication have important consequences for carrier transport.

#### Nanocrystal Size

The effect of the size of a NC on its optical properties, directly accessible through spectroscopy, is robustly understood for a large variety of systems. However, what role the NC size has on carrier transport, when the NCs are brought together in a NC-solid, has been difficult to pin down.

One of the most fundamental assumptions made for NC-solids, is that carrier transport occurs via the lowest energy quantum confined electron/hole states of the NCs. Bozyigit et al. \[58\] fabricated diodes with PbS NCs and performed temperature-dependent current-voltage (IV) measurements. They fit the saturation current \(J_0\) of the Shockley diode equation to their results,

\[
J_0 = J_{00} T^2 \exp \left[ -\frac{E_\mu}{nk_BT} \right],
\]

where \(J_{00}\) is the saturation current prefactor, \(E_\mu\) is the mobility bandgap, and \(n\) is the ideality factor of the diode (see Fig. 1.7). They performed their measurements and analysis for devices fabricated with different NC sizes, and found the mobility bandgap scales linearly with the optically extracted bandgap, \(E_\mu \sim 0.88E_g\)\(^3\). This was direct evidence that charge transport occurs through the quantum confined states of the NCs.

Another puzzle is how the NC size effects the charge transport. From eq. 1.13, we see that the ET rate should depend on the overlap

\(^3\)This comparison was done to \(E_g\) extracted from the first absorption peak. As we discuss in Chapter 3.3.1, the VBM and CBM do not optically couple in PbS NCs, and so their \(E_g\) overestimated the true bandgap.
1.2. *Charge Transport in Nanocrystal Solids*

Figure 1.7: Temperature dependent IV characterisation of PbS NC-solid Schottky diodes. Fits of the Schottky diode equation to the raw data (red lines, dots respectively), are shown on the left for a device fabricated with $E_g = 1.69\text{eV}$ NCs. The fits give the mobility bandgap $E_\mu$ and saturation current pre-factor $J_00$ for different NC bandgaps shown on the right. Adapted from Bozyigit *et al.* [58].

...of the charge carrier wavefunctions on neighbouring NCs. As the size of the NCs decreases, the quantum confinement increases, increasing the leakage of the wavefunctions outside of the NCs. Therefore, for fixed inter-NC distance, $\delta$, the ET rate should increase as the NC size decreases. Shabaev *et al.* [59] performed calculations to estimate this effect. They modelled the NCs as spherical potential wells and computed the carrier mobility as a function of size within the tight-binding formalism. Their calculations indicated a strong scaling of the carrier mobility with NC size. In Figure 1.8, we reproduce their calculations for PbS NCs.

Liu, Kang, and coworkers [49,61], extracted carrier mobilities from field effect transistor (FET) measurements (see Fig. 1.9). Their results have shown non-trivial or opposite dependences of the carrier...
CHAPTER 1. INTRODUCTION

Figure 1.8: Carrier mobility of PbS NC-solid as a function of NC size, calculated using the model of Shabaev et al. [59]. PbS NCs are modelled as spherical potential wells with radius $r$, separation $\delta$, separated by energetic barriers of height $U_0$ [60].

Figure 1.9: Carrier mobilities extracted from FET measurements on CdSe (a) and PbSe (b) NC solids. Figures adapted from (a) Kang et al. [61], and (b) Liu et al. [49]

Choice of Ligand

Beyond the choice of NC size and material, the choice of ligand is also crucial in determining the charge transport properties.
The exponential dependence of $|V|^2$ on the inter-NC separation (eq. 1.14) suggests that systematic tuning of $|V|^2$, and therefore charge carrier mobility, can be achieved via the ligand length [13, 49, 62]. Liu [49], Gao [62], and coworkers extracted charge carrier mobilities from FET measurements utilizing NC solids fabricated with aromatic-dithiols and alkyl-dithiols of varying lengths, and found $\mu(\delta) \propto |V|^2 \propto \exp[-\delta]$ (see Fig. 1.10a). Choi, [63], Koole [64], and coworkers performed absorption and photoluminescence (PL) measurements on PbS and CdTe NCs NC-solids, and found increasing red-shifts of both the absorption and PL peaks as the ligand lengths were decreased, indicating an increase in the electronic coupling of neighboring NCs (see Fig. 1.10b).

Figure 1.10: (a) Carrier mobilities extracted from FET measurements on PbSe NC solids fabricated with thiol ligands of different lengths, adapted from Liu et al. [49]. (b) Absorbance of PbS NC solids as synthesised with oleic acid ligand, and ligand exchanged with EDT and mono-, di-, and tri- benzene di-thiol (BDT, DBDT, TBDT), adapted from Choi et al. [63].

Recently, Brown et al. [65] conducted ultraviolet photoelectron spectroscopy (UPS) experiments on PbS NC-solids fabricated with a large variety of inorganic and organic ligands, from which they could extract the energetic positions of the VBM and fermi level with respect to vacuum (see Fig. 1.11). Their results indicated that the positioning of the bands in the NC solid with respect to vacuum could be tuned
by $\sim 1$eV depending on the strength of the surface dipole formed by the bound ligand.

![Figure 1.11: VB and CB energy and Fermi level for PbS NCs treated with the indicated ligands extracted from UPS. Adapted from Brown et al. [65].](image)

1.3 Electron-Phonon Coupling in Nanocrystals

With a strong theoretical understanding of the static electronic properties of semiconductor NCs and robust and well established means of experimentally controlling them, focus in the NC community is now shifting to investigation of mechanisms based on the dynamic electronic and vibrational properties. The energetic separation of states close to the band edges in semiconductor NCs are typically on the order of $\sim 100$meV, while the highest phonon frequencies are typically in the range of $\sim 30$-50meV. Phonon mediated electronic transitions in semiconductor NCs are thus multi-phonon.

We first introduce the theory of radiative and non-radiative multi-phonon mediated electronic transitions, which will be the starting point for several discussions in this thesis. We then review existing
literature pertaining to the experimental characterisation of electron-phonon coupling in colloidal NCs.

### 1.3.1 Frank Condon Principle

The theory of phonon-mediated radiative and non-radiative electronic transitions has its roots in the work of Franck [66] and Condon [67] on the role of phonons on the absorption and emission spectra of molecules. The main concept behind the Frank-Condon (FC) principle is that an electronic excitation or relaxation of a charge due to the interaction with an electric dipole \( \vec{\mu} \) (e.g., a photon) causes a shift in the equilibrium position of the nuclear coordinates, \( \Delta \). This is illustrated in Figure 1.12. The parabolas represent the potential of the lattice in the electronic ground and excited state. The \( x \)-axis corresponds to the dimensionless atomic coordinates, \( Q = \sqrt{m\omega/\hbar X} \), where \( \omega, X, \) and \( m \) are the frequency, normal coordinates, and reduced mass of the phonon mode coupled to the optical transition. The shift of the minima of the free energy parabolas indicates how the equilibrium position of the nuclei are shifted between the ground and excited states. Comparing panels a and b highlights that the larger the shift in nuclear coordinates \( (Q_{0,i} - Q_{0,f}) \) that results from the electronic transition, the larger the photon energy required for absorption.

Formally, the FC Principle describes the transition from an initial state, \( |\Psi_i(q, Q)\rangle \), where \( q \) are the electronic and \( Q \) the nuclear coordinates, to the final state \( |\Psi_f(q, Q)\rangle \) resulting from the perturbation of an electric dipole \( \vec{\mu} \). Under the Born-Oppenheimer approximation, the electronic and nuclear wavefunctions can be separated,

\[
|\Psi_i(q, Q)\rangle = |\psi_n(q, Q)\rangle|\phi_{\nu n}(Q)\rangle, \tag{1.19}
\]

\[
|\Psi_f(q, Q)\rangle = |\psi_{n'}(q, Q)\rangle|\phi_{\nu' n'}(Q)\rangle,
\]

where \( \psi \) and \( \phi \) are the electronic and nuclear wavefunctions, and \( n \) and \( \nu \) are their respective quantum numbers, the prime indicating their values in the final state. The transition rate, \( k \), is then

\[
k \propto |\langle \psi_{n'}(q, Q)|\langle \phi_{\nu' n'}(Q)|\mu|\psi_n(q, Q)\rangle|\phi_{\nu n}(Q)\rangle|^2 \tag{1.20}
\]

\[
\approx |\langle \psi_{n'}(q, Q_0, i)|\vec{\mu}|\psi_n(q, Q_0, i)\rangle|^2 F,
\]
Figure 1.12: Illustration of the Franck Condon Principle. The parabolas represent the harmonic potential of the lattice, and the horizontal lines in them their vibrational excitations. A vertical electronic transition, \( n \rightarrow n' \), can be accompanied by vibrational excitation. Figure adapted from Ruckamp et al. \[68\].

where the last step, known as the Condon approximation, assumes that the expectation value \( \langle \psi_{n'}(q, Q)|\vec{\mu}|\psi_n(q, Q) \rangle \) does not depend on the instantaneous nuclear coordinates \( Q \), and can thus be computed with some particular \( Q \), often chosen to be \( Q_{0,i} \). \[69\]. The Franck Condon factor \( F = |\langle \phi_{n'}(Q)|\phi_n(Q) \rangle|^2 \), is the overlap of the initial and final vibrational modes. We term the shift in vibrational energy (i.e. the Franck-Condon energy \( E_{FC} \)) associated with the shift in normal coordinates for each electronic transition, \( n \rightarrow n' \). If there is only one phonon mode, with frequency \( \omega \), excited in this process, then

\[
E_{FC} = \hbar \omega \Delta^2 / 2. \quad (1.21)
\]
1.3.2 Non-Radiative Multi-Phonon Mediated Electronic Transitions

Huang and Rhys [5] extended the FC principle to develop a theory of non-radiative multi-phonon mediated transitions, by thermally averaging the FC factor $F$ [40]. They expressed the non-radiative rate constant as

$$k \propto V^2 F,$$  (1.22)

where $V$ is an electronic coupling term originating from non-adiabatic effects. While we will not reproduce $F$ here, it takes particularly digestible forms for transitions driven by a single phonon mode with frequency $\omega$ in the low and high temperature limits [70]:

$$F = \left(4\pi S \hbar \omega k_b T\right)^{-1/2} e^{\frac{-(p\hbar \omega + S\hbar \omega)^2}{4S\hbar \omega k_b T}}, \quad k_b T \gg \hbar \omega$$

$$F = (\hbar \omega)^{-1} e^{-S} \frac{S^p}{p!} \approx \frac{e^{p-S}}{\hbar \omega \sqrt{2\pi p}} \left(\frac{p}{S}\right)^{-p}, \quad k_b T \ll \hbar \omega, \quad (1.23)$$

where $S$ is the Huang-Rhys factor. $S$ is related to the FC energy, $S = E_{FC}/\hbar \omega = \Delta^2/2$, and $p$ is the number of phonons emitted/absorbed as a result of the electronic transition of $\Delta E$, $p = \Delta E/\hbar \omega$ (see Fig. 1.13). From eq. 1.23 we see that in the high temperature limit, multi-phonon mediated transitions are temperature activated with activation energy

$$E_A = -(p\hbar \omega + S\hbar \omega)^2/4S\hbar \omega.$$  (1.24)

The low temperature limit results in a finite rate which is independent of temperature [40]. From the FC factors in eq. 1.23 we see that, for multi-phonon processes, $p \gg 1$, the transition rates, eq. 1.22 depend strongly on the Huang-Rhys parameter $S$, which in turn will depend on the strength of the electron-lattice coupling.

1.3.3 Experimental Evidence

While it was presumed that multi-phonon mediated processes in NCs should be inefficient, a concept often dubbed the ‘phonon-bottleneck’ [71], experimental and theoretical investigation of phonon-mediated processes in colloidal NCs point to strong coupling to optical transitions, efficient intraband carrier cooling, and fast carrier trapping.
Large thermal broadening of optical transitions is a typical feature of colloidal NCs [72, 76], which has been suggested to result from strong electron-phonon coupling [72, 73, 76–79].

Low temperature (10K) spectroscopy studies [72, 73] on cadmium selenide (CdSe) NCs were able to spectrally resolve phonon-sidebands in their PL due to coupling to LO phonons. Besombes and coworkers [77] measured the low temperature PL of single epitaxially grown CdTe NCs embedded in ZnTe barriers. They found that at very low temperatures, the PL deviated from that expected for Lorentzian broadening of the optical transition due to the exciton lifetime. Namely, phonon sidebands on both sides of the Lorentzian peak increased as the temperature was increased (Fig. 1.14). Employing a FC model, they reasoned that the phonon sidebands resulted from coupling to low energy acoustic phonon modes.

Turyanska [76], Qiao [75] and coworkers investigated the temperature dependent PL of ensembles of PbS and lead selenide (PbSe) NCs and found an increase of ~60meV in the thermal broadening of the ensemble at 300K compared to ~ 10K. Recently, Caram et al. [80] employed photon-correlation Fourier spectroscopy to measure the PL...
1.3. E-P COUPLING IN NANOCRYSTALS

linewidth of individual PbS NCs. For \( r = 1.2 \text{nm} \) PbS they found a single crystal PL linewidths of 60-100meV. Using the same technique, Cui et al. measured CdSe single crystal room temperature line-widths which increased from \( \sim 60 \text{meV} \) for \( r = 3 \text{nm} \) NCs to \( \sim 95 \text{meV} \) for \( r = 1.5 \text{nm} \) NCs.

Figure 1.14: PL spectra of epitaxially grown CdTe NCs at very low temperatures. Figure is adapted from Besombes et al. [77]

Along with the broadening of optical transitions, strong electron-phonon coupling can also induce a temperature dependence in the optical transition energies. In bulk lead-chalcogenides, thermal expansion of lattice causes a blue shift in their bandgap [76]. Olkhovets et al. [81] measured the temperature dependence of the absorption of PbS NCs as a function of temperature and NC size. As shown in Figure 1.15, they measured the extent of the blueshift to decrease with the NC size, becoming negative (red-shift with increasing temperature), for the smallest NCs measured. This can not be explained by temperature
effects on the static lattice constant alone, and the authors proposed that coupling of the states to acoustic modes in the PbS NCs.

Figure 1.15: Absorption spectra of PbS NCs as a function of temperature are shown in (a), and the shift of the first absorption peak with temperature as a function of NC size is shown in (b). Figure is adapted from Olkhovets et al. [81]

Direct visualisation of the electronic coupling to phonons in colloidal NCs were provided by the Three-Pulse Photon Echo measurements of McKimmie [79] and Krauss [78], which uses a sequence of precisely delayed fs laser pulses to measure the transient absorption. Some of the measurements for PbS and CdSe core-shell NCs are shown in Figure 1.16. For PbS, the spectrum of the peak shift indicates a coupling to acoustic modes, while for the core-shell CdSe coupling is predominately to an optical mode.

Phonon-Mediated Electronic Transitions

Hot carrier cooling rate have been measured in PbSe [82,85] and CdSe [86,88] NCs employing transient absorption. In these measurements, a fs laser pump pulse, with its energy tuned to a high energy
1.3. **E-P COUPLING IN NANOCRYSTALS**

Figure 1.16: Three-Pulse Photon Echo measurements on PbS (a), adapted from Krauss et al. [78] and CdSe-CdS-ZnS (b), adapted from McKimmie et al. [79].

The transition of the NC is used to generate an electron hole pair in an excited state of the NC (Fig. 1.17a.i). A delayed probe pulse, tuned to the lowest energy optically active transition, is then used to probe the filling of the lowest energy transition. The bleaching of the transmission of the probe pulse is measured, the idea being that if unoccupied, the probe pulse will be absorbed ((Fig. 1.17a.ii)), whereas if the electron or hole cool to the lowest energy transition, the absorption of the probe pulse will be quenched (Fig. 1.17a.iii).

Figure 1.17: Principle of transient absorption spectroscopy is shown in (a) as described in the main text. The measured $P \rightarrow S$ transition time constants for CdSe as a function of NC size. (b) is adapted from Klimov et al. [87].
Using this technique, Klimov and coworkers measured hot electron cooling rates of $2-10\text{ps}^{-1}$ for 4-1.2nm CdSe NCs, corresponding to energy loss rates approaching $10\text{eVps}^{-1}$ in the 1.2nm NCs. An increase in the hot carrier cooling rates with NC size was apparent (see Fig. 1.17b). Similar results were reported by Cooney, Rabouw and coworkers for CdSe [86, 88], and Schaller, Harbold and coworkers for PbSe [82, 85]. Spoor et al. conducted intraband transient absorption to probe the electron and hole cooling rates independently from one another in PbSe NCs [83]. They found $\sim 1\text{ps}^{-1}$ cooling rates for electron, while the hole cooling rate was found to be 4-times faster. Schaller et al. measured the temperature dependence of the $P \rightarrow S$ electron cooling rate for PbSe NCs. Their data is reproduced in Figure 1.18. At high temperatures, they observed a temperature activated rate, while at low temperatures, the rate was seemingly independent of temperature. This is precisely what is predicted by the multi-phonon mediated transition rates of Huang and Rhys (eq. 1.23).

![Figure 1.18: P \rightarrow S relaxation rate for PbSe NCs as a function of temperature. Adapted from Schaller et al. 82.](image)

Further evidence for efficient multi-phonon mediated electronic transitions was given by our work on the characterization of trap states in NC solids [89, 90]. We measured the non-radiative transition rates
of charge carriers in a variety of PbS NC-based diodes. Employing temperature impedance spectroscopy (TAS), we fit a function

$$k = k_0 \exp \left[ -\Delta E/k_BT \right], \quad (1.25)$$

on Arrhenius plots of the device capacitance (Fig. 1.19a) and the spectra of electronic states involved in the transition (Fig. 1.19b). This was done for a large number of devices fabricated with PbS NCs of bandgaps ranging from 0.8-1.7eV. Figure 1.19c summarizes the different $\Delta E$ and $k_0$ measured for all devices.

While all of the measurements showed room temperature transition rates of $k \sim k_0 \exp(-\Delta E/k_BT) = 10 - 10^{10}s^{-1}$, transitions could be divided into two groups: some transitions have small $\Delta E$ and $k_0$, while others have large $\Delta E$ and $k_0$. The frequencies $k_0$ for these two groups both scaled exponentially with $\Delta E$ (see Fig. 1.19c),

$$k_0 = k_{00} \exp[\Delta E/E_{MEE}], \quad (1.26)$$

where $E_{MEE}$ is the Multi-Excitation-Entropy. This cannot be explained by the multi-phonon theory of Huang and Rhys (eq. 1.23), as the rate computed for their model decreases with increasing $\Delta E$. While an explanation from first principles for such a form for the attempt frequency $k_0$ is lacking, it is often thought of as an entropic effect; the larger the $\Delta E$, the more ways there are to gain sufficient energy from the phonon bath to make the transition \footnote{91}. Fitting eq. 1.26 to the set of points with lower $\Delta E$ resulted in $E_{MEE} = 53$meV, while the set of points with larger $\Delta E$ gave $E_{MEE} = 17.7$meV. This suggests that the two groups of transitions correspond to two phenomenologically different processes, or are predominately driven by different phonon modes.
Figure 1.19: Temperature Admittance Spectroscopy measurements on PbS NC solids. (a) Arrhenius plots of a TAS measurement, $dCD/fdf$, can be fit to obtain the activation energy $\Delta E$ and the attempt-frequency, $k_0$ for a transition in the semiconductor. (b) Spectra of electronic states corresponding to the transitions in (a). (c) Plot of $k_0$ versus $\Delta E$ for a large number of devices fabricated with PbS NCs with band-gaps 0.8-1.7eV. [90].
Chapter 2

Experimental and Computational Techniques

Here we outline the various experimental and computational techniques used for the work in this thesis.

2.1 Computational Techniques

First principles investigation of the physical, electronic, and dynamical structure of NCs was achieved through Density Functional Theory (DFT) calculations. We give here a brief introduction to DFT and explain how we used it to determine the physical and electronic structure of NCs, and how DFT can be incorporated into molecular dynamics (MD) simulations (Ab-Initio Molecular Dynamics (AIMD)) to determine the dynamical structure of NCs.

2.1.1 Density Functional Theory

DFT is the most successful general approach to finding the ground state physical and electronic structure of materials, from infinite bulk
crystals to small molecules. Here, following Parr and Yang [92], we discuss the main principles behind DFT.

To determine the ground state physical and electronic structure of a material, we want to minimize the total energy of the system. The total energy is given by the hamiltonian,

\[ H = T + V_{ne} + V_{ee} + V_{nn}, \]  

(2.1)

where \( T \) is the kinetic energy of the electrons in the system, \( V_{ne} \) is the Coulomb energy due to the interaction of the electrons with the nuclei, \( V_{ee} \) is the electron-electron interaction energy, and \( V_{nn} \) is the nuclear-nuclear interaction. Both \( V_{nn} \) and \( V_{ne} \) depend on the nuclear coordinates, so the physical structure of the system can be found by minimizing the total energy in the ground electronic state,

\[ H\Psi_0 = E_0\Psi_0. \]  

(2.2)

For a given set of nuclear coordinates, the \( \Psi_0 \) and \( E_0 \) can be found using the variational principle,

\[ E_0 = \min_{\Psi} E[\Psi]. \]  

(2.3)

Thus \( \Psi_0 \) and \( E_0 \) can be determined by minimizing \( E_0 \) through variation of \( \Psi_0 \).

The task of minimizing \( E_0 \) through variation of \( \Psi_0 \) was greatly facilitated through the work of Hohenberg and Kohn. They showed that, as the ground state density \( \rho(\vec{r}) \) uniquely determines the external potential, \( V_{ne} \), to within a trivial additive constant, and the ground state wavefunction \( \Psi_0 \) [93]. To prove this, consider two Hamiltonians, \( H\Psi_0 = E_0\Psi_0 \) and \( H'\Psi'_0 = E'_0\Psi'_0 \), whose external potentials differ by only an additive constant, \( (H-H' = c) \). From the Variation Principle,

\[ E_0 < \langle \Psi'_0 | H | \Psi'_0 \rangle = \langle \Psi'_0 | H' | \Psi'_0 \rangle + \langle \Psi'_0 | H - H' | \Psi'_0 \rangle \]  

(2.4)

\[ = E'_0 + c \int \rho(\vec{r})d\vec{r}, \]

and

\[ E'_0 < \langle \Psi_0 | H' | \Psi_0 \rangle = \langle \Psi_0 | H | \Psi_0 \rangle + \langle \Psi_0 | H' - H | \Psi_0 \rangle \]  

(2.5)

\[ = E_0 - c \int \rho(\vec{r})d\vec{r}. \]
Adding the eqs. 2.4 and 2.5 together gives $E_0 + E'_0 < E_0 + E'_0$, a contradiction. Therefore, the density $\rho(\vec{r})$ uniquely determines both the external potential, $V_{ne}$, and the ground state wavefunction $\Psi_0$.

We can thus compute the total energy, eq. 2.3 through variation of the density $\rho(\vec{r})$,

$$E_0 = \min_{\rho(\vec{r})} E[\rho(\vec{r})],$$

(2.6)
a much simpler task than variation of the many-body wavefunction $\Psi_0$. To implement this, the Hamiltonian must be recast in terms of $\rho(\vec{r})$. This can be done within the Hartree-Fock approximation,

$$H = T[\rho(\vec{r})] + V_{ne}[\rho(\vec{r})] + V_{ee}[\rho(\vec{r})] + V_{nn}[\rho(\vec{r})] + V_{XC}[\rho(\vec{r})],$$

(2.7)

where the new term, $V_{XC}[\rho(\vec{r})]$, corresponds to the exchange-correlation energy of the electrons, which is not captured by $V_{ee}[\rho(\vec{r})]$ when expressed with the Hartree-Fock approximation in terms of $\rho(\vec{r})$. In principle, eq. 2.7 is exact. However, to date, no close-form solution for the exchange-correlation functional, $V_{XC}[\rho(\vec{r})]$, has been determined. Numerous approximations for $V_{XC}[\rho(\vec{r})]$ have been developed which are used for practical calculations.

**CP2K**

A majority of the DFT calculations in this thesis were performed within the CP2K program suite [94]. CP2K employs linear combinations of contracted Gaussian-type orbitals (GTOs) to approximate the real atomic orbitals. This greatly increases the efficiency of the calculation of the total energy (eq. 2.7), as GTOs are extremely localized in space, giving rise to sparse instead of full Hamiltonian matrices [95]. However, in this scheme, the extrapolation of results for infinite bulk systems is not automatically accounted for as in plane-wave DFT codes. CP2K is thus better suited for DFT based calculations on large non-periodic systems.

For the calculations presented in this thesis, we used the dual basis of localized Gaussians and plane waves [95], with a 300Ry plane wave cutoff. Double-Zeta-Plus-Polarization (DZVP) [96], Goedecker-Teter-Hutter pseudopotentials [97] for core electrons, and the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional are used for
all calculations. Convergence to $10^{-8}$ in Self Consistent Field calculations was always enforced. For NCs, non-periodic boundary conditions and the non-periodic wavelet Poisson solver are used. The lengths of the cubic unit cells are adjusted such that there is always a buffer of length 1.5nm from the edges of the NC to the edge of the unit cell. For bulk PbS calculations, periodic boundary conditions for the 4x4x4 cubic supercell (512 atoms) are used, and the supercell length (6.0115Å) is determined through a cell optimization using a conjugate gradient optimization. Geometry optimization is performed with the Quickstep module utilizing a Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimizer. A maximum force of 24meVÅ$^{-1}$ is used as convergence criteria. All atoms in all systems were relaxed.

2.1.2 Physical and Electronic Structure

We can employ DFT to investigate the physical and electronic structure of NCs. The first step is the choice of a well justified atomistic model for the NC of interest. Once the model is chosen, its geometry is relaxed to minimize the total energy of the NC. Finally, the Hamiltonian can be constructed from the relaxed atomistic model, and diagonalised to obtain the electronic structure. Here we outline the atomistic model we choose for PbS, give the details of the geometry relaxation and electronic structure calculations, and finally present the resulting electronic structure of a representative PbS NC.

**Atomistic Model**

As discussed in Chapter 1.1.2 during colloidal synthesis, the shape of the NC will be dictated by the surface energies of the exposed NC facets, which are either bare coordinated with surface ligands. In general, colloidal NCs will grow along a trajectory in physical configuration space which minimizes the total energy, dominated during growth by the various surface energies of the facets.

For PbS NCs, Zherebetskyy et al. published a comprehensive study where they computed the surface energies of the various facets which could result from cutting the rock-salt structure of PbS. The computed surfaces energies with and without bonding to ligands were input into a Wulff construction model, which minimizes the
surface energy for a fixed volume of material. The resulting minimisation indicated that the optimal structure consisted of Pb [111] facets of the rock-salt structure fully coordinated with ligands, and bare [100] facets. The lowest energy configuration had a Wulff ratio of $R_W = r_{[111]}/r_{[100]} = 0.82$, where $r_{[111]}$ and $r_{[100]}$ are the center to plane distances of the NC facets, shown in Figure 2.1. The resulting model is consistent with the observed shape of PbS NCs observed with TEM and with the excess Pb to S ratio typically measured via energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).

Figure 2.1: Depiction of the atomistic model proposed by Zherebetskyy et al. [98], reconstructed here with MTH ligands.

Besides minimising surface energies, overall charge balance of the NC should also be maintained to obtain an intrinsic semiconductor NC. The charge balance will depend not only on the Pb and S atoms, but also on the amount and type of ligands and whether the NC is charge compensated by counter-ions in the solution or NC-solid [99, 100],

$$2N_{Pb} - 2N_S + V_L N_L + N_{ch} = 0,$$

(2.8)

where $N_x$ refers to the number of Pb or S atoms, ligands (L), or surplus/deficiency of additional charges (ch), and $V_L$ is the valence of the ligand. Typical ligands for PbS, namely thiols and halide anions, have $V_L = -1$. In constructing atomistic models of PbS NCs, we have found that using $R_W \sim 0.82$, the charge balance condition is almost satisfied ($\pm 2e$, for all sizes of NCs we have investigated, up to $r 2.2$ nm). NCs cut with $R_W$ other than 0.82 require the removal of far more (typically > 10) ligands/Pb-ligand-pairs or strong
charging in order to satisfy \( R_W \sim 0.82 \). To fully satisfy eq. 2.8 for the case \( R_W \sim 0.82 \), either one to two ligands (-) or Pb-ligand-pairs (+) are removed. Alternatively, the NC can be charged \( (N_{ch} = \pm 2) \). With charging, in contrast to the case of ligand removal, NCs retain octahedral symmetry, greatly facilitating the analysis of their electronic and physical structure. Unless otherwise stated, the work presented in this thesis employs the latter approach. A pictorial summary of the construction of the atomic model is given in Figure 2.2.

\[ 2N_{\text{vol}} - 2N_z + N_z V_z = 0 \]

\[ 2N_{\text{vol}} - 2N_z + N_z V_z + N_z e^z = 0 \]

Figure 2.2: Atomistic model construction.

2.1.3 Dynamic Structure: Ab-Inito Molecular Dynamics

AIMD is one of the most powerful methods for the investigation of dynamical processes at the atomic scale. Like classical MD, it is a temporally discrete method, which computes the atomic trajectories by discretising Newton’s Equations of Motion. Classical MD utilizes predefined interatomic interaction potentials to compute the interatomic forces at each time step. The potentials are fit to empirical data or static electronic structure calculations (typically limited to two-body interactions). AIMD, on the other hand, computes the forces on each atom to the accuracy of DFT at each time step.

The AIMD approach is outlined in Figure 2.3. At each time step, the electronic structure is calculated by DFT using the nuclear
coordinates. The force on each atom can then be computed from the gradient of the total hamiltonian (electronic-plus-nuclear). Formally, this is expressed as:

$$m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = -\nabla \langle \Psi_0(q) | H(Q,q) | \Psi_0(q) \rangle,$$

where $m_i$ is the mass of atom $i$, $|\Psi_0(q)\rangle$ is the ground state electronic wavefunction, $q$ are the electronic coordinates, and $H(Q,q)$ includes the nuclear-nuclear interaction. The nuclear coordinates for the next time step are then determined from these forces.

An important consideration in AIMD is the selection of an appropriate time step, as maximising the time step without compromising the accuracy of the simulation can save substantial computational resources. This maximum time step is dictated by the highest phonon frequencies in the system being simulated. For the simulations conducted in this thesis, we used 1.5fs time steps for systems containing C-H bonds, and 10fs otherwise.
We perform AIMD in the canonical ensemble, i.e., states are in thermal equilibrium with a heat bath. In practice, MD simulations can macroscopically lose or gain energy due to their classical treatment of atomic motion and small errors introduced by the discretisation of Newton’s Equations of Motion. Then, to keep the temperature of the simulation constant, a thermostat is employed. We use the canonical-sampling-through-velocity-rescaling thermostat of Bussi et al. [101], which rescales all of the atomic velocities to keep the temperature fixed. For thermalization of the atomic structure and calibration of the thermostat, the time constant of the thermostat, which sets the feedback time between the system and the thermostat, is set to 15fs and the AIMD is run for 1ps. The time constant is then set to 1ps for the remainder of the AIMD (typically 5-10ps). All AIMD steps prior to thermalization are discarded.

Extracting Phonon Density of States

From the AIMD simulations, we can extract the position of each atom as a function of time. The phonon density of states, $g(\omega)$, is the power spectrum of the mass weighted velocity correlation function [102], which takes the simple form,

$$g(\omega) = \sum_i m_i \omega^2 |\mathcal{F}\{p_i(t)\}|^2,$$

(2.10)

where $i$ runs over all atoms, $m_i$ is the mass of the $i^{th}$ atom, $\mathcal{F}$ represents the Fourier Transform, and $p_i(t)$ is the time trace of the position of the $i^{th}$ atom. As the AIMD simulation is performed with discrete time steps, the Discrete Fourier Transform is employed for evaluating eq. 2.10.

Prior to calculating $g(\omega)$ using eq. 2.10, it is crucial to remove the six macroscopic translational and rotational degrees of freedom of the NC. This is achieved through post processing of the atomic trajectories using the Iterative Closest Point Algorithm of Besl and McKay [103].
2.2 Experimental Techniques

Here we outline the experimental techniques employed for the work in this thesis. A description of \textit{Time of Flight (TOF)} transient photocurrent technique is given followed by a discussion of practical considerations for implementing the technique, as well as a review of the theory developed to interpret the results of the measurement. We then turn to discussion of inelastic neutron scattering which we used to measure the phonon properties of PbS NCs and explain how we analyse the resulting data. At the end of the section, we give details regarding the preparation of samples and devices investigated in the following chapters.

2.2.1 Probing Carrier Dynamics: Time of Flight

In \textit{TOF} photocurrent measurements, the material under study is sandwiched between two contacts, which are fixed at a given potential, $V$, with respect to one another. A short laser pulse generates a charge distribution in the material peaked at the transparent contact. The resulting displacement current transient generated by one carrier type traversing the device is then measured (see Fig. 2.4).  \cite{104}

![Figure 2.4: Setup for TOF measurement.](image)

As we will discuss, the \textit{TOF} technique has comparative advantages over steady state characterisation techniques for investigating carrier transport. The principal advantage is that the extracted carrier mobilities, $\mu$, are independent of carrier density, whereas extracting carrier
mobilities from steady state measurements require precise knowledge of the carrier density. In addition, one can extract information on the density of transport states and shallow/deep trap states from the transient dynamics.

Here we give an overview of the principles of the technique, go over practical consideration required for effectively applying the technique, and lastly review theoretical work which has previously been done in order to understand and analyse TOF transients.

**Principle of Technique**

In an ideal TOF measurement where the semiconductor has an infinite attenuation coefficient, $\alpha_{abs}$, such that all absorption takes place at the semiconductor and illuminated electrode interface, and all charges drift across the device with fixed mobility, $\mu$, without trapping or diffusing, the problem is reduced to an infinitely thin sheet of charge travelling from one electrode to the other. The electric potentials of the electrodes (labeled $A$ and $B$) that sandwich the semiconductor of thickness $d$ are given by

$$V_A = 2\pi k \sigma_s x + 2\pi k \sigma_B d,$$
$$V_B = 2\pi k \sigma_s (d - x) + 2\pi k \sigma_A d,$$

where $k = 1/4\pi \epsilon$ ($\epsilon$ is the permittivity), $x$ is the axis perpendicular to the electrodes along which transport occurs, and $\sigma_s$, $\sigma_A$, and $\sigma_B$ are the surface charge densities of the sheet of charge in the semiconductor and at electrodes $A$ and $B$ respectively. As the electrodes are fixed at a given potential, $V_A - V_B = V$, we have

$$2\sigma_A d = 2\sigma_s x + (\sigma_A + \sigma_B)d - \sigma_s d - V/(2\pi k).$$

Taking the derivative of the surface charge density at electrode $A$ with time, and given conservation of charge, $\partial/\partial t(\sigma_A + \sigma_B) = 0$, gives an expression for the current transient

$$\frac{\partial \sigma_A}{\partial t} = \frac{\sigma_s}{d} \frac{\partial x}{\partial t}.$$

The drift velocity of the sheet of charge $v = \partial x/\partial t$ is by definition

$v = \mu E = \mu V/d$, and to travel between electrodes it takes a time $t_{tr} =$
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\[ d/v = d^2/\mu V. \]  

Finally, the current in the external circuit can be taken as the change in the charge of one of the electrodes, \( J(t) = \partial \sigma_A / \partial t, \) such that the resulting transient is given by

\[ J(t) = \sigma_s \frac{\mu V}{d^2}, \quad 0 < t < t_{tr}. \]  \hfill (2.14)

An example of such a transient is shown in Figure 2.5. \( t_{tr} \) defines the time of flight, i.e. the time required for the sheet of charge to travel from the transparent electrode to the counter electrode. Provided \( t_{tr} \) can be identified from the TOF transient, the mobility can then be computed,

\[ \mu = \frac{d^2 V}{t_{tr}}. \]  \hfill (2.15)

For disordered semiconductors, such as amorphous semiconductors [105–107], organics [108, 109], and NC solids [60, 110], observed TOF transients resemble the blue dash-dotted line in Figure 2.5. Transients with such a form have been dubbed ‘anomalously dispersive’ [104, 111], due to the apparent large dispersion in carrier transport times. One of the universal features of ‘anomalously dispersive’ transients is that they can be characterised by two distinct power laws,

\[ J(t) \propto t^{-(1-\alpha_-)} \quad t < t_{tr}, \]  \hfill (2.16)
\[ \propto t^{-(1+\alpha_+)} \quad t > t_{tr}. \]

The inset in Figure 2.5 shows the transients plotted on a log-log scale indicating power law fits of the form given in eq. 2.16.

A qualitative picture of how such transients are often interpreted is shown in Figure 2.6. A large number of carrier traverse the device with characteristic mobility \( \mu \), while others have their transport impeded, contributing to the dispersive portions of the transient. With such an interpretation the mobility is calculated via eq. 2.15 where \( t_{tr} \) is extracted from the transient as the intercept of the two distinct power laws (eq. 2.16).
Figure 2.5: KMC simulated TOF transients for an ideal conductor with infinite absorption coefficient $\alpha_{abs}$, an ideal conductor with finite $\alpha_{abs}$, and a material with anomalously dispersive carrier transport finite $\alpha_{abs}$. The inset shows the transients on a log-log scale, with power law fits to the pre- and post- $t_{tr}$ portions of the dispersive transient.

**Practical Considerations**

In order to reliably implement TOF characterisation, one must carefully ensure that the simplifying assumptions presumed in their analysis are sufficiently met. We first discuss what these considerations are, and then provide the details of the experimental setup.

The first key assumption of TOF analysis is that the charge density at $t = 0$ is peaked at the transparent electrode, ideally represented by a $\delta$ function at the transparent electrode/material interface. The accuracy of this assumption grows as $\alpha_{abs}$ increases and as the thickness of the device, $d$, increases. One should thus use a laser with a wavelength, $\lambda$, which is strongly absorbed by the material of interest. The thickness of the device should then be sized thick enough that
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Figure 2.6: TOF transient shaded to depict qualitative contributions to the measured displacement current, (1) carriers traversing device with mobility \( \mu \), (2) carries whose transport is impeded relative to those in region (1), (3) initial sharp peak in transient due to finite absorption effects.

The two distinct power law portions of the transient (eq. 2.16) are discernable. In addition, one must consider the power of the laser in conjunction with the density of optically active states in the material of interest. Larger laser intensity means a larger number of generated charges and therefore a larger signal to noise ratio in the measured transients. However one must ensure that there are enough optically active states in the material to absorb all of the incoming photons! In addition, TOF transients are typically performed with very low charge density to minimize carrier-carrier interactions. A reasonable target is to have 1 carrier generate per 1000 states adjacent to the transparent electrode. For typical PbS NC solids, this corresponds a laser pulse with \( \sim 10^9 \) photons per cm\(^2\). A lower photon flux compromises the signal to noise ratio, while much more would invalidate the low carrier concentration and initial charge density assumptions.

The next crucial assumption in the analysis is that the carriers in the device feel the electric field resulting from the applied bias, or put simply, that the difference in electric potential between the two electrodes is equal to the applied bias \( (V_A - V_B = V) \). This assumption has two requirements. First, the photo-injected charges must be efficiently extracted by the electrodes, otherwise they may form capacitive layers on the electrodes and screen the applied field.
Second, additional charge should not be injected into the device from the external circuit, otherwise we will have $V_A - V_B < V$. Conveniently, both of these requirements are met for measurements on heterojunction solar cells in reverse bias, due to the selectivity of both contacts \[112\]. The heterojunction device architecture thus facilitates TOF measurements.

**Theory**

We conclude the discussion of the TOF method by briefly reviewing the theory developed to interpret ‘anomalously dispersive’ transients in existing literature. To date, theoretical approaches employed to interpret TOF data has worked from the measurements backwards. That is, rather than starting from first principals to derive transport models which could reproduce experimental observations, authors have typically developed numerical models which reproduce experimental data, and attempts are then \textit{a posteriori} made to justify the numerical models from first principles.

To begin, we first consider some of the features commonly observed in TOF transient studies. It was mentioned previously that the ‘anomalously dispersive’ transients follow two distinct power laws, given in equation 2.16. In fact, some studies have found the two exponents in the relation to be equal, $\alpha_+ = \alpha_- = \alpha$ (see Fig. 2.7) \[104, 111\]. This gave theorists the clue that the same physical process was responsible for both power law components. In addition, TOF transients often exhibited a universality in their exponent $\alpha$ for different biases $V$ and thicknesses, $d$. This universality is apparent when the transients were plotted using axes scaled by their $t_{tr}$, $t \rightarrow t/t_{tr}(V,d)$ and $I(t) \rightarrow I(t)/I(t_{tr}(V,d))$. In Figure 2.7 we give reproductions of measurements plotted in this way \[111\]. With the axes scaled, the transients for different biases and thicknesses collapse onto a single curve. Universality of transient shape implies that the relative dispersion $\sigma(t)/\langle l(t) \rangle$ is independent of time, where $\sigma(t)$ is the standard deviation of the position of the carriers, and $\langle l(t) \rangle$ is their mean position at time $t$.

One of the early breakthroughs came from the work of Scher and Montroll \[111\]. They performed calculations of a time-dependent random walk on a cubic lattice. The electric field, $\vec{E}$, was modelled...
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Figure 2.7: TOF transients measured on amorphous As$_2$Se$_3$ (a) of various thickness and biases (different symbols in the plot), plotted on axes scaled by their individual TOF transit times, $t_{tr}$. Similar treatment for TOF transients measured on 2, 4, 7 trinitro-9-fluorenone/poly-N-vinylcarbazole measured at room temperature at various biases. Reproduced from Scher and Montroll [111].

in their calculations by a spatial bias their hop probabilities in the direction of $\vec{E}$. For $\vec{E}$ in the $x$-direction the hopping probabilities, $p$, were then,

$$ p(0, \pm 1, 0) = p(0, 0, \pm 1) = 1/6, $$
$$ p(1, 0, 0) = \eta/3, $$
$$ p(-1, 0, 0) = (1 - \eta)/3, $$

where $1/2 \geq \eta \leq 1$ gives the variable spatial bias in the $x$-direction. The hopping time was then pulled from a statistical distribution. The authors employed several hopping time distributions, and found that they could qualitatively reproduce all of the observed features of ‘anomalously dispersive’ transients provided that the hopping time distribution, $p(t_{hop})$, was given by a power law,

$$ p(t_{hop}) \sim t^{-(1+\alpha)}, \quad 0 < \alpha < 1. $$

The transients calculated with this distribution have the form given in eq. 2.16 with $\alpha_+ = \alpha_- = \alpha$, and collapsed onto a single curve for all $1/2 \geq \eta \leq 1$ and $d$. The distribution of hopping times can be
extracted from measurement, within the framework of this model, by simply measuring one of the power-law decay exponents (eq. [2.16]) of the transient. This type of model is often argued in terms of spatially disordered hopping transport: a large spatial disorder in the hopping sites gives rise to a power law distribution of hopping times.

Figure 2.8: Charge transport models employed to interpret TOF transients.

Other approaches, notably those of Schmidlin [113] and Noolandi [114], employed linear transport equations corresponding to a model of carrier transport through a band in the presence of shallow traps (band-tail states, see Fig. 2.8). Charge carriers drift with a velocity \( v = \mu E \), until encountering a shallow trap of depth \( E_i \), from which the release time, \( t_r \), is:

\[
t_r \sim e^{E_i/k_b T}.
\] (2.19)

Schmidlin [113] and Noolandi [114] investigated several shallow trap distributions and demonstrated that the calculated transients satisfied the criteria for ‘anomalously dispersive’ transients. In fact, if the distribution of band tail states is exponentially distributed, \( f(E_i) = m^{-1}e^{-x/m} \), it is trivial to demonstrate that the distribution of release times will be power law distributed,

\[
f(t_r) \sim t_r^{-(1+k_b T/m)}.
\] (2.20)

The take-away message of the preceding discussion is that ‘anomalously dispersive’ current transients have a power law distribution reflective of the carrier transport dynamics at long times.
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2.2.2 Measuring Lattice Dynamics

To measure the phonon density of states of NCs we turned to inelastic neutron scattering. In this section, we discuss the principles of the experiment and the data analysis, giving specific details of the experimental setup for the interested reader afterwards. Information about the preparation of the samples is given in Section 2.2.3.

Inelastic Neutron Scattering

The energy $E$ of a neutron with wavevector $\vec{k}$ is

$$E = \frac{\hbar^2|k|^2}{2m_n}. \tag{2.21}$$

The rest mass of the neutron is $1.675 \cdot 10^{-27}$kg, so a neutron with a wavelength on the order of Å thus has an energy on the order of meV. When the energy of the neutron is on the order of the energy of lattice vibrations ($\sim$meV), their wavelength is on the order of the atomic spacing in condensed matter. Neutrons are thus an excellent probe for lattice dynamics.

The setup of the experiment is given in Figure 2.9a. A monochromator is used to diffract neutrons of a particular energy, $E_0, \vec{k}_0$, from the beam from the source towards the sample. A Fermi-Chopper modulates this monochromatic beam, such that a short pulse of monochromatic neutrons impinges on the sample. The scattered neutrons are detected by a bank of time resolved detectors at different angles $\theta$. An example of what a detector would measure for a typical sample is shown in Figure 2.9b. The detectors measure the number of neutrons which arrive in a given period of time. In the figure, $t^*$, the time corresponding to the large peak, indicates the time at which the elastically scattered neutrons (i.e. 0 energy transfer to the sample) arrived at the detector. The counts for $t < t^*$ correspond to neutrons which sped up as a result of interaction with the sample ($\Delta E > 0$), while the counts for $t > t^*$ correspond to $\Delta E < 0$. Knowing the path length from the sample to the detector and the detector angles, we can calculate the dynamic structure factor $S(q, \omega)$, which is the intensity of neutrons scattered with energy transfer $\Delta E = \hbar \omega$ and momentum transfer $q$ [115].
Figure 2.9: Inelastic Neutron Scattering with the FOCUS time of flight spectrometer at PSI. The setup of the experiment is shown in (a). The bank of detectors measure the counting statistics of the scattered neutrons as a function of time. The elastic scattering peak at $t^*$ is used to define $\Delta t = 0$. Knowing the initial energy of the neutrons, the sample to detector lengths and angles, the dynamic structure factor $S(q, \omega)$ can be calculated from the energy $\Delta E = \hbar \omega$ and momentum $q$ transfer to the samples.
Provided the neutrons interact with at most 1 phonon within the sample, we can assume that the 1-phonon dynamic structure factor is equal to the measured one, $S_1(q, \omega) = S(q, \omega)$. The phonon density of states can then be calculated from $S_1(q, \omega)$. From the measured $S(q, \omega)$ we calculate the neutron-weighted phonon density of states $g(\omega)$, which ignores the different neutron scattering cross-sections of the different elements, as:

$$g(\omega) = \begin{cases} 
D_p \frac{\hbar \omega}{n(\omega)} S_1(q, \omega), & \Delta E < 0, \\
D_p \frac{\hbar \omega}{n(\omega) \exp[\hbar \omega/k_B T]} S_1(q, \omega), & \Delta E > 0,
\end{cases}$$

(2.22)

where $n(\omega) = (\exp[\hbar \omega/k_B T] - 1)^{-1}$, and $D_p$ is a factor related to the phonon structure factor and is proportional to $q^{-2}$. In practice, one uses the energy gain side ($\Delta E < 0$) of the measured $S(q, \omega)$ to calculate eq. (2.22) as the energy loss side is limited to a maximum of the initial neutron energy, $E_0$. If a neutron interacts with 2 phonons, it will scatter from the first phonon with a dynamic structure factor $S_1(q, \omega)$, which would then scatter again with $S_1(q, \omega)$, such that the observed dynamic structure factor would be $S_2(q, \omega) \propto S_1(q, \omega) \ast S_1(q, \omega)$. In fact, the multi-phonon $S_n(q, \omega)$ can be obtained recursively as

$$S_n(q, \omega) = \frac{1}{n} S_1(q, \omega) \ast S_{n-1}(q, \omega).$$

(2.23)

Since the measured $S(q, \omega) = \sum S_n(q, \omega)$, we can determine $S_1(q, \omega)$ as

$$S_1(q, \omega) = F^{-1} \{ \ln [1 + F\{S(q, \omega)\}] \}. \quad (2.24)$$

From the measured $S(q, \omega)$, we can also determine the mean square thermal displacement of the atoms in the samples, $\langle u^2 \rangle$. $\langle u^2 \rangle$ is related to the Debye-Waller factor, $W$, which can be calculated from the ratio of the total scattering $I_{TOT}(q)$ and total inelastic scattering, $I_0(q)$ for fixed $q$:

$$q^2 \langle u^2 \rangle = 2W = \log(I_{TOT}/I_0). \quad (2.25)$$

As the energy range is limited to the initial neutron energy $E_0$ on the energy loss side of the measurement, it is customary to calculate eq. (2.25) using detailed balance,

$$S(q, |\omega|) = \exp[\hbar \omega/k_B T] S(q, -|\omega|). \quad (2.26)$$
We can then calculate the total scattering as,

\[ I_{TOT}(q) = \int_0^\infty (1 + \exp[\hbar\omega/k_B T]) S(q,\omega) d\omega. \quad (2.27) \]

The total elastic scattering, \( I_0(q) \) is typically determined by fitting a Gaussian to the elastic peak. The calculated \( \langle u^2 \rangle \) should be independent of \( q \), and calculations are often double checked by ensuring convergence of \( \langle u^2 \rangle \) for different \( q \) \([90,102,115]\).

**Experimental Details**

We performed the inelastic neutron scattering experiments at the cold-neutron time-of-flight neutron spectrometer FOCUS at the Swiss Spallation Neutron Source (SINQ, Paul Scherrer Institute, Villigen, Switzerland). An incident neutron energy of 14.2meV (wavelength of 2.4Å) was used. The neutron energy resolution was optimized using the time-focusing technique with a focusing energy of 2.5meV, and the energy resolution was measured to be 0.97meV at 0meV energy transfer. The simulated resolution was 1.22meV at 6.0meV energy transfer and 2.25meV at 18.0meV energy transfer. All samples contain between 5-8 g of powder, distributed over the cross section of 4.5cm by 1cm resulting in 2-19% scatterers (as determined experimentally in comparison with a Vanadium standard). The powder is contained only by 6-layers of aluminum foil (\( \sim 0.1 \)mm) to minimize scattering from the sample holder. The foil is supported by an aluminum frame, which was shielded by Cadmium. The empty sample holder with Cadmium shielding was measured as background for the experiment. The measurements were performed in reflection geometry at a slab angle of 45°. The absorption shadow that is cast by the Cadmium shield covered detectors at small scattering angles, resulting in a usable \( q \) range of 2.6Å\(^{-1}\) - 4.6Å\(^{-1}\). Data reduction was done using DAVE38. A 5.0cmx1.5cmx0.2mm thick Vanadium standard was used for detector efficiency calibration, to measure the incident neutron energy and the energy resolution. All measurements were measured over 8 hours to ensure sufficient counting statistics \([90]\).
2.2.3 Materials and Devices

Here we summarise the materials and devices used for the experimental work presented in this thesis. A short summary of the PbS NC synthesis is followed by a description of the devices used for TOF measurements. Finally, the preparation procedure for samples for inelastic neutron and X-ray scattering is given.

**Lead-Sulfide Nanocystal Synthesis**

Colloidal oleic-acid capped PbS NCs dispersed in toluene were synthesized using the hot injection method, where size-tunability is primarily achieved via different concentrations of oleic acid in the starting solution. Details of the synthesis can be found in Hines et al. \[117\]. Lead (II) oxide (99.999%) is purchased from Strem Chemicals, while the remaining chemicals used in the synthesis are purchased from Sigma Aldrich. Where specified, the Hines recipe was modified according to that of Ip et al. \[110\] to include a cadmium chloride (CdCl) treatment of the NCs during cooldown. After synthesis, the NCs are washed by precipitating the NCs out of toluene via addition of acetone, followed by re-dispersion in toluene. This is done three time sequentially. Solutions are stored at \(\approx 100 \text{ mg mL}^{-1}\) in toluene. Prior to device fabrication, the PbS NCs are washed an additional three times using mixtures of methanol and ethanol as antisolvent, and finally dispersed in hexane with a concentration of \(\approx 5 \text{ mg mL}^{-1}\).

Absorption of PbS NCs was carried out with an Agilent Cary 5000, and PL of the NCs was measured with an Ocean Optics NIRQuest512 spectrometer. To do so, 100\(\mu\text{L}\) of 5 mg mL\(^{-1}\) PbS solution in hexane was introduced to a quartz cuvette, and the hexane was evaporated. 3mL of trichloroethene (TCE) was then used to re-disperse the NCs. TCE has the advantage that it is transparent over a wide range of visible and infrared (IR) frequencies. In Figure 2.10, the absorption spectra of typical PbS solutions used for device fabrication are shown, along with TEM images taken by O. Yarema. A strong scaling of the position of the first absorption peak with NC size is evident.

The reported radii of the PbS NCs in this thesis are computed from the position of the first absorption peak using the empirical model of Cademartiri et al. \[118\], which we crosschecked with TEM imaging.
Devices for Time of Flight

As we have discussed in Section 2.2.1, the heterojunction solar cell device architecture facilitates TOF measurement. We therefore fabricated [titanium dioxide (TiO$_2$), PbS, molybdenum oxide (MoO$_x$), gold (Au)] heterojunction solar cells with the structure depicted in Figure 2.11 based on recipes adapted from literature [119, 120]. The PbS layer was fabricated via a solid-state ligand exchange, as discussed in Section 1.1.3. While in 2014 the best performing heterojunction solar cells utilised 3-mercaptopropionic acid (MPA) for
ligand exchange [120], we employed EDT. We chose EDT to enable
direct comparison with previous work done by our group [89,121].

Figure 2.11: SEM image of the cross section of a heterojunction solar
cell.

With this architecture, in reverse bias, electrons are pulled out
from the TiO\textsubscript{2} electrode while the holes must traverse the length of
the device to be extracted at the MoO\textsubscript{x}/Au electrode. The standard
heterojunction solar cell architecture is thus suited for investigating
hole transport. To measure electron transport, we had to either make
the back contact transparent, or fabricate inverted-heterojunction de-
vices. One may think of the possibility of replacing the MoO\textsubscript{x}/Au
back contact with sputtered indium tin oxide (ITO) or nickel oxide
(NiO); however, oxygen-plasma assisted sputtering deposition irre-
versibly damages the PbS layer. We therefore developed an inverted
device architecture employing the stack: NiO, PbS, lithium fluoride
(LiF), aluminium (Al).

Plots of the current-voltage response of the devices in dark and
with AM 1.5 illumination are shown in 2.12. The measurements in
Figure 2.12 also show that the difference between the illuminated/dark
currents in reverse bias differ by 4-5 orders of magnitude. This gave
Figure 2.12: Dark (black) and light (AM 1.5, red) current-voltage measurements on heterojunction (employing CdCl treated PbS NCs) and inverted-heterojunction devices.

us confidence that our assumption for TOF analysis that the photo-generated carriers are efficiently extracted while injection of carriers from the electrodes is suppressed.

Heterojunction Device Fabrication

A titania nanoparticle paste (DSL 90-T, Dyesol), diluted to 125mg mL$^{-1}$ in acetone, was spun at 2500rpm for 60s on fluorine-doped tin oxide (FTO)/glass substrates (Solaronix or Thin Film Devices). Samples were placed on a hotplate at 500°C for 60min, then immersed in a 60mM titanium-tetrachloride/deionized water solution at 70°C for 30min, thoroughly rinsed with deionized water, and then placed on a hotplate at 500°C for 60min. PbS NC layers were deposited by sequential dipcoating in a PbS NC solution (5 mg mL$^{-1}$ in hexane), a crosslinking solution (6mM EDT in acetonitrile), and a rinsing solution (acetonitrile). The cross linking and rinsing solutions use anhydrous acetonitrile, stored and prepared in an N$_2$ glovebox, and brought into ambient immediately prior to dip-coating. Dip-coating was carried out in air. To adjust PbS NC solid thickness, the number of dip-coating cycles was varied, and the thicknesses were measured.
from SEM cross-sections of the device following TOF measurements. The top MoO$_x$/Au/silver (Ag) electrodes were deposited by thermal evaporation. Ag serves to improve the electrical contacts.

**Inverted-Heterojunction Device Fabrication**

NiO is deposited on patterned ITO/glass substrates (Thin Film Devices). Deposition of NiO is by RF magnetron sputtering using a 99.95% purity NiO target. The plasma is ignited at a pressure of $1.5\times10^{-2}$ mBar with a nominal Ar flow of 50sccm and a starting power of 40W. Once burning, the power is ramped up to 80W over 30s. At this point the pressure is lowered to $5\times10^{-3}$ mBar and 10% partial pressure of oxygen is added to the Ar flow. After 2 minutes, the power is ramped up further to 120W over 30s. After 2 further minutes, the power is ramped up over 30s to its final value of 140W. The pre-sputtering is done for 30min under the same conditions as the main sputtering. The substrate holder rotates at 10rpm during the entire deposition. Dip coating of the NiO coated substrates proceeds identically to that of the inverted device architecture. The top LiF/Al/Ag electrodes were deposited by thermal evaporation.

**Samples for Inelastic Neutron Scattering**

As a result of the small scattering cross-section of neutrons (element dependent but typically on the order of $10^{-24}$ cm$^2$), large amounts of material are required for inelastic neutron scattering. For our measurements on PbS NCs the experiment required $\sim$8g of PbS NCs per sample, this necessitated the design of an upscaled synthesis technique, discussed in detail in [90, 122]. We prepared 7 PbS samples for the experiment, a reference bulk sample (Sigma Aldrich (Lead(II) sulfide) 99%), a powder of $r = 8.2$ nm NCs, a NC solid powder with $r = 1.33$ nm NCs ligand exchanged with deuterated 1,2-ethanedithiol (EDT-d4) and a size series of NC solids using NCs with radii between 1.59 nm and 3.50 nm ligand exchanged with EDT.

Fabrication of $\sim$8g of PbS NCs solids also presented a unique challenge, as the large quantity of sample needed necessitated a solution based ligand exchange procedure. The samples were all fabricated by the following procedure, with the details of each ligand exchange
described separately below \[90\]. Each sample was composed of NCs from the same synthesis, but the ligand exchange was carried out on 10 portions of the NC solution in parallel, due to the limitations of a lab-scale centrifuge. We first mix 10-15mL of 70-90mg/mL PbS NCs in hexane, 10mL of the ligand exchange solution, 25mL of methanol (MeOH) in a 50mL centrifuge tube. The solutions were centrifuged at 13000g for 5min. The supernatant was poured away, and then we added in 20mL toluene. We then repeated the ligand exchange a second time with 1/3 of the ligand exchange solution. After centrifugation and removal of the supernatant, the paste-like material from each of 10 centrifuge tubes was transferred to a nitrogen glovebox and compressed into a Petri dish. The paste was dried in the glovebox at 50°C for 5h into a brittle cake, which was then transferred into the aluminum holder for the neutron scattering measurements. All samples were stored in a nitrogen glovebox, with only brief air exposure when mounting the samples for measurement.

Figure 2.13: SEM images of the bulk PbS sample, 8.19nm PbS NCs sample, and 1.33nm PbS/EDT-d4 NC sample. Their XRD patterns with refinement to Fm3m crystal structure are shown below. \[90\]

To fabricate the powder of \( r = 8.2 \text{nm} \) NCs, we used sodium sulfide (Na\(_2\)S) to remove the native ligand. The ligand exchange solution was comprised of 11.6g Na\(_2\)S·9H\(_2\)O + 96mL MeOH. From XRD (see Fig. 2.13), we find that the ligand exchange procedure fuses the original NCs into NCs with crystallite radius (8.18 nm). These larger crystals
are visible in SEM images, as seen in Figure 2.13. For NC-solid powder with $r = 1.33$ nm NCs ligand exchanged with EDT-d4, the ligand solution was comprised of 1.01 mL EDT-d4 (EQ Laboratories GmbH in Augsburg, Germany) in 120 mL acetonitrile (8.4 µl/ml)). For the size series samples, we followed the same procedure as for the EDT-d4 but use regular EDT. Due to the lower cost of EDT compared to EDT-d4, we increase the amount of EDT-solution in both steps by 75% to speed-up the ligand exchange. All samples were characterized via SEM and XRD. SEM was performed on a Hitachi S-4800, and the XRD on a Stoe Stadi P powder X-ray diffractometer.

Electrical Characterisation Setup

For all of the electrical characterisation presented in this thesis, samples were mounted into a cryostat (Janis ST-500) after 2 min of air exposure, where they remained in vacuum during the measurements.

Current-voltage measurements were carried out using a Keithley 2400 source measure unit, and AM1.5G illumination was provided by a mercury(xenon) DC arc lamp (Newport) and an air mass filter, calibrated using a piezoelectric sensor and an optical power meter (Thor Labs S302C, PM100D).

For TOF measurements, devices were mounted using a custom holder on a Nikon Eclipse Ti-U optical microscope. A 405 nm, 100 ps excitation pulses was provided by a Hamamatsu picosecond pulsed laser (PLP-10). Temperature was controlled with a Lakeshore temperature controller, and voltage biases were applied using an Agilent 33522A arbitrary waveform generator and the current was measured on a Rohde & Schwarz RTM1054 oscilloscope through the 50Ω input. Measurements were averaged over 1024 cycles at a frequency of 10 kHz. Initial rise times of the transients due to the capacitance of the devices were approximately $\sim 10$ ns, much shorter than the typical $t_{tr}$ times of $\sim 200-1500$ ns extracted from the TOF transients. $t = 0$ for the transients was thus taken as the initial peak of the measured transients.
Chapter 3

Phonon Properties in Nanocrystals

As we have discussed in Chapter 1.3.3, there is an overwhelming amount of experimental evidence pointing to strong electron-phonon coupling and efficient multi-phonon mediated electronic transitions in colloidal NCs and NC-solids. While there exists a variety of suggestions as to the origins of these fast transition rates \[123, 124\] and attempts have been made to estimate them \[125, 127\], fundamental questions surrounding electron-phonon interactions in NCs remain.

3.1 Measuring the Phonon Density of States

†The first step in the study of electron-phonon interactions is a knowledge of the phonon-density of states, \(g(\omega)\). To this end, we performed inelastic neutron scattering (INS) on PbS NCs. Details of the sample preparation, INS measurements and analysis are given in Chapter 2.2.2.

Figure 3.1: Results from inelastic neutron scattering. a) Elastic line ($\omega = 0$) and the dynamic structure factor ($S(q, \omega)$) measured for bulk and NC PbS. b) $g(\omega)$ for the same samples with calculated $g(\omega)$ for bulk PbS below. c) $g(\omega)$ for various NC radii. INS analysis performed by Bozyigit [90].
3.1. MEASURING THE PHONON DENSITY OF STATES

In Figure 3.1a, we plot the measured dynamic structure factor, \( S(q, \omega) \) where \( q \) is the momentum transfer and \( \omega \) is the energy transfer, for bulk PbS \( r \sim 8.2 \text{nm} \) PbS crystallites, and a \( r = 1.33 \text{nm} \) PbS NCs solid, prepared with EDT-d4. The integrated scattering intensities about \( \omega = 0 \), corresponding to elastic scattering, are also shown.

For bulk PbS we observe the expected distinct peaks in the elastic line corresponding to Bragg reflections of the PbS lattice, and structure along the \( q \) axis with finite energy transfer, \( \omega \neq 0 \), indicating a dispersion in the phonon-band-structure due to the long range translational symmetry of the lattice. Both features in the \( q \) axis progressively disappear as the size of the crystallites decreases, indicating a break-down of the plane-wave symmetry of the phonon modes in the NCs. As described in Chapter 2.2.2 we also extract the mean thermal displacement, \( \langle u^2 \rangle \), of the atoms from \( S(q, \omega) \), as labelled in 3.1a. We observe a two-fold increase in \( \langle u^2 \rangle \) going from bulk PbS to the \( r = 1.33 \text{nm} \) NCs.

The measured phonon density of states, \( g(\omega) \), for each sample are shown in Figure 3.1b. While the optical phonon modes are at too high an energy to resolve reliably at the temperature of the experiment, \( T = 300 \text{K} \), we can clearly resolve features of the transverse acoustic (TA) (48.8 cm\(^{-1}\)) and longitudinal acoustic (LA) (84.4 cm\(^{-1}\)) modes. For reference DFT calculations for bulk PbS \( g(\omega) \) are shown below, from which we can see excellent agreement with INS measurements of the bulk \( g(\omega) \).\(^1\) As the crystallite size is decreased, we observe a reduction in the relative weight of the TA and LA modes, and the emergence of new low energy phonon modes (\( \sim 25 \text{cm}^{-1} \)).

We additionally investigated the impact of varying the NC size within the strong quantum-confined regime, from \( r = 1.5 - 3.3 \text{nm} \), corresponding to an absorption bandgap of \( E_g = 1.4 - 0.75 \text{eV} \), respectively. Despite the strong dependence of \( E_g \) on the NC radius in this regime, no systematic influence on their \( g(\omega) \) was observed, as seen in Figure 3.1.

Furthermore, one ligand exchange was performed with EDT-d4 while the other samples were ligand exchanged with EDT. Hydrogen has a large neutron scattering cross-section (\( 8 \times \) that of Pb), while its

\(^1\) Details of bulk PbS calculations are provided in appendix C.1 and a plot of the bulk phonon bandstructure is given in Fig. B.1.
deuterated form has an appreciably weaker scattering cross-section (≈ that of Pb). We performed AIMD simulations on various EDT/Pb complexes, and determined that the additional peaks in the $g(\omega)$ for the EDT samples can be attributed to the disproportionate scattering of the EDT molecules.

In summary, our INS measurements for NC $\sim < 3$nm show the breakdown of the plane-wave symmetry of the phonon modes, with the emergence of low frequency modes and an increase in atomic motion. To investigate the origin of these effects, predict their impact on electron-phonon coupling, and determine how one can tune these effects, we turned to large-scale AIMD simulations.

3.2 Origins of Low Frequency Modes

† From the INS results, we have seen that the main features distinguishing the PbS NCs from the bulk was the emergence of low frequency phonon modes ($\sim 25$cm$^{-1}$) below the energy of the TA peak (50cm$^{-1}$), and an increase in the mean-squared thermal displacement of the atoms, $\langle u^2 \rangle$, effects which were found to be relatively insensitive to the NC size for small NCs ($r < 3$nm). To investigate the origin of these effects in the NCs we implemented large scale AIMD simulations.

We constructed a $\sim 3$nm PbS NC similar to the methodology outlined in 2.1.2 except here we did not employ ligands. To satisfy charge balance (eq. 2.8) we randomly removed Pb atoms from the surface of the NC until charge balance was satisfied. A picture of the atomistic model is shown in Figure 3.2. AIMD at 100K was performed as explained in 2.1.3. In Figure 3.2 we plot the $g(\omega)$ for both the NC and bulk PbS. In agreement with the INS data, the simulated $g(\omega)$ shows the presence of low frequency modes ($\sim 25$cm$^{-1}$) below the TA peak (50cm$^{-1}$), accompanied by a general loss of structure in the modes at higher frequencies, including the appearance of optical modes with frequencies above the highest frequency modes in the

3.2. ORIGINS OF LOW FREQUENCY MODES

Figure 3.2: $g(\omega)$ for Pb and S atoms calculated via AIMD for the PbS NC shown in the left. The filled lines correspond to the bulk PbS $g(\omega)$. [$^90$]

bulk ($\sim 240 \text{cm}^{-1}$). In addition, we see a small but finite contribution of S atoms to the low frequency modes, which breaks the real-space symmetry observed for the bulk.

To investigate where in the NCs these new modes and the increase in $\langle u^2 \rangle$ originate, we calculate the partial $g(\omega)$ and average $\langle u^2 \rangle$ for different regions of the NC (Fig. 3.3a). The plot of the average $\langle u^2 \rangle$ as a function of depth below the surface of the NC is given in Figure 3.3b. The $\langle u^2 \rangle$ matches the value in bulk PbS (0.015 Å$^2$ [$^{128}$]) in the core of the NC ($d > 10\text{Å}$), while it is substantially larger (0.027 – 0.074Å$^2$) at the surface of the NC ($d < 10\text{Å}$). The increased 2-fold increase in $\langle u^2 \rangle$ found via INS for the NCs compared to the bulk stems from the surface of the NCs.

We then calculate the partial $g(\omega)$ for both Pb and S atoms in three regions of the NC (Fig. 3.3a): the surface region consisting of the outermost 2 atomic layers (Region 3), followed by a 2 atomic layer subsurface region (Region 2), and the core of the NC (Region 1). The partial $g(\omega)$ are plotted in Figure 3.3c, along with the bulk partial $g(\omega)$ as reference. We see that in the core of the NC, the partial $g(\omega)$ of both Pb and S in the NC match those calculated from the bulk. The partial $g(\omega)$ of the atoms on the surface of the NC show a significant departure from the bulk, from which we see that both
Figure 3.3: Breakdown of the partial $g(\omega)$ and $\langle u^2 \rangle$ in the PbS NC. The NC is decomposed into three regions (a) for calculating partial $g(\omega)$, while $d$ measures the depth of the atoms from the surface. The mean $\langle u^2 \rangle$ as a function of $d$ is plotted in (b) while (c) shows the partial $g(\omega)$ for the three regions as well as as a function of $d$. The low ($\sim 25 \text{ cm}^{-1}$) and high ($> 240 \text{ cm}^{-1}$) frequency modes observed for the NC originate from Pb and S surface atoms. From structural calculations on 2D PbS slabs (see Fig. B.2), we observed a surface reconstruction of the PbS surface with a characteristic length scale of $\sim 3 \text{Å}$, consistent with the convergence of the partial $g(\omega)$ to the bulk. In addition, surface atoms will be under-coordinated, leading to a mechanical weakening of the NC surface. The $\langle u^2 \rangle$ of a phonon
mode is inversely proportional to the effective spring constant of the phonon mode, $\kappa_{\text{eff}}$,

$$\langle u^2 \rangle = k_B T / \kappa_{\text{eff}}. \quad (3.1)$$

$\kappa_{\text{eff}}$ will depend on the strength and number of bonds. Therefore lower-coordinated atoms will have larger $\langle u^2 \rangle$.

We thus conclude that reconstruction and mechanical weakening of the surface of the NCs allows both low ($\sim 25\text{cm}^{-1}$) and high ($> 240\text{cm}^{-1}$) frequency modes with large thermal displacements. For small NCs changes in $g(\omega)$ stemming from the surface this should be relatively insensitive to the NC size. With the atomistic model for PbS outlined in Section 2.1.2, we calculate that surface atoms comprise 34% and 27% of the total number of atoms for 1.2nm and 2.2nm NC, respectively.

### 3.3 Engineering Surface Modes

†The efficiency of semiconductor NC devices has benefitted tremendously from advances in NC surface chemistry [21, 129]. High photoluminescent quantum yields in NCs are linked to engineering of the NC surface, where core/shell structures have been used [130] to optimize radiative rates [131], emission wavelengths [132], and hot carrier cooling rates [74, 133]. NC-based solar cell performance has been improved with the evolution of termination strategies to increase charge carrier mobility [24, 49], reduce charge carrier recombination [110], and increase carrier extraction through optimizing inter-NC band alignment [65].

To date, the benefits resulting from surface engineering have predominately been discussed in terms of modification of the electronic properties. The introduction of a shell on a NC can be used to confine the electron, hole, or exciton in the core of the NC, an engineering approach to increase radiative recombination rates or decrease non-radiative rates by for example spatially separating the electron and hole from electronic defects stemming from surface states [133, 134], decreasing the rates of nonradiative Auger processes [86], or minimize

exciton polarization in the presence of an electric field \[135\]. In the case of NC solar cells, most literature emphasizes the role of surface termination on the passivation of defect states at the surface of NCs \[110,136,137\].

As we have seen, the surface of the NC plays an important role in determining the vibrational structure of NCs. Here, we show what effects modifying the surface termination has on the vibrational and electronic properties of the NCs. To this end, we turned to large-scale DFT and AIMD calculations on \(r \sim 1.4\) nm PbS NCs constructed according to the atomistic model described in Section 2.1.2, consisting of \(N_{Pb}=201\) Pb atoms and \(N_{S} =140\) S atoms, and terminated with \(N_L=120\) ligands. For the ligands, we employed Iodide (I), Bromide (Br), Chloride (Cl), and methanthiol (MTH). The atomistic models are shown in Figure 3.4.

### 3.3.1 Electronic Structure

In the bulk, PbS is a direct-gap semiconductor with the band gap occurring at the \(L\)-point, as shown in Figure 3.5\(^2\). Both the valence and conduction band are 8 fold-degenerate including spin due to the four-fold symmetry. The VBM states are of mixed \(3p\)-S / \(6s\)-Pb character, while the CBM states are of mixed \(6p\)-Pb / \(3s\)-S character.

For NCs, shape has been shown to effect the splitting and energetic ordering of quantum confined levels due to inter-valley coupling \[139-142\]. For our NCs, the 4-fold degeneracy of the VBM and CBM in

\(^2\)Details of bulk PbS calculations are provided in appendix C.1
Figure 3.5: Electronic band-structure of bulk PbS calculated within the GGA and with no SO interaction (a), and including HF and SO (b). The second column shows a closeup about the bandgap, and the last two columns show the orbital character of the wavefunctions [138].

bulk PbS is broken due to the [100] facets of the NCs. Both the VBM and the CBM bands give rise to 3 degenerate states and a singly degenerate level, all with S-type envelope functions for the electron densities, as shown in Figure 3.6. The CBM is singly degenerate (which we label \( \psi_{1e} \)) followed by triply degenerate states (\( \psi_{2ea} \)), while the VBM is triply degenerate (\( \psi_{1ha} \)) followed by a singly degenerate state (\( \psi_{2h} \)). The plot of the number of electronic states indicates that the NCs exhibit (1) no electronic states in the bandgap, which is to be expected for a defect-free NC, and (2) a larger density of states in the VB than in the CB, which is consistent with previous calculations on PbSe NCs [141].

In agreement with recent calculations by Voznyy et al. [143], while the envelope function for all 8 band edge states are S-type, the underlying lattice wavefunctions have differing symmetries. In Figure 3.7a we show the dipole matrix elements between the four VB and CB states for the PbS Cl NC (all analysis shown here yields quantitatively similar results for the other surface terminations). We find that the
dipole matrix elements for the lowest energy transitions $\psi_{1h\alpha} \rightarrow \psi_{1e}$ are small. The optically allowed transitions, through which absorption will occur, are the $\psi_{1h\alpha} \rightarrow \psi_{1e\alpha}$ and $\psi_{1h} \rightarrow \psi_{1e\alpha}$ transitions. The results can be understood by considering the symmetries of the wavefunctions and explains the observed stoke-shift in PbS NCs.

For our calculations, SO and HF contributions are not included. To gauge how these effects may impact the electronic fine structure of the NCs, we compute the bulk bandstructure of PbS including SO and HF contributions, as shown in 3.5b. We find that while SO interactions narrow the band-gap, HF opens it up, and the net result is an increase of the bandgap from 0.37eV (GGA) to 0.47eV (SO + HF). Another significant effect of SO and HF is a splitting of the 16-fold degenerate bands deeper within the CB and VB, shown in 3.5b. However, the VBM and CBM as well as the inter-valley peaks in the $\Gamma - K$ and $\Gamma - X$ directions and the peak at the W point, remain 4-fold degenerate with only slight shifts in energy. As the first few quantum confined states will primarily derive from these points, we conclude that SO and HF interactions should not effect the fine-structure beyond a slight increase of the calculated bandgap.
3.3. ENGINEERING SURFACE MODES

Figure 3.7: (a) Plot of the dipole matrix elements for the PbS/Cl NC. Calculations for the other NCs yield similar results. (b) Plots of the wavefunctions of the $\psi_{1e}$, $\psi_{1e\alpha}$, $\psi_{1h\alpha}$, and $\psi_{1h}$ states, with the viewing axis fixed to show the minimal symmetry of the wavefunctions.

Finally, we consider the impact of changing the surface termination of the NCs on their electronic structure. In Figure 3.8, we plot cross-sections of the electron density for the VBM and CBM for the NCs with different surface terminations. The density plotted for the VBM is the average of the three-fold degenerate states, while for the CBM it is the density in the lowest singly degenerate state. Consistent with previous calculations on Cl-terminated NCs [99], the wavefunctions for our halide-terminated NCs are confined in the NC away from the [111] facets. The total carrier density on the two outermost atomic layers on the [111] facet decreases by 40% (0.17→0.10) in the CBM and 60% (0.27→0.11) in the VBM from mth to Cl surface termination. The extent of electronic confinement increases with increasing electronegativity of the anion (S, I, Br, Cl), which is evidenced by the increasing electronic bandgaps, printed in Figure 3.8.
Figure 3.8: Slices through the NCs showing the electron density in the conduction band minimum (CBM) state and the 3-fold degenerate valence band maxima (VBM) states for all four surface terminations: mth, Cl, Br, and Cl. The calculated bandgaps of the NCs (indicated) are underestimated as is typical for density functional theory calculations [138].

3.3.2 Vibrational Structure

We now consider the vibrational structure of the NCs and determine the impact of the halide anion and thiol surface terminations. We performed AIMD at 100K, as explained in 2.1.3, for all surface terminations. The \( g(\omega) \) for each is shown in Figure 3.9 along with the \( g(\omega) \) for bulk PbS as reference.

For the NCs, regardless of surface termination, low frequency modes emerge below the TA peak of PbS bulk (48.8 cm\(^{-1}\)) and the LA peak shifts to lower energies (50-80 cm\(^{-1}\)), as observed for the ligand-free/NC in Section 3.2. For the PbS/mth NC, the partial \( g(\omega) \) for S-atoms extends to lower frequencies and the carbon (C) and hydrogen (H) atoms of the mth show vibrational modes in the range of 0-150 cm\(^{-1}\). Due to the larger mass of Br and I compared to Cl, the partial \( g(\omega) \) from the Br or I atoms is located at lower frequencies (0-150 cm\(^{-1}\)) while that for Cl extends over the entire range (0-250 cm\(^{-1}\)).
Figure 3.9: $g(\omega)$ (black line) for bulk PbS and for the mth-, I-, Br-, and Cl-terminated NCs. The partial $g(\omega)$ for Pb (brown shading), S (dark yellow shading), and the different terminations are also shown [138].
Figure 3.10: Spatially resolved vibrational properties of atoms within the NC. (a) Three regions of interest in the NC. For NCs with halide anions, there are no S atoms on the outer [111] surface. (b) Partial $g(\omega)$ for Pb (brown line) and S atoms (yellow line) for each of the 3 regions of the PbS/mth (left) and PbS/Cl (right) NCs. (c) Plot of $\langle u^2 \rangle$ for Pb (left) and S, I, Br, and Cl atoms (right) in the three regions. [111] and [100] facets in Region 1 are plotted separately. The bars represent the range ($-\sigma, +\sigma$). The thick black lines are the $\langle u^2 \rangle$ calculated for Pb and S from bulk PbS [138].
is particularly pronounced in the PbS/mth NC while it is weaker in the Cl-terminated NC.

Figure 3.10 shows the $\langle u^2 \rangle$ at 100K for Pb, S, and halide anion atoms in the three NC regions plotted for all four NC surface terminations. Values for Pb and S calculated for bulk PbS as provided for reference (black lines). Three trends are evident. First, the $\langle u^2 \rangle$ values for both Pb and S atoms decrease towards the value for bulk PbS the further the atoms are from the surface. Second, the $\langle u^2 \rangle$ values for the Pb and S atoms at the surface are smaller for PbS NCs with halide terminations than for the PbS/mth NC. Third, extremely large $\langle u^2 \rangle$ are observed for anions (S, I, Br, and Cl) on the [111] surface facets.

We can explain these observations by recalling that the atomic displacement is inversely related to the effective spring constant of the phonon mode, $\kappa_{eff}$ (see eq. 3.1). $\kappa_{eff}$ is associated with number and strength of the bonds between neighboring atoms. Pb and S atoms in the interior of a NC have a coordination number of 6, while the surface Pb and S atoms on the [100] facets of the NCs have a coordination number of 5, and surface anions such as S, I, Br, and Cl on the [111] facets have a coordination numbers of 2 or 3 (ignoring the S-C bonds in the PbS/mth NC). Thus larger $\langle u^2 \rangle$ are linked to decreased coordination number. Furthermore, the large $\langle u^2 \rangle$ of the Pb atoms on the outermost [111] facet for PbS/mth NC compared to halide terminated NCs can be explained by the strength of the bond. The effective spring constants associated with the Pb-X (X=mth, I, Br, Cl) bonds with the [111] surface atoms should scale with the percentage ionic character of the bonds [144], and the decrease in $\langle u^2 \rangle$ with the increase in ligand electronegativity is therefore expected (see table 3.1).

### 3.3.3 Implications of Surface Engineering

Our results for the electronic and phononic properties of the NCs indicates that halide anion surface termination confines the electronic wavefunctions away from the [111] surfaces, reducing the overlap of the electronic wavefunctions with the large thermal displacement surface phonons, and reduces the large mean thermal displacement of the Pb and S atoms close to the [111] surfaces. At least qualitatively speaking, this reduction of the overlap of the band-edge wavefunctions
Table 3.1: Results for the electronic and phononic properties of the NCs with X-surface terminations. The effective electronegativity of the surface termination X in Pauling units ($\chi(X)$) and the percent ionic character of the X-Pb bond, computed by the Pauling formula $100(1 - \exp[-1/4(\chi(X) - \chi(Pb))]$ are given for reference. $\chi(mth)^\ast$ was taken form Huheey [145]. The total carrier density ($n_c[111]$) on the outer Pb and X atoms on the [111] facet for both bands, and the mean square thermal displacement ($\langle u^{2}[111]\rangle$) at 100K of the same atoms are given. In the last column, the computed $A_{ue}$ values (eq. 3.2) are shown for both bands at 100K. 

<table>
<thead>
<tr>
<th>X</th>
<th>$\chi(X)$</th>
<th>IC (%)</th>
<th>$n_c[111]$</th>
<th>$\langle u^{2}[111]\rangle$</th>
<th>$A_{ue}$ ($A^2 e^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mth</td>
<td>2.45*</td>
<td>13.5</td>
<td>0.17</td>
<td>0.044</td>
<td>0.033</td>
</tr>
<tr>
<td>I</td>
<td>2.66</td>
<td>17.9</td>
<td>0.11</td>
<td>0.035</td>
<td>0.021</td>
</tr>
<tr>
<td>Br</td>
<td>2.96</td>
<td>23.9</td>
<td>0.10</td>
<td>0.037</td>
<td>0.019</td>
</tr>
<tr>
<td>Cl</td>
<td>3.16</td>
<td>27.6</td>
<td>0.10</td>
<td>0.035</td>
<td>0.019</td>
</tr>
<tr>
<td>Bulk</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.017</td>
</tr>
</tbody>
</table>

with these phonon modes should reduce the coupling of the states to those modes. To quantify this argument, we define a parameter $A_{ue}$, the overlap of the carrier density with the mean thermal displacement of the atoms,

$$A_{ue} = \sum_i \left[ \langle u_i^2 \rangle \sum_\sigma |\phi_{n,i\sigma}|^2 \right], \quad (3.2)$$

where $i$ runs over all atoms in the NC and $\phi_{n,i\sigma}$ are the components of the $n^{th}$ wavefunction projected onto the atomic orbitals $\sigma$ of the $i^{th}$ atom. The results at 100K for the CBM and VBM (averaged over the three degenerate VBM states) are tabulated in table 3.1. This reduction in overlap suggests that the electron-phonon coupling should decrease as the effective electronegativity of the ligands increases.
3.4 Electron-Phonon Coupling

With an established understanding of the electronic and vibrational structure of PbS NCs, we now investigate their interaction. We will first discuss the methods we use to quantify the electron-phonon coupling from the AIMD simulations, and then present the results for the PbS NCs investigate in Section 3.3.

3.4.1 Methodology

We are in general interested in two phonon-mediated processes, the thermal broadening of optical transitions and non-radiative multi-phonon mediated electronic transitions. Here we outline the methodology we used to quantify these processes from our AIMD calculations.

Figure 3.11: Time dependent energies of a PbS/mth NC at 300K.

The thermal broadening and temperature dependent shifting of optical transitions can be gauged directly from the time dependent energies, $E_n(t)$, of the states extracted from the AIMD simulation. A plot of $E_n(t)$ for states with $n$ around the bangap for a PbS/mth NC simulated at 300K is shown in Figure 3.11. From this data, we can

simply compute the distribution of transition energies for a particular transition. For example, in the figure we show four samples from the distribution of the lowest energy transition. The standard deviation of the resulting distribution would give our expected thermal broadening. In a complete treatment, one should include the optical matrix elements and overlap of the vibrational coordinates\(^3\) in computing the spectra. For example, if coupling is only to higher energy optical modes, one would observe a series of phonon peaks, such as those observed at low temperatures for CdSe NCs [72, 73], rather than a continuous spectra. However, for the purposes of determining the extent of the thermal broadening, we can ignore these effects.

Figure 3.12: Configurational diagram for non-radiative multi-phonon mediated transitions for a two state system coupled to a single phonon.

To examine the influence of surface termination on phonon-mediated electronic transitions, we consider the loss of coherence of the wavefunctions extracted from AIMD. Atomic motion serves as a perturbation to the electronic Hamiltonian for the nuclear ground state. In general, perturbations will add to a state, \( |\psi_n \rangle \), components from all other states, \( |\psi_{n'} \rangle \). The perturbed, time dependent state \( |\psi_n(t) \rangle \) can in general be expressed as

\[
|\psi_n(t)\rangle = \sum_\nu c_{n\nu}(t)|\psi_\nu(t)\rangle, \quad (3.3)
\]

where the time dependent coefficients \( c_{n\nu}(t) \) will depend on the perturbation.

\(^3\)This would introduce terms enforcing energy conservation.
3.4. ELECTRON-PHONON COUPLING

In Figure 3.12, we consider a two-state system with electronic states $\psi_{0,1}$ and $\psi_{0,2}$ in the nuclear ground state $Q_0$, assuming the states interact with a single phonon. At $T = 0K$, only small oscillations about $Q_0$ due to zero point motion of the phonon mode will be present (indicated by the dark-blue double sided arrow in the figure) and $\psi_1(t) \approx \psi_{0,1}$ and $\psi_2(t) \approx \psi_{0,2}$. As the temperature is increased, oscillations about $Q_0$ will increase, and the mixing of $\psi_{0,1}$ and $\psi_{0,2}$ will increase as the nuclear coordinates approach the avoided crossing of the two states where a non-adiabatic transition between the two states can occur. At the avoided-crossing, indicated by the point in the figure,

$$\psi_1(t) = \frac{1}{\sqrt{2}} (\psi_{0,1} - \psi_{0,2}),$$

$$\psi_2(t) = \frac{1}{\sqrt{2}} (\psi_{0,1} + \psi_{0,2}).$$

We can therefore expect an oscillatory component with the frequency of the coupled phonon in the inner product $|\langle \psi_{0,i} | \psi_i(t) \rangle|^2$, whose magnitude will increase with increasing $T$ and with increased electron phonon coupling. The electron phonon coupling (given by the Huang-Rhys parameter, $S$) and transition rates could then in principle be determined through investigation of $|\langle \psi_{0,i} | \psi_i(t) \rangle|^2$.

For a system where there is coupling of many phonon modes to many electronic states, there can be many spectral contributions to $|\langle \psi_{i,0} | \psi_i(t) \rangle|^2$. For systems with a large number of atoms, it can also be difficult to identify the true $Q_0$, which will in general depend on temperature. To avoid a definition of the $\psi_{0,i}$, one can calculate the wavefunction overlap autocorrelation function

$$R_n(\tau) = \langle \langle |\psi_i(t)| \psi_i(t-\tau) \rangle \rangle_t,$$

where the outer brackets indicate an averaging over time $t$. $R_n(\tau)$ indicates the rate and extent to which $\psi_n(t)$ loses its coherence due to nuclear motion. In general, the rates for transitions to and from $\psi_n$ will depend on $R_n(t)$. For example (within the single particle approximation implementation of the fewest switches surface hopping

$^4Q_0^4$ is the nuclear coordinates which minimize the free energy of the system, if the carrier is in the state $\psi_{0,1}$. 
time domain density functional theory), the probability of transition to/from \( \psi_n \) to/from state \( \psi'_n \) within a time step of \( \Delta t \) is proportional to \( (R_n(\Delta t))^{-1/2} \).\footnote{The perturbation caused by atomic motion will dynamically break this degeneracy, however their energies will fluctuate about the same value.}

### 3.4.2 Effects of Surface Engineering

Here we examine the impact of the surface termination on electron-phonon coupling, using the NCs investigated in Section 3.3. Additional AIMD simulations were performed on the PbS-mth and PbS-Cl NCs at 10K and 300K.

**Thermal Broadening and Energy Shifting of Optical Transitions**

Let us first consider the thermal broadening of time dependent band gap. As we discussed in Section 3.3.1, the lowest energy transition from which the PL will originate, \( \psi_{1h\alpha} \rightarrow \psi_{1e} \), is nominally 3-fold degenerate.\footnote{The perturbation caused by atomic motion will dynamically break this degeneracy, however their energies will fluctuate about the same value.} We compute the expected PL distribution, assuming the optical matrix elements do not change as a result of the atomic motion, by binning the time dependent energy differences of these three transitions, \( E_g(t) = E_{1e}(t) - E_{1h\alpha}(t) \). The distributions of \( E_g(t) \) for the PbS/mth and PbS/Cl NCs at 10K, 100K, and 300K are shown in Figure 3.13a, and the standard deviations of the distributions, \( \sigma_{E_g} \), are given in Table 3.2. For both NCs, the \( E_g(t) \) distributions broaden and red shift with increasing temperature.

The results predict the thermal broadening of the lowest energy transition to have a \( \sigma_{eV} \) of 72meV for the PbS/mth NC at 300K, which corresponds to a line-width of 190meV. For this size of NC (\( r = 1.3nm \)), this line-width is \( \sim 13\% \) of the absorption band-gap! This finding is consistent with the recent measurements of Caram et al.\footnote{The perturbation caused by atomic motion will dynamically break this degeneracy, however their energies will fluctuate about the same value.} who measured the PL linewidth of \( r = 1.2nm \) individual PbS NCs to be 60-100meV.

The red shift of the \( E_g \) distributions with increasing temperature also stem from the electron-phonon interactions. As discussed in Chapter 1.3.3, changes to \( E_g \) with increasing temperature that arise from thermal expansion of the lattice are expected to lead to a blue
3.4. ELECTRON-PHONON COUPLING

Figure 3.13: Phonon induced thermal broadening of the PL of PbS NCs. (a) Histograms showing the band gap energy for a PbS/mth (top) and PbS/Cl (bottom) NC. The spectral densities of the time dependent band gap energy ($E_g(t)$) for both NCs are shown in (b) [138].

shift for bulk Pb-chalcogenides [75,76], however have been observed to red shift for very small NC sizes ($r < 3$nm) [81]. We computed the electronic structure of the PbS/Cl NC with the atoms fixed at their mean positions calculated from the AIMD at 300K. The band gap increases from $E_g(0K)=1.29$eV to $E_g(300K)=1.31$eV, thus the observed red shift in the $E_g(t)$ distributions results from the lattice dynamics.

The results show that the broadening and blue shift, which are related to electron-phonon coupling, are significantly reduced in the

Table 3.2: Variance of the distribution of band gap energies, $E_g(t) = E_{1e}(t) - E_{1h\alpha}(t)$, at various temperatures.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{E_g}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS/mth</td>
<td>10K</td>
</tr>
<tr>
<td>PbS/Cl</td>
<td>7</td>
</tr>
</tbody>
</table>
Phonon-Mediated Electronic Transitions

Here we look at the coupling of the phonons in the NCs to non-radiative multi-phonon mediated electronic transitions using the methodology described in Section 3.4.1. Namely, we will compute the wavefunction-autocorrelation functions for the VBM and CBM of the NCs (eq. 3.5).

For the CBM, we thus calculate

\[
R_{CBM}(\tau) = \langle |\langle \psi_{1e}(t)|\psi_{1e}(t-\tau)\rangle|^2 \rangle_t ,
\]  

(3.6)

where the outer brackets \( \langle \cdots \rangle_t \) indicate averaging over the time trace of the AIMD. The VBM of the NCs are three-fold degenerate in the absence of atomic motion. During the AIMD this degeneracy is lifted as the energies of the three states uniquely fluctuate, leading to avoided crossings in the energies of the 3 degenerate VBM states throughout the simulation and strong mixing of all three states with one another. For the VBM we therefore calculate

\[
R_{VBM}(\tau) = \frac{1}{3} \left\langle \sum_{\alpha,\beta} |\langle \psi_{1h\alpha}(t)|\psi_{1h\beta}(t-\tau)\rangle|^2 \right\rangle_t .
\]  

(3.7)

For bulk PbS we average over the four-fold degenerate VBM and CBM

\[
R_{VBM,\text{bulk}}(\tau) = \frac{1}{4} \left\langle \sum_{i,j=1}^4 |\langle \psi_{VBM,i}(t)|\psi_{VBM,j}(t-\tau)\rangle|^2 \right\rangle_t ,
\]  

(3.8)
3.4. ELECTRON-PHONON COUPLING

\[ R_{CBM, bulk}(\tau) = \frac{1}{4} \left\langle \sum_{i,j=1}^{4} |\langle \psi_{CBM,i}(t) | \psi_{CBM,j}(t-\tau) \rangle|^2 \right\rangle_t. \]

In Figure 3.14, we plot \( R_{CBM}(\tau) \) and \( R_{VBM}(\tau) \) for the \( \text{PbS/mth} \) and \( \text{PbS/Cl} \) NCs at 10K, 100K, and 300K. \( R_{CBM}(\tau) \) and \( R_{VBM}(\tau) \) for both NCs indicate strong initial loss of coherence, which levels out to mild fluctuations with a defined mean within the first ps. The initial decoherence time depends on what frequency phonon modes are coupled to the electronic wavefunctions. As we discuss below, the initial decoherence in the \( \text{VBM} \) stems from their larger coupling to the high-energy modes (150-250cm\(^{-1}\)). The extent of dephasing indicates how well phonons drive electronic transitions, with smaller mean values indicating a higher rate of transition.

![Figure 3.14: Wavefunction overlap autocorrelation function for the CBM (eq. 3.6) and VBM (eq. 3.7) of the PbS/Cl and PbS/mth NCs at 10K, 100K, and 300K [138].](image)

For both NCs, the extent of the decoherence of the VBM states is significantly larger than the CBM. This indicates faster phonon-mediated transition rates in the VB resulting from a denser density
of states in the VB (Figure 3.6), and the stronger coupling of the VBM states to phonons. This is consistent with recent experimental measurements, which indicate much faster carrier cooling rates in the VB compared to the CB in isotypic PbSe NCs [83].

For all temperatures, the extent of the dephasing is significantly larger in the PbS/mth NC than the PbS/Cl NC. This indicates a significant reduction in the coupling of the phonons to electronic transitions upon Cl termination. In Figure 3.15, we plot $R_{CBM}(\tau)$ and $R_{VBM}(\tau)$ for bulk PbS, and the PbSX (X=mth, Cl, Br, I) NCs at 100K. In both the CB and VB the extent of the decoherence progressively increases from bulk to halide-terminated NCs to thiol-terminated NCs. The extent of the dephasing is in good agreement with the ordering predicted by the overlap of the carrier density with the mean thermal displacement $A_{ue}$ (eq. 3.2, table 3.1).

To elucidate which phonons are responsible for the loss of coherence of the wavefunctions, we plot the spectral densities of $R_{CBM}(\tau)$ and $R_{VBM}(\tau)$ (Fig. 3.16), for the PbS/mth and PbS/Cl NCs at 100K. Both spectral density plots show coupling to the low (5-50 cm$^{-1}$) and high (150-250 cm$^{-1}$) energy modes, the same mode we found to couple to the thermal broadening. Again we see that halide passivation suppresses the electron-phonon coupling.
3.5. DISCUSSION

To summarize, we have shown that the reconstruction and mechanical weakening of the surface of PbS NCs admits low (∼25 cm⁻¹) frequency modes with large thermal displacements, and a reorganization of the higher energy (∼150−250 cm⁻¹) optical phonons, effects which should be relatively insensitive to the NC size. AIMD simulations indicate that these modes are strongly coupled to the quantum confined states of the NCs. As a result, we observed large thermal broadening of optical transitions, and indications that the strong electron-phonon coupling should enable multi-phonon mediated non-radiative electronic transitions. Experimental evidence of the role of phonons in such transitions was given by Bozyigit [90], via TAS measurements on PbS NC solids, as discussed in Chapter 1.3.3 (see Fig. 1.19). The assignment of the two classes of efficient electronic transitions to coupling to low and high frequency modes are consistent with our findings here.
Our results also indicate that electron-phonon interactions are reduced in halide terminated NCs compared to thiol-terminated NCs via (1) reduction of the mean square displacement of Pb and S atoms in the NC and (2) confinement of the conduction and valence band wavefunctions away from the [111] surface where the largest atomic displacement modes occur. We further show that this reduction in electron-phonon interactions reduces thermal broadening of optical transitions and should suppress phonon-mediated electronic transitions. These findings explain the experimental results on thermal broadening, hot electron relaxation, and the improved performance of NC-based solar cells that used halide treatments and underscores the important and multifaceted role surface engineering can play optimizing NCs for different applications.
Chapter 4

Measuring Carrier Mobilities

As we discussed in Section 2.2.1, the TOF technique provides a robust approach to investigate carrier dynamics in disordered low mobility materials. In this chapter, we employ the TOF technique to investigate carrier dynamics in PbS NC solids.

4.1 Mobility dependence on Nano-Crystal Size

†As discussed in Section 1.2.1 theoretical calculations have predicted that, assuming the inter-NC spacing in a NC-solid remains the same, as the size of the constituent NC decreases, the mobility should increase. This stems from the fact that decreasing NC size increases the kinetic energy of a charge carrier on a NC, reducing the effective energy barrier between NCs seen by the carrier. This enhances the

leakage of the wavefunction outside of the NC increasing the coupling between neighboring NCs.

To experimentally study the impact of NC size on carrier mobility, we performed TOF measurements at room temperature on heterojunction solar cells to determine the room temperature hole mobility, $\mu_h(T = 300K)$. For the remainder of this chapter, we will drop the temperature dependent notation, $\mu_h(T = 300K) \equiv \mu_h$. Devices were fabricated with PbS NC sizes ranging from $r = 1.2\text{nm}$ to $2.2\text{nm}$, (see Fig. 2.10), according to the procedure outlined in Section 2.2.3. Details of the experimental setup for TOF measurements are also provided in Section 2.2.3. The NC radii, device thicknesses, and current-voltage characterisation of all of the devices are tabulated in Table 4.1.

![Figure 4.1: Example TOF transients measured at bias voltages of 3V, 5V, and 7V on a device incorporating NCs with a radius of 1.27 nm. The plot below shows the same transients on a log-log scale with power law fits to short and long time portions of the transients.](image)

In Figure 4.1, we plot three of the TOF transients for the device with 1.27nm NCs at various applied biases ($V = 3, 5, 6V$, corresponding to electric fields of $\sim 65 - 150kV/cm$). The transients exhibit a long tail, indicative of ‘anomalous dispersion’ [104,111]. On a log-log scale, the transients are fit well by two power law decays at short and long times (eq. 2.16). Fits are performed by least squares fitting over manually selected time windows. We extract $t_{tr}$ as the intersection of the two power law fits, indicated by the downwards arrows in the
4.1. MOBILITY DEPENDENCE ON NANO-CRYSTAL SIZE

figure. The $t_{tr}$ are extracted for each bias, and we then compute $\mu_h$ via a least squares fitting to

$$\mu_h = d^2 \frac{\partial t_{tr}^{-1}}{\partial V}. \quad (4.1)$$

Plots of the extracted $d/t_{tr}$ versus $V/d$ for two devices are provided in Figure 4.2 along with the fits defining the extracted $\mu_h$.

![Figure 4.2: Plots of $d/t_{tr}$ vs. $V/d$ for two NC sizes (a: $r = 2.11\text{nm}$ and b: $r = 1.27\text{nm}$).](image)

We followed the above procedure for all devices, and the resulting dependence of $\mu_h$ on NC size is plotted in Figure 4.3 and given in table 4.1. The mobilities scale with the NC radius as $\mu_h \sim r^{-\beta}$ with $\beta = 4.5 \pm 0.2$. This strong scaling is in agreement with the theoretical predictions discussed in 1.2.1, albeit with a smaller exponent than we calculated for PbS ($\beta \sim 6$). Since the publication of this work, other studies have found similar scaling as that presented here [53,58].

Our finding that carrier mobility increases with decreasing NC size, in agreement with theory, was in contrast to other carrier mobility measurements in NC-solids, which have shown non-trivial or opposite dependences of the carrier mobility on NC size [49,50,61]. These studies, as most studies of mobility in NC-solids [23,27,148,150], were carried out in FET structures. Due to the presence of deep traps (i.e., traps which are more than a few $k_B T$ away from the effective
conduction or valence band) in NC-solids, FET measurements yield an effective mobility, which includes the contribution from carriers localized in deep trap states. The fraction of trapped charge carriers is exponentially dependent on the energetic depth of the trap states. Since we showed that the energetic depth of traps increases with increasing NC band gap (i.e. decreasing NC size), a larger fraction of charge carriers would be trapped in NC-solids composed of NCs with smaller size. Therefore in a FET structure, the effective mobility could thus be measured to decrease with decreasing NC size, even if the free carrier mobility increases.

While the carrier mobilities we found with TOF in heterojunction solar cells should be insensitive to the presence of deep traps, as the release time from deep traps is far larger than the time scale of the measurement, from the measurements presented thus far, it is not possible to determine to what extent, if any, the extracted mobility underestimates the free carrier mobility due to the presence of shallow traps or a large dispersion in carrier hopping times. One can also raise the question, that in a highly energetically and spatially disordered system, what does the free carrier mobility even represent? To delve further into these questions, we first extended our TOF characterisation to include the dependence on temperature.

Figure 4.3: \( \mu_h \) as a function on NC radius extracted from TOF transients at 300K.)
Table 4.1: Physical and electrical characterisation, and extracted $\mu_h$ for the various devices. [60]

<table>
<thead>
<tr>
<th>$r$ (nm)</th>
<th>$d$ (nm)</th>
<th>$\mu_h$ (cm$^2$(Vs)$^{-1}$)</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.11</td>
<td>102 ± 4</td>
<td>(1.1 ± 0.1) · 10$^{-4}$</td>
<td>0.7</td>
<td>0.37</td>
<td>3.9</td>
</tr>
<tr>
<td>1.67</td>
<td>400 ± 13</td>
<td>(3.7 ± 0.2) · 10$^{-4}$</td>
<td>2.5</td>
<td>0.51</td>
<td>11.9</td>
</tr>
<tr>
<td>1.54</td>
<td>339 ± 10</td>
<td>(5.4 ± 0.5) · 10$^{-4}$</td>
<td>2.5</td>
<td>0.51</td>
<td>10.9</td>
</tr>
<tr>
<td>1.42</td>
<td>443 ± 13</td>
<td>(6.5 ± 0.4) · 10$^{-4}$</td>
<td>3.7</td>
<td>0.53</td>
<td>15.0</td>
</tr>
<tr>
<td>1.36</td>
<td>408 ± 5</td>
<td>(8.2 ± 0.2) · 10$^{-4}$</td>
<td>1.8</td>
<td>0.43</td>
<td>8.7</td>
</tr>
<tr>
<td>1.27</td>
<td>509 ± 5</td>
<td>(10.4 ± 0.2) · 10$^{-4}$</td>
<td>1.0</td>
<td>0.44</td>
<td>6.9</td>
</tr>
<tr>
<td>1.22</td>
<td>463 ± 10</td>
<td>(13.3 ± 0.6) · 10$^{-4}$</td>
<td>2.1</td>
<td>0.68</td>
<td>8.5</td>
</tr>
</tbody>
</table>

4.2 Temperature Dependent Time of Flight

Temperature dependent measurements enable more detailed understanding of thermally activated processes, such as carrier transport.

We again fabricated heterojunction devices with PbS NC sizes ranging form $r = 1.4$nm $r = 2.2$nm according to the procedure outlined in Section 2.2.3, and performed TOF measurements with the setup described in Section 2.2.3. We measured transients at various biases, $V$, at fixed temperatures, $T$. We kept an upper limit for $T$ of 330K as we observed irreversible degradation of the devices around $\sim 350K$. Lower limits on $T$ varied from sample to sample, but was typically in the range of 200-230K. We found that at low temperatures, the transients would become increasingly featureless ($\alpha_+ \approx \alpha_-$), rendering TOF analysis difficult. Interestingly, this is the range in temperature where Kang et al. observed a transition of transport mechanisms in PbSe NC solids [50], which they attributed to variable range hopping at low temperatures to nearest-neighbour hopping at higher temperatures.

Some of the transients measured for a device with 2.2nm NCs at various $V$ and $T$ are shown in Figure 4.4. The transients again have the form corresponding to ‘anomalous dispersion’ and are well fit by two power law decays at short and long times, eq. 2.16. We again take the intercept of the two power laws as $t_{tr}$. $t_{tr}$ was extracted in this way for each sample at all $V$ and $T$ measured.
We found that the extracted $t_{tr}(V,T)$ could be excellently fit with a function with Arrhenius form,

$$\frac{d}{t_{tr}(V,t)} = \mu_{h0} e^{-E_A/k_B T \left( V + V_0 \right) / d},$$

(4.2)

where $\mu_{h0}$ is the pre-factor of the hole mobility, $E_A$ is the activation energy for the mobility, and $V_0$ is the built in field resulting from the heterojunction in the device. We fit simultaneously for $\mu_{h0}$, $E_A$, and $V_0$, by minimising the residuals of the fit function with the extracted $t_{tr}(V,T)$. The fit function evaluated as a function of $V$ at fixed $T$ is overlaid as a solid line on plots of $d/t_{tr}$ versus $V/d$ in Figure 4.5.

We performed the same analysis on all devices, and plots of $d/t_{tr}$ versus $V/d$ and the corresponding fits are provided in appendix B.2. Values of $\mu_{h0}$, $E_A$, and $V_0$ for the various devices are summarised in table 4.2 and the extracted $\mu_{h0}$ and $E_A$ are plotted in Figure 4.6 as a function of NC size.

The excellent fit of eq. 4.2 for all NC sizes indicate that the mobility extracted from TOF can be accurately described with an Arrhenius form for the $T$ and $V$ ranges investigated here. Both $\mu_{h0}$ and $E_A$ are found to scale strongly with NC radius. As we will discuss in Section 4.4, the value of the extracted parameters depend on the extent of the energetic and spatial disorder in the sample and the charge transport model employed. Nevertheless, we note a clear size dependence of both $\mu_{h0}$ and $E_A$. The increase of $\mu_{h0}$ with decreasing NC size is
4.3. ELECTRON MOBILITY

Figure 4.5: Plot of hole $d/t_{tr}(V,T)$ vs. $V/d$ for a device with 2.2nm NCs. Lines correspond to the fitted function (eq. 4.2) evaluated at fixed $T$

consistent with the expected increase of electronic coupling between neighboring NCs with decreasing NC radius [59]. As discussed in Section 4.4 and Chapter 5, $E_A$ is related to the reorganization of the medium surrounding the NCs and reorganization of the structure of NCs themselves upon charge transfer can contribute to $E_A$. In addition, as pointed out by Kang et al. [50], energetic disorder of NCs transport states can also contribute to $E_A$.

4.3 Electron Mobility

We also fabricated an inverted-heterojunction with 2.2nm NCs to investigate electron mobility, $\mu_e$. We followed the same procedure as that for $\mu_h$, using the function

$$\frac{d}{t_{tr}(V,t)} = \mu_{e0} e^{-E_A/k_B T} \frac{(V + V_0)}{d},$$  

(4.3)
to fit the extracted $t_r r(V,T)$. The results for $\mu_e$, $E_A$, and $V_0$ are in the last row of Table 4.2 and plotted in Figure 4.7.

For NCs of approximately the same radius, the $E_A$ for electrons is similar to that found for holes. The mobility pre-factor however is significantly larger, $\mu_e > 2\mu_h$. This is in agreement with previous experiments that have consistently measured electron mobilities to be higher than hole mobilities in lead-chalcogenide NCs [27, 49, 149], but is surprising given that the effective masses of holes and electrons in bulk lead-chalcogenides are nearly identical [152].
4.4 Interpretation of Time of Flight Mobilities

As we have previously discussed in Section 2.2.1, commonly observed ‘anomalously dispersive’ current transients, such as those we measured for PbS NC solids, are predicated by a power law distribution of the long-time limits of the carrier transport dynamics, \( \sim t^{-(1+\alpha)} \) with \( 0 < \alpha < 1 \). This power law dependence is typically ascribed to strong spatial disorder coupled with an exponential dependence of the hopping rate with inter-site distances in spatially disordered hopping models or to an exponential distribution of band tail states in effective band models. Here we briefly describe how the power law distribution in hopping times can arise and qualitatively how the exponent \( \alpha \) can be related to different physical parameters.
As discussed in Chapter 1.2, carrier transfer rates are typically taken to depend exponentially on the inter-NC distance \[49, 51–53, 153\],
\[
t_{h} \sim e^{\beta r},
\]
where \(\beta\) depends on the nature of the coupling between the two hopping sites, and \(r\) is the distance between the two sites. With spatial disorder, if the distribution of \(r\), \(f_{r}(r)\), has a component which is exponentially distributed, \(f_{r}(r) \sim m^{-1}e^{r/m}\), the hopping time distribution will have a power law component,
\[
f_{t_{h}}(t_{h}) \sim t^{-(1+1/\beta m)},
\]
from which we can identify \(\alpha = 1/\beta m\).

Alternatively, the hopping time is often taken to exponentially depend on the energetic barrier associated with the hop \[29, 47, 49–52\],
\[
t_{h} \sim e^{-E/k_{B}T}.
\]
If the distribution of the energies of the states contributing to transport has an exponential component, such as a band tail distribution, \(f_{E}(E) \sim m^{-1}e^{E/m}\), then
\[
f_{t_{h}}(t_{h}) \sim t^{-(1+k_{B}T/m)},
\]
such that \(\alpha = k_{B}T/m\). For NC solids, one could expect that the disorder in the energies of the transport states arises from the distribution in the band gaps of the NCs, often taken to be normally distributed with standard deviation \(\sigma\). The change in energy hopping from one NC to another, \(\Delta E\), would then also be normally distributed. However, with the hopping times given by eq. 4.6, the resulting \(f_{t_{h}}(t_{h})\) would be not power law distributed, but log-normally distributed.

In Chapter 5 we take a charge transfer rate of the form of Marcus charge transfer:
\[
t_{h} \sim e^{-(\lambda+\Delta E)^{2}/4\lambda k_{B}T}.
\]
\(\lambda\) is the reorganisation energy associated with a charge hop, we show in appendix C.2 that for large \(t_{h}\), \(f_{t_{h}}(t_{h})\) will have the form:
\[
f_{t_{h}}(t_{h}) \sim t^{-(1+\lambda k_{B}T\chi_{b}^{2}/\sigma^{2})},
\]
where $\chi_b$ ($b = \text{CB}||\text{VB}$) dictates how the CB and VB levels align between neighboring NCs (see eq. 1.9). In this case, $\alpha = \lambda k_b T \chi_b^2 / \sigma^2$.

Likely, in the case of NC-solids, both positional and energetic disorder are present, resulting in temperature-dependent and temperature-independent contribution to the dispersion of charge carriers.

Regardless of the origins of the distribution in hopping times, a power law distribution has an important ramification on TOF analysis. Simply put, a power law distribution means that the $\mu$ extracted from TOF will decrease with the number of hops such that the extracted $\mu$ will be proportional to the device thickness. This comes from the following: For a power law distribution $f(t) \sim t^{-\nu}$ (where we here use the exponent $\nu = 1 + \alpha$ to be consistent with statistics literature), has divergent mean values if $\nu \leq 2$. If we pull $n$ independent $t_i$ from the distribution, we can compute the expectation value of the largest encountered $t_i$, $\langle t_{\text{max}} \rangle$ [154]. Provided $\nu > 1$ and $n \gg 1$,

$$\langle t_{\text{max}} \rangle = \frac{n^{1/(\nu-1)}}{1} = \frac{n^{1/\alpha}}{1}.$$  \hspace{1cm} (4.10)

For $1 < \nu < 2$ and $n \gg 1$, the value of the sum of $n$ $t_i$, $S_n = \sum_n t_i$ which itself is a random variable, will be dominated by the maximum encountered $t_i$, which will increase with $n$ [154].

Figure 4.8: Plot of the probability distribution of the total transport time for each carrier normalized to the number of hops $n$, $S_n/n$, for various $n$. The peaks of the distributions increases with the number of hops $n$. 

CHAPTER 4. MEASURING CARRIER MOBILITIES

For the case of hopping, if the carrier undergoes \( n \) hops from one electrode to the other (\( n \) will be proportional to device thickness), the distribution of the total transport time for each carrier will be given by the distribution of \( S_n = \sum_n t_i \). In Figure 4.8, we plot the distributions of \( S_n = \sum_n t_i \) normalized to \( n \),

\[
S_n/n = n^{-1} \sum_n t_{h,i},
\]

(4.11)

where the \( t_i \) were pulled from a power law distribution \( \sim t^{-3/2} \). We plot the distribution for several values of \( n \), from which we can see that the peak of the distributions increases with \( n \). Now, the transit time extracted from TOF, \( t_{tr} \), with which \( \mu \) is calculated, corresponds to the peak in the distribution of the individual carrier transit times, \( \text{MAX} [S_n] \), which will increase with the number of hops \( n \). Simply put, a power law distribution means that the \( \mu \) extracted from TOF will decrease with the number of hops, so \( \mu \) will be proportional to device thickness! This decrease will be more and more significant as \( \alpha \) decreases from 1 to 0. As \( \alpha \) should depend on temperature in the presence of energetic disorder, the significance of the \( E_A \) extracted via TOF must also be scrutinised.

To investigate this further, we fabricated a thickness series of devices using \( r = 1.58 \text{nm} \) NCs. Four devices of thickness \( d = 460 \text{nm}, 520 \text{nm}, 560 \text{nm}, \) and \( 600 \text{nm} \) were fabricated and measured via TOF. Plots of their extracted \( t_{tr}(V,T) \) and corresponding fits of eq. 4.2 are given in appendix B.2.

In Figure 4.9(a), we plot the transients for all device thicknesses, \( d \), biases, \( V \), and temperatures, \( T \), with the axes scaled according to the \( t_{tr}(d,V,T) \) extracted for each transient. We observe that the transients for all \( d \) and \( V \) collapse onto a single curve for fixed \( T \). We fit the long time tails of the transients to extract \( \alpha(T) \). As expected in the presence of energetic disorder, \( \alpha \) decreases with decreasing \( T \). While linear with \( T \) in the range measured here, we see that \( \alpha(T) = k_B T/m \) is not logical since extrapolation of \( \alpha(T) \) at low temperatures would be negative. Nevertheless, the decreasing \( \alpha(T) \) means that the extracted \( \mu_h(d,T) = \mu_{0,h}(d)e^{E_A/k_B T} \) will vary with \( d \). If we assume
4.4. **INTERPRETATION OF TIME OF FLIGHT MOBILITIES**

Figure 4.9: **TOF** thickness series analysis. The **TOF** transients for all $d$, $V$, and $T$ plotted on axes scaled to their individually extracted $t_{tr}(d,V,T)$ are shown in (a), and the $\alpha(T)$ extracted from power law fits to the long time tails of the transients are plotted in (b). The $\mu_{h0}$ and $E_A$ extracted from fits to the devices using eq. 4.2 are plotted as a function of device thickness in (c).

$\mu_h(d,T)$ scales according to the average maximum hopping time of each carrier, eq. 4.10, then,

$$\mu_h(d,T) \sim \frac{\mu_{h0}}{d^{1/\alpha(T)}} e^{-E_A/k_bT} = \mu_{h0} e^{-(E_A/k_bT + \log d/\alpha(T))}.$$  \hspace{1cm} (4.12)

In Figure 4.9(c) we plot the extracted $\mu_{h0}$ and $E_A$ as a function of $d$ and find that both increase as the thickness increases.

The above discussion may seem like a critique of **TOF** technique since it shows that the values extracted for the $\mu_0$ and $E_A$ will depend on the thickness of the sample used. However, this is an inherent problem with the definition of carrier mobility itself for disordered systems whose carrier dynamics depend on distributions with divergent means. The existence of a well-defined macroscopic carrier mobility exists only if the distribution of transport times has a defined mean value!
Chapter 5

Electron Transfer Model for Nanocrystal-Solids

In this chapter, we motivate a more comprehensive model for charge transport in PbS NC solids, based on the what we have learned from the characterisation of charge carrier dynamics (Chapter 4) and electron phonon coupling in these systems (Chapter 3).

Having observed activation energies in charge carrier transport in Chapter 4, we consider the presence of intrinsic activation energies associated with hop of a charge carrier from one NC to another. This points us to the ET models of Marcus [36], Jortner [39, 40], Bixon [41], Efrima [42, 43], and Ulstrup [44]. As we will see, these models are analogous to those used for multi-phonon mediated non-radiative electronic transitions. Our understanding of electron-phonon coupling in PbS NCs (Chapter 3) will therefore allow us to understand and properly parameterize a charge transport model.

5.1 Charge Transfer Theory

The beginnings of the theory of ET are often credited to Franck, of the Franck-Condon principle fame (see Chapter 1.3.2), who, in a private communication to Libby, asserted that ET reactions could be interpreted in terms of the Franck-Condon principle [40]. The first
quantitative description of ET rates was, however, first provided in the pioneering work of Marcus \[36\]. In this section, we will provide an overview of the Marcus model, its relation to the non-radiative rate theory of Huang and Rhys \[5\] (as discussed in Chap. \[1.3.2\]), and extensions of the model by Jortner, Bixon, Efrima, and Ulstrup \[39\]–\[44\]. Finally, we will discuss the implications of these models in the context of charge carrier transport in NC-solids.

### 5.1.1 Reorganization Energy and Marcus Charge Transfer

The seminal work of Marcus, for which he was awarded the Nobel Prize, concerned the development of his theory for quantitative estimation of the rate of oxidation/reduction reactions in solution \[36\]. \( DA \rightarrow D^+ A^- \) (reactants \( \rightarrow \) products, with donor \( D \) and acceptor \( A \)). He abstracted the description of the dynamic configurations of the reactants, products, and solvent molecules into a single reaction coordinate, \( Q \), and that the driving force of the reaction was the Gibbs free energy. He reasoned that the reactant and products would have their equilibrium minima of free energy at different points along \( Q \), and that their free energy would depend quadratically on \( Q \), as shown in figure \[5.1\], and that the quadratic dependence of the free energy should be identical for both reactants and products.

Within the context of the Eyring Transition State Theory, Marcus determined the rate of the reaction to be

\[
k_{ET} \propto (k_B T)^{-1/2} \exp \left[-E_A / k_B T \right],
\]

where \( E_A \) is the activation energy of the reaction, the free energy the system must overcome for the reaction to proceed (Fig. \[5.1\]). The activation energy can be related to a single parameter, \( \lambda \), known as the reorganization energy.

\[
E_A = (\lambda + \Delta G_0)^2 / 4\lambda,
\]

where \( \lambda = G(D^+ A^-, Q_r) - G(D^+ A^-, Q_p) = G(DA, Q_p) - G(DA, Q_r) \), i.e. the difference in free energy of the system with the coordinates of the reactants but the charge state of the products, with the free energy of the product, or equivalently, the difference in free energy of
5.1. CHARGE TRANSFER THEORY

Figure 5.1: Configurational diagram of the Marcus model.

the system with the coordinates of the products but the charge state of the reactants, with the free energy of the reactants. The key to completing the model was the calculation of an estimate for $\lambda$. To accomplish this, Marcus employed a model of two metal spheres in a polar medium, and reasoned that the reaction coordinate is then given by the polarisation of the medium, $Q_r \rightarrow P_r$, $Q_p \rightarrow P_p$, which gives the outer shell reorganization energy $\lambda_{os}$ in eV as

$$\lambda_{os} = \Delta e \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right),$$

(5.3)

where $\epsilon_{op}$ and $\epsilon_s$ are the optical and static permittivities of the medium. This type of reorganization energy, i.e. the energy associated with reorganization of a polar medium surrounding the D+A, is referred to as ‘Outer-Shell’ reorganization energy.

One of the shortcomings of Marcus’s original formulation is that it treated the ET about the intersection of the free-energy curves
adiabatically \cite{40}. Dogonadze and coworkers \cite{37,38} replaced the polar medium of Marcus with a bath of optical phonons with a single low frequency $\omega$, their instantaneous polarisations interacting with the electron. Employing Landau-Zener theory, they computed the non-adiabatic rate
\[ k_{ET} = \frac{2\pi}{\hbar} V^2 \sqrt{\frac{1}{4\pi \lambda k_B T}} \exp \left[ -\left( \lambda + \Delta G_0 \right)^2 / 4\lambda k_B T \right], \quad (5.4) \]
where $V$ is the electronic coupling of the reactants and products.

Comparing eq. 5.4 with the high temperature limit of the thermally averaged FC factor computed by Huang and Rhys for multi-phonon mediated electronic transitions,
\[ F = (4\pi S\hbar \omega k_B T)^{-1/2} \exp \left[ -\frac{(p\hbar \omega + S\hbar \omega)^2}{4S\hbar \omega k_B T} \right], \quad k_B T \gg \hbar \omega, \quad (5.5) \]
we see their forms are nearly identical. We can identify $\lambda = S\hbar \omega$, where the Huang Rhys parameter $S = (1/2)(Q_r - Q_p)$\footnote{To our knowledge, Dogonadze and coworkers never explicitly made this connection, although many authors have since (see for example \cite{40}).} This is also clear comparing figures 5.1 to 1.13 Assuming a quadratic dependence of the free energy of the reactants $G_R(Q)$,
\[ \lambda = G_R(Q_p) - G_R(Q_r) = \hbar \omega \frac{1}{2}(Q_r - Q_p)^2 = S\hbar \omega. \quad (5.6) \]

While the rate expressions for non-adiabatic ET and multi-phonon mediated electronic transitions have the same form, they represent solutions to phenomenologically different problems. Namely, outer shell ET was concerned with the reorganization of the surrounding medium, while non-radiative transitions was concerned with reorganization of the nuclear coordinates of the donor and acceptor atoms themselves. The direct equivalence between the two theories was established upon the inclusion of the concept of internal reorganization in ET theory.

We illustrate the concept of internal reorganization energy in Figure 5.2 using a hypothetical molecule, A-B-A. We consider ET transfer between two such molecules, with one molecule positioned at a point of lower potential energy. When charged with an electron, the molecule has a $\pi/2$ angle between the two A-B bonds, and when neutral has
a $\pi$ angle between the bonds. Coupling to phonons will cause a continuous deformation of the bond lengths and angles. At some point along the reaction coordinate, the bond lengths and angles will be such that the adiabatic wavefunction will be distributed over both the donor and acceptor. Whether transfer occurs depends on the non-adiabatic transition probability at this point. The $E_A$ for this process is identical to eq. 5.2 with $\lambda = \lambda_i$. This qualitative example employs a change in bond angle as the nuclear reorganization. The same arguments can be made for systems that undergo minor changes in bond lengths with a change in charge state. What is important is that the ground state nuclear configuration between the charged and uncharged molecule are different. Marcus included these effects with his outer shell reorganization energy, $\lambda_{os}$, as $\lambda = \lambda_{os} + \lambda_i$ [155].

Till now, all of the ET theories we have discussed computed FC factors assuming coupling to a single phonon mode, which pointed in the exact direction of the reaction coordinate. The fact that these theories were so successful in describing a multitude of physical processes indicated that this is a reasonable assumption. However, the final piece of the puzzle was to rigorously justify this. Fortunately, the
solution had already been provided in the context of ET by Kubo and Toyozawa [156]. They extended the model of Huang and Rhys (see Chap. 1.3.2) to include coupling of an arbitrary number of phonons with frequencies $\omega_l$, and reduced displacements $\Delta_l$, corresponding to Huang Rhys parameters $S_l = \Delta^2_l / 2$. An example in two-dimensions is shown in Figure 5.3. They showed that in the high temperature limit, $k_BT \gg \hbar \omega_l$ for all $l$, the FC factor takes the form

$$F = \frac{1}{\sqrt{4\pi\Lambda k_BT}} \exp\left[-(\Lambda + \Delta E)^2 / 4\Lambda k_BT\right], \quad (5.7)$$

$$\Lambda = \sum_l \frac{\Delta^2_l}{2} \hbar \omega_l = \sum_l S_l \hbar \omega_l. \quad (5.8)$$

This is precisely the form of eq. 5.4 and 1.23, with $\lambda = S\hbar \omega \rightarrow \Lambda$. This process thus corresponds to thermal activation over the barrier presented by the lowest crossing point of the potential energy hypersurfaces [40] (in fig. 5.3 this corresponds in 2D to the minimum of the intersection of the two parabolas). If we know the equilibrium
coordinates of reactants, $Q_{l0,r}$, and products, $Q_{l0,p}$, for \textit{ET} we can compute

$$
\Lambda = G(D^+A^-, Q_{l0,r}) - G(D^+A^-, Q_{l0,p}). \quad (5.9)
$$

Why is this significant? Well, provided we can compute $\Lambda$, and assuming finite coupling to a quasi-continuum of low energy phonon modes, we can determine the \textit{ET} rate using the single mode expression eq. 5.4 by replacing $\lambda \rightarrow \Lambda$. We must not consider the frequencies and normalised displacements of the coupled modes!

### 5.1.2 Electronic Coupling

Calculation of the electronic coupling, $V$, for \textit{ET} between a donor $D$ and acceptor $A$ in eq. 5.12 requires the calculation of the direct exchange interaction \cite{40}

$$
V = \langle \Psi_{DA} | H_T | \Psi_{D^+A^-} \rangle, \quad (5.10)
$$

where $H_T$ is the Hamiltonian of the combined $D + A$ system. In the case of weak coupling, $V$ scales approximately with the overlap of the wavefunctions of the $D$ and $A$ atoms which are involved in the charge transfer \cite{40,157-159}. For the transfer of an electron in state $i$ of the donor, $\psi_{Di}$, to the state $j$ of the acceptor, $\psi_{Aj}$:

$$
V \approx K \langle \psi_{Di} | \psi_{Aj} \rangle, \quad (5.11)
$$

where $K$ is a constant.

Estimation of the constant $K$ involves direct computation of eq. 5.10. However, one can employ 5.11 if only the relative scaling of $V$ is desired (e.g. its dependence on the $D - A$ separation $\delta$, $V(\delta)$).

### 5.1.3 Encorporating Quantum Lattice Effects

The non-adiabatic \textit{ET} model of eq. 5.4 gives a \textit{ET} rate for a process in which coupling of the electron to a quasi-continuum of low energy phonon modes drive the system over energetic barrier resulting from nuclear displacements between the reactants and products. It does not however, include any contributions to the \textit{ET} rate from higher frequency phonon modes ($\hbar \omega > k_b T$). We demonstrated coupling of
higher frequency phonons to the electronic states in a NC in Chapter 3, and so one must consider how these modes may affect the ET rates.

The contributions of coupling to intramolecular modes (phonon modes of the donor and acceptor themselves) were determined in a series of papers by Jortner, Bixon, Efrima, and Ulstrup [39–44]. The authors considered the model shown in Figure 5.4, where excitation/de-excitation of \( \omega_h > k_B T \), occurred during the ET process. The resulting transition rate is then given by

\[
k = \frac{2\pi}{\hbar} V^2 \sqrt{\frac{1}{4\pi \Lambda k_B T}} e^{-S_h} \left[ \exp \left( -\frac{(\Lambda + \Delta G)^2}{4\Lambda k_B T} \right) + \sum_{p=1}^{\infty} \frac{S_h^p}{p!} \exp \left( -\frac{p\hbar \omega_h}{k_B T} - \frac{(\Lambda + \Delta G - p\hbar \omega)^2}{4\Lambda k_B T} \right) \right] + \sum_{p=1}^{\infty} \frac{S_h^p}{p!} \exp \left( -\frac{(\Lambda + \Delta G + p\hbar \omega)^2}{4\Lambda k_B T} \right),
\]

where \( S_h \) is the Huang Rhys factor for the coupling of the electron to the \( \omega_h \) mode. The first of the three terms in the large square brackets is just the non-adiabatic term from eq. 5.4. The second corresponds to de-excitation of phonons on the reactants before charge transfer, and is multiplied by the probability that \( p \) phonons are present, therefore if \( \hbar \omega \gg k_B T \) this term vanishes. The final term corresponds to thermal excitation of phonons on the reactants. As a final note, Efrima and Bixon pointed out that the model can be extended to account for coupling to \( m \) modes, provided their \( \omega_h \) are similar, through the replacement \( S_h \rightarrow mS_h \) [42].

### 5.1.4 Implications for Charge Transport

Here we compare the ET model of eq. 5.12 for non-adiabatic ET including the effects of excitation/de-excitation of high frequency phonons, with regards to the implications for charge transport in a 3D ensemble of energetically disordered transport sites. We assume that there is a reorganization energy \( \Lambda \) associated with charge transfer from one site to the next, and that the change in entropy from a charge hop is negligible, \( \Delta G \rightarrow \Delta E \). With disorder in the hopping site energies,
5.1. CHARGE TRANSFER THEORY

Figure 5.4: Configurational diagram for the ET models incorporating thermal excitation/de-excitation of the reactants/products, assuming coupling to a high frequency phonon mode, $\hbar \omega_h > k_B T$.

$E_i, \Delta E = E_{i+1} - E_i$ will then have some statistical distribution, depending on the distribution of the $E_i$.

In Figure 5.5a we plot the ET rate (eq. 5.12) as a function of $\Delta E$ with $mS_h = 0, 1, 2, 3$. The model with $mS_h = 0$ reduces to the non-adiabatic Marcus model of eq. 5.4 which has a Gaussian form with a maximum $k$ occurring at $\Delta E = -\Lambda$, both strongly exergonic ($\Delta E \ll 0$) and endergonic ($\Delta E \gg 0$) transfers have small rates. From a particular site, a charge carrier will hop to one of its neighbours whose energy differs not too much from its own. Importantly, this implies that it will be unfavourable for carriers to hop to sites with particularly low $E_i$. With the coupling to high frequency phonons, the situation changes, and the maximum rate is shifted to more and more exergonic transfers as $mS_h$ increases. In Figure 5.5b, we plot the model with $mS_h = 2$ at temperatures of $T = 300, 200, 100, 50K$. We can see that including excitation of phonons in the products upon ET leads to nearly temperature independent rate for exergonic transitions, while the endergonic slow down exponentially. The effect of the coupling to high energy phonon modes is to drive the charge carriers to low lying energetic sites in the ensemble.
Figure 5.5: Plots of the ET rate as a function of $\Delta E = \Delta G$ using eq. 5.12 for different $mS_h$ and $T$. With $mS_h = 0$ the model reduces to the non-adiabatic Marcus model, eq. 5.4.

### 5.2 Origin of Reorganization Energy of Nanocrystals

The activation energy for carrier mobility in NC solids has typically been assigned to outer shell reorganization \[\text{[17, 45–47]}\]. The outer shell reorganization energy, $\lambda_{os}$, depends on the frequency dependent dielectric constant $\epsilon(\omega)$. If the ET is very slow (ms to s), one can assume that all of the dipoles in the system have sufficient time to orient themselves in their lowest energy configurations after an ET event (see Fig. 5.6), and one can use the expression given in eq. 5.3, which is proportional to $(\epsilon_{op}^{-1} - \epsilon_{s}^{-1})$. If the ET is significantly faster, $\epsilon_s$ should be replaced by the dielectric constant corresponding to the ET rate $\epsilon_s \rightarrow \epsilon(2\pi k)$.

Estimation of $\lambda_{os}$ thus requires knowledge of the ET rates and the full frequency-dependent permittivity $\epsilon(\omega)$. To date, no studies have reported on the full range of the permittivity for PbS NC solids. Impedance spectroscopy on PbS NC solids have been performed \[\text{[89, 160]}\], and results indicate that although the permittivity does increase at low frequencies, it levels off at a constant value above $\sim 10^4\text{Hz.}$
5.2. ORIGIN OF REORGANIZATION ENERGY OF NCS

These measurements are typically limited to $\sim 10^6$ Hz. If the permittivity extracted by these measurements can be extrapolated to optical frequencies, then we could expect a negligible $\lambda_{os}$, as carrier hopping times are typically on the order of ns to $\mu$s. We therefore turn our attention to the inner-shell reorganization energy $\Lambda$.

5.2.1 Inner Shell Reorganization Energy

We can determine the internal reorganization energy, $\Lambda$, within the quadratic free energy approximation discussed in Section 5.1, using eq. 5.9. For the ET from one NC to another within a large ensemble of NCs, we can ignore the change in entropy, $S$, associated with the ET. If we further assume that the charge state of a NC in the ensemble of NCs does not effect the physical structure of its neighbouring NCs, which should be reasonable for low carrier concentrations in the NC-solid, we can compute eq. 5.9 using a half cell approach [161]. In the half cell approach, the total energies of the donor and acceptor are calculated individually and $\Lambda$ can be computed as,

$$
\Lambda = \left( E_{TOT}(D^+, Q_{l0,d}) + E_{TOT}(A^-, Q_{l0,a}) \right) - \left( E_{TOT}(D^+, Q_{l0,d+}) + E_{TOT}(A^-, Q_{l0,a-}) \right).
$$

Figure 5.6: Depiction of the reorganization of dipoles corresponding to an ET.
We explain this expression term by term. The first term corresponds to the total energy of a positively charged donor, but with the nuclear coordinates corresponding to the equilibrium nuclear coordinates of the neutral donor. The second term corresponds to the total energy of the a negatively charged acceptor with the nuclear coordinates of the neutral acceptor. The third and fourth term then correspond to the total energy of the charged donor/acceptor with the nuclear coordinates of the charged donor/acceptor.

To calculate \( \Lambda \) via eq. 5.13, we turn to DFT. We constructed atomistic models for a size series of PbS NCs with chlorine (Cl) termination, according to the procedure discussed in Chapter 2.1.1. Images of the atomistic models are shown in Figure 5.7.

We performed calculations for each NC with radius \( r \) in three charge states; neutral (intrinsic semiconductor, \( n_0 \)), charged with 1 electron (\( e \)), and charged with a hole (\( h \)). For each charge state, we fully relaxed the structure of each NC minimising the total energy.
Convergence of the nuclear positions to within a threshold of 100 fm was used for the relaxation. From the relaxed structures, we obtain the 0K equilibrium nuclear coordinates for each charge state, $Q_{l0,n0}$, $Q_{l0,e}$, and $Q_{l0,h}$, and corresponding total energies, $E_r(n_0,Q_{l0,n0})$, $E_r(e,Q_{l0,e})$, and $E_r(h,Q_{l0,h})$. Here we have dropped the $\text{TOT}$ subscript for the energies. We then computed the energies of various charge states, using the equilibrium nuclear coordinates from the other charge states, $E_r(x,Q_{l0,x})$. For example $E_r(h,Q_{l0,n0})$ corresponds to the total energy of a NC with radius $r$ charged with a hole, but with the nuclear coordinates of the neutral NC. In accordance with the Born-Openheimer approximation of the ET model, for the calculation of the $E_r(x,Q_{l0,x})$ the electronic structure was fully relaxed to its ground state. The internal reorganization energy associated with hole transfer from the NC with $r = r_1$ to the NC with $r = r_2$, $\Lambda_h(r_1,r_2)$, is then given by:

$$\Lambda_h = (E_{r1}(n_0,Q_{l0,h}) + E_{r2}(h,Q_{l0,n0})) - (E_{r1}(n_0,Q_{l0,n0}) + E_{r2}(h,Q_{l0,h})),$$

while for electron transfer,

$$\Lambda_e = (E_{r1}(n_0,Q_{l0,e}) + E_{r2}(e,Q_{l0,n0})) - (E_{r1}(n_0,Q_{l0,n0}) + E_{r2}(e,Q_{l0,e})).$$

In Figure 5.8a, we plot the calculated $\Lambda_h(r_1,r_1) = \Lambda_h(r)$ and $\Lambda_e(r)$ for ET between two NCs with identical radius $r$ as a function of $r$. Both $\Lambda_h(r)$ and $\Lambda_e(r)$ decrease monotonically with an increase in NC radius, and within the scatter, are approximately the same for hole and electron transfer for a given NC radius. Both data sets are well fit with an inverse square dependence on the NC radius, $\Lambda_x(r) \sim r^{-2}$. In Figure 5.8b we plot the $\Lambda_h(r_1,r_2)$ for a hop of a hole to/from the $r = 0.85$ nm NC, from/to a NC with radius $r_2$. The results indicate that $\Lambda_h(r_1,r_2) \approx (\Lambda_h(r_1) + \Lambda_h(r_2))/2$. This means that in the presence of size disorder of the NCs in a NC solid, $\langle \Lambda_x(r_i,r_i') \rangle \approx \Lambda_x(\langle r_i \rangle)$.

To determine the origin of the $\Lambda_x(r)$, we computed the Pb-Cl and Pb-S nearest neighbour bond lengths in the charged and neutral NCs, $d(x,Pb-X)$, where $x$ is the charge state and $X = Cl||S$. In Figure 5.9 we plot the mean of the change in bond length going from the
Figure 5.8: Internal reorganization energy for hole ($\Lambda_h(r)$) and electron ($\Lambda_e(r)$) transfer between two PbS NCs of equal radius ($r$), as a function of the radius $r$ is shown in (a). The black line illustrates the $\sim r^{-2}$ dependence of the $\Lambda_x(r)$. In (b) the $\Lambda_h(r_1,r_2)$ for the hop of a hole from a $r_1 = 0.85\,\text{nm}$ NC to a NC with radius $r_2$ (and vice-versa) is plot as a function of $r_2$. The resulting $\Lambda_h(r_1,r_2)$ are approximately the average of the $\lambda_h(r_1)$ and $\lambda_h(r_2)$.

neutral NC to the charged NCs $\Delta d = d(n, Pb - X) - d(x, Pb - X)$, where $x = e \parallel h$. Upon charging the NCs with a hole, the Pb-Cl bonds contract, while upon charging with an electron, they expand. The extent of the contraction/extension of the Pb-Cl bonds decreases as $r$ increases. In contrast, the extracted contraction/expansion of the Pb-S bonds upon charging with an electron or hole is below the relaxation threshold, an appears negligible compared to the change in Pb-Cl bonds.

The internal reorganization energies $\Lambda_h(r)$ and $\Lambda_e(r)$ therefore arise from the reorganization of the Pb-Cl bond lengths of the NCs upon charge transfer, and decrease as the size of the NC and therefore number of Pb-Cl bonds, increases.

To see how $\Lambda_h(r)$ and $\Lambda_e(r)$ are affected by the choice of ligand, we repeated the calculations for the PbS/Br, and PbS/I NCs with $r = 1.2\,\text{nm}$. Unfortunately, inconsistent results were obtained for the PbS/MTH NCs. This is due to the fact that the MTH ligand
have rotational degrees of freedom. The free energy surfaces of the PbS/MTH NCs presumably have many local minima with respect to the rotations of the MTH molecules, and so determining the ‘true’ equilibrium nuclear coordinates is a formidable challenge.\(^2\) The results for the halide ligands are given in Table 5.1. The results indicate a clear decrease in the \(\Lambda_h\) and \(\Lambda_e\) with decreasing electronegativity of the halide.

5.3 Superlattice and Inter-Nanocrystal Coupling

PbS NCs self-assemble into a Body-Centered Cubic (BCC) superlattice upon NC-solid formation [31, 162]. Recently, through high energy small angle X-ray scattering, Weidman and coworkers [30] also

\(^2\)We are currently applying techniques based on AIMD simulations to calculate the \(\Lambda\) for the PbS/MTH NCs.
Table 5.1: Internal reorganization energy for hole ($\Lambda_h$) and electron ($\Lambda_e$) transfer between two $r = 1.2\text{nm}$ PbS NCs and the effective electronegativity of the surface terminations in Pauling units ($\chi(X)$).

<table>
<thead>
<tr>
<th></th>
<th>$\chi(X)$</th>
<th>$\Lambda_h$ (meV)</th>
<th>$\Lambda_e$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS/Cl</td>
<td>3.16</td>
<td>58</td>
<td>82</td>
</tr>
<tr>
<td>PbS/Br</td>
<td>2.96</td>
<td>57</td>
<td>79</td>
</tr>
<tr>
<td>PbS/I</td>
<td>2.66</td>
<td>47</td>
<td>72</td>
</tr>
</tbody>
</table>

demonstrated ordering in the orientations of the individual PbS NCs. They found the [100] facets of the NCs to align perpendicular to the direction of the BCC lattice vectors, while the [111] NC facets aligned perpendicular to the [111] direction of the BCC unit cell (see Fig. 5.10). In the BCC superlattice, each PbS NC has a total of 14 nearest neighbours, 6 in the [100] directions and 8 in the 111 directions.

Figure 5.10: PbS NC-solid BCC Superlattice with lattice constant $a = b = c$. The orientation of the PbS NCs within the BCC unit cell is shown, and the wavefunction overlap integrals, $A_{[100]}$ and $A_{[111]}$, used for the ET model are indicated.
The next step in parameterising the ET model is to determine the electronic couplings \( V_{i,j} \). As we discussed in Section 5.1.2, we can gauge the relative magnitudes of the \( V_{i,j} \) through overlap of the VBM and CBM wavefunctions of the NCs:

\[
A_{i,j} = \langle \psi_{n,i} | \psi_{n,j} \rangle,
\]

where \( A_{i,j} \) is related to \( V_{i,j} \) through a constant, \( A_{i,j} = V_{i,j}/K \) (see eq. 5.11). We are interested in the \( A_{i,j} \) for two particular physical configurations of nearest neighbor NCs, where their [100] facets are aligned, or their [111] facets are aligned, which we will refer to as \( A_{[100]} \) and \( A_{[111]} \) respectively. These two orientations are indicated in Figure 5.10.

To calculate the \( A_{i,j} \), we use the wavefunctions from the DFT calculations performed on our PbS NC size series (Section 5.2.1). As with the NCs investigated in Chapter 3.3.1, we find the four-fold degeneracy of the VBM and CBM of bulk PbS is split into a 3-fold \((\psi_{1e,\alpha}, \psi_{1h,\alpha})\) and singly degenerate \((\psi_{1e}, \psi_{1h})\) set of states in the NCs. However, here we find the ordering of the states to be size dependent. Interestingly, although the ordering of the states varies, the lowest energy optical transition remains weakly coupled (see Figure B.4 in Appendix B.3). We therefore calculate both \( A_{[100]} \) and \( A_{[111]} \) for the singly degenerate states as:

\[
A_{[100]} = \langle \psi_{1x}(r) | \psi_{1x}(r + R[1, 0, 0]) \rangle,
\]

\[
A_{[111]} = \langle \psi_{1x}(r) | \psi_{1x}(r + R[1, 1, 1]) \rangle.
\]

For the triply degenerate states we compute,

\[
A_{[100]} = \frac{1}{9} \sum_{\alpha, \alpha'} \langle \psi_{1x,\alpha}(r) | \psi_{1x,\alpha'}(r + R[1, 0, 0]) \rangle,
\]

\[
A_{[111]} = \frac{1}{9} \sum_{\alpha, \alpha'} \langle \psi_{1x,\alpha}(r) | \psi_{1x,\alpha'}(r + R[1, 1, 1]) \rangle.
\]

\( R \) is adjusted in the calculations such that the facet-to-facet distance of the NCs is 3 Å. Our DFT calculations utilize linear combinations of Gaussians for the atomic orbital basis set, long range overlap calculations will be inaccurate due to the \( \exp[r^2] \) decay of the gaussian...
atomic orbitals at large $r$. The typical fix for this is to perform the calculations with small $r \sim 3\text{Å}$, and then extrapolate using the distance dependence of the form given in eq. 1.14.

![Figure 5.11: Overlap of the hole wavefunctions assuming NCs with [100] facets aligned ($A_{[100]}$), or their [111] facets aligned ($A_{[111]}$), corresponding to the superlattice model depicted in Figure 5.10. The facet-to-facet distance was set to 3Å. These results show that electronic coupling between neighboring [100] facets is stronger than between [111] facets by $\sim 2$ orders of magnitude. The $A_{[100]}$ and $A_{[111]}$ of $\psi_{1h}$ (blue squares) and $\psi_{1h\alpha}$ multiplied by a factor of 3 (red circles) coincide.](image)

Plots of the computed $A_{[100]}$ and $A_{[111]}$ as a function of NC size for the VBM states of the NCs are plotted in Figure 5.11. There are two take-aways. First, the coupling scales strongly with NC size, in accordance with the spherical potential well model discussed in Chapter 1.2.2. Second, the coupling to the nearest neighbours in the [111] directions is nearly two orders of magnitude lower than the coupling to nearest neighbours in the [100] directions. The results from the fact that the ligands residing on the [111] facets tend to confine the band edge wavefunctions away from the [111] surface, as we discussed in Chapter 3.3.1.

Finally, we show that the resulting rates are the same whether the band edges are singly or 3-fold degenerate. The resulting wavefunction overlaps for the $\psi_{1h}$ (eq. 5.17) are approximately three-times higher
than for the $\psi_{1h,\alpha}$ (eq. 5.18). However, the three fold degeneracy must be included for the ET rate between the $\psi_{1h,\alpha}$ states.

5.4 Outlook

Here we have motivated a phonon-mediated ET model. We performed DFT to compute estimates for the electronic coupling and internal reorganization energies of the model for PbS NCs. The results demonstrate dependencies on the NC size and surface termination. These estimates can be used as inputs to Kinetic Monte Carlo calculations to simulate charge transport in PbS NC solids. We are currently implementing this to compare the predictions of the model to TOF photocurrent transients.
Chapter 6

Conclusion

We have shown that the electronic and phononic properties of NCs, electron-phonon interactions, and charge transport in NC-solids are dependent on the size and surface chemistry of the NCs in a number of ways.

Characterization of charge carrier mobility in PbS-NC-solids indicated that the temperature activated charge transport strongly depends on the size of the NCs. DFT calculations were used to demonstrate that these effects result from the decrease in wavefunction overlap, and a decrease in the internal reorganization energy with increasing NC size.

The choice of ligand also modifies many of the important physical processes in NCs. We demonstrated that the coupling of phonons to the electronic states of NCs is reduced as the effective electronegativity of the ligand increased. At the same time, reorganization of the ligand-Pb bond lengths in the NCs were the predominant source of the internal reorganization energy associated with electron transfer between NCs. This suggested a coupling of the vibrational modes of the ligands to inter-NC electron transfer, which increases with the electronegativity of the ligand.

The effects of NC size and surface chemistry should be broadly applicable to other NC materials, and provide an avenue for controlling their charge carrier dynamics.
Appendix A

Publications

The work in this thesis is based in parts on the following publications:


Other publications during the doctoral studies:


Appendix B

Additional Figures

B.1 Phonon Properties in Nano-Crystals

Figure B.1: Phonon band-structure of bulk PbS

B.2 Measuring Carrier Mobilities
Figure B.2: 2D slab of PbS which was geometrically relaxed, to investigate surface reconstruction. The deviation in the bond lengths in the direction normal to the surface are shown on the right. [90]
B.2. MEASURING CARRIER MOBILITIES

Figure B.3: $\mu_h$ as a function of NC radius extracted from TOF transients at 300K.

[60]
B.3 Electron Transfer Model

Figure B.4: Optical matrix elements for 3 different sizes of PbS/Cl NCs. The $\psi_{1e,\alpha}$ and $\psi_{1h,\alpha}$ are 3-fold degenerate. The black boxes indicate the lowest energy optical transition for the NCs.
Appendix C

Additional Calculations

C.1 Density Functional Theory Calculations of Bulk Lead-Sulfide

For the bulk calculations of PbS, we use Vienna ab initio simulation package (VASP) \[163\]. The basis set for the one-electron wave functions is constructed by the projector augmented-wave (PAW) method \[164, 165\]. We choose the PAW pseudopotentials such that the \([Xe] 4f^{14} 5d^{10} ([He] 2s^2 2p^6)\) electrons of Pb (S) are selected as the core electrons. The valence electrons are \(6s^2 6p^2\) for Pb and \(3s^2 3p^4\) for S. Scalar-relativistic corrections are also taken into account. For generalized gradient approximation (GGA) calculations, we treat the exchange correlation potential within the (GGA) utilizing the parameterization from Perdew, Burke, and Ernzerhof (PBE) \[165\]. For calculations including screened hybrid functional (HF), we employ the screened HF of Heyd and coworkers (HSE03) \[166\]. A \(8\times8\times8\) G-centered Monkhorst-Pack \(k\)-point grid corresponding to 512 \(k\)-points in the reducible wedge of the Brillouin zone is carried out, while the use of symmetry is switched off completely. The partial occupancies for each wavefunction are set by the Gaussian smearing method with 50 meV smearing width. The energy cutoff of 550 eV is considered. For the electronic self-consistency loop, the convergence criteria of \(10^8\) eV/Angstrom force acting on each ion and a total energy difference
of $10^8$ eV between two subsequent iterations are implemented to assure highly converged forces. When explicitly specified in the main text, spin-orbit coupling (SOC) is included in the electronic band structure calculations. The two-atom primitive cell of PbS was rock salt with a room temperature lattice constant ($a$) of 5.963 Å. The two atoms were situated at (0, 0, 0) for Pb and (0.5, 0.5, 0.5) for S. The electronic band structures go along a discrete $k$-mesh following high-symmetry points, i.e. $G$ at the reciprocal coordinates (0,0,0), $K$ at (0.375, 0.375,0.75), $W$ at (0.5,0.25,0.75), $X$ at (0.5,0,0.5), $L$ at (0.5,0.5,0.5) in the units of (2p/a, 2p/a, 2p/a). The phonon dispersion of bulk PbS, phonon density of states ($g(\omega)$), and thermal displacement, $\langle u^2 \rangle$, are computed by the Phonopy package \[167\]. The harmonic IFCs matrix calculated by VASP is used as an input via DFPT instead of a finite-displacement approach \[168\]. For phonon frequencies $q$-mesh sampling, we used 51»51»51 Monkhorst-Pack with half mesh shift in direction along the corresponding reciprocal axes in order to assure convergence of $g(\omega)$ and partial $g(\omega)$. For thermal displacement, we chose a 21»21»21 Monkhorst-Pack $q$-mesh with half mesh shift.

### C.2 Hopping Time Distribution Function

If we assume a standard Marcus type charge transfer mechanism, the mean hopping time for a carrier to go from NC$i$ to $i + 1$ will be given by

$$t_h = A(r, \delta) \sqrt{\lambda k_b T} e^{(\lambda + \Delta E)^2 /4\lambda k_b T},\quad (C.1)$$

where $A(r, \delta)$ is constant for a given NC radius, $r$, and mean NC-NC separation, $\delta$, and $\lambda$ is the reorganization energy. We assume a normal distribution in NC bandgaps,

$$f_E(E_g) = (\sqrt{2\pi}\sigma)^{-1} e^{-(E_g - \langle E_g \rangle)^2 /2\sigma^2},\quad (C.2)$$

where $\sigma$ is the standard deviation, and define the difference in energies of the carrier transport states, $\Delta E$, to be

$$X \equiv (E_{g,i+1} - E_{g,i})/\chi_b,\quad (C.3)$$
where $\chi_b$, $b = \{CB, VB\}$, dictates how the CB and VB levels align between neighboring NCs which we approximate to be independent of $E_{i+1} - E_i$. The $\chi_b$ satisfy $\chi_b > 1$ and $\chi_{CB}^{-1} + \chi_{VB}^{-1} = 1$. The distribution of $X$ is then,

$$f_X(X) = \chi_b (\sqrt{4\pi\sigma})^{-1} e^{-X^2\chi_b^2/4\sigma^2}.$$  \hspace{1cm} (C.4)$$

The distribution of hopping times is then given by,

$$f_{th}(t_h) = f_X(X(t_h)) \frac{\partial X(t_h)}{\partial t_h}.$$ \hspace{1cm} (C.5)$$

Evaluating this and collecting terms independent of $t_h$ into a constant $C$ gives,

$$f_{th}(t_h) = C \exp \left[ \frac{\lambda k_B T}{\sigma^2} \sqrt{\frac{k_B T \log \left( \frac{t_h}{A\sqrt{\lambda k_B T}} \right)}{t_h \log (t_h/A \sqrt{\lambda k_B T})}} \right] t_h^{-1(1+\lambda k_B T \chi_b^2/\sigma^2)}. \hspace{1cm} (C.6)$$

To see how this distribution scales with large $t_h$ we define $Y \equiv \log (f_{th}(t_h))$, and $R \equiv \log (t_h)$, and calculate the derivative,

$$\frac{\partial Y}{\partial R} = \frac{-\lambda^2 k_B T \chi_b^2}{2\sigma^2 \sqrt{\lambda k_B T R - \log A \sqrt{\lambda k_B T}}} \left[ \frac{1}{2(R - \log (A \sqrt{\lambda k_B T}))} - \left(1 + \frac{\lambda k_B T \chi_b^2}{\sigma^2}\right) \right]. \hspace{1cm} (C.7)$$

In the limit of large $t_h$ (large $R$), we thus have

$$\lim_{t_h \to \infty} f_{th}(t_h) = C' t_h^{-\left(1+\frac{\lambda k_B T \chi_b^2}{\sigma^2}\right)}, \hspace{1cm} (C.8)$$

where $C'$ is a constant independent of $t_h$. 

\section{Hopping Time Distribution Function}
Appendix D

Acronyms

Acronyms and Chemical Formulae

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ag</td>
<td>silver</td>
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<td>AIMD</td>
<td>Ab-Initio Molecular Dynamics</td>
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<td>BCC</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>EDT</td>
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<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
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<td>electron-transfer</td>
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<td>Acronym</td>
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<td>FC</td>
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<td>valence band</td>
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<td>valence band maximum</td>
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Bibliography


[90] Bozyigit, D., Yazdani, N., Yarema, M., Yarema, O., Lin, W.M.M., Volk, S., Vuttivorakulchai, K., Luisier, M., Juranyi,


[115] Lovesey, S.W., *Theory of Neutron Scattering from Condensed Matter*, volume 1, Oxford University Press, **1984**.


About the Author

Nuri Abraham Yazdani was born in Ottawa, Ontario, Canada in 1984. He received his B.Sc. in Engineering Physics from Carleton University in 2007. He was awarded his M.Sc. from Simon Fraser University in 2010 for his work on dilute magnetic semiconductors under the tutelage of Prof. Malcolm Kennett. Before beginning his thesis on Carrier Dynamics in Nanocrystal Solids with Prof. Vanessa Wood at ETH Zürich in 2013, he worked on scale-free networks and dye-sensitized solar cells in the groups of Prof. H. Herrmann and Prof. H. G. Park respectively. In his free time he enjoys football, cycling, mountain sports and activities, travelling, and playing music.