Liquid-Solid Duality in Semiconductor Perovskites
or Electron Solvation in Materials Science

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Out with The Old...

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In with The New!
Collaborators

• Oleg Prezhdo, USC, AIMD Theory

• Eran Rabani, UC Berkeley, EPM Theory

• Maksym Kovalenko, ETHZ, perovskite NC synthesis
Section 1:
Thinking about new opportunities based upon classical concepts
Random thoughts during my end of my PhD. 1998 graphics here!
The 1\textsuperscript{st} decision in Quantum Mechanics: The choice of representation

\[ \psi_i(x) = \langle x|i \rangle \]

\[ E_i(x) = ??? \]

\[ \psi_i(k) = \langle k|i \rangle \]

\[ E_i(k) = ??? \]
The 2\textsuperscript{nd} decision for QM and spectroscopy: frequency domain or time domain?

$I(\omega) \leftrightarrow C(t)$

$\text{FFT}$
A new decision for the nature of material used in electronics: covalent and ordered perfection vs ionic and glassy disorder

\[ \psi(k) \text{ vs } \psi(x)! \]

\[ \Im(\omega) \text{ vs } C(t)! \]

The problem at hand:
Resolving the excitonic structural dynamics of X & MX in electronic materials
A new problem arises in ionic, glassy, disordered materials: Fluctuations and Correlations in Liquids & Glasses.

Fluctuation-Dissipation and Onsager’s Regression Hypothesis!
Section 2: Building a Better Microscope, as it were

Don Eigler, IBM Almaden ~1994
Presently sailing a boat, it appears...
Approach 1: time-resolved photoluminescence (t-PL)
The solution: picosecond Streak Camera detectors

Simultaneous time and wavelength measurement

TCSPC + PL spectrum

Down to 3ps time resolution
Approach 2: State-Resolved Pump/Probe (SRPP) or Transient Absorption (TA) spectroscopy
Moving to the femtosecond domain requires some thought about shutters and timing

Laser beam width 5 mm
Laser pulse duration desired 100 fs
Shutter speed required 5 mm / 100 fs
= $5 \times 10^{10}$ m/s

Speed of light = $3 \times 10^8$ m/s
Speed of sound = $3.4 \times 10^2$ m/s
Thinking about moving to the femtosecond domain or how to make fs laser pulses by Fourier Transform principles aka Mode Locking

\[ \delta t \propto \frac{1}{\Delta \nu} \]

\[ \delta v = \frac{c}{2L} \]

\[ \lambda_m = \frac{2L}{m} \]
Generic pump/probe or Transient Absorption Spectroscopy
State-Resolved pump/probe spectroscopy

- EMA: State 1
- EPM: State 2
- S: Singlet
- P: Triplet

- 800 nm
- Pump 1
- Pump 2
- White Light Probe
Approach 3: Two-Dimensional Electronic (2DE) Spectroscopy
Why move from 1D to 2D spectroscopy?
The hows and whys of 2DE

\[ \chi_i^{(3)}(t_1, t_2, t_3) \rightarrow \chi_i^{(3)}(E_1, t_2, E_3) \]

- \( E_1 \): Excitation energy
- \( t_2 \): Population time
- \( E_3 \): Detection energy

R. M. Hochstrasser, *PNAS*, 104, 36, June 2007,
Thinking about the three types of signals in TA and 2DE spectroscopy.
A more serious look requires a change of mindset from photons to fields

\[ |G\rangle \langle X| \]
\[ P(t) = |\mu_{eg}|^2 \exp(-i\omega_{eg}t) \exp\left(-\frac{t}{T_2}\right) \]

- Charge reorganization \( \mu_{eg} = \langle e|\hat{\mu}|g\rangle \)
- Energy gaps \( \omega_{eg} = E_{eg}/\hbar \)
- Fluctuations \( \exp(-t/T_2) = \exp[-g(t)] \)

\[ g(t) = \int_0^t d\tau \int_0^\tau d\tau' \langle \delta \omega_{eg}(\tau') \delta \omega_{eg}(0) \rangle \]
Lineshapes in 2DE

Fast dephasing

\[ C(t) = \gamma \delta(t) \]

Static inhomogeneity

\[ C(t) = \sigma^2 \]

Exponential decorrelation (« Kubo »)

\[ C(t) = \sigma^2 \exp \left( -\frac{t}{\tau_c} \right) \]
Anatomy of our 2DE spectrometer implemented via non-classical optics

- Ti:Sapph CPA 800nm, 1kHz, 130 fs
- White light generation
  Hollow core fiber (2.5m)
- Dispersion management
  GRISMs
- Pulse generator
  Dual AOPDF
- Spectrometer
- Sample
An overview of 2DE data as movies
Section 3:
New materials that interpolate between limits as a long-standing theme of investigation... From CdSe Quantum Dots to Metal Halide Perovskites
Introduction to semiconductor metal halide perovskites

• Perovskite: Material with $A^{1+}B^{2+}X^{1-}$
• Remarkable Solar PV efficiency
  - 25% vs. 26% in Si, 28% in GaAs
• Tunable chemistry at all three sites
Why study perovskites? Liquid / Solid duality. Phonon glass / electron crystal. Structural dynamics

Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation
Kiyoshi Miyata, Timothy L. Atallah, X.-Y. Zhu*

Lead halide perovskites have been demonstrated as high performance materials in solar cells and light-emitting devices. These materials are characterized by coherent band transport expected from crystalline semiconductors, but dielectric response and phonon dynamics similar to liquids. This liquid-like/dual behavior is what led to this study.

Screening in crystalline liquids protects energetic carriers in hybrid perovskites
Haiming Zhu,† Kiyoshi Miyata,† Yongping Fu,‡ Jue Wang,‡ Prakriti P. Joshi,§
Daniel Nieszner,§ Kristopher W. Williams,§ Song Jin,‡ X.-Y. Zhu†

Hybrid lead halide perovskites exhibit carrier properties that resemble those of pristine.

Large polarons in lead halide perovskites
Kiyoshi Miyata,1 Daniele Meggiolaro,2,3 M. Tuan Trinh,1 Prakriti P. Joshi,1 Edoardo Mosconi,2,3 Skylar C. Jones,1 Filippo De Angelis,2,3 X.-Y. Zhu1,†

Lead halide perovskites show marked defect tolerance responsible for their excellent optoelectronic properties. These properties might be explained by the formation of large polarons, but how they are formed and whether organic cations are essential remain open questions. We provide a direct time domain view of large polaron formation in single-crystal lead bromide perovskites CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$. We found that large polaron...
Why study perovskites? Liquid / Solid duality. Phonon glass / electron crystal. Structural dynamics
Section 4:
Applying SRPP, 2DE, and t-PL spectroscopy to unravel exciton-lattice interactions in metal halide perovskite nanocrystals... Towards a Quantum Drop?
State-Resolved Pump/Probe (SRPP) spectroscopy of CsPbBr3 P NC and CdSe QD NC

Breaking Phonon Bottlenecks through Efficient Auger Processes in Perovskite Nanocrystals
ACS nano 17 (4), 3913-3920

Polaronic quantum confinement in bulk perovskite crystals revealed by state-resolved pump/probe spectroscopy
Physical Review Research 3 (2), 023147
Optical bleach dynamics reveals remarkable behavior in P NC

- Cold exciton lineshape dynamics reveal linewidth and peak energy trajectories
- Early time (fs) blueshifting and broadening.
- Late time (ps) redshifting and narrowing
- CdSe is solid as a rock!

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**Polaronic quantum confinement in bulk perovskite crystals revealed by state-resolved pump/probe spectroscopy**
Physical Review Research 3 (2), 023147
Dynamical confinement via polarons rationalizes the dynamics

Exciton-polaron coupling?

or

Exciton solvation dynamics
With complex electronic structural dynamics... why not move from 1D to 2D spectroscopy?

Exciton–polaron interactions in metal halide perovskite nanocrystals revealed via two-dimensional electronic spectroscopy
The Journal of Chemical Physics 159 (18), 2023
Thinking about 2DE signals in the case of spectral diffusion and cooling

Spectral diffusion

Exciton relaxation / cooling

Diffusion and relaxation
2DE spectra of MHP NC reveals a previously unobserved doublet / splitting in 15 nm diameter CsPbI$_3$ and CsPbBr$_3$
2DE enables observation of hot exciton cooling
2DE enables energy resolved analysis to reveal cooling and exciton-polaron coupling.
Anti-diagonal linewidth trajectories reveal liquid-like Brownian dynamics

<table>
<thead>
<tr>
<th></th>
<th>CsPbI$_3$</th>
<th>CsPbBr$_3$</th>
<th>Ratio I/Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass (amu)</td>
<td>126.9</td>
<td>79.9</td>
<td>1.26</td>
</tr>
<tr>
<td>Spectral diffusion timescale (fs)</td>
<td>375</td>
<td>300</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Exciton–polaron interactions in metal halide perovskite nanocrystals revealed via two-dimensional electronic spectroscopy

The Journal of Chemical Physics 159 (18), 2023
Deeper investigations into coherence and motivations for Coherence Mapping

1. The system is excitonic with no coherent phonons but strong coupling to incoherent polarons

2. The polaronic motion like solvation results in fluctuations which dissipate energy and result from strong coupling between electrons and the ionic glassy lattice

3. But if there are excitons and they are fluctuating, is there coherence in their fluctuations?
Motivations for Coherence Mapping

Using coherence to enhance function in chemical and biophysical systems

Coherence phenomena arise from interference, or the addition, of wave-like states. Although coherence has been shown to yield transformative ways for improving pristine matter and coherence was considered fragile. However, recent evidence suggests that the phenomena are robust and can survive in the face of state of recent discoveries, present viewpoints that suggest that coherence can and discuss the role of coherence as a design element in realizing function.

Photovoltaic concepts inspired by coherence effects in photosynthetic systems

The past decade has seen rapid advances in our understanding of how coherent and vibronic phenomena in biological photosynthetic systems aid in the efficient transport of energy from light-harvesting antennas to photosynthetic reaction centres. Such coherence effects suggest strategies to increase transport lengths even in the presence of structural disorder. Here we explore how these principles could be exploited in making improved solar cells. We investigate in depth the case of organic materials, systems in which energy and charge transport stand to be improved by overcoming challenges that arise from the effects of static and dynamic disorder — structural and energetic — and from inherently strong electron-vibration couplings. We discuss how solar-cell device architectures can evolve to use coherence-exploiting materials, and we speculate as to the prospects for a coherent energy conversion system. We conclude with a survey of the impacts of coherence and bioinspiration on diverse solar-energy harvesting solutions, including artificial photosynthetic systems.
Evaluating coherence is not so simple
Quantum beats: electronic or vibronic?
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[Graph showing energy vs. diameter for absorption energy and PL energy.]

[Graph showing splitting energy vs. diameter for 2DE splitting energy and absorption splitting energy.]
Quantum beats: electronic or vibronic?
Quantum beats: electronic or vibronic?
Ultrafast Photoluminescence Spectroscopy Reveals the Excitonics of Light Emission from Metal Halide Perovskite Nanocrystals
Steady-state spectroscopic characterization of light emission in metal-halide perovskite nanocrystals.
Improving from 100 ps to 3 ps time resolution enables observation of spectral dynamics and moving from kinetics to dynamics.
Kinetics vs Dynamics? Words matter!

Chemical kinetics and dynamics have long been a central area of research in physical chemistry. In undergraduate courses, students are taught basic concepts in kinetics, and advanced students have studied dynamics. However, physical chemistry is always in flux, pun intended. Hence, we must be aware of the changes in the content students learn as well as the changes in the science that is done by researchers as contemporary problems evolve. We will find that, as the problems of the day evolve, the driving concepts remain the same.

Historically, physical chemists transitioned (pun intended again) from studies of chemical kinetics to chemical dynamics with the advent of molecular beams in gas phase physical...
Nanocrystals and quantum dots have electronic structure due to excitons (X) and multiexcitons (MX), of which the biexciton (XX) is the simplest.

Observing strongly confined multiexcitons in bulk-like CsPbBr3 nanocrystals
The Journal of Chemical Physics 158 (15)
The pump fluence dependence reveals the kinetics of MX populations.

Observing strongly confined multiexcitons in bulk-like CsPbBr3 nanocrystals
The Journal of Chemical Physics 158 (15)
Spectrally and temporally resolving MX from X.

Enhancing Multiexcitonic Emission in Metal-Halide Perovskites by Quantum Confinement
ACS nano 17 (24), 24910-24918
Observing hot exciton thermalization through ultrafast t-PL measurements.

Hot Excitons Cool in Metal Halide Perovskite Nanocrystals as Fast as CdSe Nanocrystals
ACS nano 18 (1), 1054-1062
Spectral dynamics of PL linewidth and their temperature dependence reveals rich spectroscopy due to a complex cascade of processes.

Light Emission from CsPbBr$_3$ Metal Halide Perovskite Nanocrystals Arises from Dual Emitting States with Distinct Lattice Couplings

Nano Letters 23 (23), 11330-11336
The spectral dynamics of the linewidth trajectories arises from a delicate interplay of kinetics and thermodynamics.

Light Emission from CsPbBr$_2$ Metal Halide Perovskite Nanocrystals Arises from Dual Emitting States with Distinct Lattice Couplings
Nano Letters 23 (23), 11330-11336
Deconstructing PL into radiative and non-radiative recombination paths and the implications upon spatial delocalization.

Excitonic Quantum Coherence in Light Emission from CsPbBr$_3$ Metal-Halide Perovskite Nanocrystals
Nano Letters 24 (1), 61-66
The radiative and non-radiative rate constants for X and XX have temperature dependences that reveals insight into mechanisms.

Excitonic Quantum Coherence in Light Emission from CsPbBr$_3$ Metal-Halide Perovskite Nanocrystals
Nano Letters 24 (1), 61-66
AIMD theory (O Prezhdo, USC) reproduces experiment quantitatively

Excitonic Quantum Coherence in Light Emission from CsPbBr$_3$ Metal-Halide Perovskite Nanocrystals
Nano Letters 24 (1), 61-66
Ultrafast measurements enable moving from measurements of kinetics to dynamics.

Breaking the Condon Approximation for Light Emission from Metal Halide Perovskite Nanocrystals
The Journal of Physical Chemistry Letters 14 (50), 11281-11285
Experimental observation of t-PL dynamics.

**Breaking the Condon Approximation for Light Emission from Metal Halide Perovskite Nanocrystals**
The Journal of Physical Chemistry Letters 14 (50), 11281-11285
AIMD (O Prezhdo, USC) reproduces experiment quantitatively by excitation induced structural dynamics

Breaking the Condon Approximation for Light Emission from Metal Halide Perovskite Nanocrystals
The Journal of Physical Chemistry Letters 14 (50), 11281-11285
Summary

1. MHP NC are interesting and important materials with remarkable properties
2. 1D TA spectroscopy provides an initial glimpse into exciton-polaron coupling or solvation dynamics in glassy solids
3. 2DE spectroscopy directly reveals glassy lattice structural dynamics
4. 2DE spectroscopy reveals exciton-polaron coupling – the possibility of a new quasiparticle or a new state of matter a quantum drop?
5. 2DE spectroscopy on different sizes of NC reveals unexpected splittings. These splittings produce an excitonic coherence that is long lived
6. t-PL spectroscopy reveals excitonic spatial coherence at low temperature
7. t-PL spectroscopy reveals a breakdown of the Condon approximation due to strong structural dynamics in these glassy solids