QUANTUM CONFINEMENT AND THE EMISSION OF VISIBLE LIGHT

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by

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Abstract

by

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This thesis is for a Doctorate of Philosophy in the field of Condensed Matter. This thesis weaves a common thread which connects together everything I have worked on from 2013-2019. The structure of materials at the atomic level dictates their appearance. Conversely, precise optical experiments performed on these materials can be used to determine details of their structure and chemistry. Multiscale modeling was used to build up from the atomic scale and to test hypotheses of lattice dynamics. This document is (hopefully) a useful reference for those who want to understand how to model complex, dynamic systems over multiple orders of magnitude of length and time.
This thesis is dedicated to my family. To my older brother, Sam, who was so enamoured by the beauty of mathematics that after a long day of learning, he would come home and teach it to me. To my sister, Maria, who appreciated each thing for what it was whether unique or appealing without regard to utility for which the rest of us were obsessed. To my mother, Julie, who taught me to look up when going under a bridge and to acknowledge a clever solution and not feel too bad about copying it. And to my father, Doug, who gave me my sense of humor. I do hope he will appreciate my attempts to condense this thesis in a visual summary.
A visual representation of this thesis - The common thread which connects together
everything I have worked on over the past 6 years.
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CHAPTER 1

INTRODUCTION

The visible spectrum conveys unparalleled information about an object. In this thesis, two projects will be presented where data from optical experiments was eventually used to discern robust structural phenomena over lengths scales ranging from angstrom to micrometers. Our primary point of comparison is two experiments: optical absorption and photoluminescence as well as their trajectories over time. We will see that absorption and emission form a synergistic pair. Each (roughly 10 nm x 10 nm x 10 nm) volume of material has its own absorption spectrum prescribed by the electronic structure. An absorption measurement probes a larger area which averages and combines heterogeneous spectra. And thus, optical absorption measurements probe the electronic structure of the material as a whole. Following optical absorption, an electron and hole, charge carriers, are released into the material. The electron and hole follow "channels" of the electronic structure - the conduction band and valence band respectively. The charge carriers may diffuse, accumulate, separate or pair. In the end, if there are electron(s) and hole(s) in the same region, they may recombine and emit visible light. And so, the visible light which is emitted by a material following illumination conveys the electronic structure of where charge carriers were generated, where they went, how long their journey lasted, and what path they took to get there. In turn, emission provides an exceptionally detailed view of regions of the material which are optically bright - the phases most suitable for optical devices.

The first project presented in this thesis is the culmination of our efforts to
understand why fluorescence intermittency was observed during photoreduction of graphene oxide. Graphene oxide’s emission was decomposed into the emission of a distribution of fluorophores. This atom-level simulation eventually lead to the conclusion that fluorescence intermittency was due to creation and destruction of small luminescent clusters. The second project started from a basic premise for the photosegregation phenomenon in mixed-halide perovskites. Simulating this premise lead to a multitude of testable conclusions which were experimentally verified and ultimately proved the premise itself.

Multiscale modeling which connects local structural transformations to optical observations will be the main topic of discussion. This discussion would not be complete without an inclusion about how behavior changes across different length scales and a discussion of dimensionality. A basic treatment of how confinement alters the electronic structure of a material is illustrated in the appendix. This treatment produces a natural length scale of $\sim 10$ nanometers that separates bulk and confined matter. For the purposes of determining electronic structure from physical structure at the local level, our gold standard will be Density Functional Theory. Density Functional Theory is a collection of numerical techniques and software packages for calculating electronic properties from a known structure. The many-electron problem is treated as a single-body problem via the Kohn-Sham equations. The optical properties over a wider area are constructed by invoking multiple, heterogeneous structures. Heterogeneities in physical structure manifest in ensemble absorption measurements as weighted averages of absorption spectra and through their influence on charge carrier dynamics in optical emission. Kinetic Monte Carlo is the primary means by which we sample the heterogeneity produced by (photo)chemical processes. Kinetic Monte Carlo is a technique where trajectories for a dynamic process are randomly sampled. These multiscale simulations will in the end contain an array of structures from Kinetic Monte Carlo simulations, how these structures change over time, a list of the
optical properties of each structure, and rules for how to combine the heterogeneous properties into a single measurement. We will have absorption spectrum, percent absorption, photoluminescence spectrum, and photoluminescent quantum yield over time. All of these can be compared to experiment. Finally, we can tweak the rules governing the chemical processes which result in the dynamic environment and observe how this changes the optical response. In the end, we evaluate the rules themselves by how well their consequences match reality. We will see that the surgical precision of photoluminescence in particular ensures this is a well-constrained problem and the rules can be deduced.

In our graphene oxide project, we calculate the emission and absorption over time of a graphene oxide sheet as it disintegrates due to repeated photo-reduction reactions. This reduction eventually breaks the sheet down into electronically-isolated islands. Within a certain size range, these islands become highly-emissive. We connect the creation and destruction of these highly-emissive graphenic clusters to the observation of fluorescence intermittency. The "aha" moment was when we realized that the fluorescence intermittency was spatially uncorrelated. If we consider the "on" and "off" states to be some order, the fluorescence intermittency in graphene oxide was purely local. In turn, the order conveyed by the fluctuation between on and off states was only observable at experimental scales because there were sufficiently few blinking emitters. Had there been more blinkers within an experimental pixel, their stochastic variations would have washed out the effect leaving behind only gradual changes to quantum yield. The broad photoluminescence spectrum supports the hypothesis that charge carriers are generated and combine within small graphenic clusters - they do not migrate between clusters. Through repeated simulation and comparison with experimental emission and absorption trajectories we gradually developed more-accurate representations of the chemical reactions. These reactions include sublimation of carbon where the local bond structure was critically
important as well as removal of surface hydroxide ($OH^-$) and epoxide (COC). The modeling matched the experiment better when the epoxide desorbed as CO, rather than just oxygen on its own. That fine detail of graphene oxide reduction chemistry is indicative of the power that multiscale modeling has and the types of discoveries that resulted from trying to understand optical phenomena.

In methylammonium mixed-halide perovskites ($MAPb(I_{1-x}Br_x)_3$) another interesting optical phenomenon was observed. The emission spectrum is tunable between limits of pure iodine and pure bromine, and under illumination, the spectrum red-shifts. The scientific community proposed that the spectrum is narrow and sharp because carriers are free to diffuse over long distances ($\sim 1\mu m$) and thus many carriers accumulate in the same place. Furthermore, it is believed that the redshifting is due to segregation of iodine and bromine. We showed that the two effects are related - the former causes the latter. A thermal model is used for charge carrier distribution and ionic motion is dictated by carrier energy. The ionic motion is hypothesized to be vacancy-mediated which has experimentally verifiable consequences on the final structure formed and on the optical trajectories.
CHAPTER 2

FLUORESCENCE INTERMITTENCY IN GRAPHENE OXIDE: AN EXPERIMENTAL OVERVIEW

2.1 Observation of Fluorescence Intermittency During Graphene Oxide Photoreduction

Graphene oxide (GO) is a 2D material formed by the oxidation of graphene.\[17\] Unlike graphene, GO possesses a band-gap that gives rise to strong fluorescence in the visible spectrum\[19\] that can be tuned by gradual reduction into reduced graphene oxide (rGO) (cf. figure 2.1).\[44\] Prior single sheet absorption and emission microscopy/spectroscopy studies\[65, 46\] have shown that this novel system’s photophysical properties evolve dramatically during photoreduction; GO’s emission first quenches and then brightens under continuous 405 nm irradiation (figure 2.2). This behavior is linked to reduction monitored through synchronous absorption microscopy, emission spectroscopy, and ensemble characterization techniques.\[65, 46\] Intriguingly, the brightening phase is punctuated by spatially heterogeneous fluctuations in emission intensity with 1/f power spectral densities (PSDs) typical of fluorescence intermittency.\[62\].

2.2 Fluorescence Intermittency: An Introduction and Background

For decades, researchers have been trying to determine the finite states of a system undergoing fluorescence intermittency, a phenomenon in which a fluorophore consistently cycles between power-law distributed bright periods and power-law dis-
Figure 2.1. Photoluminescence map of a graphene oxide flake. The x and y scale is pixels and each pixel is approximately 200 x 200 nm.
Figure 2.2. Trajectory of emission intensity and percent absorption for a single pixel in figure 2.1. Emission exhibits rapidly fluctuating intensity coinciding with the peak in average emission intensity (ca. 1000 s).
tributed dark periods. Many models have been developed to explain the contrast between fast radiative recombination (ns) and slow timescales seen in fluorescence intermittency (s-min)[25, 66, 14, 11, 20]. One of first and most widely used microscopic models assumes that the dark state is charged[21, 52], and it is often invoked to justify the existence of long intermittent periods in colloidal quantum dot blinking trajectories. In this model, an on-to-off transition occurs due to Auger ionization of a nanocrystal. The implicit assumption is that a charged quantum dot remains non-emissive until neutralized by return of the ejected electron. Although some of the predictions of the original Efros-Rosen model are in contradiction with experiments[37, 87], recent work by Osad’ko et al[52] showed that a modified version of the charging model is consistent with power law kinetics. However, as shown by Guyot-Sionnest[37], charged quantum dots are emissive, and alternative blinking scenarios also have to be considered. Quantum dot blinking has also been attributed to light-induced surface ligand reorganization[76] and even to light-induced defect rearrangement in nanocrystals[75]. Beyond quantum dots, blinking has been observed in a host of other systems. Examples includes instances of fluorescence intermittency in single molecules[45] and in single polymer strands[7]. Explanations for blinking in these other systems hence range from surface electron (hole) traps to oxidation. Consequently, within the broader context of single particle microscopy, and even within the realm of quantum dot blinking, there exists no consensus as to the microscopic origin of blinking.

2.3 Evidence of Localization

The inherent sensitivity of photoluminscence revealed that an interesting, complex, and dynamic process was occurring during photoreduction. I would like to point out one piece of evidence in particular from the photoluminscence experiments. The emission spectrum was too broad (figure 2.3). A single emitter has a well-defined
emission energy. It may be broadened slightly by thermal energy (∼25 meV) but a ∼ 200 meV emission peak width was observed experimentally. This peak width could be explained through ensemble emission involving many emitters each with a different emission energy. However, this postulate created a new problem: blinking should not be measurable if there are a very large number of uncorrelated blinkers. In the next two chapters, we finally resolved this issue. Blinking was uncorrelated, but there were few enough blinkers that the effect was observable.
In GO, concerted single-particle optical microscopies are coupled to multiscale spatial ($nm^2$-$mm^2$) and temporal (ms-h) simulations of relevant photolytic reactions to demonstrate how the chemical reactivity of individual graphene oxide sites leads to different reduced graphene oxide domain structures exhibiting distributed absorption and fluorescence properties. The agreement between simulation and experiment additionally grows with model parameterization until new optical behavior, fluorescence intermittency, emerges from rules governing single chemical reactions. This has broader implications beyond GO/rGO blinking since despite the nearly three decades of work on the matter, the current study is the first study to link blinking to a definitive chemical process.

To determine if rGO’s blinking and reduction mechanism are implicitly connected, we have carried out multiscale theoretical modeling of GO-to-rGO interconversion. Fig. 3.1 shows Density Functional Theory (DFT)/Time-dependent Density Functional Theory (TDDFT) and Kinetic Monte Carlo (MC) simulations which connect the photoreduction-induced, structural evolution of GO to the optical response of its individual $sp^2$ domains. GO features a $sp^2$-coordinated carbon honeycomb lattice, which contains vacancies, defects, and functional groups distributed across its basal plane and edges. Different models suggest that epoxide (COC) and hydroxide (COH) groups predominantly decorate GO’s basal plane while edges are carbonyl- (CO), carboxyl- (COOH), or hydrogen-terminated. Consequently,
graphenic domains are embedded within a disordered, $sp^3$-hybridized matrix with photolytic reduction leading to GO-to-rGO interconversion through changes to the local number, size, and overall density of aromatic $sp^2$ clusters.\textsuperscript{[17, 44, 28]}

In order to provide molecular insight into optically measured experimental data, the developed model scales six orders of spatial magnitude in a series of steps. First, DFT and TDDFT is carried out to determine gap energies, radiative recombination rates, nonradiative recombination rates, and thus quantum yields on Å - nm scaled fluorescent domains (cf. Fig. 3.2). The domains we studied via DFT/TDDFT span the entire visible range and are representative of all $sp^2$ domains which contribute to the photoluminescence of graphene oxide. Next, MC simulations use this information to model larger regions of a GO sheet during dynamical chemical reactions. During the simulation, cluster detection is used to count the number of connected carbon atoms; the gap energy, associated absorption cross-section, and quantum yield expressions are applied to calculate the color, absorption, and emission intensity of that cluster. Clusters whose gap energy exceeds the photon excitation energy are excluded. The absorption cross-section and emission intensity of all clusters within the region is summed up. The absorption is rescaled to calculate a percent absorption. Finally, in order to simulate a region comparable to a pixel in the experiment many small regions are simulated and the results are averaged.

3.1 Density Functional Theory

All DFT calculations were performed with the Gaussian 09 software package. Structures were relaxed to a force of less than 0.01eV/Angstrom before optical calculations were performed. All calculations were performed with the 6-31G* basis set at the B3LYP\textsuperscript{[5 42 68 74]} level.
Figure 3.1. Cascade of domain and length scales used in the study of optical properties of graphene oxide.

Optical properties of each size range are connected to the next larger size range. Color is used to represent emission intensity as indicated by the scale bar on the right. (a) Typical domain used in DFT calculations to characterize the absorption/emission properties of individual carbon nanoclusters; (b) Structure of GO at a specific time-step generated by MC simulation; (c) A 200 x 200 nm composite of 100 MC-simulated domains equivalent to the optical response of one pixel monitored in the experiment; (d) Time-averaged emission intensity for one sample used in the study. Scale bars: 0.2 nm, 2 nm, 20 nm, and 2 µm for (a), (b), (c), and (d) respectively.
3.2 Optical Properties of Individual Graphenic Domains

DFT/TDDFT\cite{26} are first used to establish minimum transition energies, absorption cross-sections/emission intensities, and quantum yields (QYs) for a series of successively larger graphenic clusters: C24H12, C54H18, C96H24, C150H30, and C216H36. Clar’s pioneering work\cite{32} demonstrated that the optical response of polynuclear aromatic hydrocarbons (PAHs) depends exquisitely on the number of carbon atoms as well as the maximum number of possible aromatic sextets. Different PAHs, which conserve the number of carbon atoms and aromatic sextets, possess near identical optical properties. Consequently, the chosen graphenic clusters enable construction of a calibration curve, linking $sp^2$ domain size to QY and spanning the visible spectrum. Corresponding graphenic cluster emission energies (QYs) are 4.16 eV (31.8%), 2.90 eV (12.5%), 2.18 eV (4.52%), 1.69 eV (1.25%), and 1.32 eV (0.092%) respectively.\cite{19,39,79}

3.3 Life Time vs. Oscillator Strength

The rate constant of spontaneous radiation transition is given by
### TABLE 3.1

OPTICAL PROPERTIES OF CARBON NANOCLUSTERS

<table>
<thead>
<tr>
<th></th>
<th>$C_{24}H_{12}$</th>
<th>$C_{54}H_{18}$</th>
<th>$C_{96}H_{24}$</th>
<th>$C_{130}H_{30}$</th>
<th>$C_{214}H_{36}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>0.74</td>
<td>1.23</td>
<td>1.73</td>
<td>2.22</td>
<td>2.71</td>
</tr>
<tr>
<td>Clar Number</td>
<td>3</td>
<td>7</td>
<td>12</td>
<td>19</td>
<td>27</td>
</tr>
<tr>
<td>Emission Energy (eV)</td>
<td>4.16</td>
<td>2.90</td>
<td>2.18</td>
<td>1.69</td>
<td>1.32</td>
</tr>
<tr>
<td>Radiation Lifetime</td>
<td>2.14 ns</td>
<td>2.95 ns</td>
<td>4.22 ns</td>
<td>6.31 ns</td>
<td>10.2 ns</td>
</tr>
<tr>
<td>Internal Conversion Lifetime</td>
<td>1.00 ns</td>
<td>422 ps</td>
<td>200 ps</td>
<td>80 ps</td>
<td>9.44 ps</td>
</tr>
<tr>
<td>Quantum Yield (%)</td>
<td>31.8</td>
<td>12.5</td>
<td>4.52</td>
<td>1.25</td>
<td>0.0925</td>
</tr>
<tr>
<td>Emission Intensity (a.u)</td>
<td>7.63</td>
<td>6.75</td>
<td>4.34</td>
<td>1.88</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Comparison of 5 carbon nanoclusters from 0.74 to 2.71 nanometers in diameter. The nanoclusters completely cover the visible range and have emission energies from infrared to ultraviolet. Although our TDDFT results are for absorption, the relative change in the electronic structure of the excited state is quite small. Consequently, the electronic transition energies for absorption and emission can be approximately regarded as the same.

$$A_{ng} = \frac{2e^2(\omega_{ng})^2}{4\pi \epsilon_0 mc^3} f_{ng}$$

Or its corresponding life time is given by

$$\tau_{ng} = \frac{1}{A_{ng}} = 2.30508 \times 10^{-8} \frac{1}{f_{ng}(\omega_{ng}[eV])^2}$$

where $f_{ng}$ The oscillator strength of the transition between the ground state $g$ to the excited state $n$. $\omega_{ng}$ Its corresponding transition frequency ($s^{-1}$) e: $1.602 \times 10^{-19}$
C $\epsilon_0$ is the Permittivity of vacuum ($8.85418781762 \times 10^{-12}$ F/m) c is the Speed of light (299792458 m/s)

### 3.4 Calculation of Internal Conversion Rate

The rate constant of the internal conversion is given, under single promoting mode approximation, by

$$W_{n\rightarrow g} = \left| \frac{R_{ng}^p}{\hbar} \right|^2 \frac{\omega_p}{2\hbar} Re \int_0^\infty dt \exp[it(-\omega_{ng} + \omega_p) - \gamma t] G_{ng}(t)$$

where $R_{ng}^p = -\hbar^2 < \Phi_g | \frac{\partial}{\partial Q_p} | \Phi_n >$ is an electronic coupling matrix element due to the break-down of the Born-Oppenheimer approximation, $\Phi_g(\Phi_n)$ is the electronic ground (excited) state wave function, $\hbar\omega_p$ and $Q_p$ are the vibrational energy of the promoting mode and its normal coordinate, respectively, $\hbar\omega_{ng}$ is the electronic transition energy, and $\gamma$ is a convergence factor. The term $G_{ng}(t)$ in Eq. (3.4) is given, $\hbar\omega_l \gg k_B T$, by

$$G_{ng}(t) = \exp[-\sum_l S_l (1 - e^{it\omega_l})]$$

Expansion of Eq. (3.4) leads to

$$G_{ng}(t) = \exp[-\sum_l S_l] \sum_{n=0}^\infty (S_l)^n e^{itn\omega_l} \sum_{m=0}^\infty (S_S)^m e^{itn\omega_s}$$

Substituting Eq. (3.4) into Eq. (3.4) yields

$$W_{n\rightarrow g} = \left| \frac{R_{ng}^p}{\hbar} \right|^2 \frac{\omega_p}{2\hbar} \exp[-\sum_l S_l] \sum_{n=0}^\infty \sum_{m=0}^\infty \ldots (S_l)^n (S_S)^m \frac{n!}{n!} \frac{m!}{m!} : Re \int_0^\infty dt \exp[it(-\omega_{ng} + \omega_p + n\omega_l + m\omega_s + \ldots) - \gamma t]$$
Under two-accepting-mode approximation, Eq. (3.4) becomes

\[
W_{n \rightarrow g} = |R_{ng/h}|^2 \frac{\omega_p}{2\hbar} exp[-(S_1 + S_2)] \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(S_1)^n (S_2)^m}{n! m!} \frac{\gamma}{(\omega_{ng} - \omega_p - n\omega_1 - m\omega_2)^2 + \gamma^2}
\]

If we assume \(|R_{ng/h}|^2 \frac{\omega_p}{2\hbar} exp[-(S_1 + S_2)]\) does not depend on the size of graphene clusters, Eq. (3.4) leads to

\[
W_{n \rightarrow g} = A \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(S_1)^n (S_2)^m}{n! m!} \frac{\gamma}{(\omega_{ng} - \omega_p - n\omega_1 - m\omega_2)^2 + \gamma^2}
\]

where \(A = |R_{ng/h}|^2 \frac{\omega_p}{2\hbar} exp[-(S_1 + S_2)]\).

3.5 Photolysis and Rate Constants

Photolytic reactions follow selection rules, and rates of selected processes scale with temperature like thermally-activated Arrhenius rates.\[72\] \(k = A e^{-\frac{E_a}{k_B T}}\) is an activation or barrier energy, \(k\) is the Boltzman constant, and \(A\) is a reaction dependent prefactor which varies from \(10^{12} \text{ sec}^{-1}\) to \(10^{15} \text{ sec}^{-1}\) for unary reactions or \(10^6 \text{ sec}^{-1}\) to \(10^8 \text{ sec}^{-1}\) for binary reactions.\[72\] The intensity of the laser used in the photoreduction experiments was only capable of raising the temperature by 1-2 °C.\[65\] The main features of photoreduction show up on timescales of 0.1s to 1000s. If we consider the maximum range of \(A\), \(10^6 \text{ sec}^{-1}\) to \(10^{15} \text{ sec}^{-1}\), then the activation energies must lie within \(0.35eV < E_a < 1.09eV\). In this regard, theoretical activation energies for hydroxide desorption (0.54eV)\[29\], hydroxide dissociation into epoxide and water (0.5eV)\[87\], epoxide abstraction as \(O_2\) (1.0eV)\[87, 63\], and oxygen (0.98eV)\[55\] or hydroxide (0.32eV)\[29\] hopping agree well with this energy range. However, the mechanism of lattice disintegration remains elusive because carbon sublimation from edges has activation energies of 4.5eV and 7.5eV for arm-
chair and zigzag edges respectively. A process for dissociation of carbon with more than one carbon neighbor is necessary for lattice disintegration. It has been demonstrated that the photo-Fenton process can create holes in rGO. A possible mechanism was proposed where adsorbed hydroxide groups migrate to edges and they assist in carbon abstraction through the formation of carboxyl (COOH) groups. Energy barriers for dissociation of carboxyl groups were calculated to be 0.57eV and 2.26eV for armchair and zigzag edges respectively. However, the energy for carboxyl dissociation on zigzag edges is still too high to be reachable. Additionally, another mechanism is necessary for conversion of edge carbon atoms which have 2 C-C bonds to single C-C bond carboxyl groups. Strain due to $sp^3$ bonding has been shown to cause wrinkling in GO. Wrinkled graphene is more susceptible to an oxidative cutting reaction which has activation energies less than 1eV. Even if we had energy barriers for all of the relevant reactions in the system, those energy barriers would still refer to ideal cases which differ greatly from the local structure in graphene oxide. For instance, the hydroxide hopping barrier was calculated for a single hydroxide molecule on an infinite graphene lattice with no defects, other functional groups, or vacancies. Low-barrier diffusion reactions can lead a molecule to a new lattice site with lower desorption barriers, and so the most relevant activation energies are for the lowest energy desorption accessible pathways. We propose that functional group abstraction happens primarily through groups hopping to edges or vacancies/defects and then desorbing. For these reasons, we treat the rate constants phenomenologically. We restrict the rate constants to within 4 orders of magnitude of each other and we order them based upon their idealized activation energies locking in well-known differences.
3.6 Chemical Reactions Used in Monte Carlo

\[ C_nOH \rightarrow C_n + OH^- \]

(Rate = \( k_{OH} \))

\[ C_nO \rightarrow C_{n-1} + CO \]

(Rate = \( k_O \))

\[ C_n \rightarrow C_{n-1} + C \]

(Rate = \( k_{C1}, k_{C3}, k_{C zig}, k_{C arm} \))

\( k_{C1} \) (the least stable) was applied to carbon atoms with a single nearest neighbor carbon, \( k_{C3} \) (the most stable) was applied to carbon with three nearest neighbor carbon atoms, \( k_{C zig} \) was applied to carbon atoms with 2 nearest neighbors and 4 next-nearest neighbors, and \( k_{C arm} \) was applied to carbon atoms with 2 nearest neighbors and less than 4 next-nearest neighbors. Based upon the timescales present in the experimental data, the rate constants of the fastest removal process and the fastest process capable of destroying the carbon lattice must be within 4 orders of magnitude of each other. For instance even if \( k_{C3} = 0 \), then the other carbon removal processes are sufficient to disintegrate a lattice. However if \( k_{C3} = k_{C zigzag} = k_{C armchair} = 0 \), then the remaining process, \( k_{C1} \), is insufficient to disintegrate the lattice on its own. In the simulation a phenomenological estimation of rate constants was used, below a description of the connection between the rate constants and activation barriers is provided. Figure 4.1a, 4.1b, and the yellow dashed-dotted line in figure 4.1 used the following rate constants: \( k_{OH} = 1000, k_O = 10, k_{C1} = k_{C3} = k_{C zigzag} = k_{C armchair} = 1 \)

The blue dotted line in figure 4.1 used the following rate constants: \( k_{OH} = 1000, k_O = 10, k_{C1} = 1, k_{C zigzag} = k_{C armchair} = 0.1, k_{C3} = 0 \) Figure 4.1c, the red dashed in figure 4.1, and the data presented in figures 4.3 and 4.5 used the following rate
constants: $k_{OH} = 1000$, $k_O = 10$, $k_{C1} = 10$, $k_{C{armchair}} = 1$, $k_{C{zigzag}} = 0.1$, $k_{C3} = 0$

3.7 Simulation of Photoreduction with Kinetic Monte Carlo

MC simulations then model the evolution of GO’s graphenic clusters during photoreduction (cf. figs 3.3, 3.4). A 20 x 20 nm carbon honeycomb lattice is first generated whereupon functional groups are incorporated into the lattice by randomly placing hydroxide and epoxide groups across the basal plane. Three chemical reactions are simulated to evolve the lattice during reduction: hydroxyl abstraction equation (1), 1,3 epoxide abstraction equation (2), and direct carbon sublimation equation (3).[29, 63]

\[
C_nOH \rightarrow C_n + OH, (Rate\text{Constant} = k_{OH})(1)
\]

\[
C_nO \rightarrow C_{n-1} + CO, (Rate\text{Constant} = k_O)(2)
\]

\[
C_n \rightarrow C_{n-1} + C, (Rate\text{Constant} = k_C)(3)
\]

Although the actual chemical reactions which occur during GO photoreduction are more complicated and numerous[63], equations (1-3) produce photoreduction and lattice disintegration which dictate GO’s long-term structural evolution.[17, 19, 28]

3.8 Optical Properties of Clusters in Monte Carlo Simulations

DFT/TDDFT results are incorporated into MC simulations. Specifically, graphenic clusters, possessing suitable emission energies and QYs to be experimentally observed, are monitored. The absorption of an individual graphenic domain is proportional to its $sp^2$ carbon content while its corresponding emission intensity is the product of its absorption cross-section and associated quantum yield. $C_{24}H_{12}$ and $C_{216}H_{36}$ have emission energies outside the visible range. Therefore, only clusters in the
range of 50 to 150 carbon atoms contribute significantly to the observed emission (cf. Table 3.1 and Fig. 3.2). Counterintuitively, smaller clusters emit more despite their lower absorption cross-section. By adding the response of all spectroscopically-relevant graphenic clusters within suitably large areas of the GO lattice, theoretical emission/absorption intensity time trajectories are obtained, which can be directly compared to experiment. [65]

Quantum yields are calculated by comparing the rate of radiative recombination with the total recovery rate to the ground state. The absorption in MC simulations was calculated by comparing the number of $sp^2$ carbon atoms in the simulation with a piece of graphene of the same area. The ratio was then multiplied by 2.3% (The absorption of graphene at 520 nm)[79]. Emission quantum yields of the five selected clusters were calculated by starting with the lowest energy level which has a significant dipole element to the ground state and then comparing photoluminescence rates to internal conversion rates. The gap energy, absorption cross-section, and emission quantum yield of individual clusters formed in MC simulations was subsequently estimated through TDDFT-established calibration curves, $\epsilon(eV) = \frac{20.5}{\sqrt{N}}$, $\sigma(a.u.) = N$, and $QY(\%) = 274.5e^{-0.44\sqrt{N}}$, where $N$ is the number of carbon atoms in the cluster. Kinetic Monte Carlo simulations were performed with 17280 carbon lattice sites [21.3 nm x 21.3 nm] with larger regions represented by averaging many such simulations. Each kinetic step removed a carbon atom/functional group from the simulation, and the reaction to be performed was chosen randomly with probability proportional to rate, rate constant times number of reactants, and site of reaction chosen randomly.

3.9 Calculation of Power Spectral Density

The power spectral density (PSD) of the trajectory is calculated based on Welch’s method.[25] First, the trajectory of total length is divided into overlapping segments with length of $\Delta t_0$. The overlapping rates of the segments are chosen to be 50%,
Simulation proceeds through initialization which creates a graphene oxide lattice, and then cycles through photoreduction reactions. Each reaction is weighted based upon the number, $N$, ways that the reaction can proceed (reactants) and by the rate constant for that reaction. Every M steps, the connectivity of the lattice is analyzed and clusters are identified. $M$ is chosen to produce a sampling rate similar to the experimental sampling rate.
Figure 3.4. Depiction of a single step in the Monte Carlo chemical reaction simulation.

The same parameterization was used as in figure 4.1a and 4.1b. The simulation contains a graphene sheet with most carbon sites filled in. The large circles in the honeycomb lattice represent carbon atoms and the smaller circles represent either OH groups or O atoms depending on their location. OH groups adhere above the atom, and epoxide (COC) forms above a bond. In this image, the black and grey carbons atoms are neither absorbing nor emitting and the colored carbon atoms are absorbing and emitting. Every grey carbon atom is considered non-absorbing/emitting because it is in an $sp^3$ configuration with a surface oxide (either OH or O) attached to it. The yellow and blue clusters are separated by a wall of adsorbates. The black carbon atoms belong to $sp^2$ clusters that are too small to emit or absorb. There is also a third option (not depicted) where a cluster becomes too large to emit, but can still absorb.
which means there are segments. Then the modified periodogram, as defined in (3.9) is calculated for each of the segments.

\[
\hat{S}_M(f) = \frac{\Delta t_0}{M} \left( \sum_{n=1}^{M} w_n x_{mM-n+1} \exp[i2\pi f \Delta t_0 (n-1)] \right)^2
\]

Here, \(\Delta t_0\) is the unit time difference between discrete temporal signals, \(w_n\) is the window function that convolves with the signal trajectory, for which we used Hamming window in our calculation. Then the periodograms are averaged to reduce the variance in the periodogram estimator.

\[
\hat{S}_{MAP}(f) = \frac{1}{K} \sum_{m=1}^{K} K \hat{S}_m(f)
\]

Before the estimation of the trajectory PSD, the dependence of window size and frequency of the periodogram estimator is evaluated to find the no-bias region of the estimator, as shown in Figure 3.5. A small value for the window size of a given frequency is chosen in the non-bias region to minimize the variance. Since the trajectory of blinking shows long range self-correlation, we utilize an extended version of central limit theorem in estimation of the variance of the periodogram estimator, in which

\[
\hat{\kappa}_{MAP}(f) = \frac{1}{K} (\hat{\kappa}_0(f) + 2 \sum_{m=1}^{K-m} m c (1 - m K) \hat{\kappa}_m(f))
\]

\[
= \frac{1}{K - m} \sum_{n=1}^{K-m} \hat{S}_n(f) \ast \hat{S}_{n+m}(f)
\]

are defined. Variance of the periodogram estimator is determined by the maximum value of \(\hat{K}_{MAP}(f)\) when \(m_c\) goes from 1 to \(K\).
Figure 3.5. Contour plot of the dependence of periodogram estimator on the choice of window size and frequency.

The area showing near vertical contours of estimator values are the non-bias regions. The blue round dots connected by red line are examples of the choice of frequency and window size combination for PSD estimation.
3.10 Monte Carlo with Counting Statistics and Reversible Processes

In order to account for both experimental counting statistics (shot noise) and the likely existence of reversible reactions, we consider the impact of introducing Poisson noise to the Monte Carlo results. In the former case, Poisson noise just models experimental shot noise. In the latter case, Poisson noise can be used to model the effects of chemical reversibility in the equations of section 3.6. Specifically, when reverse reaction timescales are comparable to the experimental integration time, variations in the number of active (emissive) domains will cause fluctuations to the overall integrated emission intensity. This will then manifest itself as apparent noise in the data. Hence, the inclusion of additional stochastic noise intensity variations to the Monte Carlo simulation approximates the tangible effects of chemical reversibility.

The following are implicit assumptions and limitations of the approximation that should be noted: (a) First, if reversible reaction rates are significantly faster than the experimental binning time (second timescale), intensity fluctuations stemming from these reversible reactions will be averaged out. (b) The stochastic noise approximation is based on many emitters with equal photoluminescence intensity, and it assumes that each switching event is a single emitter event. Therefore, the intensity distribution can deviate from a Poisson distribution. (c) Next, if reversible reaction rates are significantly slower than the experimental binning time, intensity fluctuations will exhibit time-correlations, which are not captured by Poisson noise. (d) The use of Poisson noise to represent the tangible effects of reversible reactions therefore implicitly assumes that reverse reaction rates exhibit timescales comparable to the experimental binning time. In the absence of detailed activation energies and a full accounting of all possible reversible reactions, beyond those associated with the equations in section 3.6, an accurate estimation of relevant reverse reaction rates cannot be established. Thus, at present, a fully rigorous accounting of reversibility is beyond the scope of this study. In practice, to include counting statistics, for
each data point in the Monte Carlo trajectory, the number of photons that would have been counted in a detector is randomly generated by choosing a value from a Poisson distribution. The mean of the Poisson distribution is set to the number of counts (max $\sim 3000$) seen in the original MC trajectory. To include stochastic noise, associated with reversible reactions, the same methodology is applied. The number of active clusters is generated randomly by choosing a value from a Poisson distribution. The mean of the Poisson distribution in this case is given by the number of Monte Carlo-estimated emissive clusters (max $\sim 300$). Then the number of clusters is multiplied by the average counts/cluster to obtain a new estimate for the total number of counts observed. Fluctuations in cluster number thus more significantly impacts the Monte Carlo trajectories than variations due to counting statistics.

3.11 Data Availability

The Monte Carlo simulation code is available at:

https://github.com/aruth2/GOMonteCarlo
4.1 Emission and Absorption Time Trajectories

Here we show that unexpected blinking during graphene oxide to reduced graphene oxide photoreduction is attributed, in large part, to the redistribution of carbon \( sp^2 \) domains. This reclustering generates fluctuations in the number/size of emissive graphenic nanoclusters wherein multiscale modeling captures essential experimental aspects of reduced graphene oxide’s absorption/emission trajectories while simultaneously connecting them to the underlying photochemistry responsible for graphene oxide’s reduction. These simulations thus establish causality between currently unexplained, long timescale emission intermittency in a quantum mechanical fluorophore and identifiable chemical reactions that ultimately lead to switching between on and off states.

Fig. 4.1a shows emission/absorption trajectories resulting from using equations (1-3)\((k_{OH} > k_O > k_C)\) in the MC simulation. The percentage of epoxide:carbon (COC:C) has been varied from 0-25% to find the trajectory in best agreement with experiment. This yields an optimal 20%, consistent with previous studies showing C:O ratios between 4:1 and 2:1 if one assumes that half of the oxygen is in epoxide form.\(^{[17]}\) In all cases, remaining \( sp^2 \) sites have been OH decorated. Fig. 4.1b compares an experimental emission/absorption trajectory to the best match from 4.1a (20% epoxide). This value was chosen by comparing absorption maximum and
valley-to-peak emission intensity ratio. Evident in either case is that the emission exhibits an initial decay, followed by a low plateau. Meanwhile the absorption exhibits an initial rise followed by a high plateau. The emission then exhibits a second photobrightening peak with blinking prior to apparent photobleaching and irreversible sample damage. While the emission is intermittent, the absorption follows a smooth decay. The calculated emission trajectory remarkably reproduces the two-peaked structure of the experiment. Additionally, the optimal epoxide percentage simultaneously reproduces the maximum absorption value as the experiment (1.2%) and the emission valley-to-peak ratio. The simulations indicate that the first peak in the emission trajectory arises from OH removal, equation (1). The plateau stems from COC removal, equation (2). The final photobrightening peak occurs due to the sublimation of carbon, equation (3) (cf. Fig. 4.2).

4.2 Local Structure Model of Carbon Sublimation

Given that blinking occurs during carbon sublimation, we focus on more realistically modeling this phenomenon by allowing carbon sublimation rate constants to differ. This accounts for the varied local structure found in GO/rGO [e.g. singly-coordinate sites versus armchair edges, zigzag edges, and triply-coordinated sites]. Specifically, we set $k_{C1} > k_{Carm} > k_{Czig} > k_{C3}$ in equation (3), and this parameterization is used in simulations yielding figures 4.1c, 4.1d, 4.3 and 4.5.

Fig. 4.1c shows the resulting superb agreement with experiment. Not only is clear intermittency evident in the calculated trajectories but the magnitude of intensity fluctuations is comparable to experiment.

Since emission and absorption are intimately tied to $sp^2$ domain structure, the improved emission vs. absorption correlation shown in Fig. 4.1d, reveals that the local structure model for carbon sublimation reproduces the number and size distribution of $sp^2$ domains that were created in the experiment both leading up to and
during blinking.

4.3 Blinking from Carbon Sublimation

In Figure 4.3, the frequency domain has been used to illicit features of fluorescence intermittency in the experimental and MC trajectories. Panels 4.3a and 4.3b show the trajectories after Fourier filtering. This process removes the long-term evolution of GO’s emission and more clearly reveals the fluorescence intermittency that is present. Blinking begins and ends at approximately the same time in the MC and the experiment. This leads us to conclude that the MC simulation captures the key difference between the stable emission and the fluorescence intermittency phase of the system. Subsequent analyses of their power spectral densities reveal that both simulated and experimental trajectories exhibit $1/f^\alpha$ power law behaviors (Fig. 4.3c). Experimental and theoretical power law exponents of $0.5 < \alpha < 0.9$ and $\alpha = 1.9$ are found, which fall within the range of exponents (i.e. 0.5 to 2.0) typically seen for other nanoscale emitters exhibiting fluorescence intermittency.

The quantitative discrepancy between experiment and theory is narrowed by including Poisson noise. In this regard, Poisson noise accounts for counting statistics and also provides a simple model for intensity fluctuations arising from reversible reactions. The latter, in particular, stems from dynamic changes to the number of emissive domains, which contribute to the overall observed emission intensity. Including counting statistics to the Monte Carlo simulation reduces its power law exponent to 0.7, which is closer to the range of exponents seen in the experiment. Furthermore, after including cluster fluctuations to model reversible processes, we recover substantial spectral weight at high frequencies. Additional details regarding the effect of Poisson noise on the Monte Carlo results and the methods used to calculate PSD can be found in Fig. 4.4 and 3.5.

Figure 4.4 shows the impact of adding Poisson noise to Monte Carlo trajecto-
Figure 4.1. Comparison of experimental and MC time trajectories.

(a) Theoretical emission/absorption trajectories for different epoxide concentrations determined by the ratio of epoxide to total carbon content (COC:C). (b) Typical experimental emission/absorption trajectory compared to the best theoretical trajectory from panel a. (c) Close-up of emission profile during the blinking phase. (d) Emission versus absorption correlation plots.
Figure 4.2. Emission and absorption trajectories versus remaining reactants.

The parameterization is the same as in figure 4.1a and 4.1b. The y axis of the second panel is a ratio between the number of that chemical species, and the initial number of carbon lattice sites.
ries. Namely, adding counting statistics to the Monte Carlo trajectory reduces its power law exponent to $\alpha = 0.7$. When only noise from reversible processes is considered, the power law exponent becomes even smaller $\alpha = 0.3$. It is therefore evident that improved modeling of reversible reactions will lead to better agreement between experiment and theory.

In whole, the model reproduces the two peaked absorption/emission trajectories in Fig. 4.1b. Subsequently accounting for local structure immediately reproduces the emission versus absorption correlation seen experimentally in Fig. 4.1d and the appearance of emission intermittency seen in Fig. 4.1f, 4.1h, and 4.3. This last success is especially important, because it points to a structural mechanism, which underlies blinking in graphene oxide.

4.4 Reclustering Mechanism of Blinking

To explore deeper mechanistic aspects of GO/rGO blinking, Fig. 4.5 highlights specific features of emission/absorption trajectories and associated structure in a 20 x 20 nm area. MC simulations illustrate that relatively few spectrally-relevant clusters exist per unit area in GO/rGO during the blinking segment of its trajectories. In fact, approximately one emissive cluster exists per 100 $nm^2$ at any given time. Reclustering of these graphenic domains is therefore responsible for corresponding fluctuations in the associated emission intensity (e.g. Fig. 4.5). The structure at subsequent time steps reveals how emissive domains separate from large networks and subsequently photobleach. This explains why blinking shows up in emission but not absorption. Blinking is thus a consequence of an evolving equilibrium between the photolytic separation and disintegration of graphenic clusters of the correct, spectrally-relevant size. Such light-induced structural changes are also the likely cause of blinking in other fluorophores[51] although there may not be a universal mechanism for blinking.
Figure 4.3. Frequency domain analysis of emission trajectories.

(a) Fourier filtered experimental trajectory. (b) Fourier Filtered MC trajectory. In both cases, frequencies below 0.01 Hz have been removed. The envelope of the experimental Fourier filtered trajectory grows around ca. 500 s and decays around ca. 3000 s. The magnitude of the Monte Carlo Fourier filtered trajectory grows and decays at nearly the same time as the experiment. (c) Power Spectral Density of Expt. and MC trajectories. Error bars are s.e.m. The error in the power-law exponent reflects the quality of the fit, and shows that both experimental and MC trajectories fit well to power-law distributions.
Figure 4.4. Monte Carlo power spectrum altered by introducing Poisson noise.

The parameterization of the MC matches figures 4.1, 4.1d, 4.3 and 4.5 (The local structure model). The figure compares power spectral densities of the experiment, the MC simulation, the MC with counting statistics, and the MC with stochastic noise using a 500 sec window of the trajectory when blinking was strongest. Error bars are s.e.m. In each case, power law exponents are indicated in the legend. For the raw MC PSD, a line has been included to indicate the existence of data points below the shown y axis limits.
Figure 4.5. Simulated emission, absorption and domain structure during rGO blinking.

Cluster color coding reflects the energy of light emitted by clusters. Black $sp^2$ domains do not emit although they do absorb light.
4.5 Discussion

A multiscale numerical simulation of GO-rGO photoreduction reproduces essential experimental features characterizing the evolution of GO’s optical properties. Specifically, the modeling successfully explains experimentally-observed emission/absorption trajectories with strong temporal fluctuations about a second photobrightening feature. Additionally, both experimental and simulated PSDs exhibit power-law behavior characteristic of universal emission intermittency seen other fluorophores. The explicit link established between emission/absorption trajectories and the structural/chemical transformation of GO/rGO strongly suggests that blinking in rGO originates from reclustering – $sp^2$ cluster creation and destruction processes as well as processes which distort $sp^2$ domains in a reversible manner. Reclustering alters the size, shape, and ultimately the quantum yield of underlying graphenic nanoclusters leading to emergent emission intermittency. This conclusion is especially important from a mechanistic standpoint since it has been a longstanding mystery\cite{75,24} as to how an inherently quantum mechanical system – such as a quantum dot, rod, wire, but also rGO – exhibits fluctuations over timescales much longer than those of fundamental electronic processes.
CHAPTER 5

MIXED-HALIDE PEROVSKITE SOLAR CELLS : AN INTRODUCTION AND BACKGROUND

5.1 A Tunable Platform for Solar Materials Development

Hybrid mixed halide perovskites [e.g. $MAPb(I_{1-x}Br_x)_{3}$, $MA = CH3NH3^+$] are near ideal materials for top cell light harvesting layers in multi-junction solar cells. Desirable properties include sharp absorption onsets, large absorption coefficients, sizable carrier diffusion lengths and long carrier lifetimes. Further complementing these photovoltaic properties are their tunable bandgaps ($E_g$) which can be modified by changing $Br^-$ to $I^-$ anion ratios. Figure 5.1 displays the bandgap tunability through optical absorption measurements.

5.2 Halide Phase Segregation Under Illumination in Mixed Halide Perovskites

Unfortunately, $MAPb(I_{1-x}Br_x)_{3}$ perovskites exhibit instabilities under continuous optical illumination. Prior photoluminescence (PL) studies have found that under visible light irradiation the overall PL from $MAPb(I_{1-x}Br_x)_{3}$ exhibits a dramatic time-dependent redshift. Under dark conditions, the redshifted emission slowly recovers. Figure 5.2 exhibits the photoluminescence observed following illumination. Through concerted optical and structural measurements, this phenomenon has since been attributed to light-induced halide phase segregation and stems from nucleation and growth of I-rich and Br-rich domains within the parent mixed halide...
Figure 5.1. Absorption spectra of $MA\text{Pb}(I_{1-x}Br_x)\text{3}$ for various compositions.

The band edge can be tuned from red to green by $I \rightarrow Br$ substitution. Throughout the tunable range, band edge absorption remains sharp indicating low electronic disorder.
perovskite.\textsuperscript{34, 64, 9, 84, 85, 8, 43, 13, 3, 35, 82, 10, 16, 6} A structural representation of halide phase segregation is shown in figure 5.3.

5.3 The Role of Halide Vacancies

At present, few models rationalize light-induced anion photosegregation in MAPb(I\textsubscript{1-x}Br\textsubscript{x})\textsubscript{3}.\textsuperscript{10, 16, 6} General consensus exists on several aspects of anion photosegregation, namely that: (a) entropic considerations stabilize mixed halide perovskites at room temperature\textsuperscript{10, 16}, (b) only partial phase segregation occurs under illumination\textsuperscript{34, 64, 9, 84, 16}, (c) nucleated iodide-rich domains act as carrier recombination centers so that phase-segregated perovskite emission is dominated by I-rich domain photoluminescence\textsuperscript{34, 64, 9, 16, 6}, and (d) recovery occurs in the dark albeit on significantly slower timescales.\textsuperscript{34, 64, 9} Despite this, a number of important open questions remain. Central among them is the identity of anion migration channels in hybrid perovskites and, by the same token, the role played by defects such as halide vacancies.\textsuperscript{9, 85, 3}
Figure 5.2. Post-Illumination photoluminescence spectra of MAPb(I_{1-x}Br_x)₃ for various compositions.

For compositions $x = [0.2, 0.9]$ the photoluminescent peak position converges on 1.7eV ($x \sim 0.2$).
In the dark, iodine, bromine, and vacancies are entropically mixed. Following illumination they segregate and an iodine-rich region is formed.

Figure 5.3. Depiction of the photosegregation phenomenon.
CHAPTER 6
BUILDING KINETIC MONTE CARLO SIMULATIONS OF PHOTOSEGREATION

Kinetic Monte Carlo simulations consider vacancy-mediated $I^-$ and $Br^-$ hopping under the influence of $n$ charge carriers with local composition-dependent bandgaps. $n$ is connected to an effective photoexcitation intensity, $I_{\text{exc,\text{effective}}}$, via photon energy, $h\nu$, absorption coefficient, $\alpha$, carrier lifetime, $\tau$, and carrier diffusion length, $l_{e/h}$.

In practice, relevant excitation densities must first be established to inform our kinetic Monte Carlo simulations. Our colleagues have previously suggested that band gap differences are responsible for inducing photosegregation. Implicit to the model is an excitation density of 1 excitation/formula unit where each excitation carries an excess energy equivalent to the perovskite bandgap. In practice, an approximate photoexcitation density is $10^{-4}$/formula unit where $n$ is the number of photoexcitations and $V$ is the corresponding excitation volume. The estimate assumes $h\nu = 3eV$, an excitation intensity of $I_{\text{exc}} = 100mW/cm^2$, a corresponding absorption coefficient of $\alpha = 10^5cm^{-1}$, and a carrier lifetime of $\tau = 100$ ns.

6.1 Estimate of Carrier Accumulation

At first glance, $n/V$ would seem to be too low to induce anion photosegregation given that the entropic contribution to the free energy is of comparable magnitude to thermal energy at room temperature (25 meV/atom). Long carrier diffusion lengths ($l_{e/h}$) and lifetimes, however, imply that photogenerated carriers can accumulate at local potential minima within hybrid perovskite films. These minima entail
either potential energy fluctuations due to electronic disorder or may arise from local bandgaps of stochastically-generated iodide-rich regions. I-rich domains are known to possess favorable energies for both electron and hole localization and explain why dominant I-rich domain emission is seen in mixed halide perovskites during illumination despite only partial phase segregation.\cite{16, 34} Consequently, a relationship between the excitation intensity and $n$ that explicitly accounts for carrier diffusion and which leads to conditions amenable to nucleating at least one I-rich domain can be given as follows: $I_{\text{exc, effective}} = n \left( \frac{h \nu}{\tau a V_D} \right)$ where $V_D = \frac{4}{3} \pi r^3 \epsilon / \hbar$ is a geometric volume linked to carrier diffusion length. In subsequent kinetic Monte Carlo simulations, $n$ is set, and $I_{\text{exc, effective}}$ is reported.

6.2 Defect Physics

Next, for the majority of its composition range (i.e., $x = 0.2-1.0$) MAP$_{1-x}$Br$_x$$_3$ exhibits a cubic perovskite structure with corner sharing halide octahedra surrounding MA cations. In this structure, halide anions primarily migrate by hopping from occupied sites to adjacent halide vacancies as opposed to interstitial hopping.\cite{86, 18, 80, 48} This is supported by measured/calculated vacancy-mediated hopping barriers ($V_I = 0.17-0.25$ eV; $V_{Br} = 0.23-0.43$ eV) which support vacancy hopping ionic conductivity in hybrid perovskites.\cite{77} By contrast, anti-site hopping processes possess much larger barriers\cite{11}, making them less likely to be relevant anion migration channels in these materials. Furthermore, although interstitial hopping barriers have been suggested to take similar magnitudes as vacancy-hopping barriers\cite{86, 18, 78, 48}, their abundance under halide deficient conditions is significantly smaller than that for vacancies. Low (high) interstitial (vacancy) densities are additionally corroborated by high (low) Frenkel (Schottky) defect formation enthalpies [2.1 eV] (0.14 eV).\cite{77}
6.3 Construction of Simulation Cell

To simulate light-induced halide phase segregation, we construct supercells with sizes ranging from 4x4x4 (64 formula units) to 12x12x12 (1728 formula units), assuming periodic boundary conditions and x=0.5. The x=0.5 stoichiometry is a representative value for consistency with prior measurements. Following construction of the lattice, the system is mixed via unbiased hopping. Additionally, a variable fraction of halide sites is made vacant. Corresponding y-values range from y=0.01-0.2.

Although MAPb(I_{1-x}Br_x)_3(1-y) supports large halide vacancy concentrations, these defects do not introduce electronic disorder in the material. Indeed, theoretically calculated energy levels of halide vacancy-related trap states lie above the conduction band edge. Halide vacancies also do not affect either the bandgap or mixing enthalpy of MAPb(I_{1-x}Br_x)_3(1-y).

6.4 Calculation of Photocarrier Energy

Light-induced anion migration is subsequently modeled as follows. We first establish a grid of local bandgaps (E_{g,i}) based on the number of bromine and iodine atoms surrounding each Pb atom in the supercell. Local gap energies are established using a geometrical bandgap volume (V_{gap}). V_{gap} represents a physical volume in space that defines local bandgap energies due to local anion stoichiometry. As such, it represents the smallest volume of space within the supercell from where photosegregation can commence. V_{gap} scales with supercell size. In all cases though, whether 4x4x4, 8x8x8 or 12x12x12, V_{gap} encompasses less than 1/10th the total supercell volume. This volumetric ratio is found to be sufficiently small so as not to unduly influence the outcomes of Monte Carlo simulations between supercell sizes. Consequently, theoretical photosegregation rate constants are evaluated using 4x4x4 supercells so that multiple Monte Carlo runs can be averaged (32 runs for each y value) to achieve
a sufficient confidence level in extracted $k_{MC}^{\text{forward}}$ values. For simulations where the chemical structure of the phase segregated domain is of primary interest, larger supercell sizes (i.e. 8x8x8 and 12x12x12) are used. This is because the smallest system to show evidence of trapped $Br^-$ is the 8x8x8 supercell.

Local bandgaps are evaluated using the halide composition-dependent expression derived from fits to experimentally-obtained $MAPb(I_{1-x}Br_x)_3$ bandgaps by Noh[50], $E_{g,i} = 1.57 + 0.39x_i + 0.33x_i^2$. A weight ($w_i = e^{-\frac{E_{g,i}}{kT}}$) is assigned to each local bandgap based on the Boltzman distribution. This assumes the rapid thermalization of photoexcitions.[16] The total energy associated with an existing anion configuration in the lattice, $E_{\text{tot}} = n \sum_i w_i E_{g,i}$, is then evaluated where $n$ is the number of excitations contained in the simulation volume.

6.5 Enumeration and Selection of Moves

For every vacancy within the simulation volume, adjacent anions are identified. Assuming a possible hop is found, the change in total energy resulting from the hop ($\Delta E_{\text{tot}}$) is calculated. The associated probability of a hop is estimated using an Arrhenius expression of the form $p = e^{-\frac{\Delta E_{\text{tot}} + E_{b,l}}{kT}}$ where $E_{b,l}$ is a local hopping barrier associated with halide migration from an occupied to vacant site and the index $l$ denotes a particular hop. $E_{b,l}$ is nominally set to 250 meV for both $I^-$ and $Br^-$. Under these conditions, $p$ simplifies to $p = e^{-\frac{\Delta E_{\text{tot}}}{kT}}$. Here, little consensus exists as to exact barrier energies for each species; the literature [86] is replete with vacancy activation energies for $I^-$ and $Br^-$. Control simulations, which consider the case of asymmetric barriers, however, reveal that both $Br^-$ and $I^-$ barriers are equally important to establishing photosegregation rates, justifying the use of symmetric $E_{b,l}$ values in what follows. Finally, the corresponding rate constant for a given hop is $k_l = e^{-\frac{\Delta E_{\text{tot}} + E_{b,l}}{kT}}$. Since the rate constant prefactor is difficult to evaluate from first principles, we use an arbitrary time unit (t. u.) and
scaling factor in order to compare Monte Carlo rate constants to experiment. During
the simulation, $E_{tot}$ is recorded for each step where the effective time, $\Delta t$ for a given
step is given by $\Delta t \propto \frac{1}{\sum k}$.

By fitting $E_{tot}$ as a function of $t$ (averaged over 32 4x4x4 Monte Carlo simulations for each $y$ value), an overall photosegregation rate constant
$(k_{MC}^{forward})$ is obtained. A reverse recovery rate constant $(k_{MC}^{reverse})$ can be calculated
the same way except that $\Delta E_{tot} = 0$ since no photoexcitation exists. This leads to
an intrinsic asymmetry between $k_{MC}^{forward}$ and $k_{MC}^{reverse}$.

6.6 Calculation of Optical Properties from Photocarrier Local Bandgap Spectrum

To simulate linear absorption and emission spectra, the above photoexcitation
weighting scheme is used. Each timestep in the Monte Carlo simulation yields
an emission spectrum for the current anion configuration expressed as $I_{em}(E_g) = \sum_i w_i(E_{g,i})$. A line broadening factor proportional to $kT$ is applied to thermally
broaden the theoretical emission spectrum. For the linear absorption, the lineshape
derived by Saba et al.\cite{57} is employed with thermal broadening included.

6.7 Calculation of Radial Distribution Functions

Radial distribution functions, $g(r)$, were calculated from structures that emerged
during 12x12x12 kinetic Monte Carlo simulations. To calculate $g(r)$, the center Pb
atom of I-rich, photosegregated domains was first identified in the atomic configu-
racion, following the simulation. Next, halide sites at fixed distances, $r$, from the
center were grouped, with the number of $I^-$, $Br^-$, and vacancies counted for each
group. The vacancy fraction, $y$, is defined as the number of vacancies present divided
by the total number of sites in the group. The corresponding $Br^-$ fraction, $x$, is
likewise determined by the total number of $Br^-$ present divided by the total number
of bromine and iodine atoms in the group. What results is a list of x- and y-values
versus r. This process is repeated for atomic configurations at different steps during
Monte Carlo simulations, using the same center Pb atom. To retain the utility of reported r-values, they are given relative to the domain/surrounding film interface by subtracting the resulting I-rich domain radius. The location of the interface is established from the final atomic configuration, resulting from the simulation.
CHAPTER 7

MONTE CARLO SIMULATION OF PHOTOSEGREGATION VS. EXPERIMENT

It has been established\cite{64, 9} that spectral changes, as well as growth of I-rich domain PL, provide a means of accessing the underlying kinetics and ultimately the mechanism behind light-induced halide phase segregation. In this study, we couple kinetic Monte Carlo simulations with absorption- and emission-based measurements of light-induced anion segregation in MAPb(I$_{1-x}$Br$_x$)$_3$ to directly connect the migration of individual anions to the evolution of MAPb(I$_{0.6}$Br$_{0.4}$)$_3$ emission/absorption spectra. A critical question we seek to resolve is the role played by halide vacancies by measuring/simulating segregation kinetics of MAPb(I$_{1-x}$Br$_x$)$_3$(1-y) systems with different halide vacancy concentrations (y). In this way, we establish detailed mechanistic insight into relevant anion migration pathways responsible for the phenomenon and establish useful insights necessary to develop new strategies for controlling anion photosegregation. The simulations further suggest that near ubiquitous emission energies, which converge on that for MAPb(I$_{0.8}$Br$_{0.2}$)$_3$ (i.e. x\~{}0.2) following photosegregation, arise from the existence of kinetically trapped Br- within nucleated I-rich domains. An established photosegregation excitation intensity threshold is independent of the number of vacancies and instead depends critically on parameters such as carrier diffusion length, lifetime and bandgap tunability. The study thus sheds new light on important parameters that define halide photosegregation and presents opportunities for controlling the phenomenon.
Figure 7.1. Evolution of optical spectra under illumination.

8\times8\times8 MAPb(I_{0.5}Br_{0.5})_3(1-y) (a) PL and (b) absorption spectra for y = 0.01 under $I_{\text{exc, effective}} = 10\, \text{mW/cm}^2$ illumination. Selected times for simulated PL spectra are 0 (blue), 1 (orange), 9 (green), and 42 (red) time units (t. u.). Corresponding experimental (c) PL and (d) absorption spectra for y = 0.014. Selected times for PL spectra are 0 (blue), 13 (orange), 48 (green), and 120 (red) seconds. Analogous experimental (e) PL and (f) absorption spectra for y=0.111. Both experimental PL and absorption spectra have been acquired using illumination from a 405 nm CW laser ($I_{\text{exc}} = 40\, \text{mW/cm}^2$).
7.1 Vacancy-Mediated Anion Photosegregation Kinetics.

Seven different y-value MAPb(\(I_{0.6}Br_{0.4})_{3(1-y)}\) (\(0.014\leq y\leq0.111\)) films were synthesized using modified literature procedures.\([85, 11]\) Figures 7.1 a,b show simulated emission and absorption changes that arise due to light-induced anion segregation in a (\(y=0.01\)) MAPb(\(I_{0.5}Br_{0.5})_{3(1-y)}\) film. Comparison of corresponding experimental results for a nominally stoichiometric film (\(y=0.014\); Figures 7.1 c,d) and a halide deficient film (\(y=0.111\), Figures 7.1 e,f) reveal that the kinetic Monte Carlo simulations capture qualitative trends in the experimental results. This correlation between Monte Carlo simulations and experiment is especially apparent in computed emission spectra (Figure 7.1a) which redshift from 1.83 eV to 1.60 eV. By comparison, the corresponding experimental PL shifts from 1.82 eV to 1.71 eV (\(y=0.014\), Figure 7.1c) while that from a halide deficient film (\(y=0.111\), Figure 7.1e) shifts from 1.92 eV to 1.70 eV, both over the course of 120 seconds of \(\lambda_{exc}=405\) nm CW illumination (\(I_{exc} = 40mW/cm^2\)). In all cases, resulting emission spectra after prolonged illumination converge on 720-730 nm (1.70-1.72 eV). This has been near-universally reported in the literature and has been suggested to be linked with an observed cubic-to-tetragonal crystallographic phase transition when \(x\leq0.2\).\([50, 34, 9]\) For corresponding Monte Carlo simulations, the emission energy converges to a value consistent with \(x\sim0.1\). This limiting \(x\) increases with increasing simulation system size and possibly grows to \(x\sim0.2\). Of note is that the Monte Carlo simulations do not consider a crystallographic phase transition. This will be discussed in greater detail below. Associated absorption changes under comparable CW illumination conditions (\(\lambda_{exc} = 405nm; I_{exc} = 40mW/cm^2\)) are subtler. The most notable difference to emerge in either calculated (Figure 7.1b) or experimental (Figures 7.1d,f) absorption spectra are overall decreases of their band edge absorbance.

Figure 7.2 shows associated photosegregation kinetics of MAPb(\(I_{0.5}Br_{0.5})_{3(1-y)}\), acquired by monitoring the integrated I-rich PL as well as changes to the band edge
Figure 7.2. Photosegregation Kinetics

4x4x4 $MAPb(I_{0.5}Br_{0.5})_{3(1−y)}$ kinetic Monte Carlo (a) PL- and (b) absorption-based forward phase segregation kinetics for $y=0.01-0.100$ and $I_{\text{exc, effective}} = 2mW/cm^2$. Corresponding experimental (c) PL- and (d) absorption-based phase segregation kinetics under CW illumination ($\lambda_{\text{exc}} = 405nm; I_{\text{exc}} = 40mW/cm^2$) for $y=0.014-0.111$. 

51
absorbance during illumination. The data clearly show that with increasing $y$, photosegregation rates increase. By fitting these time-dependent kinetic traces using monoexponential or biexponential functions, forward phase segregation rate constants have been estimated. The obtained rate constants are $k_{forward,em}^{MC}$, $k_{forward,abs}^{MC}$, $k_{forward,em}$, and $k_{forward,abs}$ for the Monte Carlo and experimental emission/absorption results respectively.

Figure 7.3 now plots $k_{forward,abs}$ and $k_{forward,em}$ versus vacancy fraction. In either case, forward emission- [Monte Carlo: Figure 7.3a; experiment: Figure 7.3c]
and absorption-based [Monte Carlo: Figure 7.3b; experiment: Figure 7.3d] photosegregation rate constants increase with increasing halide deficiency. This agrees with prior results;[85, 3] however, the current study is the first to experimentally quantify vacancy concentrations and to directly link them to $k_{\text{forward}}$. The most striking result in Figure 7.3 is that both Monte Carlo and experimental rate constants depend linearly with $y$. For $k_{\text{MC,em}}^{\text{MC}}$, the observed linear dependency can readily be rationalized since bandgaps, formation energies and thus activation energies are not altered by vacancy concentration.[11] As a result, the one factor directly responsible for the $y$-dependency of $k_{\text{MC,em}}^{\text{MC}}$ is the number of available pathways for anion hopping. Here, we note that several reports suggest possible interstitial-mediated transport due to similar interstitial and vacancy hopping barriers.[78, 48] However, interstitial densities only become significant in excess halide conditions.[11, 78, 48, 83] Together, the data and especially the observed linear $y$-dependency of $k_{\text{forward,em}}$ strongly point to vacancy-mediated anion kinetics as responsible for anion segregation in $MAPb(I_{1-x}Br_x)_{3(1-y)}$. This corroborates prior measurements of ionic conductivity in perovskites.[80, 18, 1, 31, 49, 80, 40, 12] The Monte Carlo results additionally rationalize prior empirical observations which report phase segregation sensitivities to halide deficiency[85, 3] and establish that relevant photosegregation anion migration channels are linked to the existence of vacancies, whether intrinsic[77] or deliberately[85, 3] introduced.

7.2 Structure of Photosegregated Domain

The Monte Carlo simulations simultaneously yield other significant insights into $MAPb(I_{1-x}Br_x)_{3(1-y)}$ photosegregation. To illustrate, Figures 7.4 a-c show snapshots of the $MAPb(I_{0.5}Br_{0.5})_{3(1-y)}$ ($y=0.01$) lattice during illumination (12x12x12 supercell). Three snapshots are shown, the first at the outset, prior to illumination (Figure 7.4a), the second at 1000 Monte Carlo steps (Figure 7.4b) and the third at
Figure 7.4. Evolution of a 12x12x12 $MAPb(I_{0.5}Br_{0.5})_3(1-y)$ ($y=0.01$) model during illumination.

Snapshots (a) at the outset, (b) after 1000 Monte Carlo steps, and (c) after 9,400 steps. Red, green and white spheres represent iodine, bromine and vacancies respectively. Corresponding iodine, bromine and vacancy distribution functions (d) at the outset, (e) after 1000 Monte Carlo steps, and (f) after 9,400 steps. The interface is established by examining the final atomic configuration, following the simulation. In (a-c) highlighted (dark) atoms are inside (outside) the domain.

9400 steps (Figure 7.4c). Beneath Figures 7.4 a-c are corresponding radial distribution functions [$g(r)$] that illustrate the distribution of iodine (red) and bromine (green) anions as well as vacancies (white). At the outset of photosegregation, Figures 7.4 a,d illustrate a stochastically-generated I-rich (Br-poor) region. Vacancy distributions are generally radially homogeneous across models. During illumination, vacancies facilitate the exchange of Br- and I- anions. This leads to increasing I- and simultaneously decreasing Br-/vacancy concentrations as the latter are pushed outwards towards domain edges. Figures 7.4 b,e illustrate the enrichment of the I-
rich domain. In Figure 7.4e, plotted radial distribution functions clearly reveal I-enrichment (Br-depletion). In tandem, Br- and vacancy concentrations increase towards the edges of the I-rich core. This is evident through g(r) functions that peak further away from the core center. The emergence of both Br- and vacancy “shells”, which surround the core, is evident. Upon prolonged illumination, Figures 7.4 c,f reveal continued I-enrichment. This is especially clear in Figure 7.4f, which shows a strongly peaked I\(^-\) g(r) function. At the same time, both Br- and vacancy g(r) functions are now unambiguously peaked outside the I-rich domain. The simulations thus reveal the formation of apparent core/shell structures in MAPb(I\(_{1-x}\)Br\(_x\))\(_3(1-y)\) films during photosegregation. The predicted core/shell structure may be detected using techniques sensitive to the local halide ion environment such as X-ray absorption near edge spectroscopy.\[53\] Perhaps one of the more intriguing results of these Monte Carlo simulations is evidence of trapped Br\(^-\) within the I-rich core. Since most vacancies have been expelled from the I-rich core, Br\(^-\) still within the I-rich domain have difficulty escaping. What results, as demonstrated by Figure 7.4f, is a sizable trapped Br\(^-\) fraction within the core. Interestingly, the resulting core composition, which includes the trapped Br\(^-\) fraction, is x~0.1. This is very similar to empirical literature observations which near-universally report that prolonged photosegregation of MAPb(I\(_{1-x}\)Br\(_x\))\(_3\) leads to I-rich domains having stoichiometries consistent with x~0.2.\[50, 34\] We expect the fraction of trapped Br\(^-\) to increase with simulation size and in this way, the Monte Carlo results rationalize the stabilization of MAPb(I\(_{0.8}\)Br\(_{0.2}\))\(_3\) domains upon photosegregation without invoking a cubic-to-tetragonal crystallographic phase transition. For reference, a theoretical percolation threshold is x=0.27.\[73\] Of note is that control simulations, show that a tetragonal distortion to the MAPb(I\(_{1-x}\)Br\(_x\))\(_3\) lattice does not suppress anion photosegregation.
7.3 Photosegregation Rate Constant vs. Br Hopping Barrier

Throughout the previous studies, we employed the same hopping barrier for $Br^-$ and $I^-$ ($E_b=250$ meV). Here we test the effects of reducing the $Br^-$ barrier relative to that for $I^-$. This is done by systematically reducing $Br^-$ hopping barriers from 250 meV to 150 meV in control Monte Carlo simulations. Resulting values are then compared with predictions from two scenarios: A) that $I^-$ hopping is the rate limiting step for anion photosegregation (i.e. the overall rate constant is independent of $Br^-$ barrier) and B) that $Br^-$ hopping is the rate limiting step for anion photosegregation, irrespective of the actual $Br^-$ barrier used (i.e. the overall rate constant is independent of $I^-$ barrier). Note that all Monte Carlo rate constants contain a $\Delta E_{\text{tot}}$ term. Consequently, the effects of varying barrier heights are not immediately obvious and require full simulations to see the impact these changes have on observed rates and rate constants.

7.3.1 Predicted Behavior of the Two Limiting Scenarios

Scenario A: Scenario A implies that there will be no change to observed Monte Carlo values since no dependence with Br- barrier exists (Figure 7.5, dashed green line). Scenario B: The predicted behavior of this scenario is found by reducing both $Br^-$ and $I^-$ barriers symmetrically. This yields an overall rate change of $\exp(-\Delta E_b/kT)$ and represents the limiting (i.e. maximum) values that can be achieved (Figure 7.5, dashed blue line) when barrier heights are lowered.

Observed response from Monte Carlo simulations when the Br- barrier is reduced: Monte Carlo $k_{\text{MC}}^{\text{forward}}$ values have been obtained by systematically reducing the $Br^-$ barrier. Figure 7.5 shows that resulting $k_{\text{forward}}^{\text{MC}}$ values increase exponentially across the range of $Br^-$ barriers tested (Figure 7.5 open red circles). The exponential increase of (Figure 7.5 dashed red line) consequently argues against Scenario A as this case predicts no change in rate constant with decreasing $Br^-$ barrier. We
7.4 Phase Segregation in a Tetragonally-Distorted Crystal

Throughout the previous studies, a cubic crystal structure for $MAPb(I_{0.5}Br_{0.5})_3(1-y)$ has been assumed. Here we test the case where $MAPb(I_{0.5}Br_{0.5})_3(1-y)$ adopts a tetragonal structure to investigate whether phase segregation can be suppressed...
through a crystallographic phase transition. This directly addresses a hypothesis posited in the literature, which suggests that a cubic-to-tetragonal phase transition at $x \sim 0.2$ stabilizes I-rich domains and prevents further photosegregation. First, Figure 7.6 shows an idealized, tetragonally-distorted $MAPb(I_{0.5}Br_{0.5})_{3(1-y)}$ lattice, stretched along the z direction. Blue and green atoms denote halide anions on the equatorial ($PbX_2$) and axial (MAX) planes respectively. Lead atoms are depicted in brown while vacancies are in pink. MA cations are shown using faded black, white, and orange atom clusters. Next, three hopping pathways, depicted by the arrows in Figure 7.6 are considered. These vacancy hopping pathways include: equatorial-to-equatorial ($e \to e$), equatorial-to-axial ($e \to a$) and axial-to-equatorial ($a \to e$) hops along with associated hopping barriers of $E_{e\to e}$, $E_{e\to a}$, and $E_{a\to e}$. At this point, two scenarios are considered to model the effects of a tetragonal lattice distortion on anion photosegregation:

Scenario 1: $E_{e\to a} = E_{a\to e} > E_{e\to e}$=250 meV. In this model, equatorial-to-equatorial ($e \to e$) vacancy hops are common. Rare equatorial-to-axial ($e \to a$) jumps also occur. However, once in an axial position, vacancies spend a significant amount of time in this position (about the same amount of time spent within the equatorial plane) before returning to an equatorial plane, whether the original plane or a new plane. Scenario 2: $E_{a\to e} < E_{e\to e} = 280 meV < E_{e\to a}$. Asymmetric axial-to-equatorial and equatorial-to-axial barriers are considered. This model originates from Meloni et al. [48] who have shown through experiment and molecular dynamics simulations that anion migration barrier asymmetries in exist in $MAPb(I_{1-x}Br_x)_3$. In this scenario, when a rare $e \to a$ hop occurs, the vacancy quickly moves back to an equatorial plane, whether the original plane or a new plane.

Figure 7.7 shows results of the tetragonal simulation assuming Scenario 1. Plotted is the change in $k_{f,em}^{MC}$ versus extent of tetragonal distortion, as defined by $\Delta E_{tetragonal} = E_{e\to a} - E_{e\to e}$. In the plot, values are normalized to the value observed at
Figure 7.6. Idealized representation of a $MAPb(I_{0.5}Br_{0.5})_3$ tetragonal distortion, resulting in anisotropic hopping barriers.

Green halides on the axial position and blue halides on the equatorial position are considered different in this representation. Vacancies indicated using pink. One axial vacancy and one equatorial vacancy are shown.
\( \Delta E_{tetragonal} = 0 \) (the cubic case). The simulations show that as \( \Delta E_{tetragonal} \) increases, \( k_{MC}^{forward, em} \) decreases, eventually converging to a value approximately an order of magnitude smaller than the cubic rate. The plateauing of \( k_{MC}^{forward, em} \) in Figure 7.7 indicates that at large tetragonal distortion, \( a \rightarrow e \) and \( e \rightarrow a \) hops are suppressed. Anion movement therefore occurs near-exclusively within the equatorial plane. However, photosegregation still occurs due to \( e \rightarrow e \) hops and consequently these kinetic Monte Carlo simulations reveal that a tetragonal distortion of the lattice would not stop photosegregation. Next, Figure 7.8 shows results of the tetragonal simulation assuming Scenario 2. Here \( k_{MC}^{forward, em} \) increases with increasing \( \Delta E_{tetragonal} \). Although the \( e \rightarrow a \) barrier increases, the \( a \rightarrow e \) barrier simultaneously decreases. Though difficult to predict a priori, what results is a net increase in \( k_{MC}^{forward, em} \). The Monte Carlo simulations thus again indicate that a tetragonal distortion would not suppress anion photosegregation.
7.5 $I_{\text{exc}}$ Dependence of Halide Photosegregation.

We now address two remaining aspects of MAPb$(I_{1-x}Br_x)_3$ photosegregation observed in the literature: (a) nonlinear $I_{\text{exc}}$-dependencies of photosegregation rates\cite{16}, including saturation of forward rate constants at large $I_{\text{exc}}$, and (b) a threshold intensity, $I_{\text{exc},\text{threshold}}$, below which photosegregation is suppressed.\cite{16}

Figure 7.9a first plots $k_{\text{forward,em}}$, acquired for two MAPb$(I_{0.6}Br_{0.4})_3(1-y)$ thin films ($y=0.014$ and $y=0.111$), both as functions of $I_{\text{exc}}$. Figure 7.9b likewise plots corresponding Monte Carlo values for two vacancy fractions ($y=0.005$ and $y=0.01$), against $I_{\text{exc,\text{effective}}}$. $I_{\text{exc,\text{effective}}}$ implicitly incorporates a carrier diffusion length with $l_{e/h}=1 \mu\text{m}$ assumed here (see SI). In either experiment or simulation, forward rate constants saturate, the former at $I_{\text{exc}} \sim 10 - 40 \text{mW/cm}^2$ and the latter at $I_{\text{exc,\text{effective}}} \sim 0.4 \text{mW/cm}^2$.

Figures 7.9a,b likewise reveal the existence of a photosegregation intensity thresh-
Figure 7.9. Intensity dependence on photosegregation kinetics

(a) Experimental [$y=0.014$ (solid red circles) and $y=0.111$ (solid blue triangles)] and (b) 8x8x8 Monte Carlo [$y=0.005$ (open red circles) and $y=0.01$ (open blue triangles)] photosegregation rate constants as functions of $I_{\text{exc}}$ and $I_{\text{exc, effective}}$. Dashed lines are rising exponential fits to the data. In (b) $I_{\text{exc, effective, threshold}}$ is denoted using a vertical dashed line.
old below which photosegregation is suppressed. Table 1 lists experimental $I_{\text{exc,threshold}}$ values obtained for different vacancy fractions. These values agree with prior photosegregation thresholds reported in the literature (i.e. $I_{\text{exc,threshold}} \sim 40 \mu W/cm^2$). They also agree with the Monte Carlo derived thresholds observed in Figure (7.9) ($I_{\text{exc,effective,threshold}} \sim 200 \mu W/cm^2$). In what follows, we rationalize the saturation of $k_{\text{forward,em}}$ and $k^M_{\text{forward,em}} C$ and explain the existence of a photosegregation intensity threshold.

### Table 7.1

$I_{\text{exc,threshold}}$ FOR $MAPb(I_{0.6}Br_{0.4})_3(1-y)$ FILMS WITH VARIABLE VACANCY CONCENTRATION.

<table>
<thead>
<tr>
<th>$y$</th>
<th>$I_{\text{exc,threshold}}(\mu W/cm^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014</td>
<td>92.9</td>
</tr>
<tr>
<td>0.029</td>
<td>219.8</td>
</tr>
<tr>
<td>0.043</td>
<td>146.2</td>
</tr>
<tr>
<td>0.049</td>
<td>146.9</td>
</tr>
<tr>
<td>0.058</td>
<td>350.4</td>
</tr>
<tr>
<td>0.074</td>
<td>207.2</td>
</tr>
<tr>
<td>0.111</td>
<td>229.9</td>
</tr>
</tbody>
</table>

#### 7.5.1 Saturation

To address the first observation, our colleagues have previously suggested that $k_{\text{forward,em}}$ saturates with $I_{\text{exc}}$ due to an exponentially converging probabil-
ity of a mobile carrier finding an I-rich domain. The Monte Carlo simulations similarly predict $k_{\text{forward}}$ to exponentially converge when carrier densities are sufficiently large (i.e. $n \sim 40$) to maximize photosegregation kinetics. Differences in required saturation intensity (Reference [16]: $I_{\text{exc, effective}} \sim 10mW/cm^2$; Monte Carlo: $I_{\text{exc, effective}} \sim 0.4mW/cm^2$) primarily stem from the parameters assumed in each model (Ref [16]: $l_e/h = 337nm, \tau 10ns$; Monte Carlo: $l_e/h = 1\mu m$ and $\tau \sim 100ns$).

7.5.2 Threshold

Next, the kinetic Monte Carlo photosegregation intensity threshold of $I_{\text{exc, effective, threshold}} \sim 200\mu W/cm^2$ ($n \sim 20$) is similar to that found experimentally (Table 1). The number of excitations $n$ is an order of magnitude larger than that implied by Bischak et al. ($n \sim 1$). This primarily stems from different estimates of the minimum photocarrier energy required to achieve photosegregation.

Given that the Monte Carlo simulations do not provide physical insight into $I_{\text{exc, threshold}}$ or its numerical value, we develop an accompanying minimal probabilistic model that describes phase segregation. This allows us to better understand the origin of $I_{\text{exc, threshold}}$ and simultaneously enables us to link its existence to material parameters and experimental conditions. Although our colleagues have previously [16] established an analogous photosegregation suppression criterion, it was premised on linking theoretically-described forward rate constants to experimentally-observed (empirical) reverse recovery rate constants. Specifically, photosegregation was said to be suppressed when $k_{\text{forward}} \leq 1/10 k_{\text{reverse}}$.

7.6 Probabilistic Model for Photosegregation

Here we develop a general model to describe the photostability of a material in the presence of ion exchange processes that lower the energy of localized, photogenerated carriers. The model’s underlying premise is that the additional energy, due
to the presence of photogenerated carriers, influences ion dynamics. The following are assumptions of the model, which considers the fraction (x) of ion 1 ($Br^-$) and the fraction (1-x) of ion 2 ($I^-$) in two regions of a material, a photosegregated region and the rest of the film:

- First, $x_q$ refers to the fraction of ion 1 in the photosegregated region. Likewise, $x_f$ refers to the fraction of ion 1 elsewhere in the film.
- As a limit, a phase comprised of only ion 1 (i.e. $x=1$) possesses the largest carrier energy.
- As a second limit, a phase comprised of only ion 2 (i.e. $x=0$) possesses the smallest carrier energy.
- A phase possessing a mixture of ions 1 and 2 (i.e. $0 < x < 1$) possesses a carrier energy intermediate between the two limits.
- The mixed phase (i.e. $0 < x < 1$) is entropically favored.
- Under illumination, charge carriers form and influence ion dynamics.
- The energy of charge carriers can be lowered by forming an ion 2-rich phase.
- A parameter $\Delta E_{g,\text{domain}}$ accounts for electron and hole energies and includes their binding energy.
- A generic Arrhenius expression for rate constants is invoked such that corresponding (second order) rates for ion exchange at the interface between the photosegregated region and the rest of the film take the form
  \[
  R_{12} = A x_q (1 - x_f) e^{-\frac{-E_h + n \Delta E_{g,\text{domain}}}{kT}} \\
  R_{21} = A (1 - x_q) x_f e^{-\frac{-E_h - n \Delta E_{g,\text{domain}}}{kT}}
  \]
  \(R_{12}(R_{21})\) is the forward (reverse) rate for replacing ion 1 with ion 2 (ion 2 with ion 1) in the photosegregated region of the film. A is a prefactor, $E_h$ is a hopping energy barrier, kT is thermal energy, and $\Delta E_{g,\text{domain}}$ is the system’s bandgap change, which stems from replacing a single atom of ion 2 with ion 1. Based on the above assumption that carrier energies are higher in a region dominated by ion 1, $\Delta E_{g,\text{domain}}$ is positive.
- $\Delta E_{g,\text{domain}}$ is estimated for $MAPb(I_{0.5}Br_{0.5})_3$ using the empirical expression developed by Noh et al. $E_g(x) = 1.57 + 0.39x + 0.33x^2$. In particular, $\Delta E_{g,\text{domain}}$ is found by dividing the linear coefficient of the Noh expression, 0.39 eV, by the number of halide atoms used in the local composition-dependent bandgap: $3 \times \frac{V_{gap}}{V_c}$ where $V_{gap}$ and $V_c$ are the bandgap volume (discussed above) and unit
Figure 7.10. Energetic preference for phase segregation under charge accumulation

Plot of $x_q$ versus $\frac{n\Delta E_{g,\text{domain}}}{kT}$ with $x_f = 0.5$.

cell volume respectively. Consequently, assuming a 3.6 nm $V_{gap}$ of similar order to that reported in Reference [61] ($V_{gap} = 8.2 nm^3$) and a lattice constant of 6.107 Å [50] ($V_c = 0.23 nm^3$), we find $\Delta E_{g,\text{domain}} \sim 3.6 \text{ meV/atom}$.

Finally, at equilibrium (i.e. $R_{12} = R_{21}$) solving for $x_q$ gives the desired fraction of ion 1 ($Br^-$) in the photosegregated region.

$$x_q = \frac{x_f}{x_f + (1 - x_f)e^{\frac{2n\Delta E_{g,\text{domain}}}{kT}}}$$

Equation 7.6 thus reveals that photoinduced phase instability depends upon $\frac{n\Delta E_{g,\text{domain}}}{kT}$, which is the ratio of the change in carrier energy per ion, $n\Delta E_{g,\text{domain}}$, and the thermal energy per ion, kT. Figure 7.10 provides a plot of $x_q$ versus $\frac{n\Delta E_{g,\text{domain}}}{kT}$ for $x_f = 0.5$.

The following criterion therefore dictates phase stability: $\frac{n\Delta E_{g,\text{domain}}}{kT} < 1$. Above 1, the energetic term in Equation 7.6 dominates entropic contributions such that the
system becomes unstable with ion 1 leaving the photosegregated region and being replaced with ion 2. An alternative stability criterion, expressed as an excitation intensity threshold, is

\[ I_{\text{exc,threshold}} \geq \left( \frac{kT}{\Delta E_{g,\text{domain}}} \right) \left( \frac{h\nu}{\alpha} \right) \left( \frac{1}{\tau V_D} \right) \]

where \( \Delta E_{g,\text{domain}} \) is the bandgap change associated with replacing a single anion (e.g. \( I^- \) replacing \( Br^- \) in the domain or vice versa). The threshold excitation intensity (n~20) corresponds to a carrier density in the photoquenching domain of 0.04/formula unit.

Equation 7.6 reveals that the very parameters which make MAPb\((I_{1-x}Br_x)_3\) such a good solar cell material (large \( E_g \) tunability\[50\], large \( \alpha \), large \( \tau \)[15], and large \( l_{e/h} \)) lead to its phase instability. Of these parameters, \( l_{e/h} \) is readily accessible and we have previously demonstrated[16] that reducing \( l_{e/h} \) suppresses halide photosegregation. At a more quantitative level, by using \ 3.6 \text{ meV/atom}[50] , \( h\nu = 3 \text{ eV} , kT = 25 \text{ meV} , \alpha = 10^5 \text{cm}^{-1} , \tau = 100 \text{ns}[16] , \) and \( l_{e/h} = 1 \mu m \) in Equation 7.6 we predict a photosegregation intensity threshold of \( I_{\text{exc,effective,threshold}} = 80 \mu W/cm^2 \) that is independent of vacancy fraction. This value is in general agreement with Monte Carlo derived thresholds as well as with the experimentally-observed intensity thresholds listed in Table 7.1. More relevantly, the absence of a \( y \)-dependency appears to be borne out by the experimental data.

Finally, Equation 7.6 shows that decreasing carrier diffusion lengths increases \( I_{\text{exc,threshold}} \) as \( I_{\text{exc,threshold}} \propto l_{e/h}^3 \). As an illustration, when \( l_{e/h} 100 \text{ nm} , I_{\text{exc,threshold}} = 80mW/cm^2 \). This illustrates the exquisite sensitivity of \( I_{\text{exc,threshold}} \) to \( l_{e/h} \) and highlights how \( l_{e/h} \) can be used to control photosegregation in mixed halide hybrid perovskites. The photostability of mixed halide nanomaterials[16], where \( l_{e/h} \) is controlled by crystallite sizes of 10 nm, is especially intriguing given recently reported 13% power conversion efficiencies of nanocrystalline CsPbI3 solar cell[70 59].
makes mixed halide nanocrystals of potential use in multi-junction photovoltaics. Along the same line of thought, it may be possible to engineer device geometries so as to accelerate carrier extraction (i.e. reduce $\tau$), in turn, preventing charge accumulation and photosegregation.

7.7 Discussion

Kinetic Monte Carlo simulations and complementary optical experiments, conducted on $MAPb(I_{0.6}Br_{0.4})_3(1-y)$ thin films, reveal that, (1) to a significant extent, halide vacancies enable and control the rate of anion photosegregation in these materials. (2) Simulations further rationalize linear growth of experimentally-observed forward rate constants with vacancy fraction. (3) The simulations additionally reveal the formation of core/shell structures following photosegregation. (4) Trapped $Br^-$ exists within central I-rich domains due to kinetic barriers which repel vacancies. This provides an alternate explanation for the observation of $x\sim0.2$ emission following photosegregation. (5) More importantly, the modeling reveals the existence of a critical excitation intensity threshold below which photosegregation is suppressed. This study thus sheds new light on defining features of photoinduced halide segregation and presents opportunities for ultimately controlling light-induced anion photosegregation in mixed anion hybrid perovskites.
CHAPTER 8

CONCLUSION AND FUTURE OUTLOOK

Multiscale simulations of optical phenomena revealed essential details of photochemical processes in graphene oxide and mixed-halide perovskites. Still, much there are many questions left unanswered, and some of these questions are tractable through extensions of the methodology shown herein. Notably the modeling of ion dynamics under illumination may have broad applicability for the study of photolysis.

The graphene oxide project came first in chronological order, and as such there were improvements made in the perovskite study. The most significant difference is that in the graphene-oxide simulations the chemical reactions proceed on their own following forward reaction kinetics. In contrast, for the perovskite Monte Carlo, the chemical reactions were coupled to optical excitations. Chemical reactions were preferred which reduced the energy of the excitations. The vacancy-mediated hopping employed in the perovskite case is reversible, and therefore different than the forward reactions employed in GO. Applying similar methodology back to graphene oxide would have substantial consequences for the structures that are formed. Chemical reactions may be applied to only those regions which are able to absorb light. Removal of oxygen-containing functional groups would proceed primarily around $sp^2$ regions. Later in the simulation, a rule could be imposed that only absorbing clusters undergo chemical reactions. This would apply a selection rule such that large bandgap clusters are stabilized. Invoking the carrier energy as a driving force for chemical reactions would favor expansion of $sp^2$ regions. Larger carbon structures would be preferred as would structures with lower bandgap. Charge carriers could even encourage carbon-
containing molecules to deposit on the graphene oxide. A dynamic treatment of the charge carriers themselves would result in different preferred structures when the cluster is excited than when it is not. This could provide a firm theoretical basis for the missing reversible reactions as part of fluorescence intermittency.

The primary problem preventing commercial deployment of perovskites solar cells at this point is stability. The solar cells are cheap and have an adequate power conversion efficiency, but their efficiency decreases over time. Ideally the cell should be stable for \( \sim 30 \) years. As the stability of the materials created increases, the speed of development is decreasing. While we had been studying methylammonium based perovskites, the scientific community has been considering formamidinium, methylammonium, and cesium alloys as an effective solar material. At present stability tests of \( \sim 10 \) days are being performed on mixed cation perovskites, but as we get closer to fully usable devices this testing length will continue to increase. Data from the Kuno group has shown an interesting trend in these stability tests. The photoluminescence is consistent for several days before suddenly starting to change. We believe this is hiding a gradual process of degradation which is actually occurring long before the PL changes. We believe a similar thermal distribution of charge carriers across heterogeneous structures applied in this case, however the we hypothesize that the structural changes responsible for eventual PL loss are nonquenching. In nanocrystals the same changes would result in a substantial shift in the PL much sooner. Therefore, by studying nanocrystals with similar composition to the materials desired for thin film solar cells, we would be able to more-rapidly detect long-term stability issues by leveraging the high-precision of photoluminescence. A first order test of this hypothesis would involve applying modified simulations to both bulk and nanocrystals to test the hypothesis that the same process results in PL blindness in bulk but PL sensitvity in nanocrystals.

What could be causing this PL blindness effect? Some clues are found in the lit-
erature. It has been reported that in $CsPb(I_{1-x}Br_x)_3$ thin films, under illumination the photoluminescent peak position blue-shifts and the photoluminscent quantum yield decreases - in sharp contrast to $MAPb(I_{1-x}Br_x)_3$ which shows a red-shifting of PL peak position and an increase in quantum yield. To date, several authors have proposed hypotheses for this observation. One hypothesis is that photosegregation couples to a phase instability so that $CsPbI_3$ transitions to an orthorhombic, optically-dark state following segregation. Another hypothesis is that segregation causes evaporation of iodine. The contrast between MA-based and Cs-based mixed-halide perovskites is further emphasized by differences in nanocrystal photosegregation. Our model clearly shows that $MAPb(I_{1-x}Br_x)_3$ nanocrystals do not segregate because there is insufficient light absorption for charge carrier buildup. This is also what has been observed experimentally. However, $CsPb(I_{1-x}Br_x)_3$ nanocrystals exhibit a photo-induced change in photoluminscence similar to that seen in bulk films. The photoluminscent peak position blue-shifts and the quantum yield decreases. However, in nanocrystals the change appears less-reversible. I believe that our model with slight extension could be made to work for $CsPb(I_{1-x}Br_x)_3$, and that doing so would tell us more about segregation, and more about these materials in general. Finally, I would like to point out that some amount of reversibility has been seen in the changes of optical properties. If a process that causes loss of PL quantum yield in $CsPb(I_{1-x}Br_x)_3$ thin films is reversible, then in a nanocrystal it could cause fluorescence intermittency.
APPENDIX A

EXCITON BINDING ENERGY FROM FIRST-ORDER PERTURBATION THEORY IN A SPHERICAL DIELECTRIC PARTICLE

Here, we will treat the problem of exciton binding energy versus nanoparticle size. We will assume that the wavefunction is determined by the exciton in the bulk and we will calculate the expected energy of that wavefunction due to the potential of a dielectric sphere with a charge at the center. The answer is analytic, and it illustrates well the interplay between dielectric screening and confinement. For an exciton in the bulk, we will use a hydrogen-like orbital which arises from an electron orbiting a positive charge. This assumption is central to the Elliot model\cite{22} of optical excitations where the squeezed $\frac{1}{n^2}$ spectrum of the hydrogen atom shows up in absorption transitions.

A.1 Exciton in Bulk Dielectric Medium

The dielectric screening has the effect of reducing the voltage in proportion the dielectric constant, and this in turn increases the size of the wavefunction and decreases its energy. $E_b = \frac{E_H}{\epsilon_r}$ where $E_b$ is the exciton binding energy in the bulk, $E_H = 13.6eV$ is the energy of the hydrogen atom, and $\epsilon_r$ is the relative dielectric constant. The correction to the size is $r'_B = \epsilon_r r_B$ where $r'_B$ is the effective Bohr radius, and $r_B = 0.529\text{Å}$ is the Bohr radius. We will use $\epsilon_r = 26$ for our comparison with hybrid perovskites which results in $r'_B = 1.375nm$ and $E_b = 25meV$.

To begin the calculation for confinement, we will start with the potential due to a dielectric sphere with a charge at the center:
\[
V = \begin{cases} 
  r > a & -\frac{e^2}{4\pi\varepsilon_0 r} \\
  r > a & -\frac{e^2}{4\pi\varepsilon_0} \left( \frac{\varepsilon_r - 1}{\varepsilon_r a} + \frac{1}{\varepsilon_r r} \right) 
\end{cases}
\]

Where \(a\) is the radius of the sphere. We will also use for the wavefunction:

\[
\psi = \frac{e^{-r \rho}}{\sqrt{\pi r \rho^3}}
\]

Along with the previous assertion \(r'_{\rho} = r_{\rho} \varepsilon_r\). Now we evaluate the expectation value of the potential energy.

\[
E_b = \langle V \rangle = \langle \psi | V | \psi \rangle = \int_0^\infty d^3 r \psi(r)^2 V(r)
\]

\[
= \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\pi r_{\rho}^3} \left[ \int_0^a d^3 r e^{-\frac{2r}{r_{\rho}}} \left( \frac{\varepsilon_r - 1}{\varepsilon_r a} + \frac{1}{\varepsilon_r r} \right) + \int_a^\infty d^3 r e^{-\frac{2r}{r_{\rho}}} \frac{1}{r} \right]
\]

Evaluating these integrals gives:

\[
E_b = \frac{1}{4\pi\varepsilon_0 \varepsilon_r b} \left[ (\varepsilon_r - 1)(-e^{-\frac{2a}{r_{\rho}}} (1 + \frac{r'_{\rho}}{a} + \frac{r'_{\rho}}{a}) + 1 \right]
\]

We will also use the assumption from the above discussion of the Elliot model that \(\frac{1}{4\pi\varepsilon_0 \varepsilon_r r_{\rho}^3} = \frac{E_H}{e^2} \).

Then:

\[
E_b = \frac{E_H}{e^2} \left[ (\varepsilon_r - 1)(-e^{-\frac{2a}{r_{\rho}}} (1 + \frac{r'_{\rho}}{a}) + \frac{r'_{\rho}}{a}) + 1 \right]
\]

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Figure A.1. Exciton binding energy in the soft-confinement regime

Left exciton binding energy versus nanoparticle size from theory. Right: Observed Stoke’s shift versus nanoparticle size. Data courtesy of Michael Brennan from the Kuno group. Because the nanocrystals were cubic a conversion $a = L/2$ was applied where L is the side length.

A.2 Discussion

This model gets quite a few things right: the binding energy converges to the right value for large particle size. The order of magnitude is correct (only off by a factor of 4). The curve is almost the right shape with the inflection point at almost the correct nanoparticle size. The only parameter in this plot is the dielectric constant, and this
in turn results in differences between the materials. Volumes have been written about the differences between this basic view and reality and some very sophisticated and very computationally costly theories have been developed to address this difference at a more fundamental level but still from first principles. For our own purposes in this story, the main importance is that at some point in the range of 5-20 nm, the behavior changes and the size of the container becomes important. Realize that the wavefunction here is assumed to be 1.375 nm, so the change occurs when the container itself is still larger than the wavefunction. This is typically referred to as the soft confinement regime.

When we look at the radial wave function density $\psi^2 r^2$, the integrand from the first-order perturbation theory, and the potential, it becomes apparent that the screening occurring far from the wavefunction itself is still especially important.
Figure A.2. Primary contributions to exciton binding energy calculation

Wave function density, integrand (energy density), and potential of a 10 nm sphere.

This example still has a few well known problems. The most glaring problems are treated by a better ab initio treatment - the Coulomb Hole Screened Exchange method [33]. The main problems are electron self-interaction, dynamic and frequency-dependent dielectric screening, and the exchange interaction. The difference between a dielectric cube and dielectric sphere also has some contribution.


