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

Australia, February 2024

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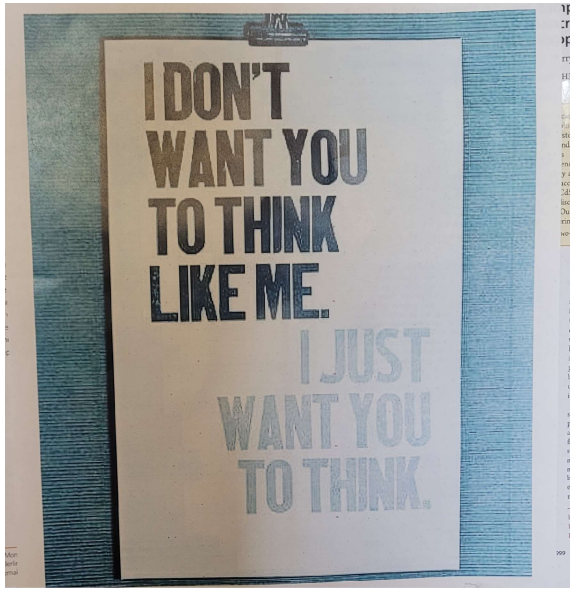
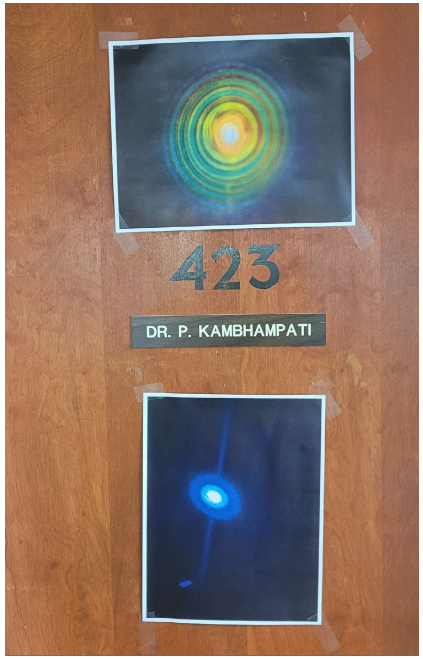
Out with The Old…



In with The New!



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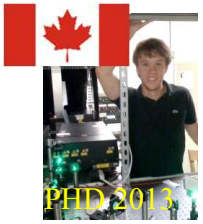

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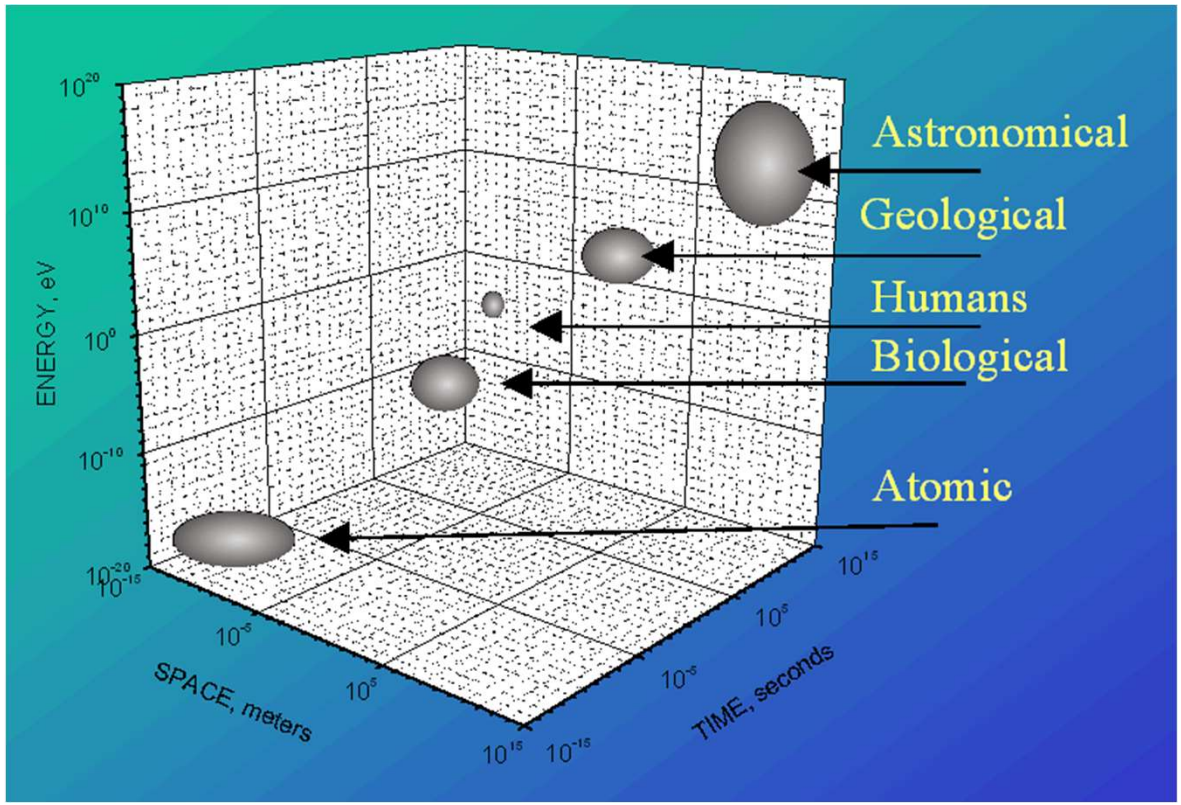
- Eran Rabani, UC Berkeley, EPM Theory
- Maksym Kovalenko, ETHZ, perovskite NC synthesis

Section 1:
Thinking about new opportunities based upon classical concepts

Random thoughts during my end of my PhD. 1998 graphics here!

Complexity

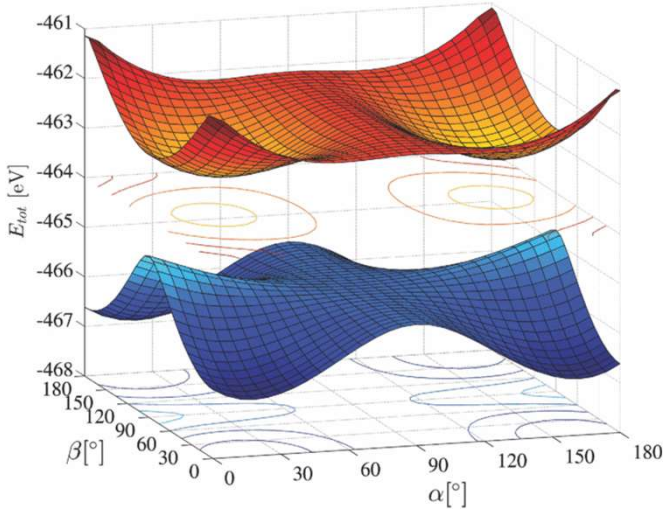
universe
galaxy
solar system
planet
ecosystem
population
human
chimpanzee
mammal
reptiles
insect
plant
bacteria
cell
virus
DNA
protein
molecule
atom
nucleon
quark

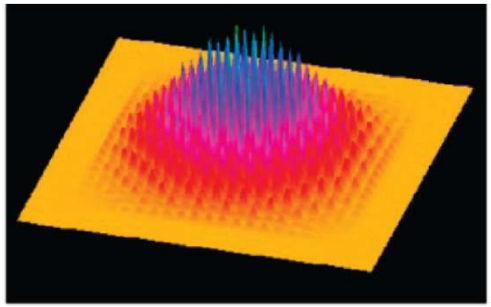


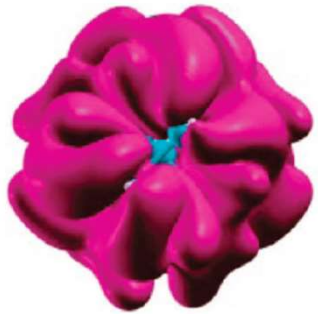
The 1st decision in Quantum Mechanics: The choice of representation

$\psi_i(\mathrm{x}) = \langle \mathrm{x}|i\rangle$

$E_i(\mathrm{x}) = ???$

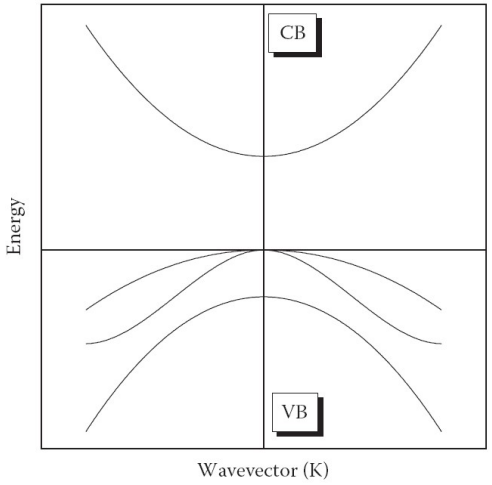






$\psi_i(\mathrm{k}) = \langle \mathrm{k}|i\rangle$

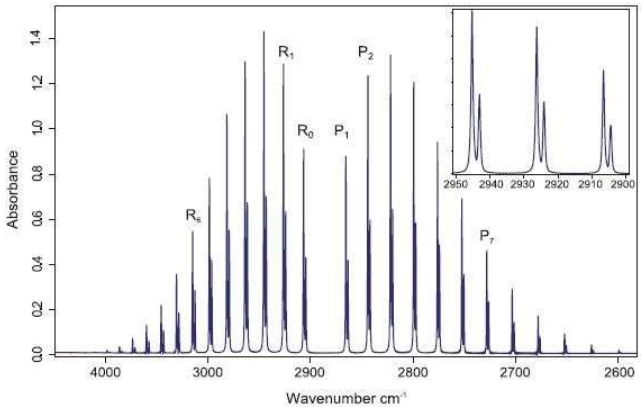
$E_i(\mathrm{k}) = ???$

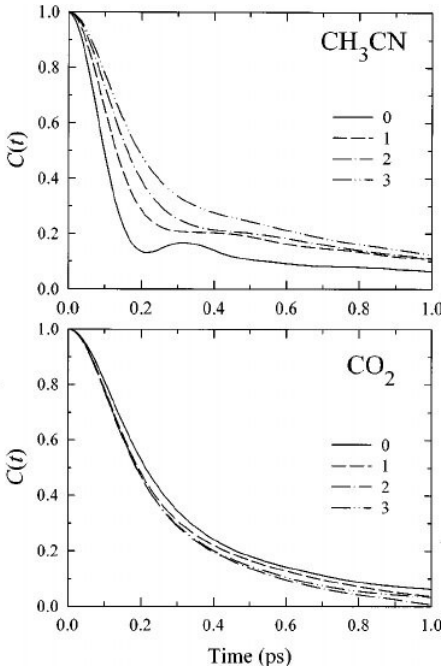


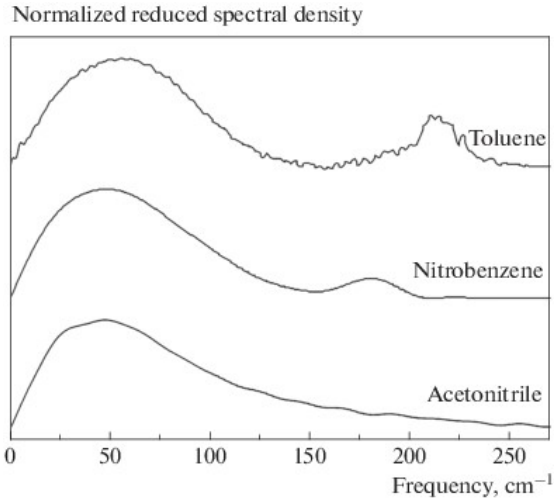
The 2nd decision for QM and spectroscopy: frequency domain or time domain?

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

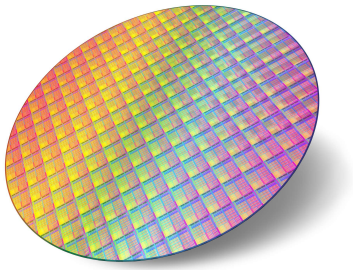
FFT



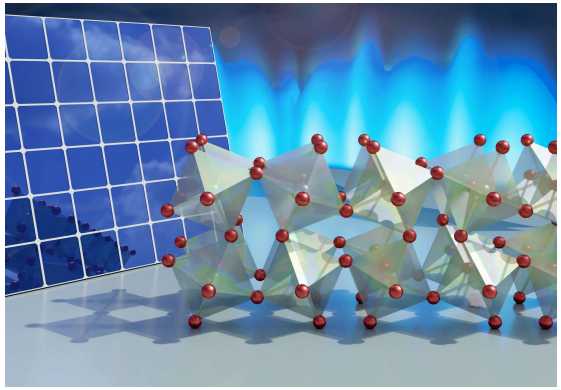


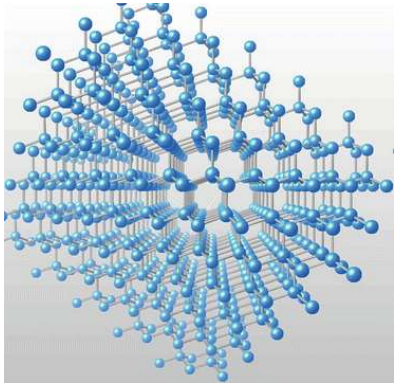


A new decision for the nature of material used in electronics: covalent and ordered perfection vs ionic and glassy disorder

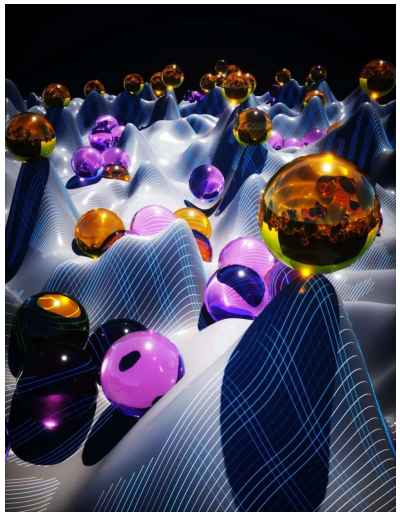


$\psi(k)$ vs $\psi(x)$!





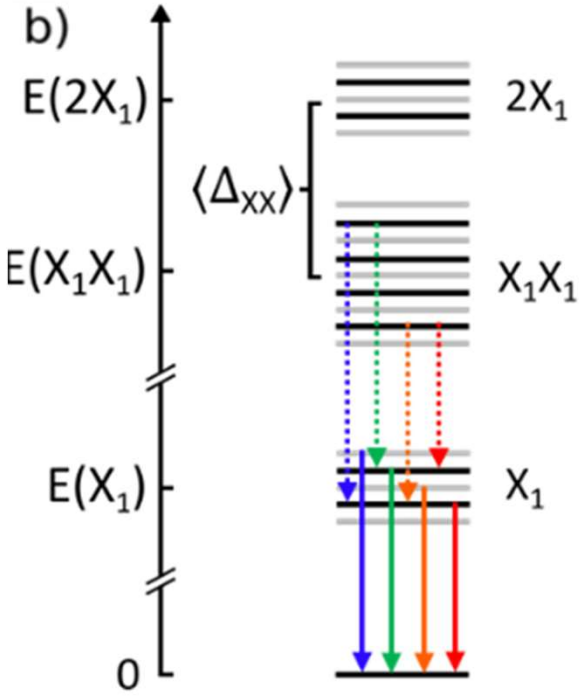
$I(\omega)$ vs $C(t)$!

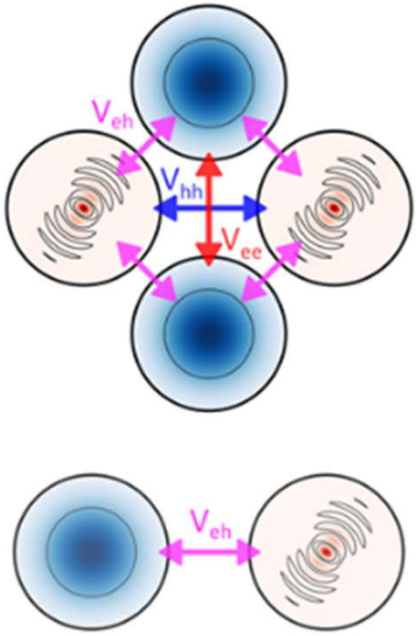


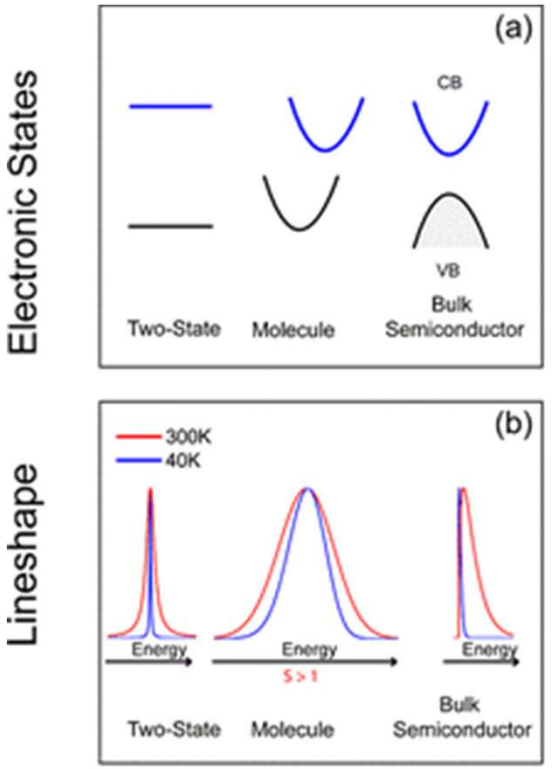
https://www.pv-magazine.com/2019/11/12/orderly-disorder-cambridge-scientists-make-surprising-perovskite-discovery/

The problem at hand:

Resolving the excitonic structural dynamics of X & MX in electronic materials

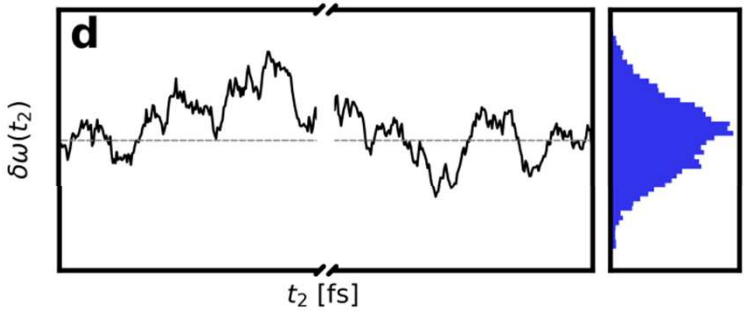


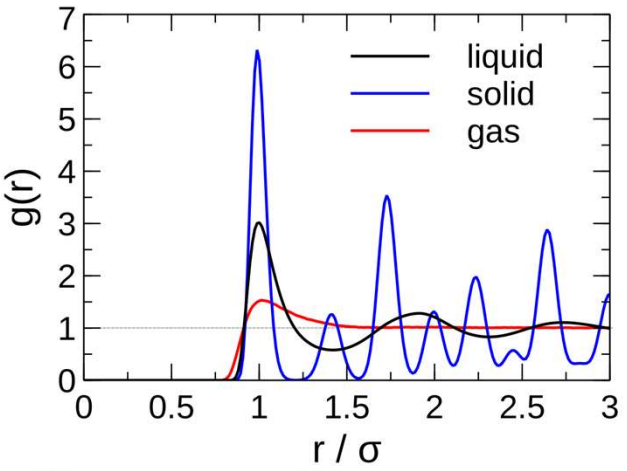


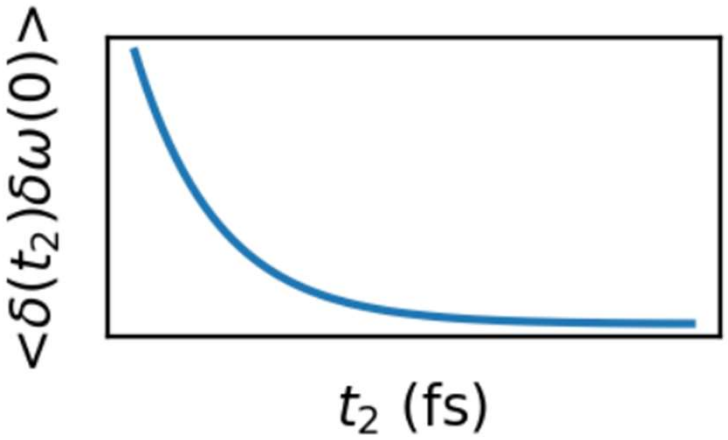


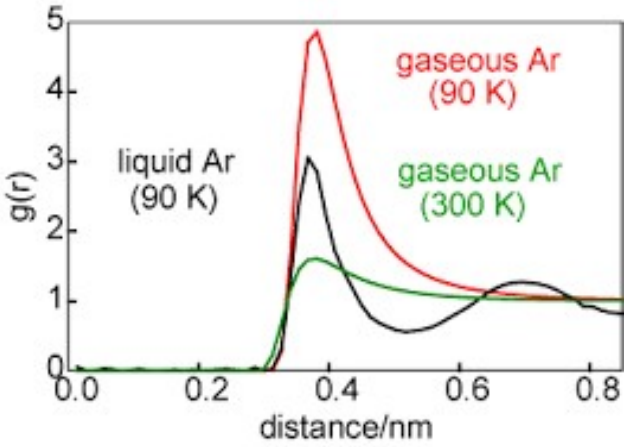
A new problem arises in Ionic, glassy, disordered materials: Fluctuations and Correlations in Liquids & Glasses

Fluctuation-Dissipation and Onsager's Regression Hypothesis!

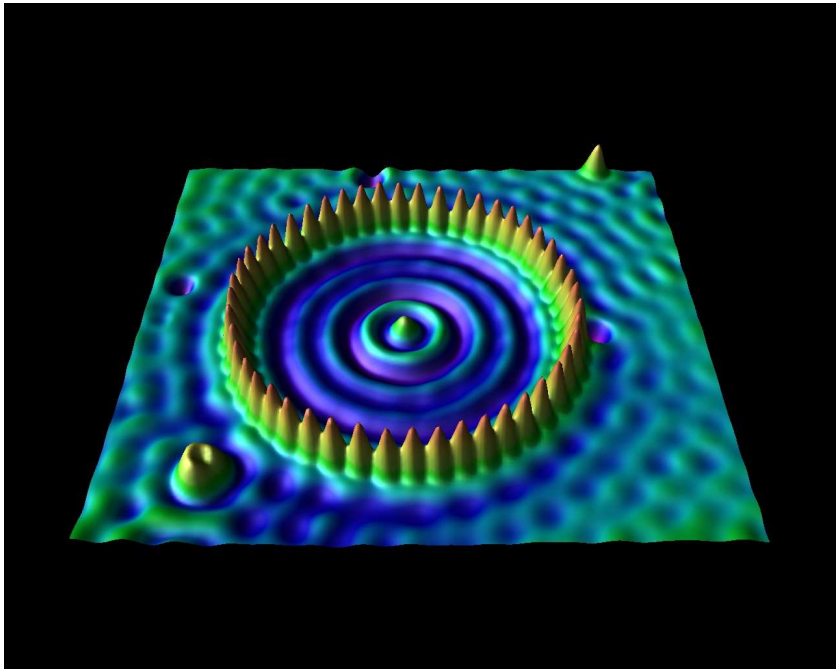


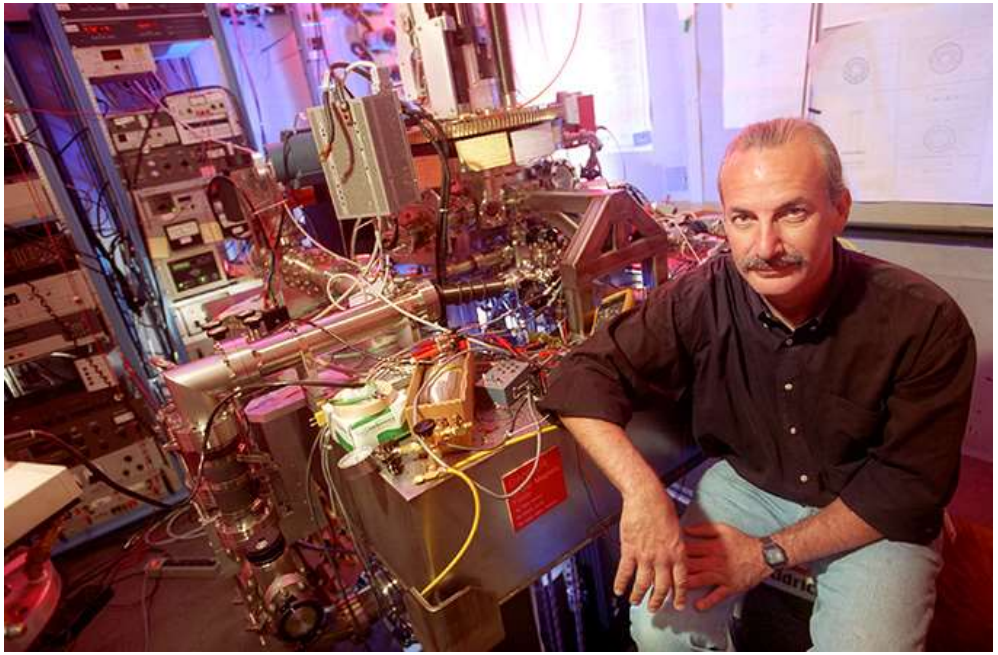






Section 2:
Building a Better Microscope, as it were

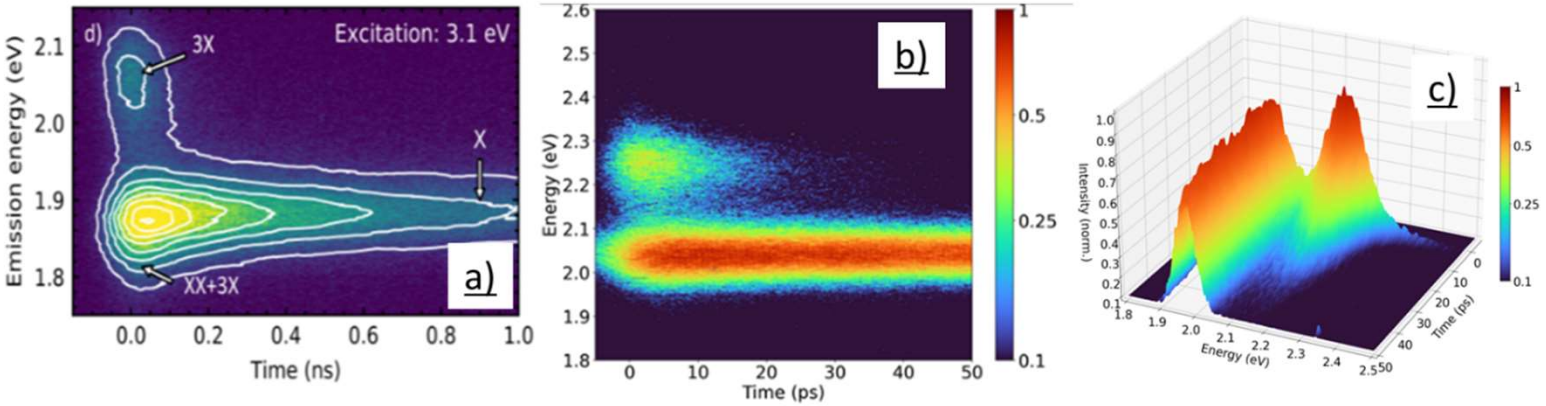




Don Eigler, IBM Almaden ~1994
Presently sailing a boat, it appears…

Approach 1:
time-resolved photoluminescence (t-PL)

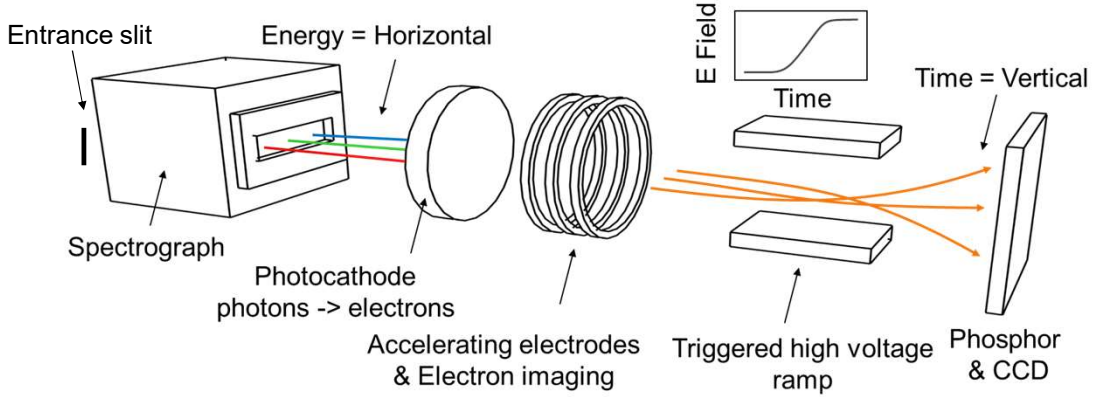
The solution: picosecond Streak Camera detectors



Simultaneous time and wavelength measurement

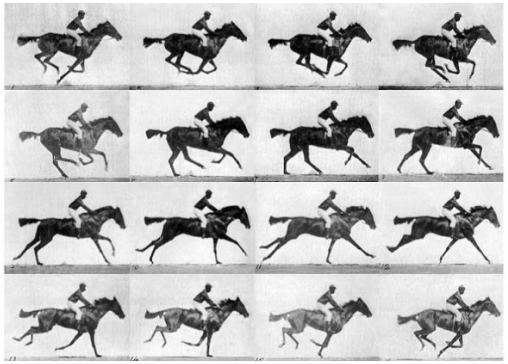
TCSPC + PL spectrum

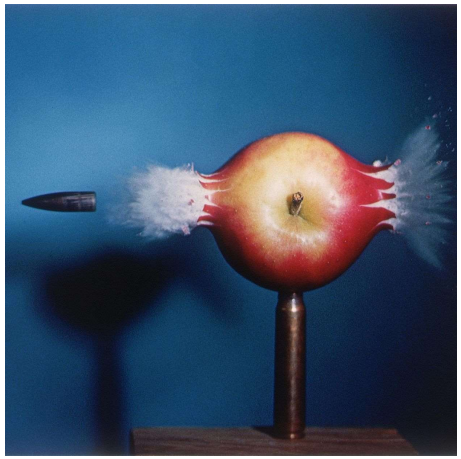
Down to 3ps time resolution



Approach 2:
State-Resolved Pump/Probe (SRPP)
or Transient Absorption (TA) spectrosocpy

Moving to the femtosecond domain requires some thought about shutters and timing



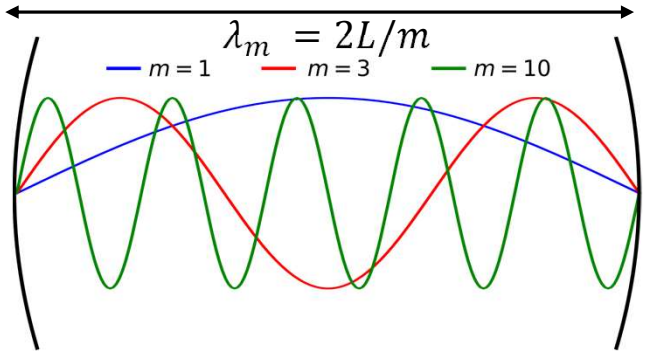


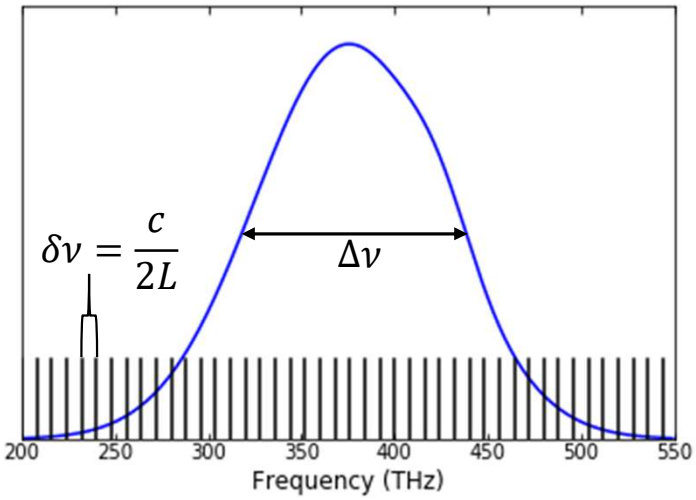
Laser beam width 5 mm
Laser pulse duration desired 100 fs
Shutter speed required 5 mm / 100 fs
= 5 x 10^10 m/s

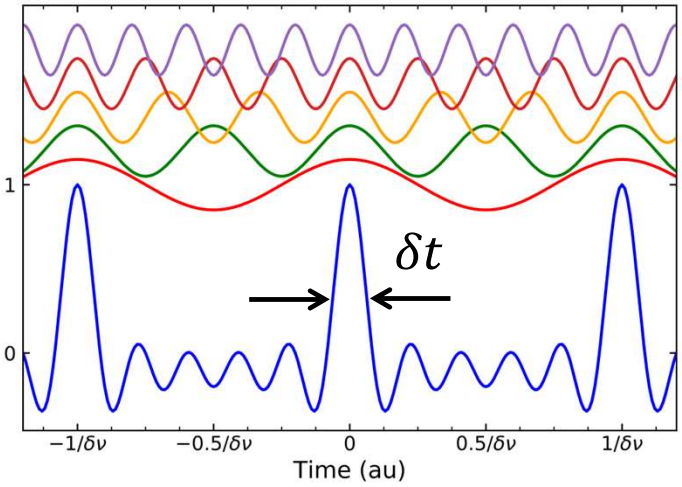
Speed of light = 3 x 10^8 m/s
Speed of sound = 3.4 x 10^2 m/s

Thinking about moving to the femtosecond domain

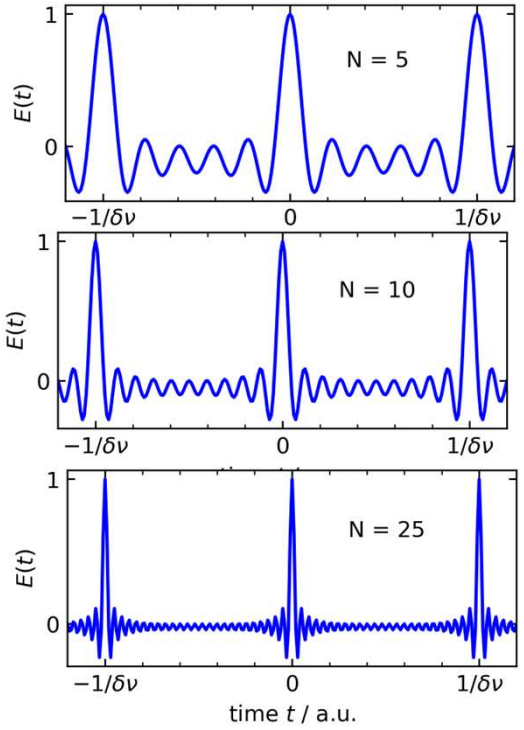
or how to make fs laser pulses by Fourier Transform principles aka Mode Locking



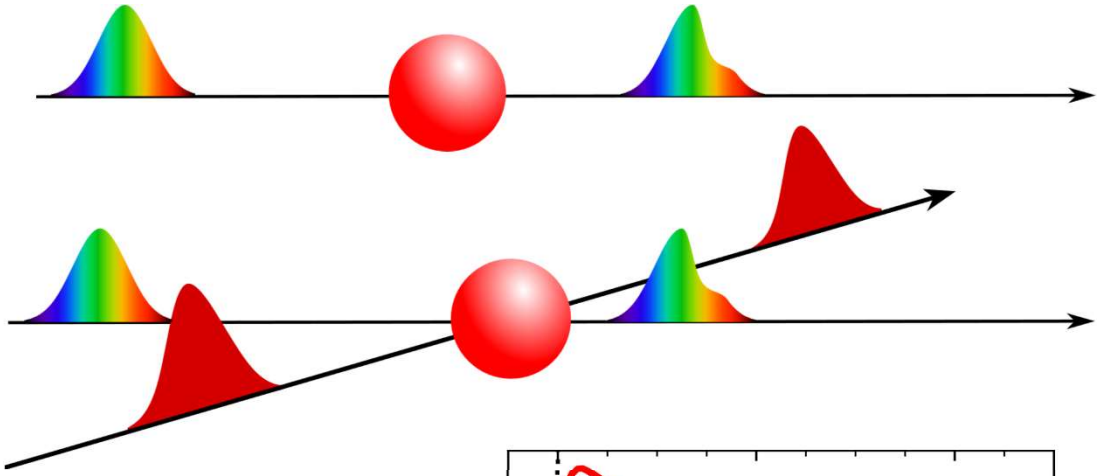


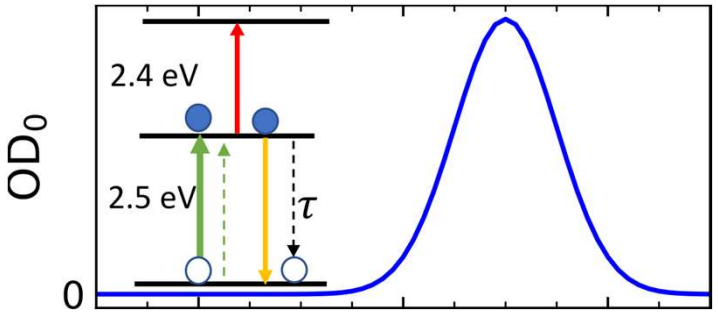


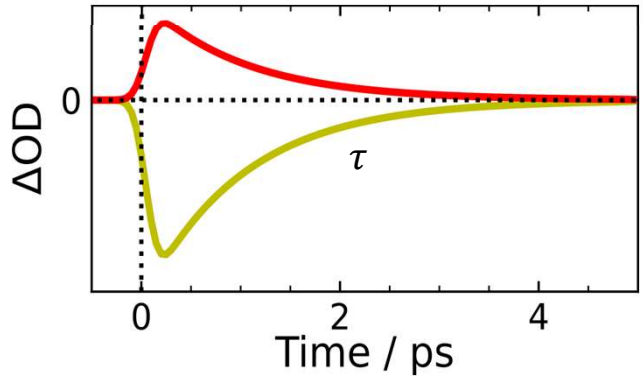
$$\delta t \propto \frac{1}{\Delta\nu}$$

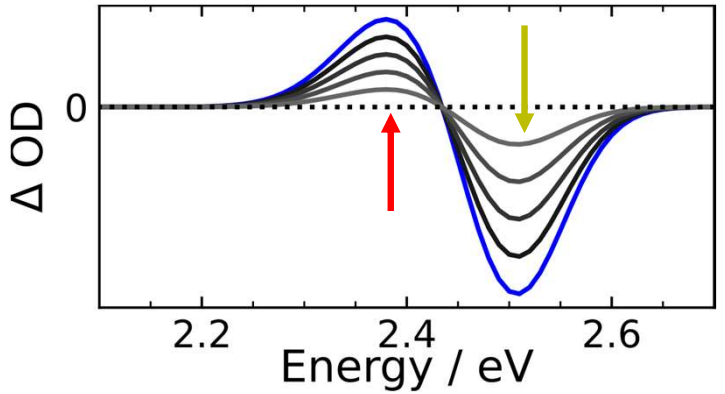


Generic pump/probe or Transient Absorption Spectroscopy

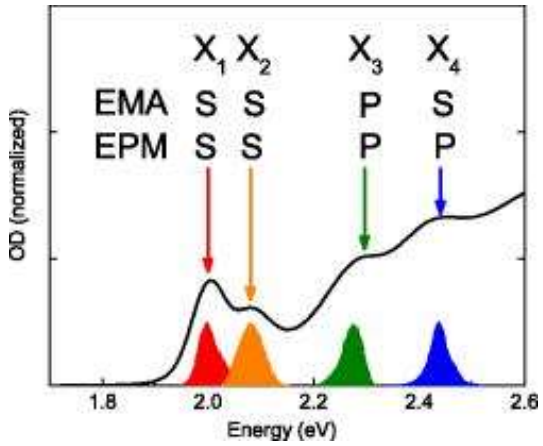


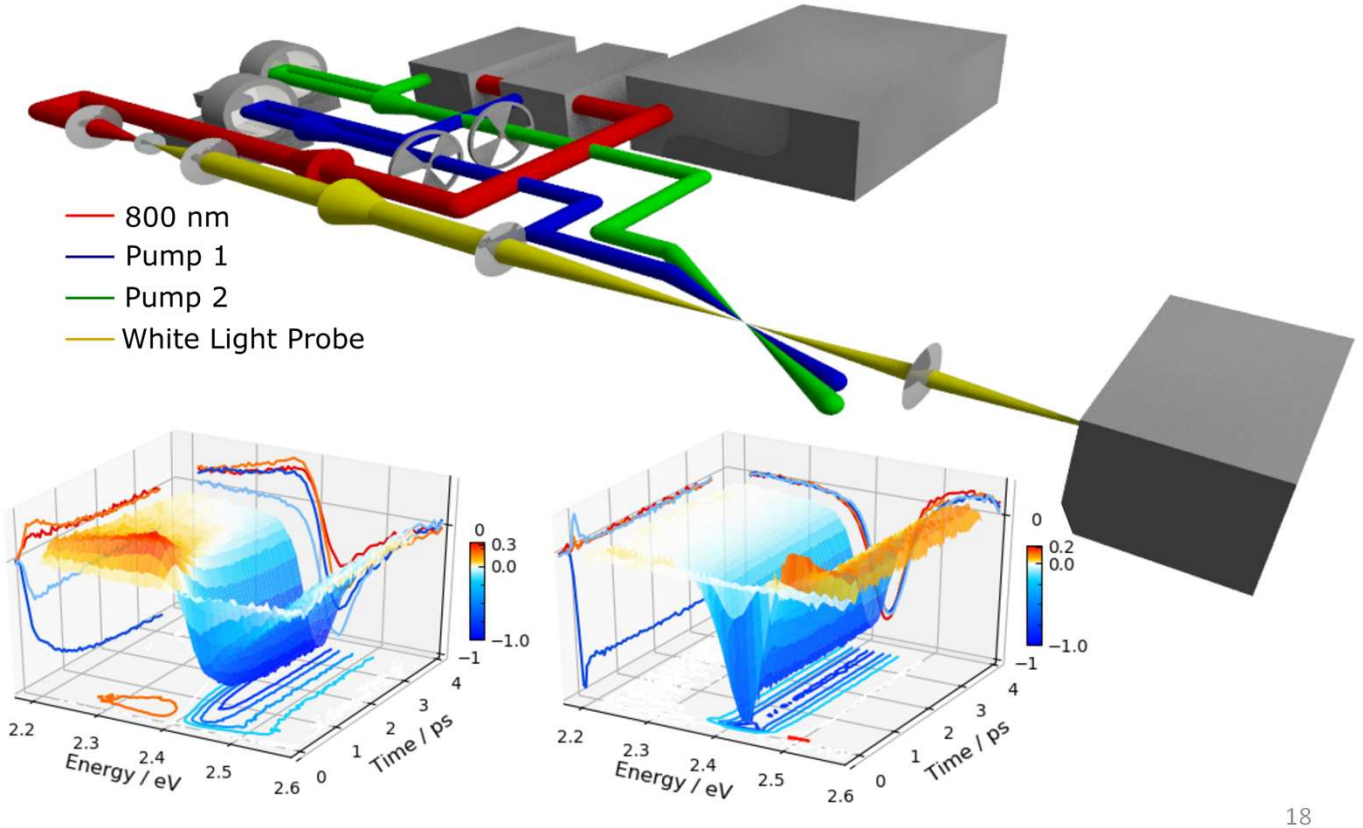






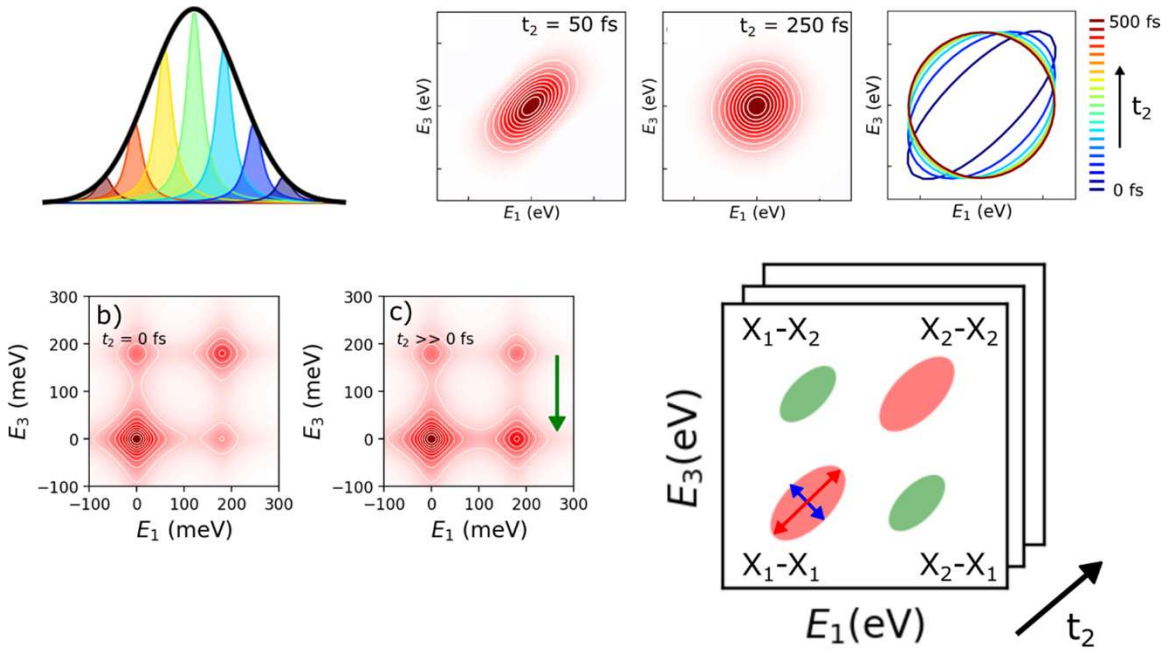
State-Resolved pump/probe spectroscopy



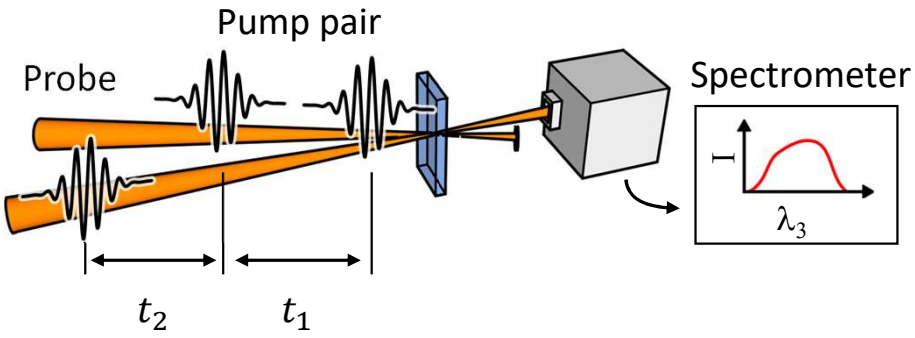


Approach 3:
Two-Dimensional Electronic (2DE) Spectroscopy

Why move from 1D to 2D spectroscopy?



The hows and whys of 2DE



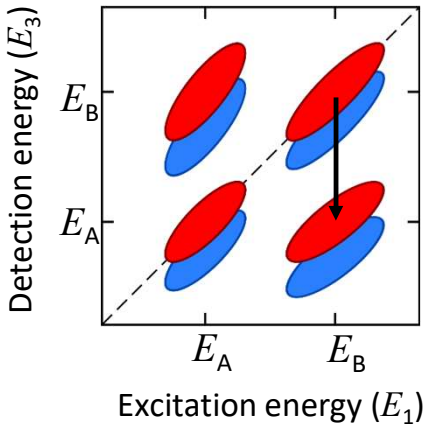
$$\chi_i^{(3)}(t_1, t_2, t_3) \Rightarrow \chi_i^{(3)}(E_1, t_2, E_3)$$

E_1: Excitation energy

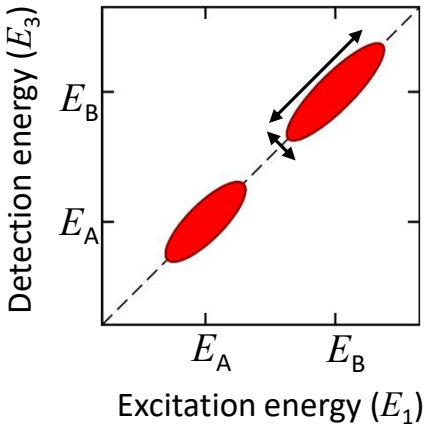
t_2 : Population time

E_3: Detection energy

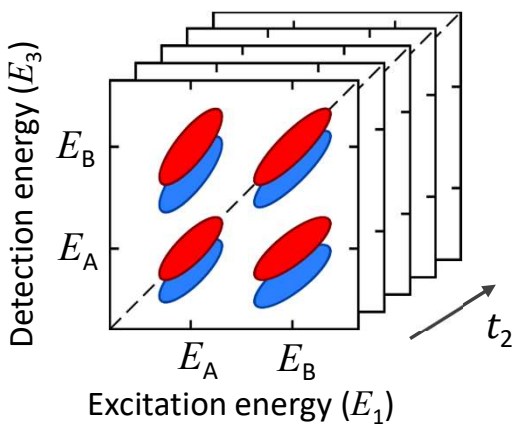
Couplings
Relaxation



Lineshapes

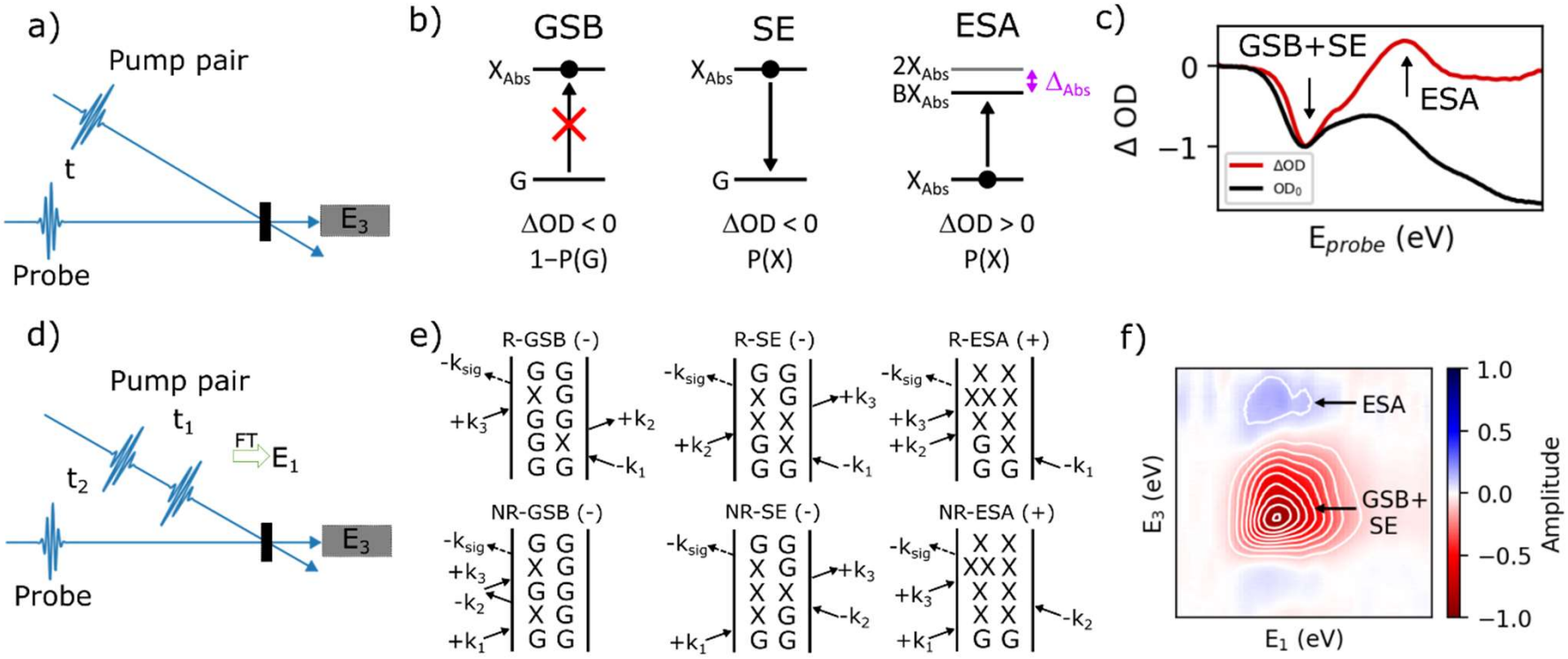


Dynamics

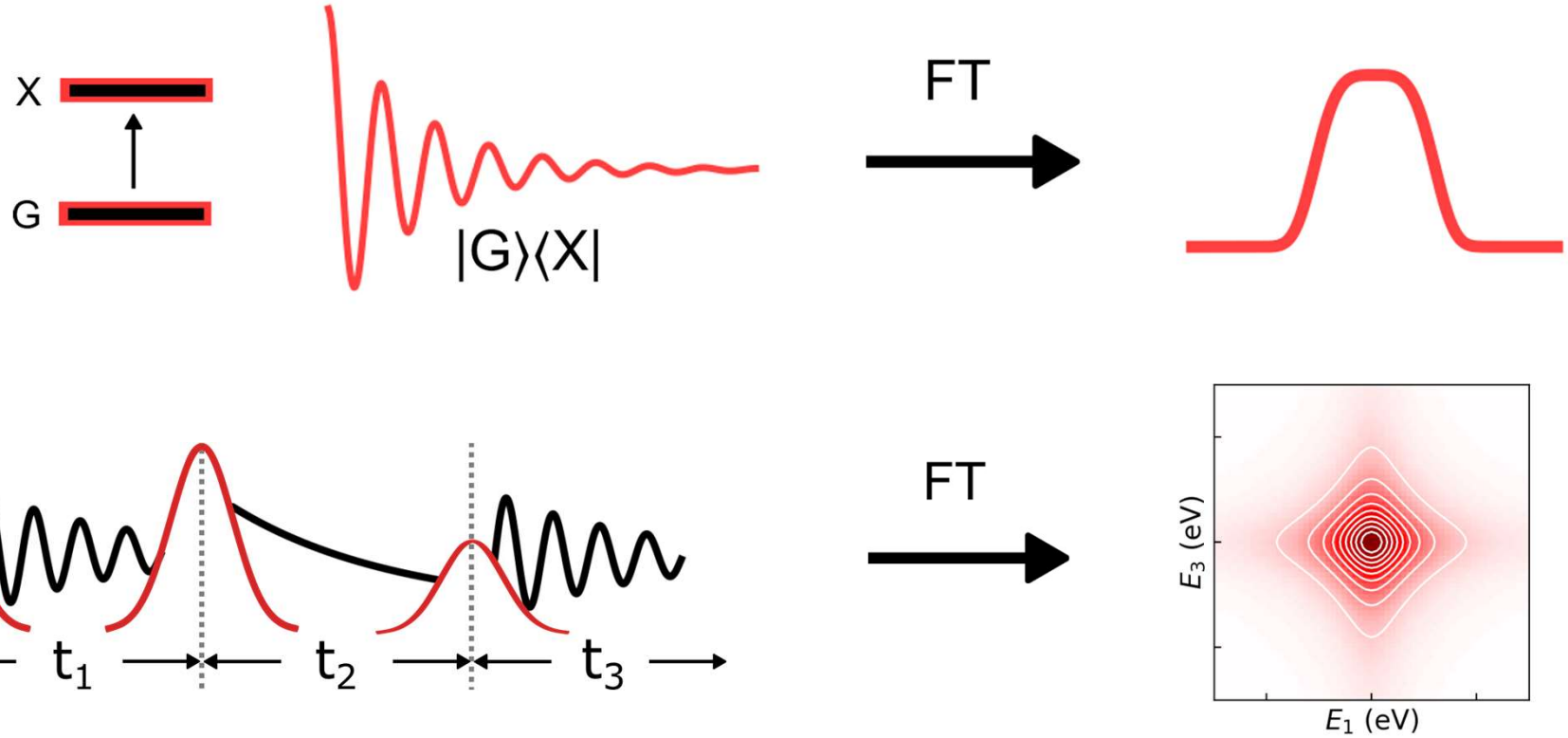


R. M. Hochstrasser, *PNAS*, **104**, 36, June 2007,

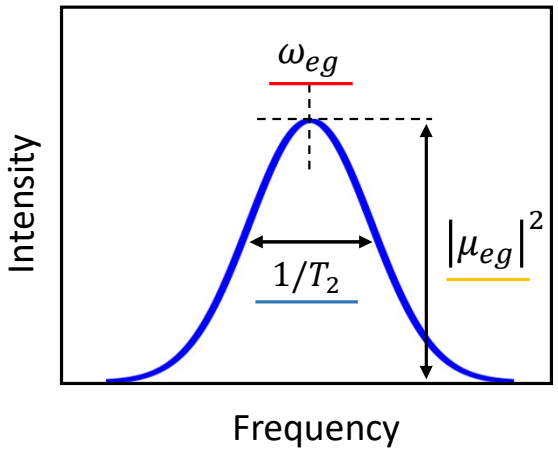
Thinking about the three types of signals in TA and 2DE spectroscopy



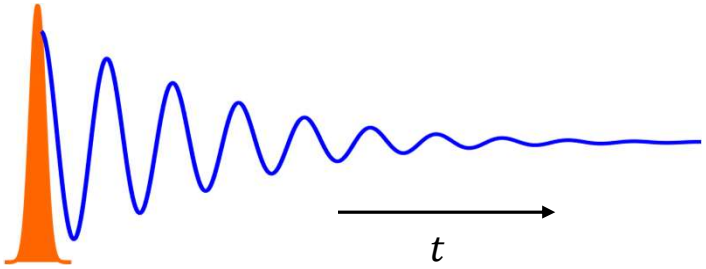
A more serious look requires a change of mindset from photons to fields



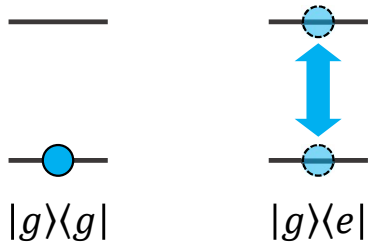
Lineshapes



$\mathcal{F}$



$$P(t) = |\mu_{eg}|^2 \exp(-i\omega_{eg}t) \exp\left(-\frac{t}{T_2}\right)$$



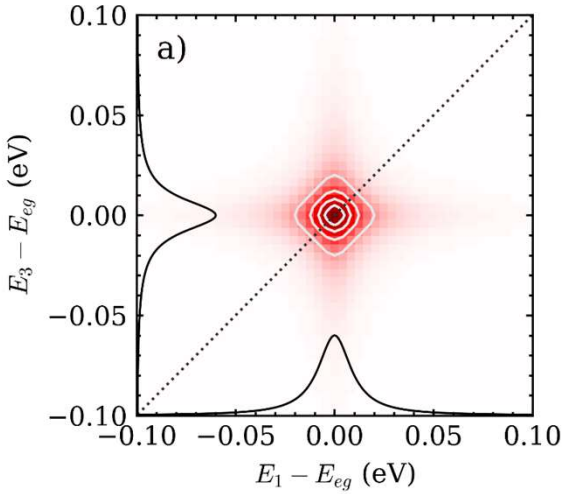
- Charge reorganization $\mu_{eg} = \langle e|\hat{\mu}|g\rangle$
- Energy gaps $\omega_{eg} = E_{eg}/\hbar$
- Fluctuations $\exp(-t/T_2) = \exp[-g(t)]$

$$g(t) = \int_0^t d\tau \int_0^\tau d\tau' \langle \delta\omega_{eg}(\tau')\delta\omega_{eg}(0)\rangle$$

Lineshapes in 2DE

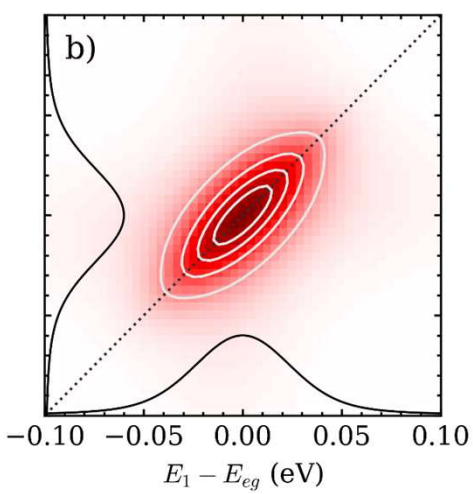
Fast dephasing

$$C(t) = \gamma\delta(t)$$



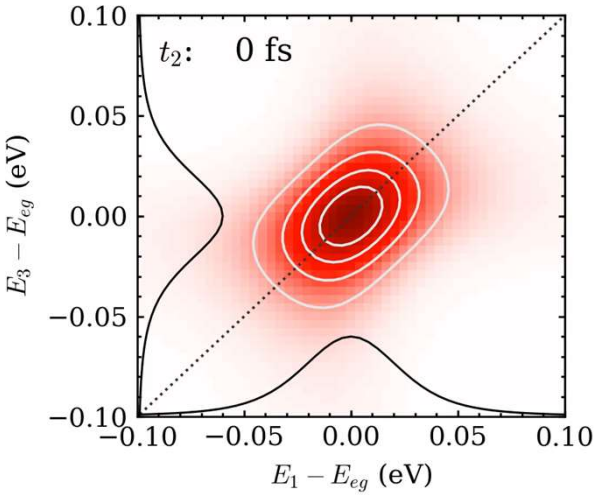
Static inhomogeneity

$$C(t) = \sigma^2$$

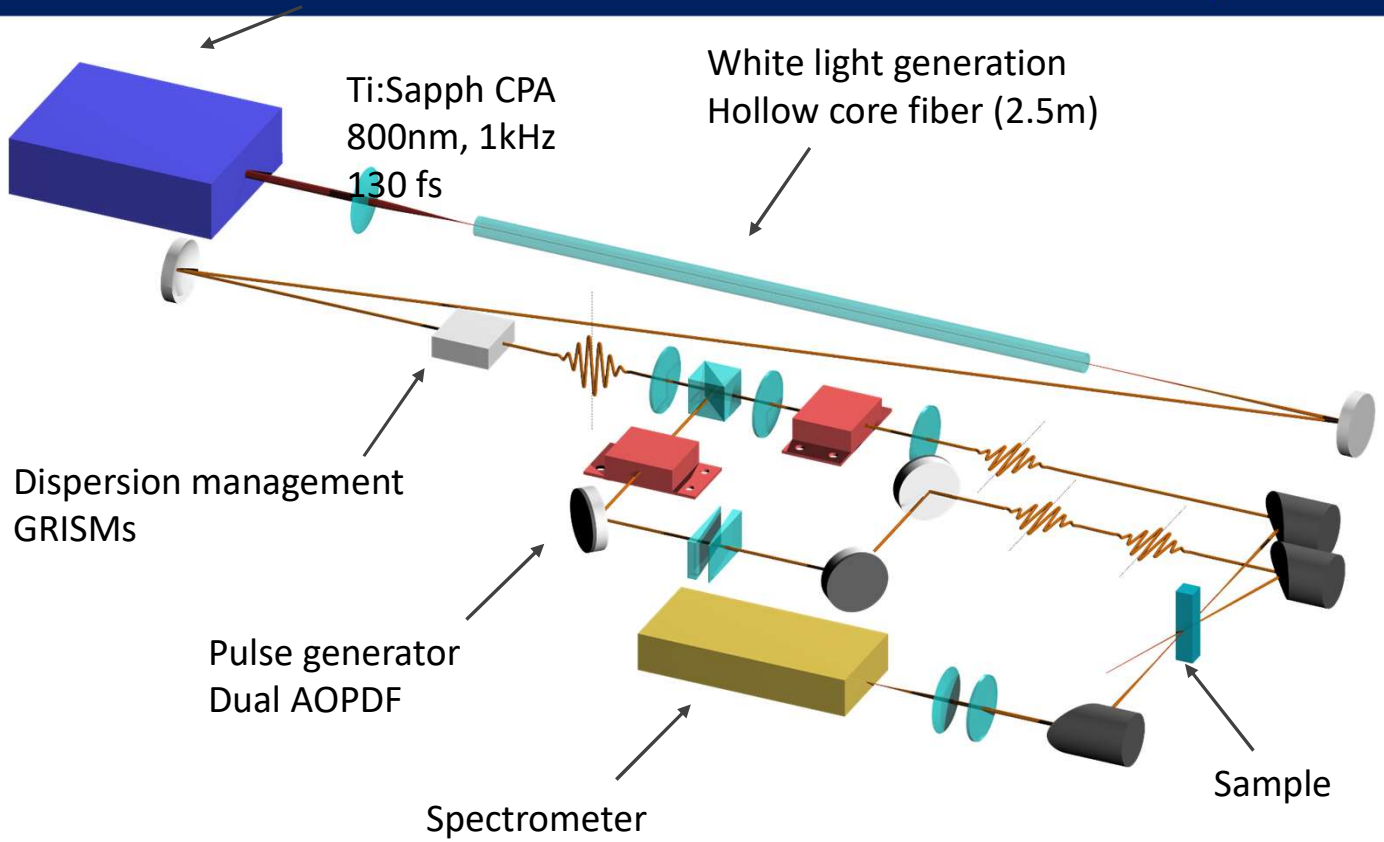


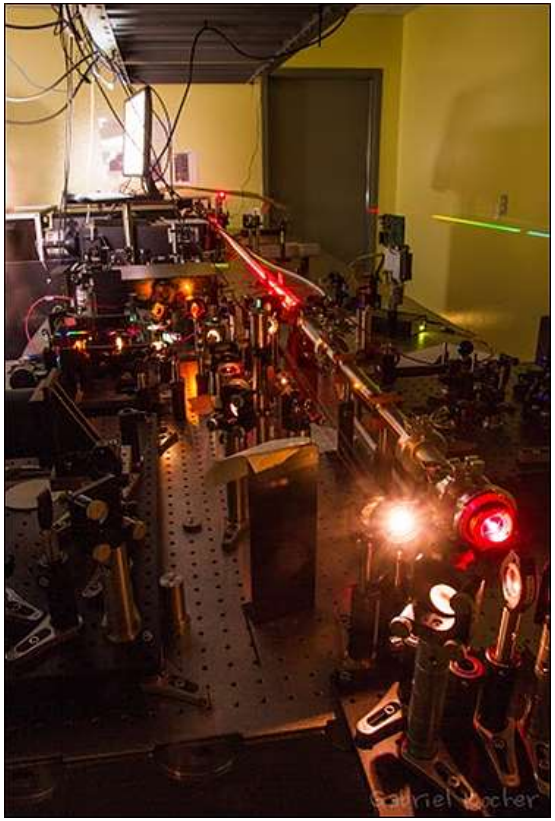
Exponential decorrelation (« Kubo »)

$$C(t) = \sigma^2 \exp\left(-\frac{t}{\tau_c}\right)$$

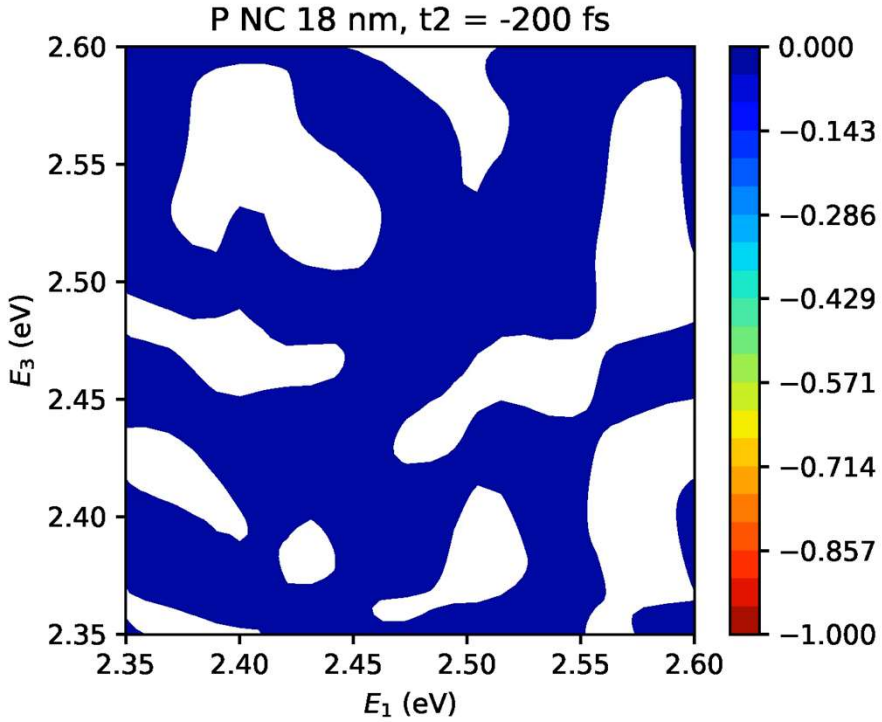


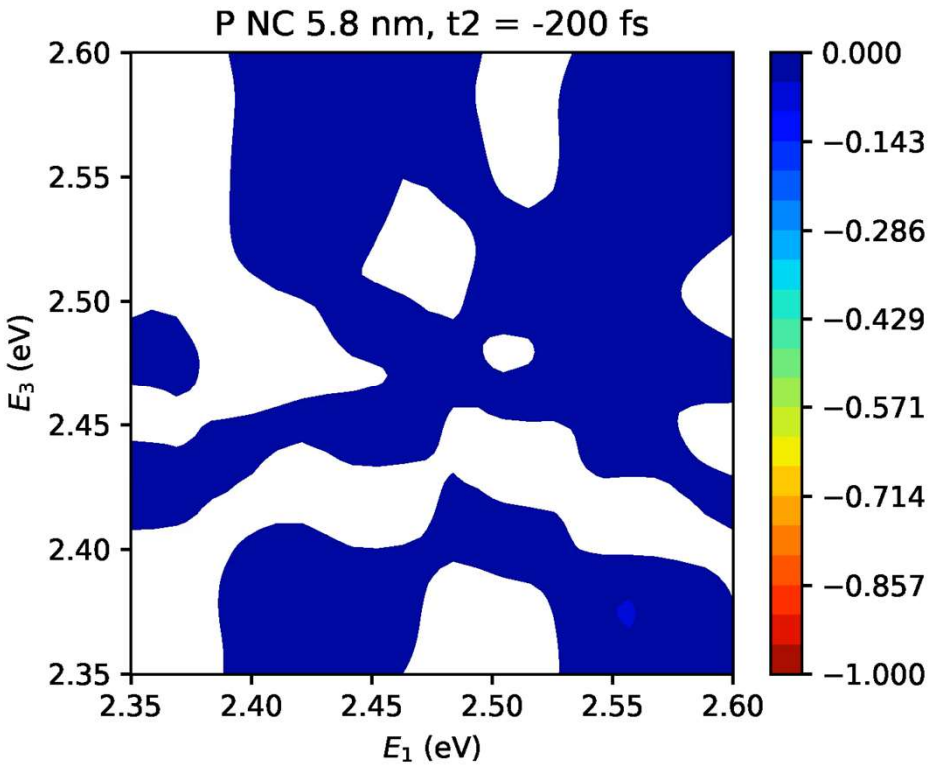
Anatomy of our 2DE spectrometer implemented via non-classical optics



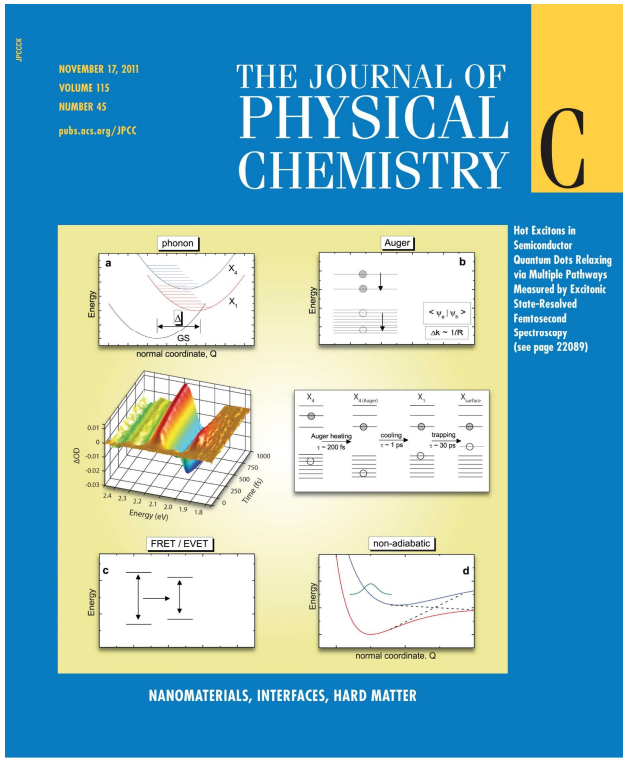


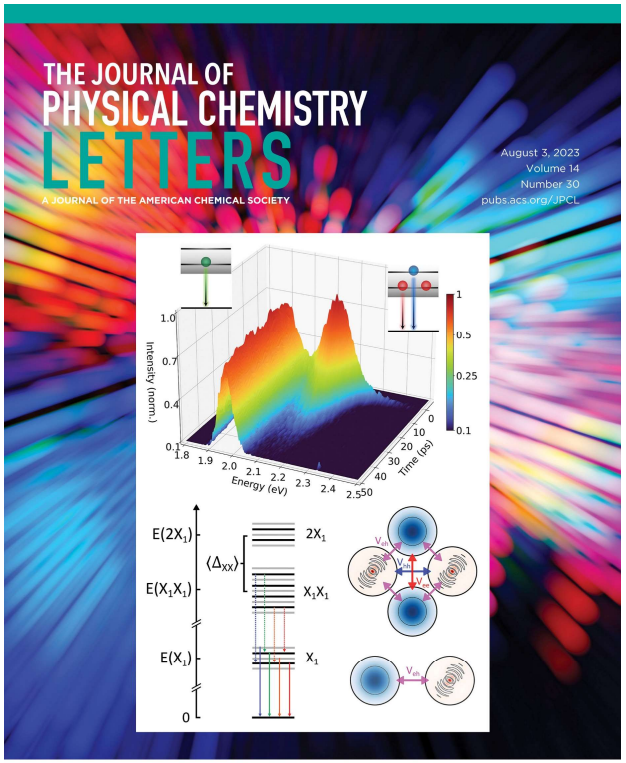
An overview of 2DE data as movies





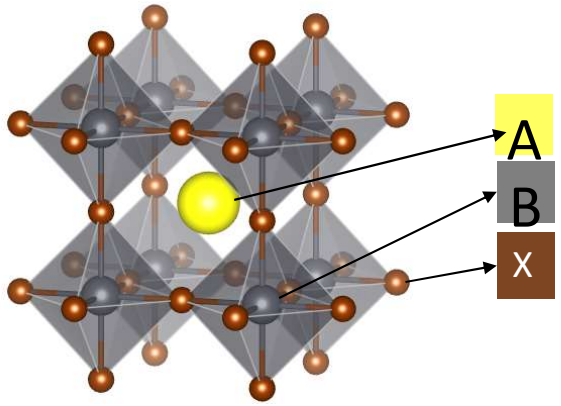
Section 3:
New materials that interpolate between limits as a long-standing theme of investigation… From CdSe Quantum Dots to Metal Halide Perovskites

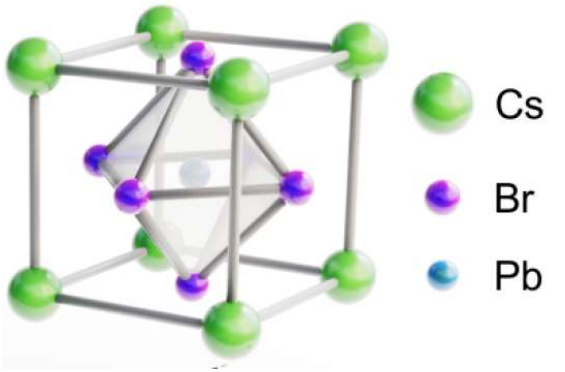




Introduction to semiconductor metal halide perovskites

- Perovskite: Material with $A^{1+}B^{2+}X^{1-}{}_3$
- Remarkable Solar PV efficiency
  - 25% vs. 26% in Si, 28% in GaAs
- Tunable chemistry at all three sites





Why study perovskites? Energy.

nature photonics

REVIEW ARTICLE

PUBLISHED ONLINE: 28 APRIL 2016 | DOI: 10.1038/NPHOTON.2016.62

Perovskite photonic sources

Brandon R. Sutherland and Edward H. Sargent*

The field of solution-processed semiconductors has made great strides; however, it has yet to enable electrically driven lasers. To achieve this goal, improved materials are required that combine efficient (>50% quantum yield) radiative recombination under high injection, large and balanced charge-carrier mobilities in excess of 10 $cm^2 V^{-1} s^{-1}$, free-carrier densities greater than 10^{17} cm^{-3} and gain coefficients exceeding 10^4 cm^{-1}. Solid-state perovskites are — in addition to galvanizing the field of solar electricity — showing great promise in photonic sources, and may be the answer to realizing solution-cast laser diodes. Here, we discuss the properties of perovskites that benefit light emission, review recent progress in perovskite electroluminescent diodes and optically pumped lasers, and examine the remaining challenges in achieving continuous-wave and electrically driven lasing.

nature nanotechnology

REVIEW ARTICLE

PUBLISHED ONLINE: 7 MAY 2015 | DOI: 10.1038/NNANO.2015.90

Metal-halide perovskites for photovoltaic and light-emitting devices

Samuel D. Stranks and Henry J. Snaith*

Metal-halide perovskites are crystalline materials originally developed out of scientific curiosity. Unexpectedly, solar cells incorporating these perovskites are rapidly emerging as serious contenders to rival the leading photovoltaic technologies. Power conversion efficiencies have jumped from 3% to over 20% in just four years of academic research. Here, we review the rapid progress in perovskite solar cells, as well as their promising use in light-emitting devices. In particular, we describe the broad tunability and fabrication methods of these materials, the current understanding of the operation of state-of-the-art solar cells and we highlight the properties that have delivered light-emitting diodes and lasers. We discuss key thermal and operational stability challenges facing perovskites, and give an outlook of future research avenues that might bring perovskite technology to commercialization.

CHEMICAL REVIEWS

Review

Cite This: Chem. Rev. 2019, 119, 3036−3103

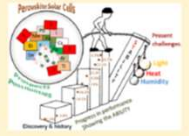
pubs.acs.org/CR

Halide Perovskite Photovoltaics: Background, Status, and Future Prospects

Ajay Kumar Jena,[†] Ashish Kulkarni,[†] and Tsutomu Miyasaka[*,†,‡]

[†]Graduate School of Engineering and [‡]Faculty of Medical Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8503, Japan

ABSTRACT: The photovoltaics of organic−inorganic lead halide perovskite materials have shown rapid improvements in solar cell performance, surpassing the top efficiency of semiconductor compounds such as CdTe and CIGS (copper indium gallium selenide) used in solar cells in just about a decade. Perovskite preparation via simple and inexpensive solution processes demonstrates the immense potential of this thin-film solar cell technology to become a low-cost alternative to the presently commercially available photovoltaic technologies. Significant developments in almost all aspects of perovskite solar cells and discoveries of some fascinating properties of such hybrid perovskites have been made recently. This Review describes the fundamentals, recent research progress, present status, and our views on future prospects of perovskite-based photovoltaics, with discussions focused on strategies to improve both intrinsic and extrinsic (environmental) stabilities of high-efficiency devices. Strategies and challenges regarding compositional engineering of the hybrid perovskite structure are discussed, including potentials for developing all-inorganic and lead-free perovskite materials. Looking at the latest cutting-edge research, the prospects for perovskite-based photovoltaic and optoelectronic devices, including non-photovoltaic applications such as X-ray detectors and image sensing devices in industrialization, are described. In addition to the aforementioned major topics, we also review, as a background, our encounter with perovskite materials for the first solar cell application, which should inspire young researchers in chemistry and physics to identify and work on challenging interdisciplinary research problems through exchanges between academia and industry.



SPECIAL SECTION PEROVSKITES

REVIEW

Properties and potential optoelectronic applications of lead halide perovskite nanocrystals

Maksym V. Kovalenko,[1,2*] Loredana Protesescu,[1,2] Maryna I. Bodnarchuk[2*]

Semiconducting lead halide perovskites (LHPs) have not only become prominent thin-film absorber materials in photovoltaics but have also proven to be disruptive in the field of colloidal semiconductor nanocrystals (NCs). The most important feature of LHP NCs is their so-called defect-tolerance—the apparently benign nature of structural defects, highly abundant in these compounds, with respect to optical and electronic properties. Here, we review the important differences that exist in the chemistry and physics of LHP NCs as compared with more conventional, tetrahedrally bonded, elemental, and binary semiconductor NCs (such as silicon, germanium, cadmium selenide, gallium arsenide, and indium phosphide). We survey the prospects of LHP NCs for optoelectronic applications such as in television displays, light-emitting devices, and solar cells, emphasizing the practical hurdles that remain to be overcome.

Why study perovskites? Liquid / Solid duality. Phonon glass / electron crystal. Structural dynamics

SCIENCE ADVANCES | REVIEW

PEROVSKITES

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 responses and phonon dynamics typical of liquids. This "crystal-liquid" duality implies that lead halide

SOLAR CELLS

Screening in crystalline liquids protects energetic carriers in hybrid perovskites

Haiming Zhu,[1]* Kiyoshi Miyata,[1]* Yongping Fu,[2] Jue Wang,[1] Prakriti P. Joshi,[1] Daniel Niesner,[1] Kristopher W. Williams,[1] Song Jin,[2] X.-Y. Zhu[1]†

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

SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

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] Skyler C. Jones,[1] Filippo De Angelis,[2,3]* X.-Y. Zhu[1]*

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 $CH_3NH_3PbBr_3$ and $CsPbBr_3$. We found that large polaron

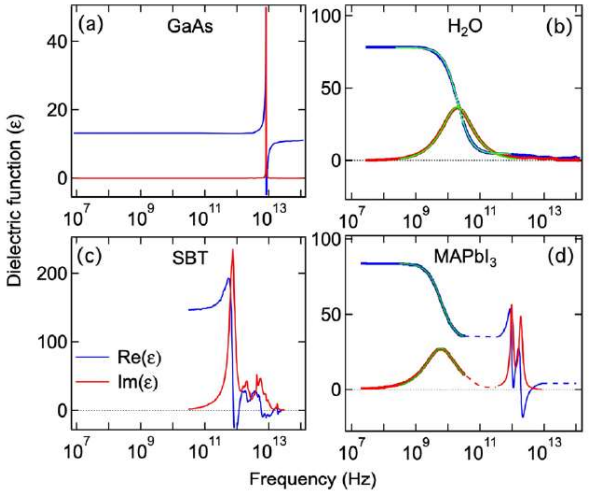


Figure 1. Comparison of dielectric functions in different media. (a) A conventional semiconductor GaAs; (b) water; (c) a ferroelectric material $SrBi_2Ta_2O_9$ (SBT); and (d) the hybrid methylammonium lead iodide perovskite, $MAPbI_3$, all at room temperature. Adapted from ref 1.

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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Perspective

Solvated Electrons in Solids—Ferroelectric Large Polarons in Lead Halide Perovskites

Feifan Wang, Yongping Fu, Mark E. Ziffer, Yanan Dai, Sebastian F. Maehrlein, and X.-Y. Zhu*

Cite This: J. Am. Chem. Soc. 2021, 143, 5−16
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Why study perovskites? Liquid / Solid duality. Phonon glass / electron crystal. Structural dynamics

THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Feature Article

Learning about the Structural Dynamics of Semiconductor Perovskites from Electron Solvation Dynamics

Patanjali Kambhampati*

Cite This: *J. Phys. Chem. C* 2021, 125, 23571−23586
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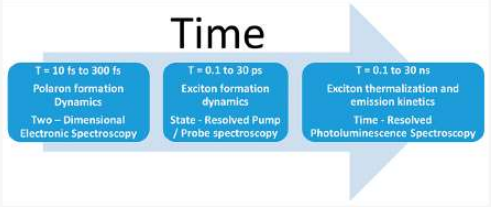
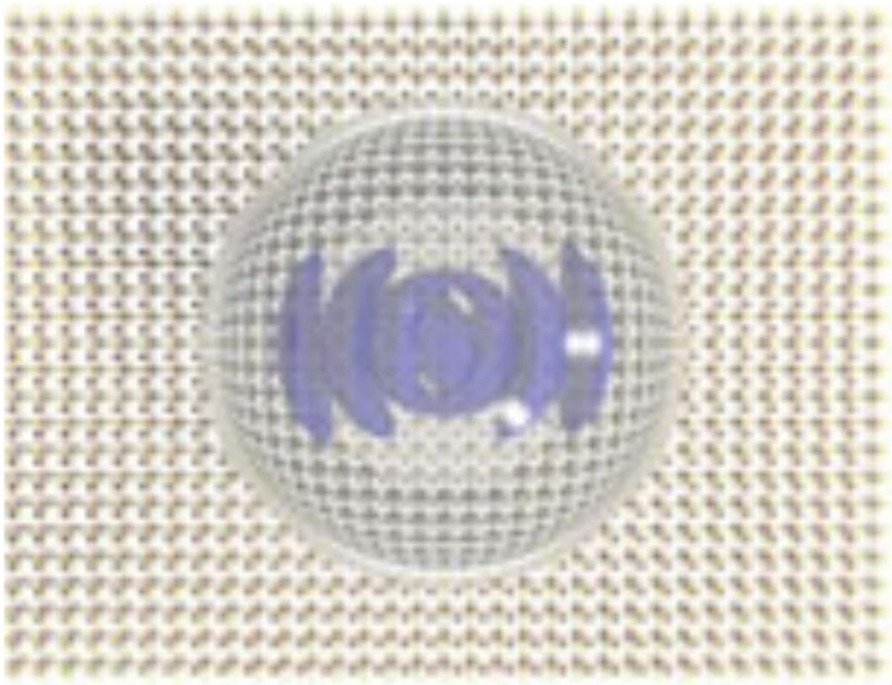
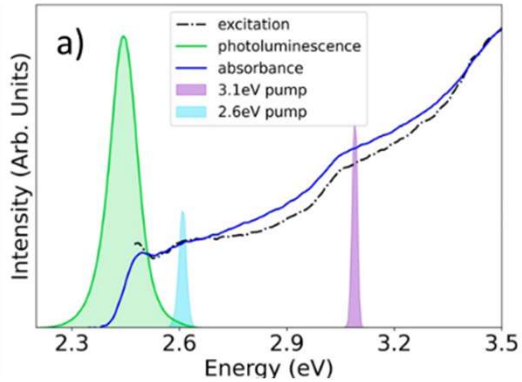
ABSTRACT: Semiconductors of the perovskite form have attracted considerable attention in recent years, most notably for their performance in photovoltaics. One key puzzle was how a disordered film could support such performance. A number of investigations have led to a current picture of defect tolerance due to a soft, ionic lattice giving rise to dynamic disorder. Moreover, the presence of polarons may be connected to this defect tolerance and ultimately in the device performance, whether photovoltaics or light emitting diodes. How do these ionic semiconductors relate to their covalent cousins, for which defect-free perfection is a main goal? In this Perspective, the question of ionicity as it gives rise to glassy structural dynamics is considered. How do these glassy structural dynamics control the optical response and thus the optoelectronic properties of the system? The recent literature is reviewed with a focus on ultrafast structural dynamics. Highlighted in the discussion of the structure/function relation is our recent work which maps the chronology of events from electronic coherence to photon emission using a suite of three time-resolved spectroscopies: two-dimensional electronic spectroscopy, state-resolved pump/probe spectroscopy, and time-resolved photoluminescence spectroscopy. These works collectively advance our understanding of liquid−solid duality in these defect-tolerant ionic semiconductors. With the connection to liquid-like dynamics made, a brief discussion of ultrafast solvation dynamics is presented. The specific connection between excess charges in liquids and solids can be found in the solvated electron, which once again serves as a prototype for electronic structure and dynamics in the condensed phase. We hope that finding isomorphisms between phases can provide insight into these new materials.



Section 4:
Applying SRPP, 2DE, and t-PL spectroscopy to unravel exciton-lattice interactions in metal halide perovskite nanocrystals… Towards a Quantum Drop?

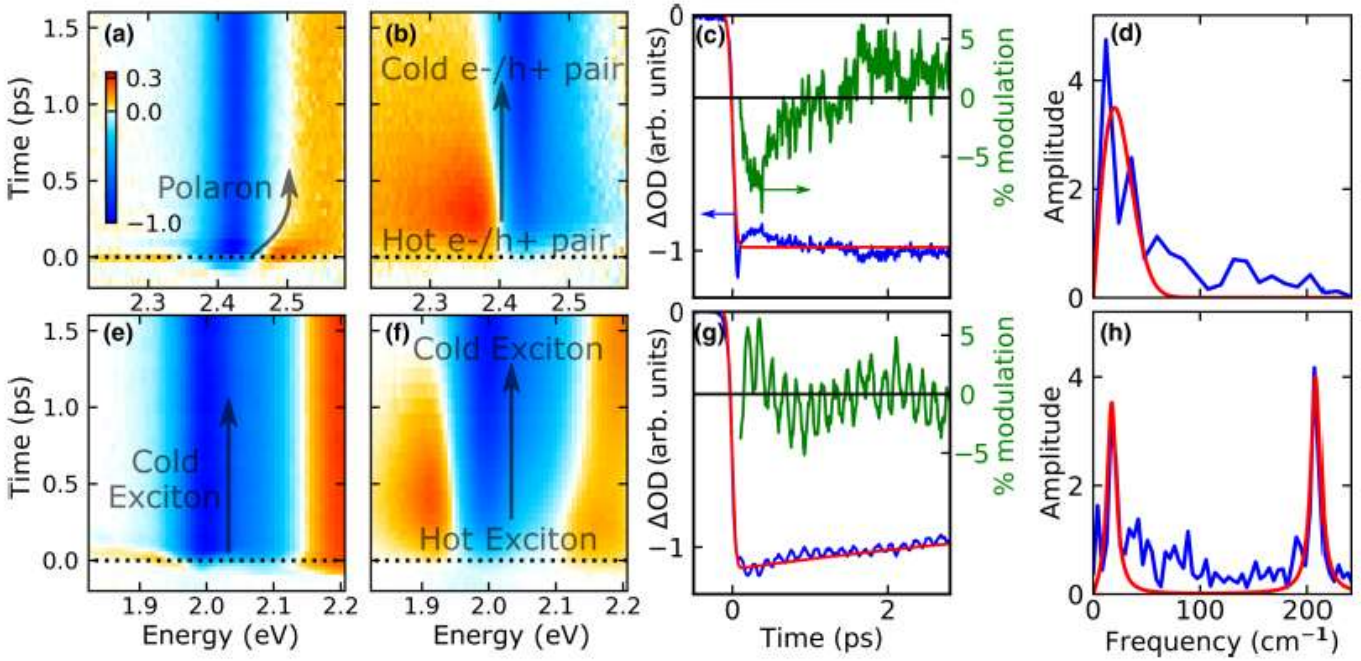


State-Resolved Pump/Probe (SRPP) spectroscopy of CsPbBr3 P NC and CdSe QD NC

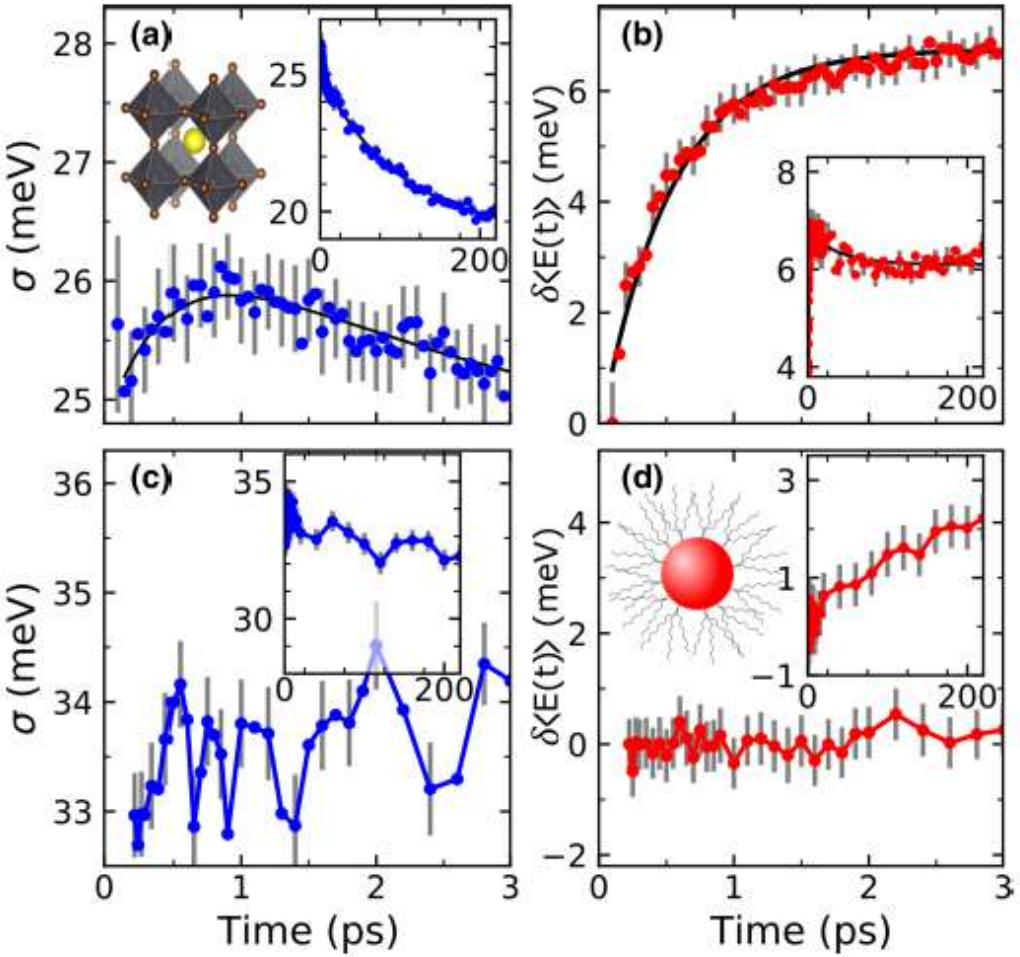


[Breaking Phonon Bottlenecks through Efficient Auger Processes in Perovskite Nanocrystals]
ACS nano 17 (4), 3913-3920

[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

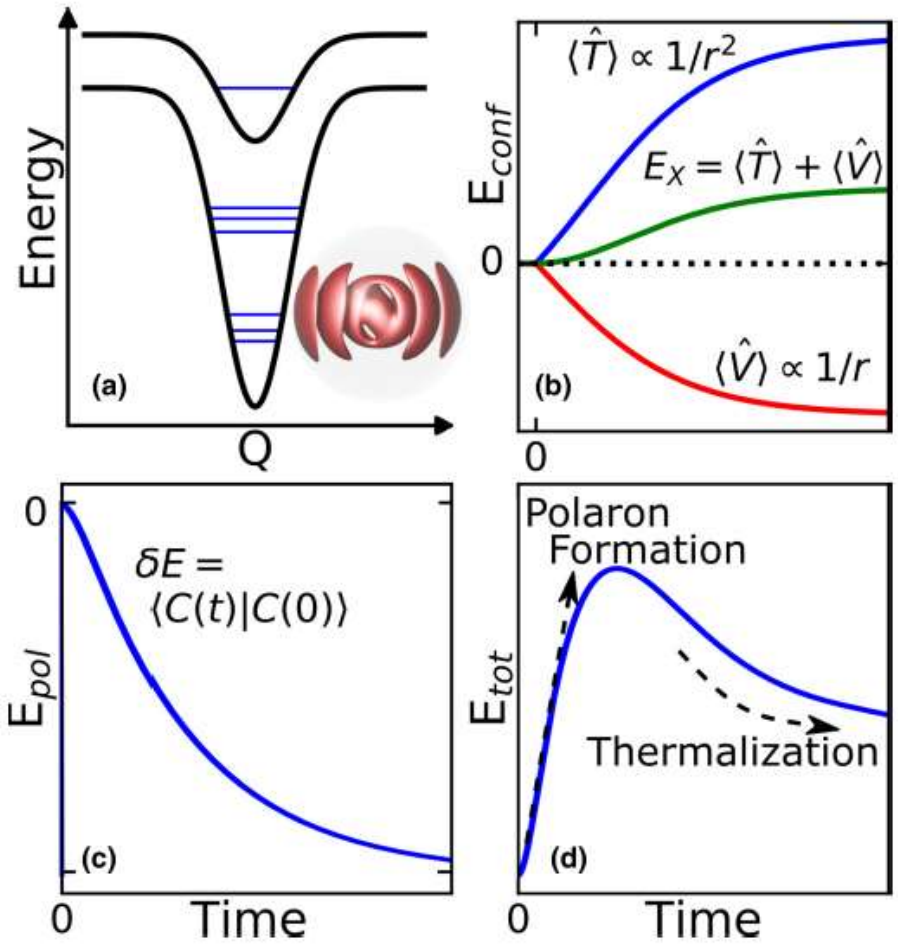


- Cold exciton lineshape dynamice reveal linewidth and peak energy trajectories
- Early time (fs) blueshifting and broadening.
- Late time (ps) redshifting and narrowing
- CdSe is solid as a rock!

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

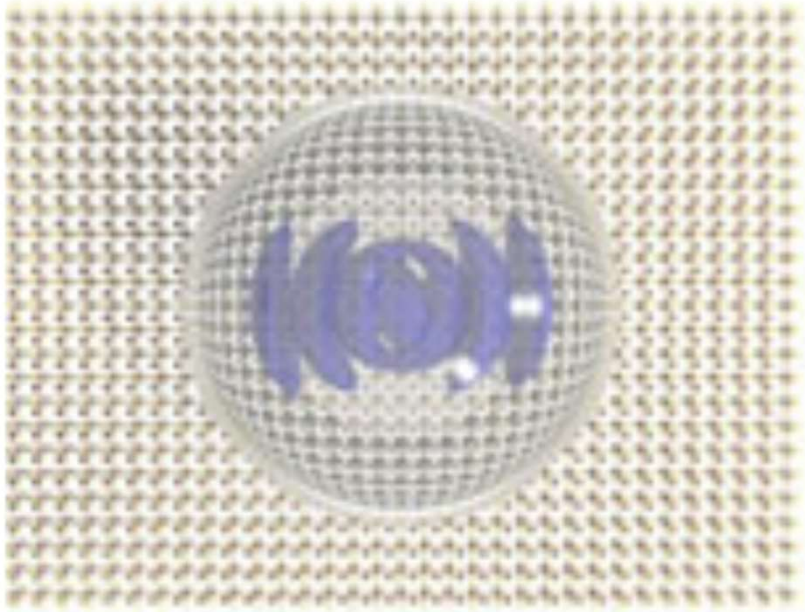
Dynamical confinement via polarons rationalizes the dynamics



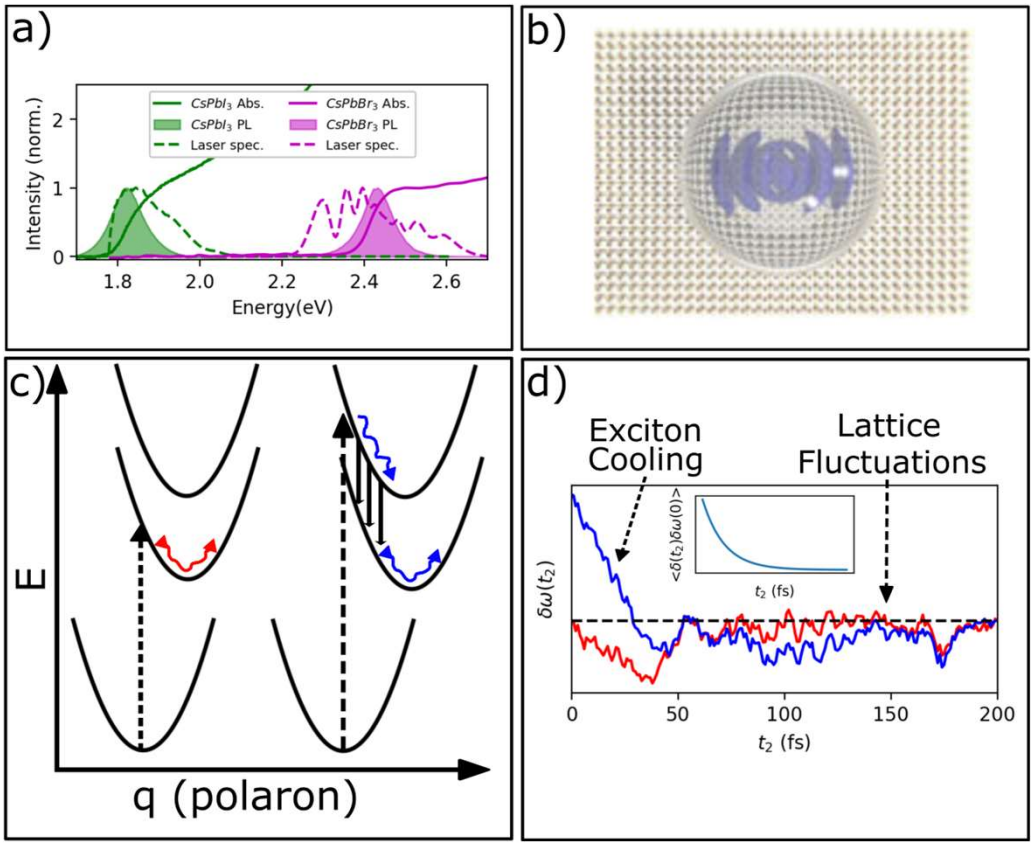
Exciton-polaron coupling?

or

Exciton solvation dynamics



With complex electronic structural dynamics… why not move from 1D to 2D spectroscopy?



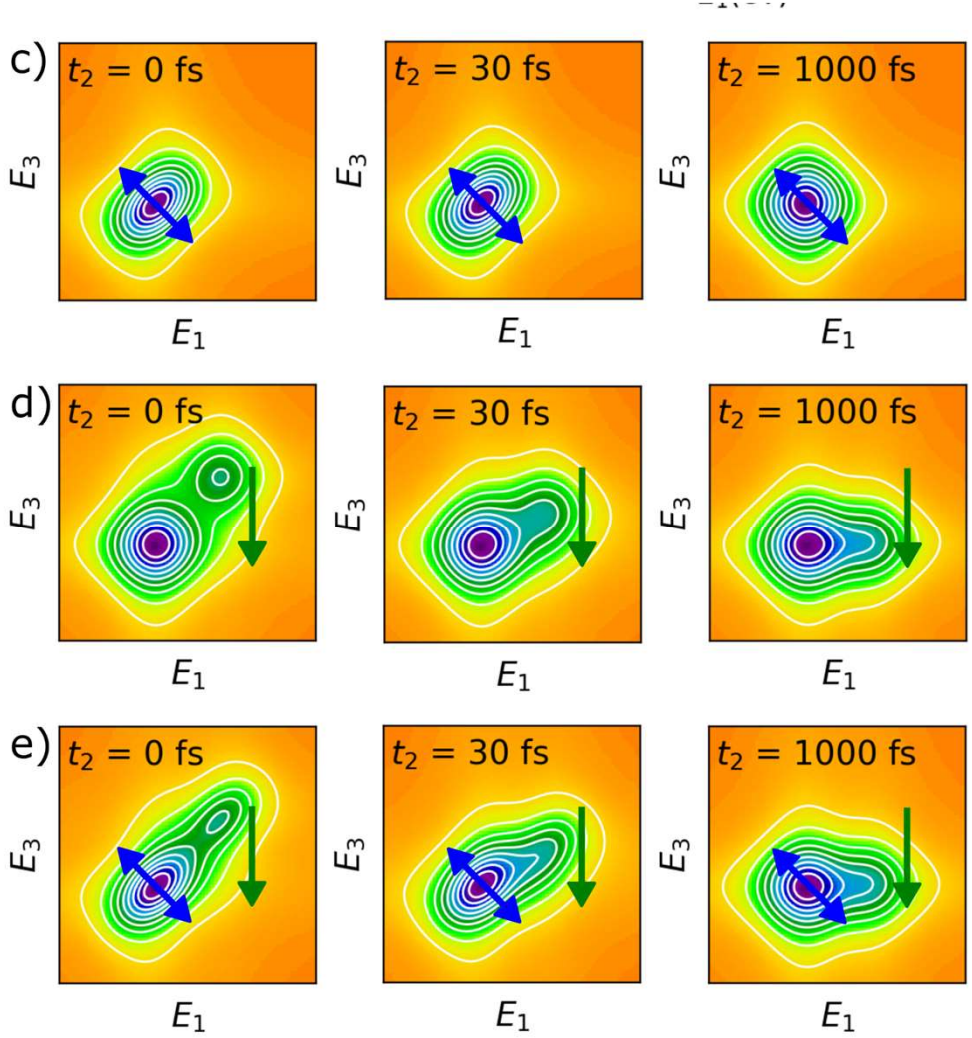
[Exciton–polaron interactions in metal halide perovskite nanocrystals revealed via two-dimensional electronic spectroscopy](#)
The Journal of Chemical Physics 159 (18), 2023

Thinking about 2DE signals in the case of spectral diffusion and cooling

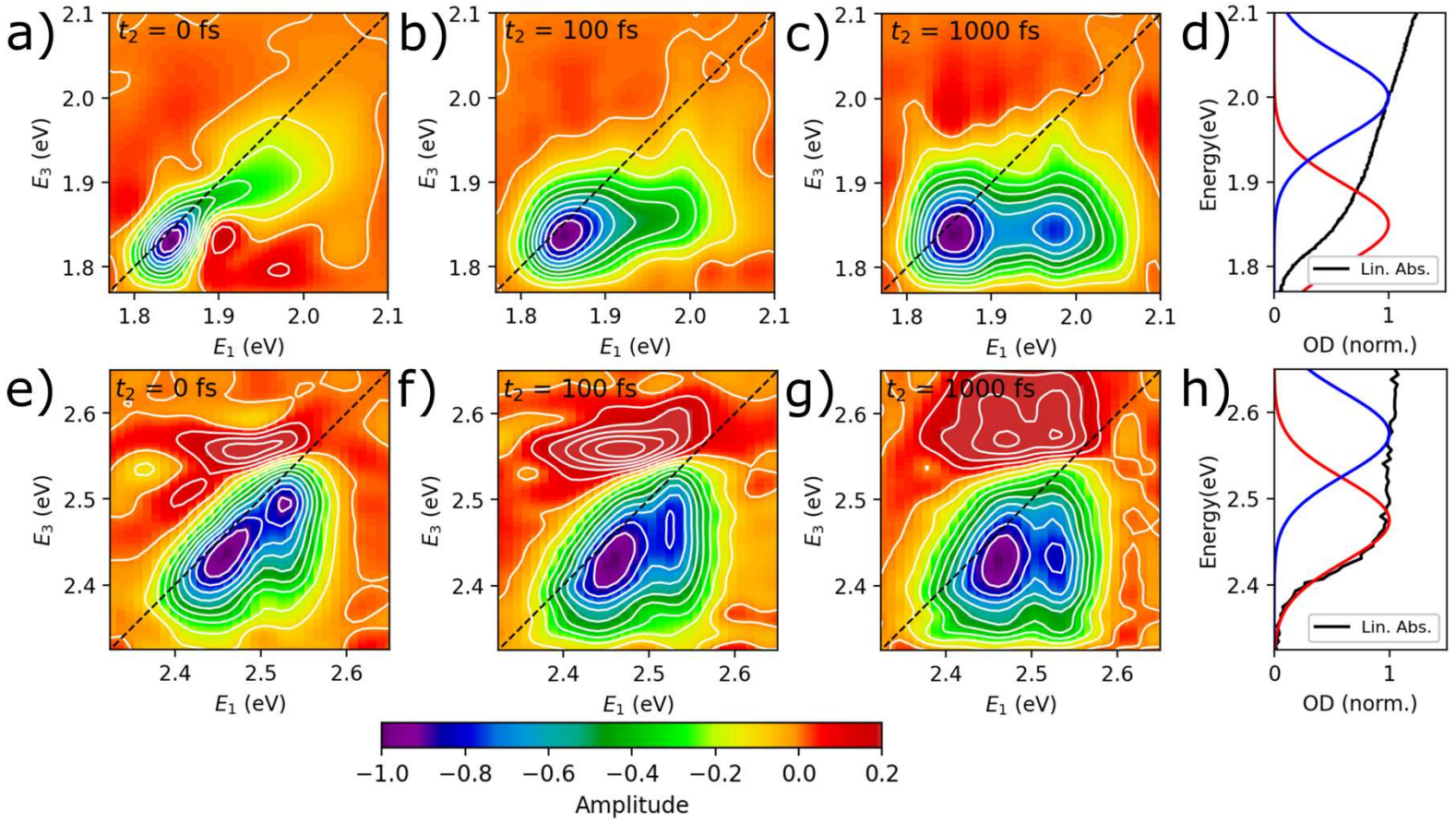
Spectral diffusion

Exciton relaxation / cooling

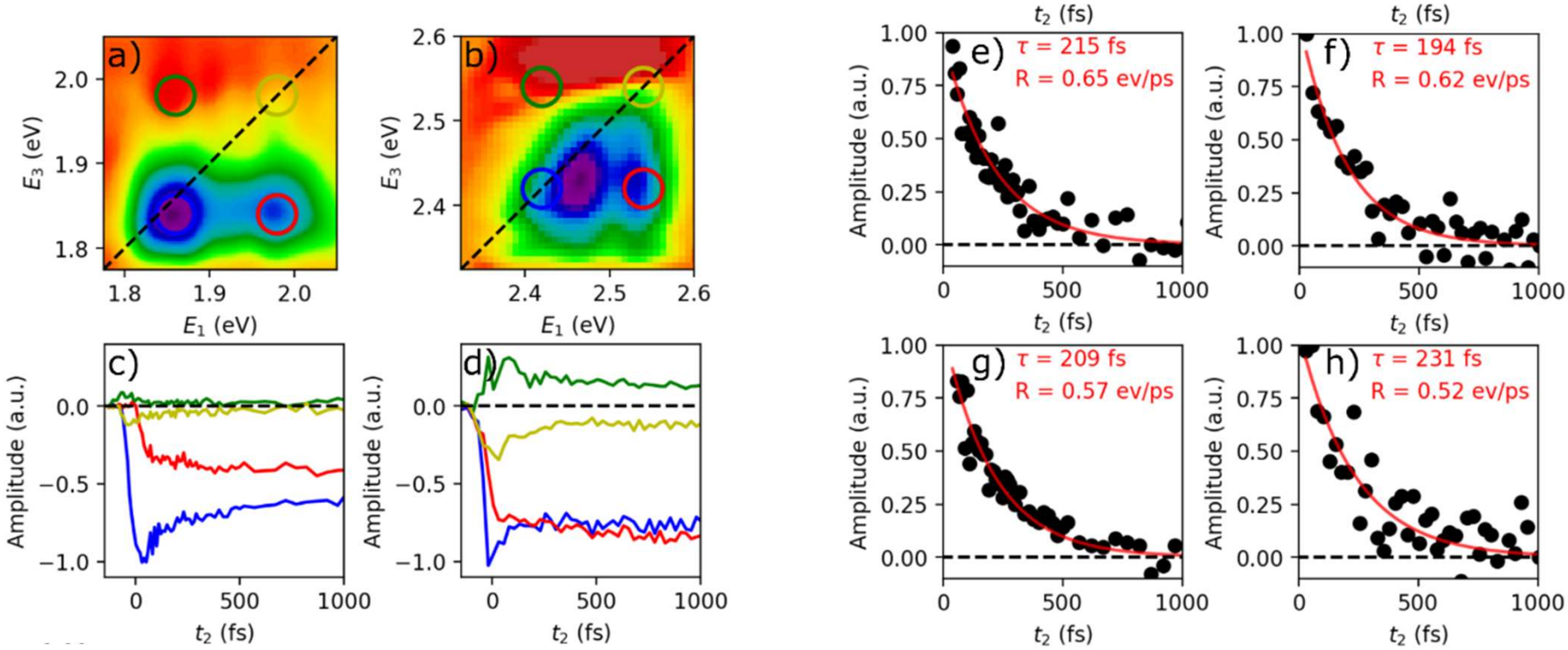
Diffusion and relaxation



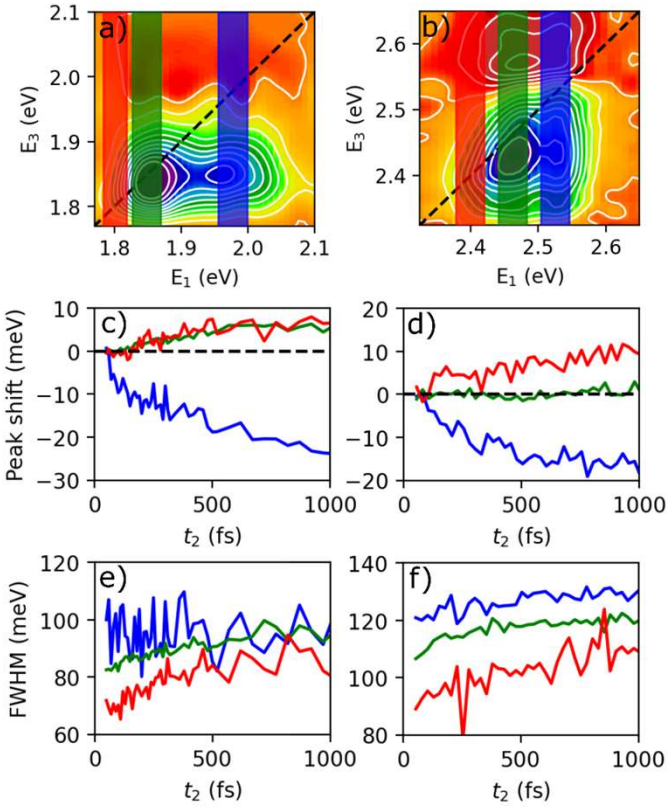
2DE spectra of MHP NC reveals a previously unobserved doublet / splitting in 15 nm diameter $CsPbI_3$ and $CsPbBr_3$

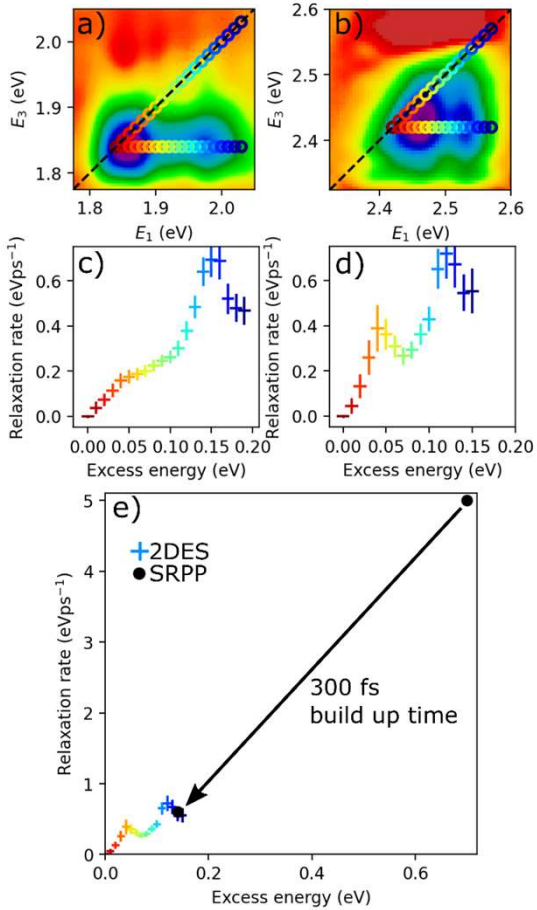


2DE enables observation of hot exciton cooling

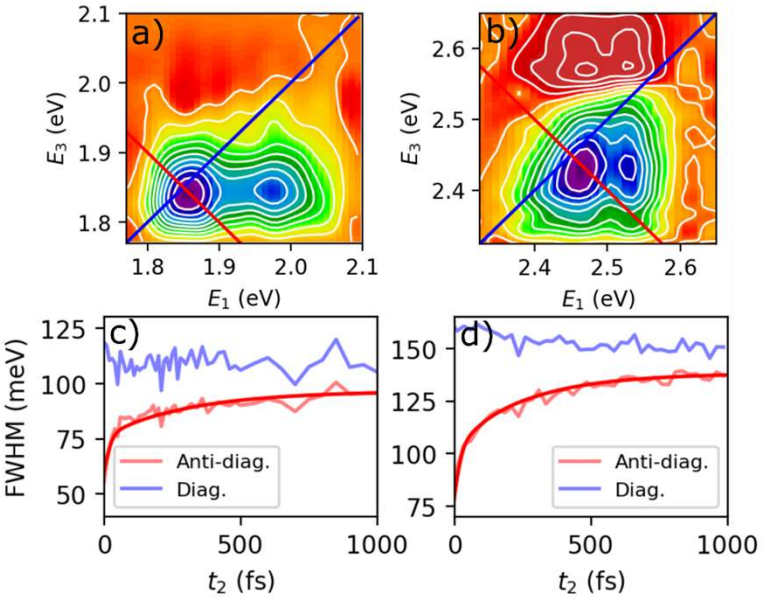


2DE enables energy resolved analysis to reveal cooling and exciton-polaron coupling

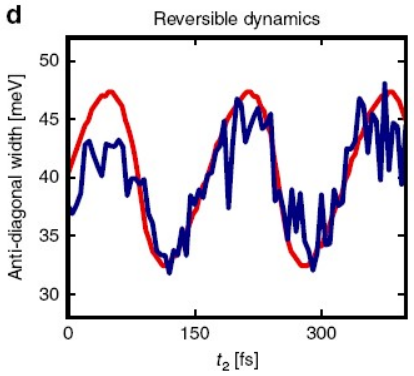


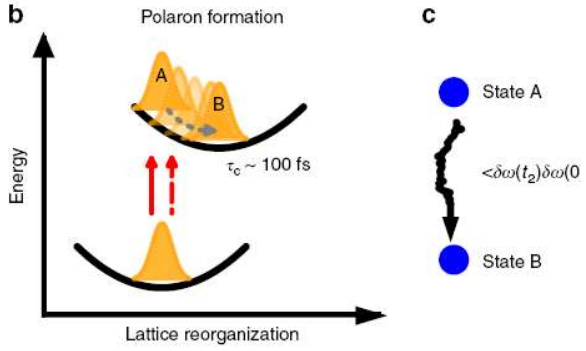


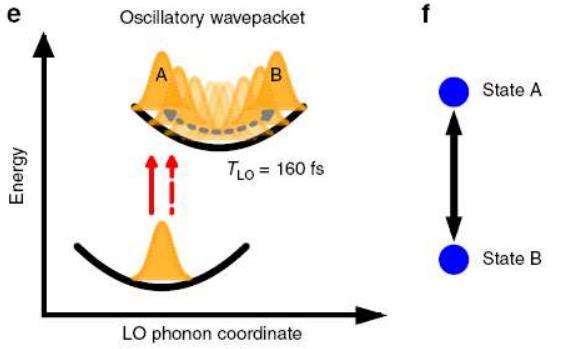
Anti-diagonal linewidth trajectories reveal liquid-like Brownian dynamics



	$CsPbI_3$	$CsPbBr_3$	Ratio I/Br
Atomic mass (amu)	126.9	79.9	$\sqrt{R}$= 1.26
Spectral diffusion timescale (fs)	375	300	1.25







[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

REVIEW

doi:10.1038/nature21425

Using coherence to enhance function in chemical and biophysical systems

Gregory D. Scholes[1], Graham R. Fleming[2], Lin X. Chen[3,4], Alán Aspuru-Guzik[5], Andreas Buchleitner[6], David F. Coker[7], Gregory S. Engel[8], Rienk van Grondelle[9], Akihito Ishizaki[10], David M. Jonas[11], Jeff S. Lundeen[12], James K. McCusker[13], Shaul Mukamel[14], Jennifer P. Ogilvie[15], Alexandra Olaya-Castro[16], Mark A. Ratner[17], Frank C. Spano[18], K. Birgitta Whaley[19,20] & Xiaoyang Zhu[21]

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

nature materials

INSIGHT | REVIEW ARTICLES

PUBLISHED ONLINE: 20 DECEMBER 2016 | DOI: 10.1038/NMAT4767

Photovoltaic concepts inspired by coherence effects in photosynthetic systems

Jean-Luc Brédas[1], Edward H. Sargent[2] and Gregory D. Scholes[3]*

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

Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence

Hohjai Lee, Yuan-Chung Cheng, Graham R. Fleming*

The role of quantu
is an open and int
bacterial reaction
reaction center. Th
formed by mixing
This coherence car
fluctuations in the
correlated protein
allow the excitatio
trapping in photos

nature

LETTERS

Coherently wired light-harvesting marine algae at ambient tempera

nature

LET

Elisabetta Collini[1]*†, Cathy Y. Wong[1]*, Krystyna E. Wilk[2], Paul M. G. C

ARTICLES
PUBLISHED ONLINE: 25 MARCH 2012 | DOI: 10.1038/NCHEM.1302

nature chemistry

Electronic coherence lineshapes reveal hidden excitonic correlations in photosynthetic

ARTICLES
PUBLISHED ONLINE: 12 JANUARY 2014 | DOI: 10.1038/NCHEM.1834

nature chemistry

Two-dimensional spectroscopy of a molecular dimer unveils the effects of vibronic coupling on exciton coherences

Alexei Halpin[1], Philip J. M. Johnson[1], Roel Tempelaar[2], R. Scott Murphy[3], Jasper Knoester[2], Thomas L. C. Jansen[2] and R. J. Dwayne Miller[1,4]*

Evidence for wavelike ener quantum coherence in phot

Gregory S. Engel[1,2], Tessa R. Calhoun[1,2], Elizabeth L. Read
Yuan-Chung Cheng[1,2], Robert E. Blankenship[3,4] & Graham

Received 21 Jan 2015 | Accepted 4 Jun 2015 | Published 9 Jul 2015

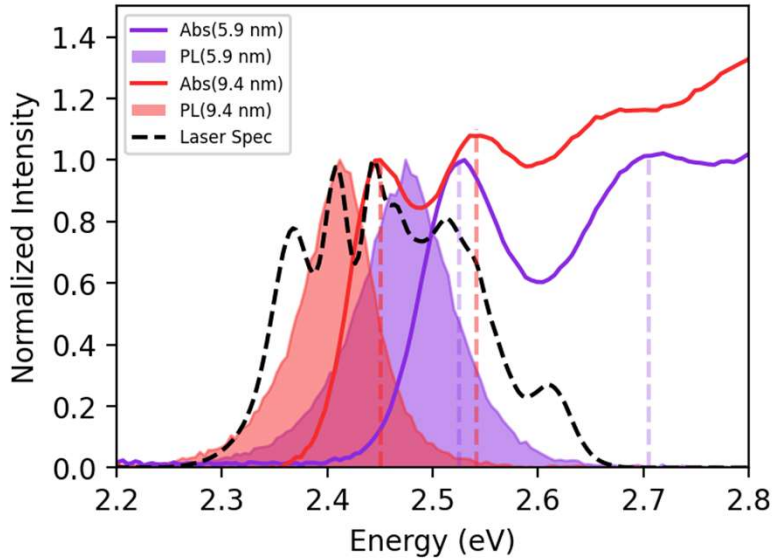
DOI: 10.1038/ncomms8755 OPEN

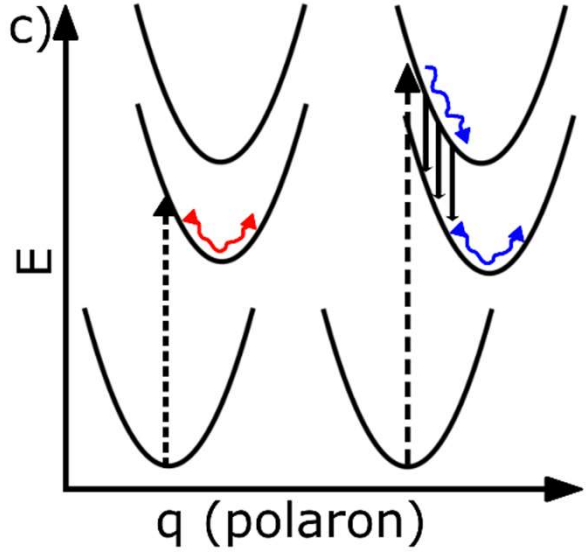
Vibronic origin of long-lived coherence in an artificial molecular light harvester

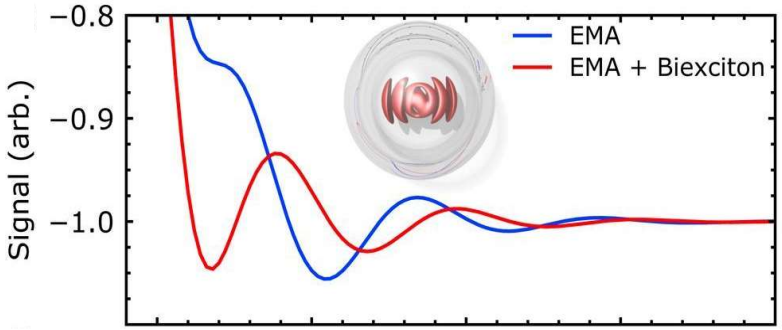
James Lim[1,*], David Paleček[2,3,*], Felipe Caycedo-Soler[1], Craig N. Lincoln[4], Javier Prior[5], Hans von Berlepsch[6], Susana F. Huelga[1], Martin B. Plenio[1], Donatas Zigmantas[2] & Jürgen Hauer[4]

lexes has spurred a
osynthesis. Vibronic
beatings. However,
unds are needed to
solvated molecular
ugh analysis of the
coherence. We find
bination of dynamic
nic dephasing time.

Quantum beats: electronic or vibronic?







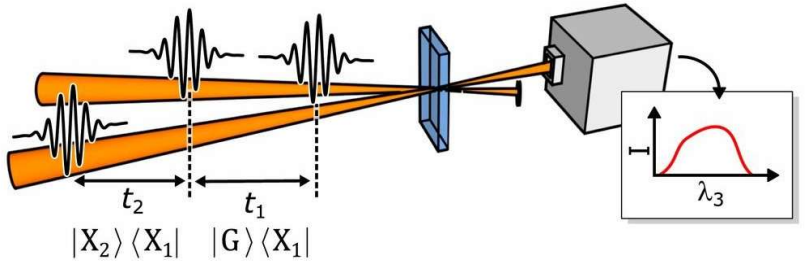
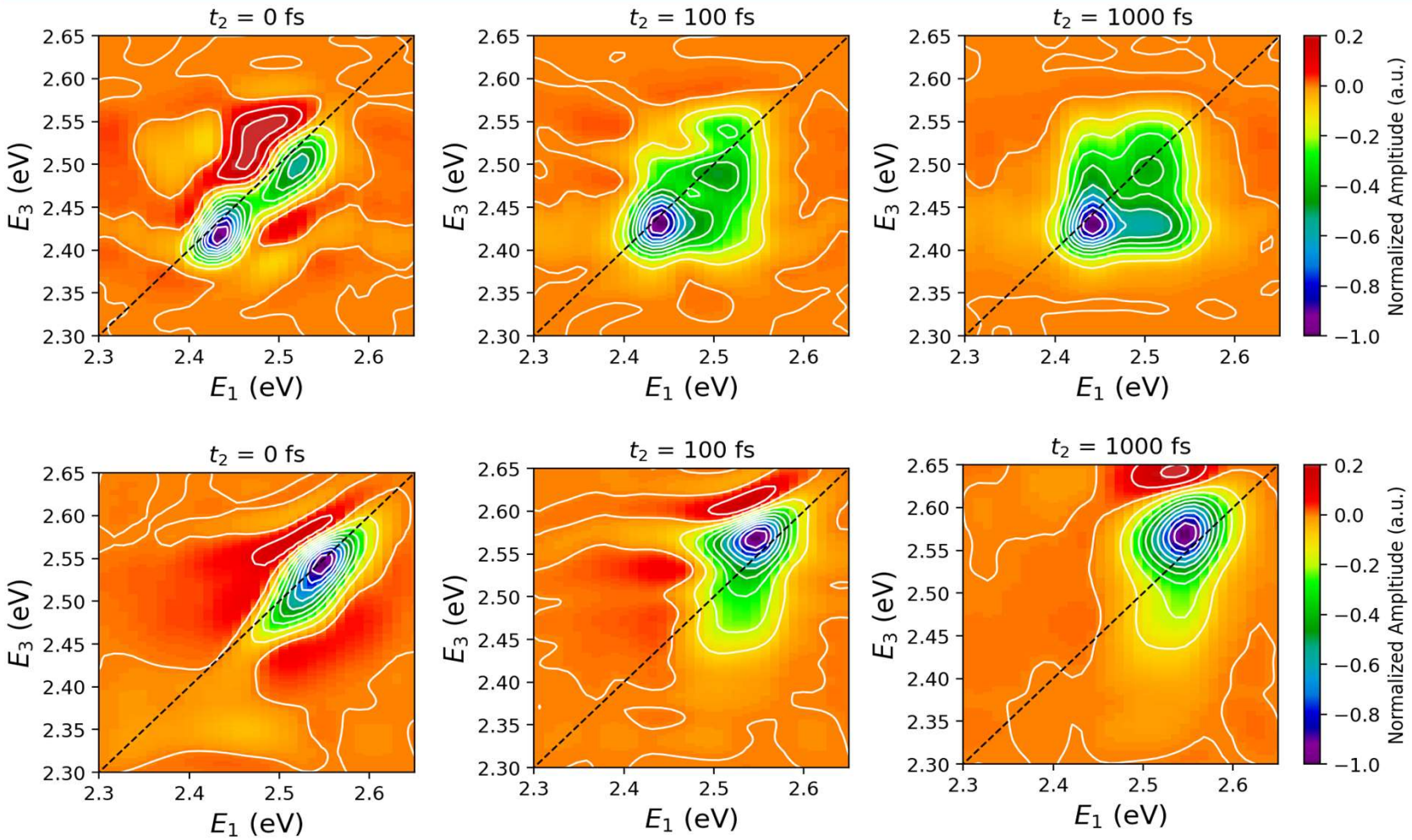


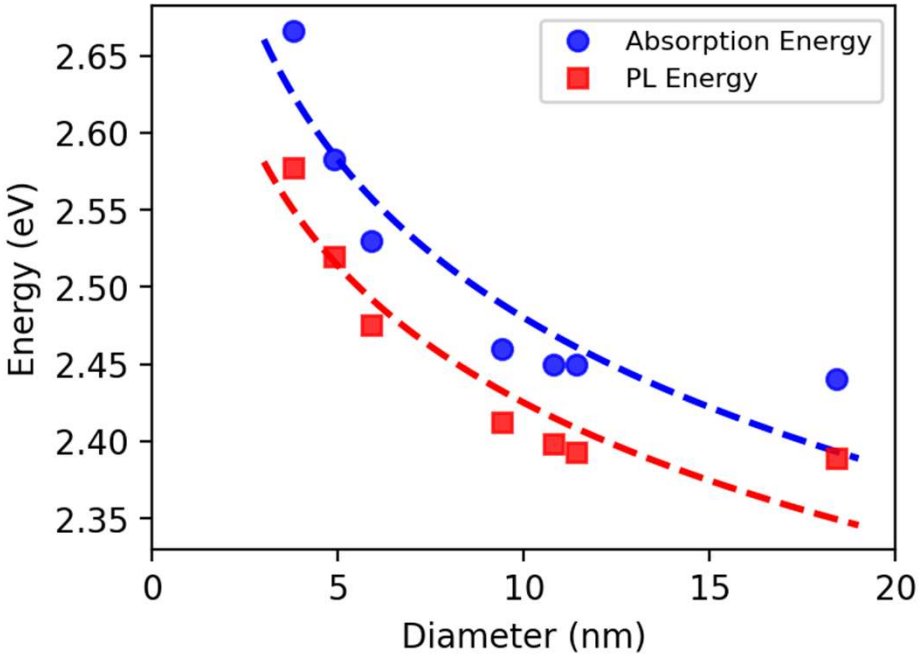
Fig 2

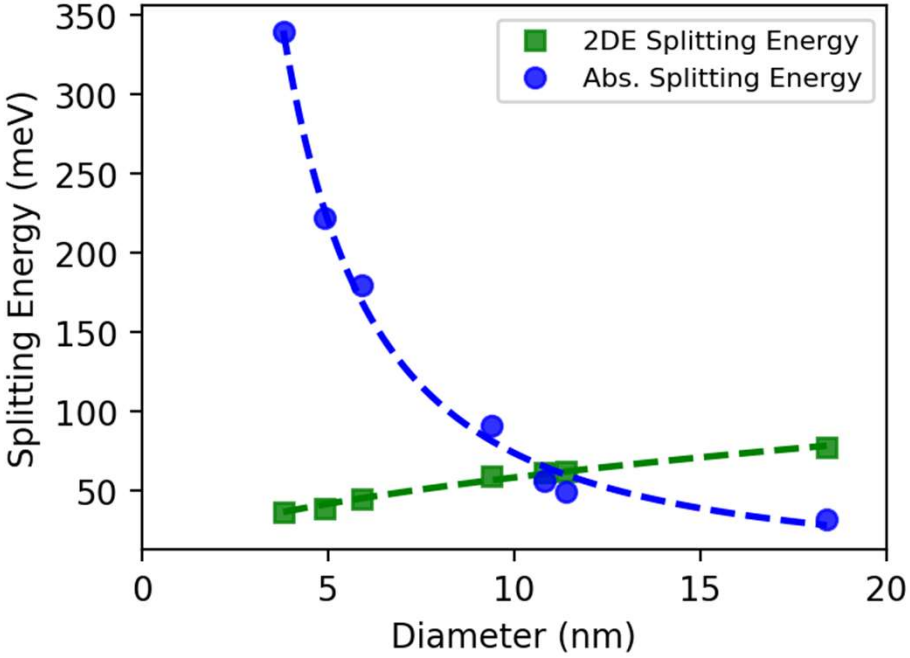
a)

Quantum beats: electronic or vibronic?

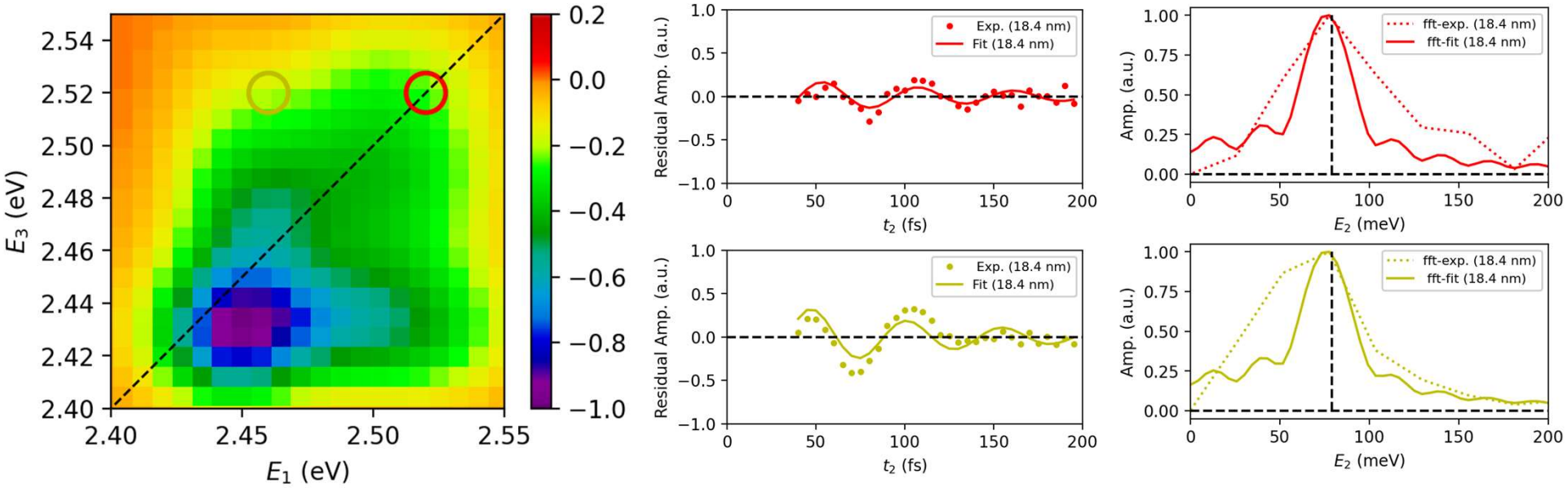


Quantum beats: electronic or vibronic?

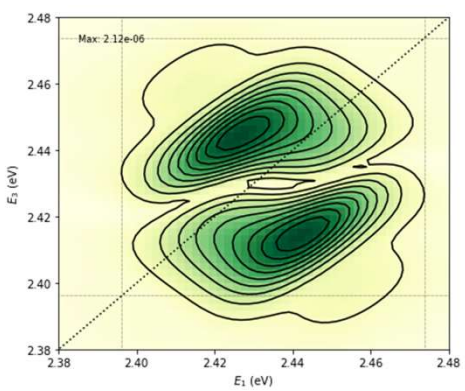


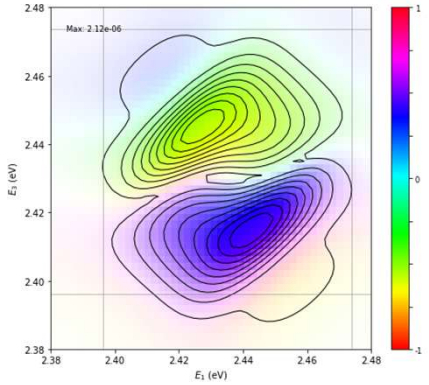


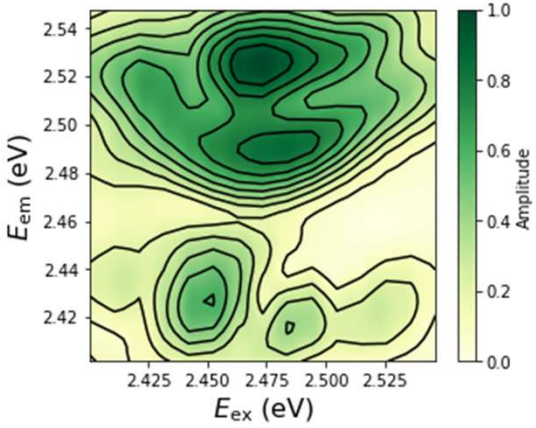
Quantum beats: electronic or vibronic?

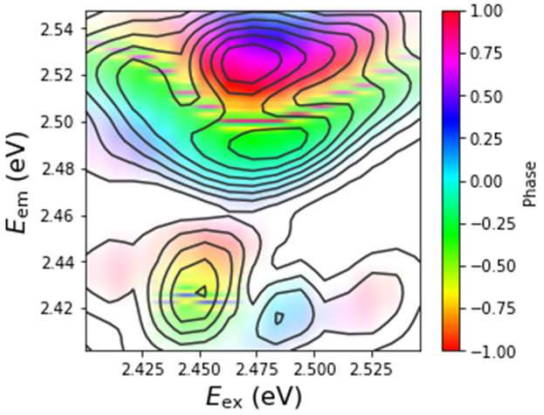


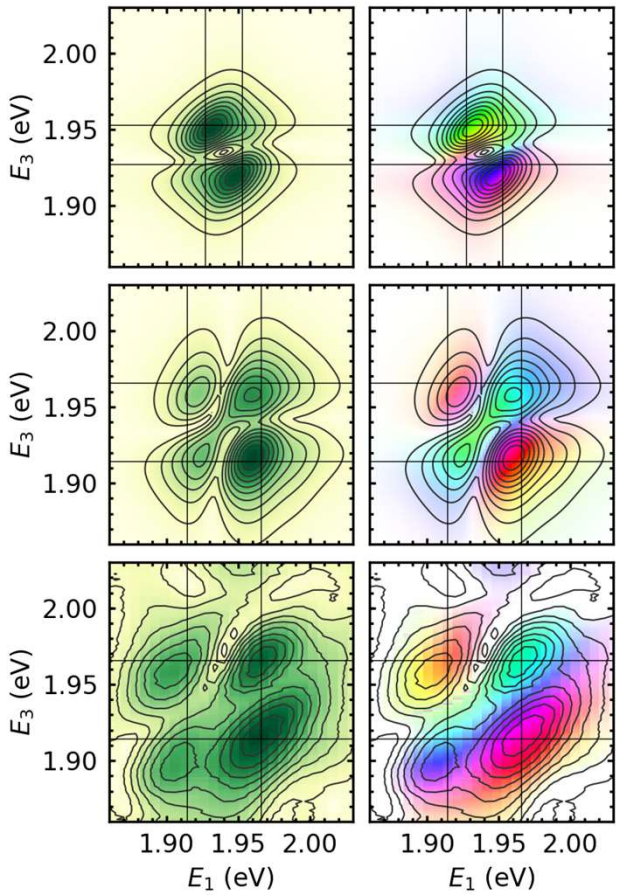
Quantum beats: electronic or vibronic?



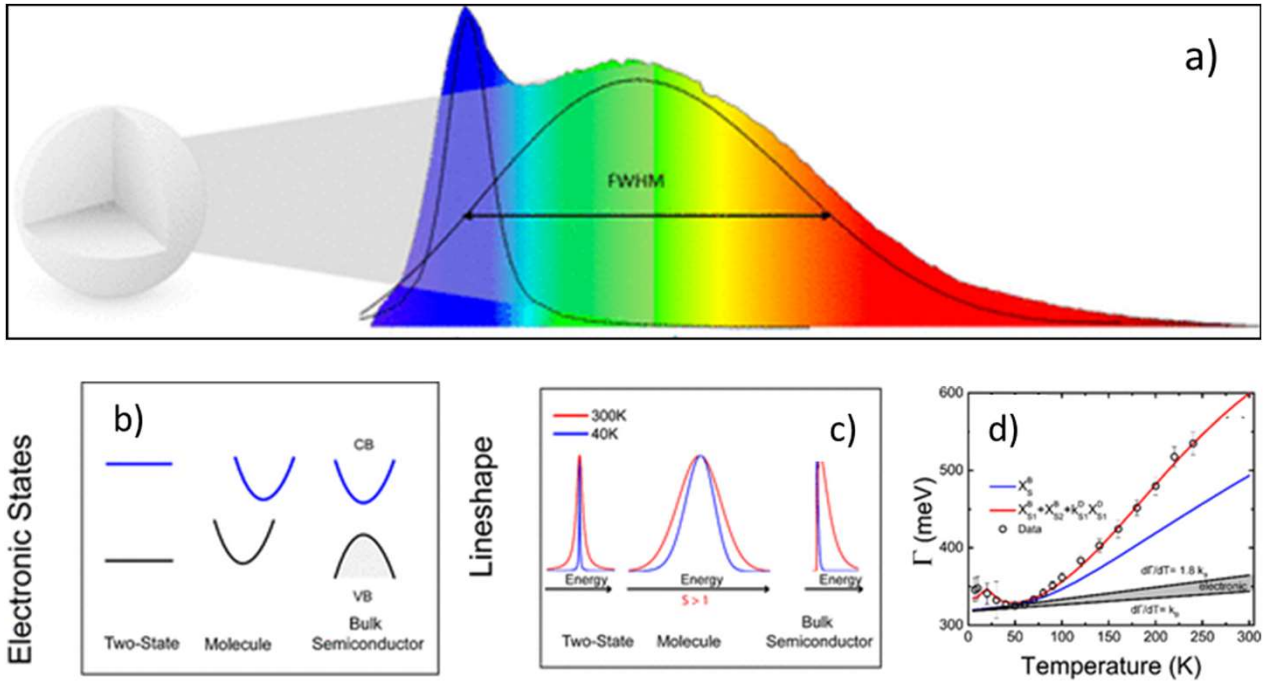




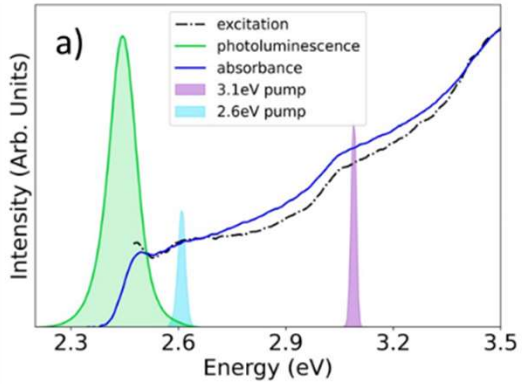


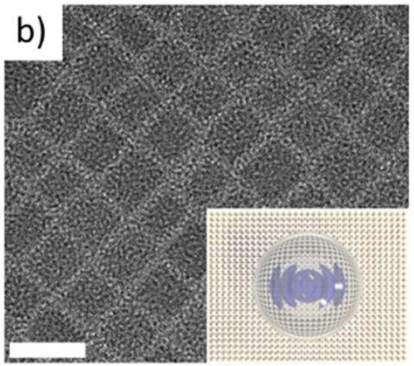


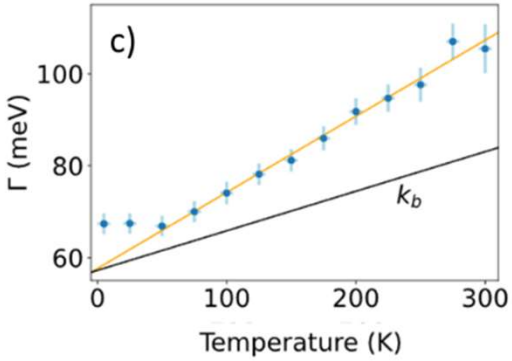
Ultrafast Photoluminescence Spectroscopy Reveals the Excitonics of Light Emission from Metal Halide Perovskite Nanocrystals

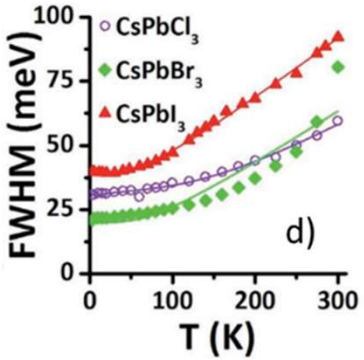


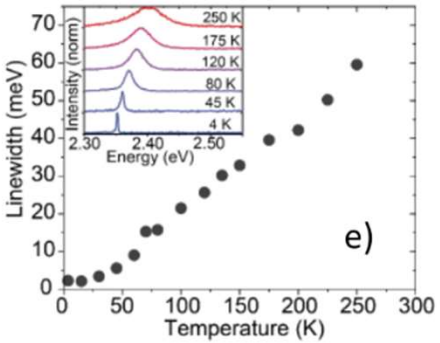
Steady-state spectroscopic characterization of light emission in metal-halide perovskite nanocrystals.

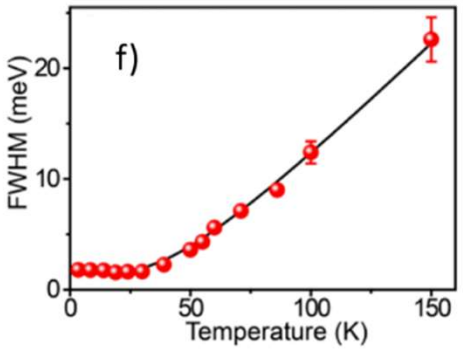




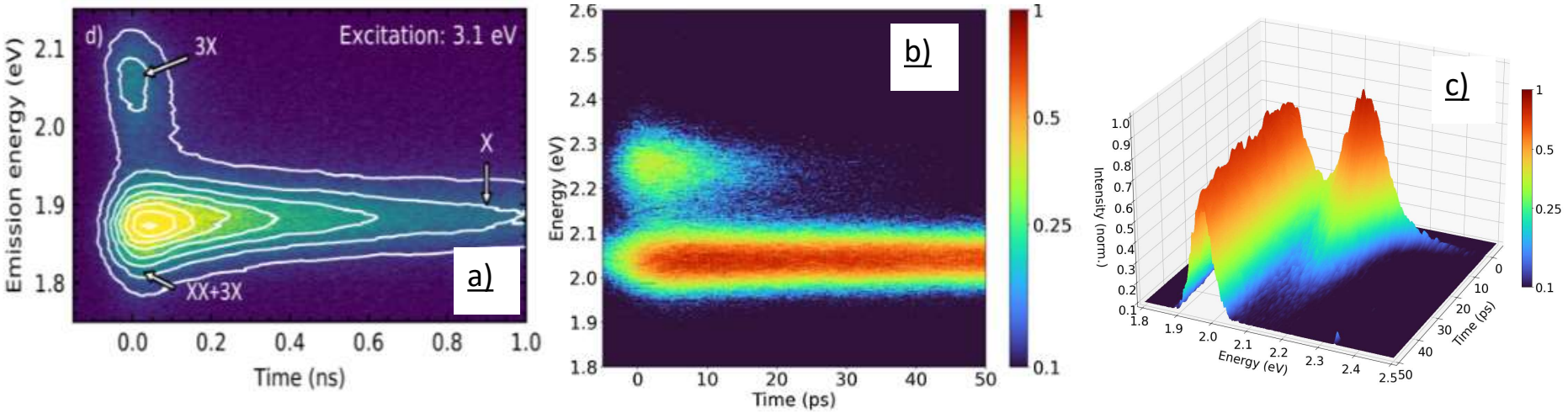








Improving from 100 ps to 3 ps time resolution enables observation of spectral dynamics and moving from kinetics to dynamics



Kinetics vs Dynamics? Words matter!

THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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A Brief Discussion of Chemical Kinetics versus Chemical Dynamics

Patanjali Kambhampati*

Cite This: *J. Phys. Chem. Lett.* 2023, 14, 2996–2999 Read Online

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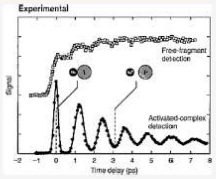
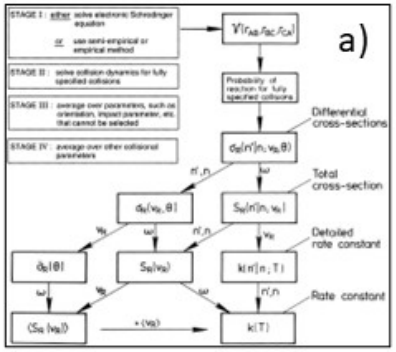
ABSTRACT: Chemical kinetics and chemical dynamics are distinct but related topics. They arise again in contemporary physical chemistry often in terms of charge carrier processes in new materials which interconvert light and electrical energy on a distribution of time scales. With this recent rise in the application of concepts in kinetics and dynamics to new problems, there has also arisen confusion about the differences and connections between the two. Here, we briefly review the relationship between kinetics and dynamics in chemical processes, with particular emphasis on the photochemical and photophysical response of a system.

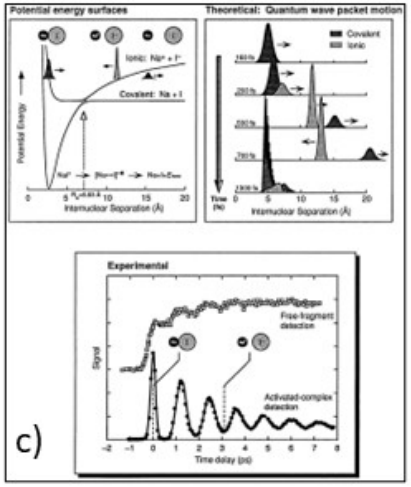


Chemical kinetics and dynamics have long been a central area of research in physical chemistry. In undergraduate courses, students are taught basic concepts in kinetics, and advanced students have studied dynamics. However, physical chemistry is always in flux, pun intended. Hence, we must be aware of 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.

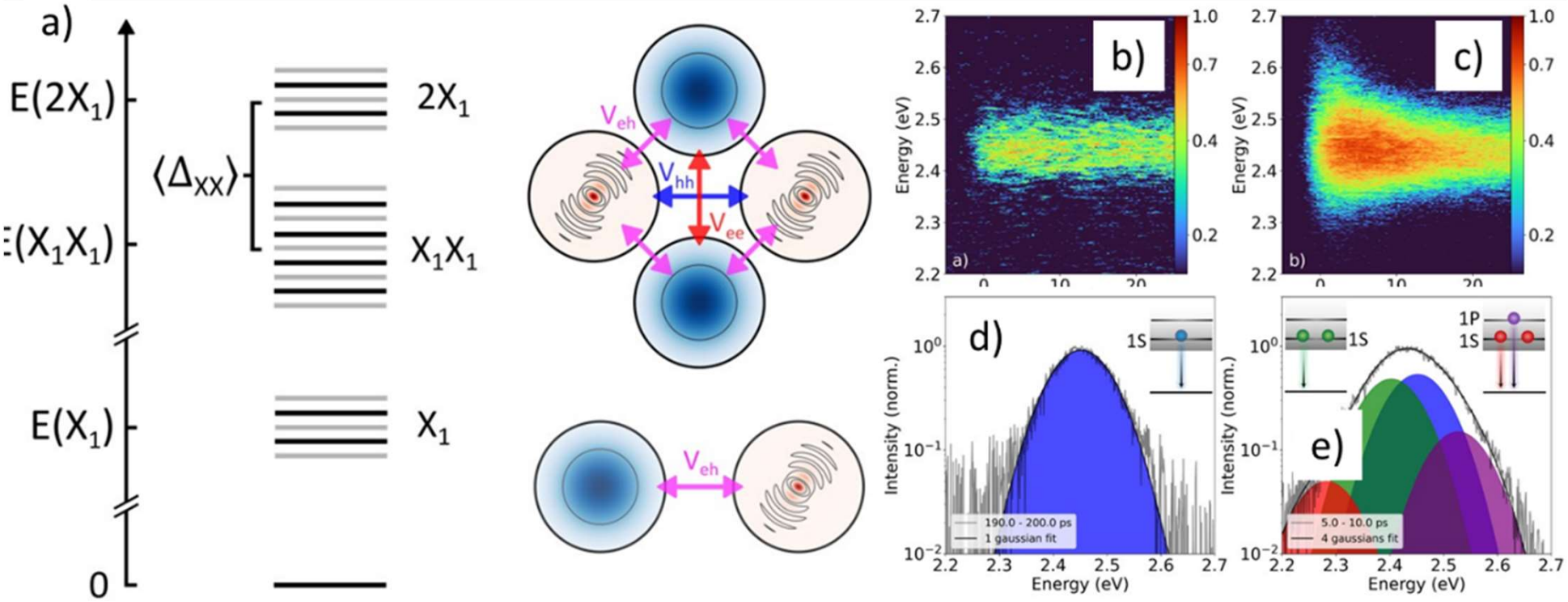
Historically, physical chemists transitioned (pun intended again) from studies of chemical kinetics to chemical dynamics with the advent of molecular beams in gas phase physical

As much of the foundational work on chemical kinetics and dynamics had been explored in the 20th century and are now the topic of textbooks, the current Century brings to us explorations in complex systems in the condensed phase, evolving in time, on a distribution of time scales.



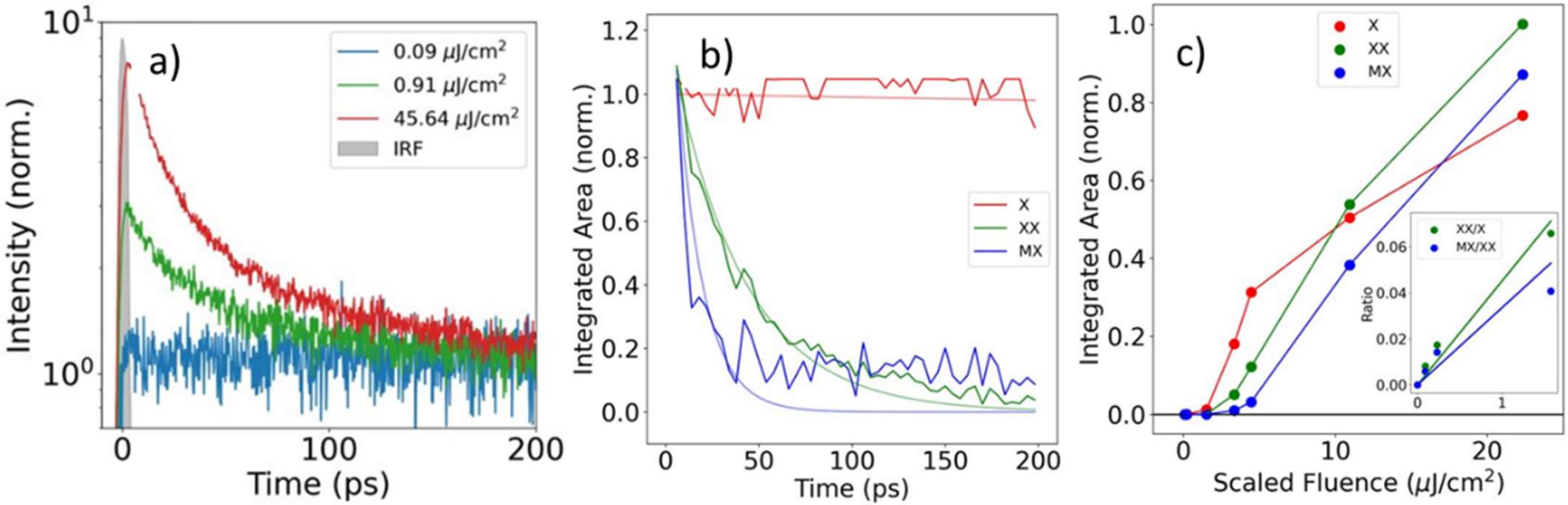


Nanocrystals and quantum dots have electronic structure due to excitons (X) and multiexcitons (MX), of which the biexciton (XX) is the simplest.



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
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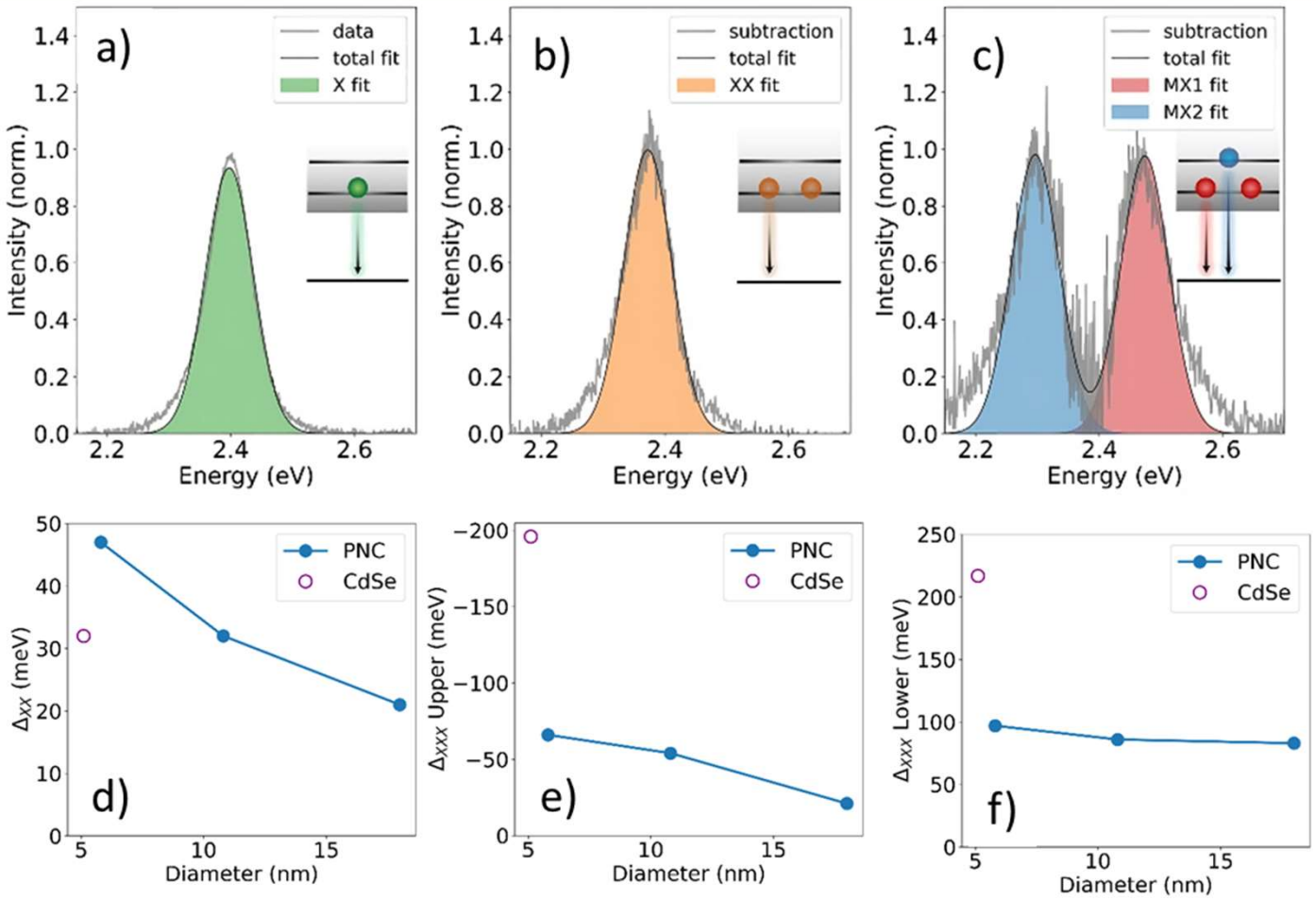
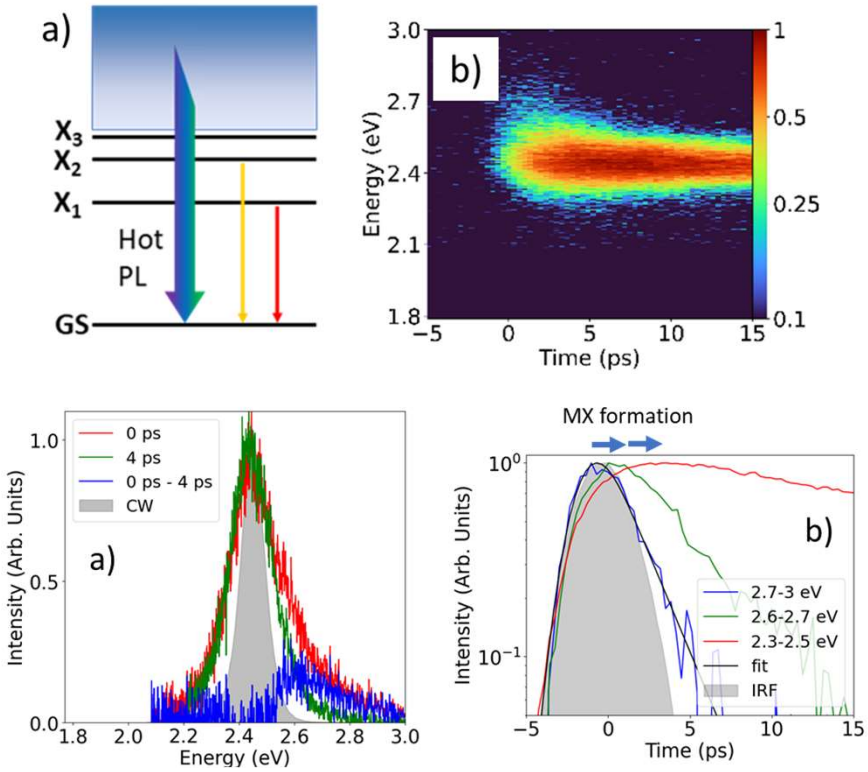
Spectrally and temporally resolving MX from X.



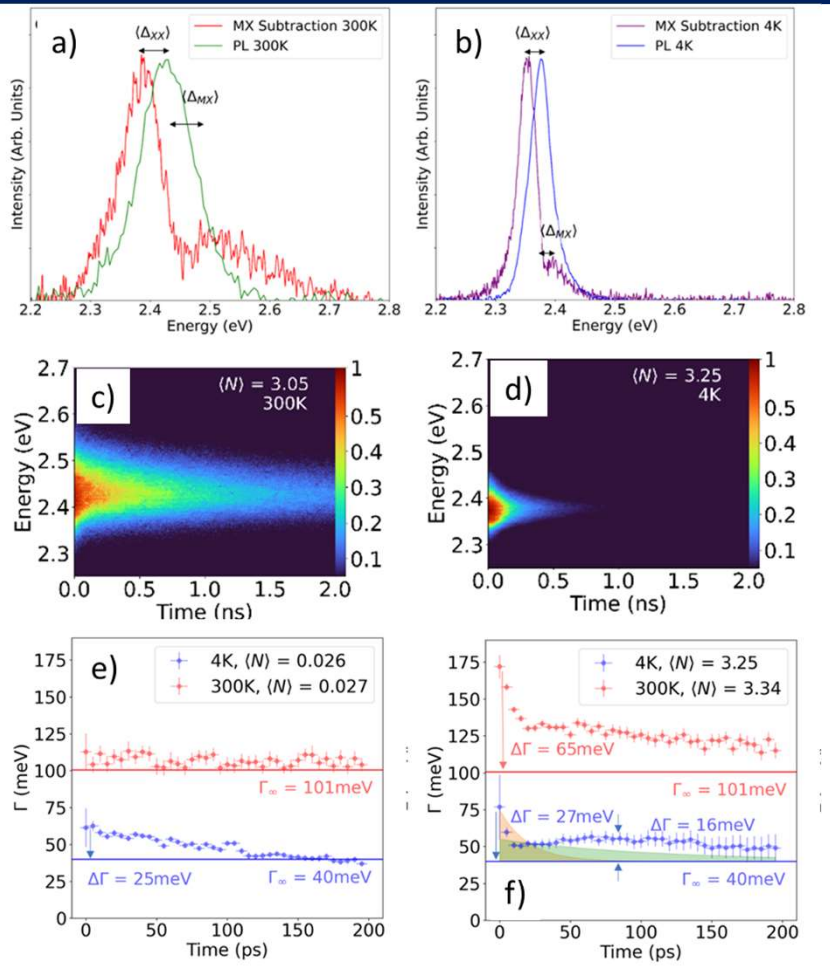
[Enhancing Multiexcitonic Emission in Metal-Halide Perovskites by Quantum Confinement]
ACS nano 17 (24), 24910-24918

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

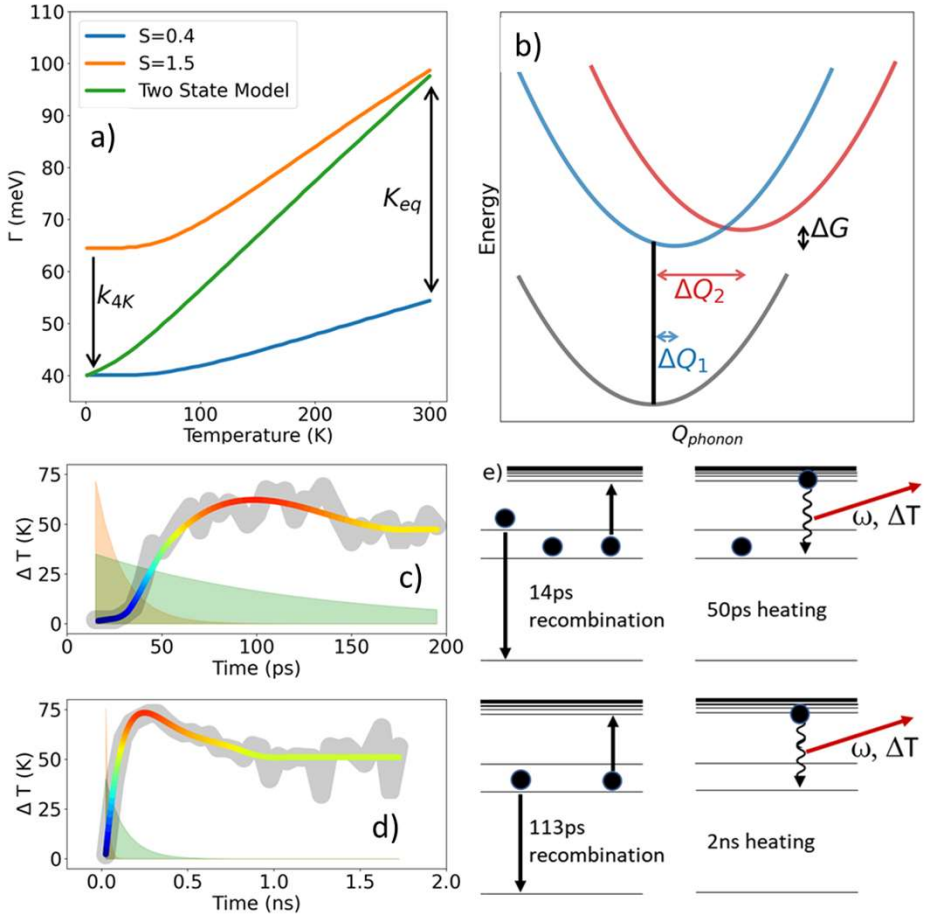
Spectral dynamics of PL linewidth and their temperature dependence reveals rich spectroscopy due to a complex cascade of processes.



Light Emission from $CsPbBr_3$ Metal Halide Perovskite Nanocrystals Arises from Dual Emitting States with Distinct Lattice Couplings

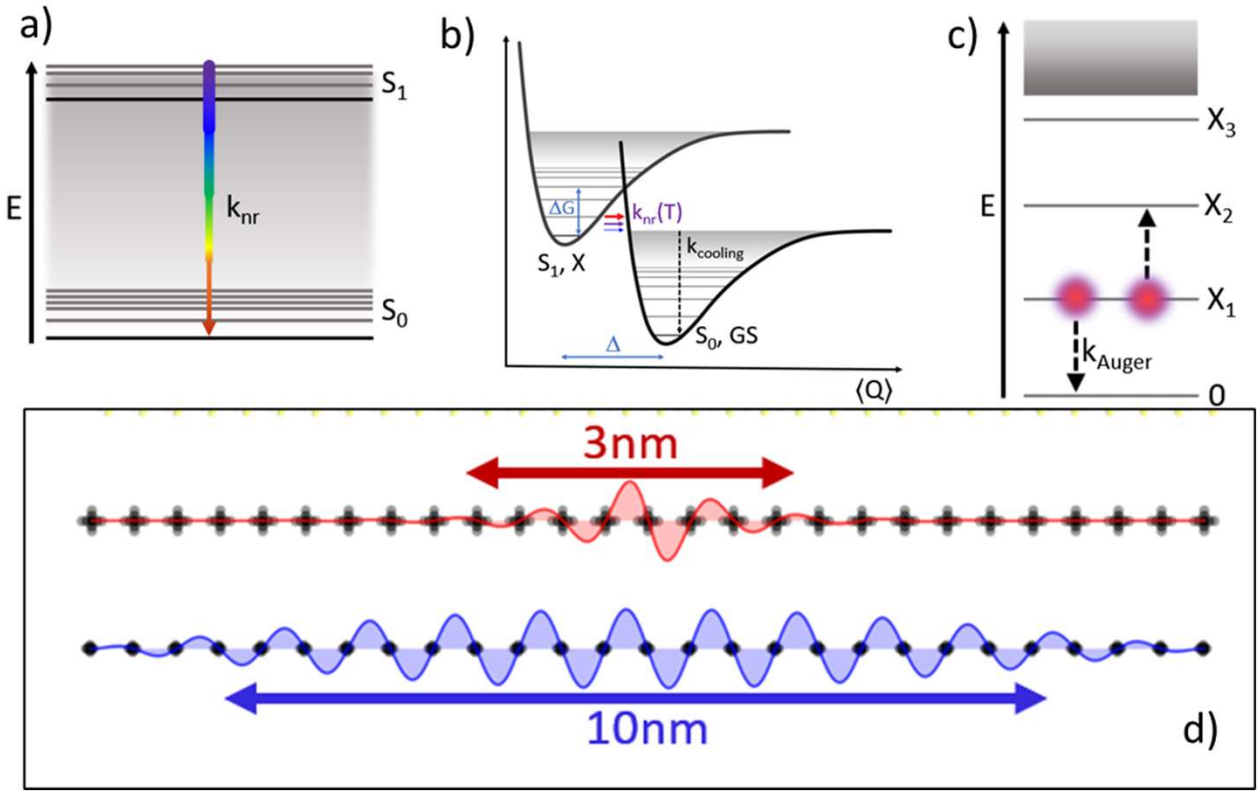
Nano Letters 23 (23), 11330-11336

The spectral dynamics of the linewidth trajectories arises from a delicate interplay of kinetics and thermodynamics.



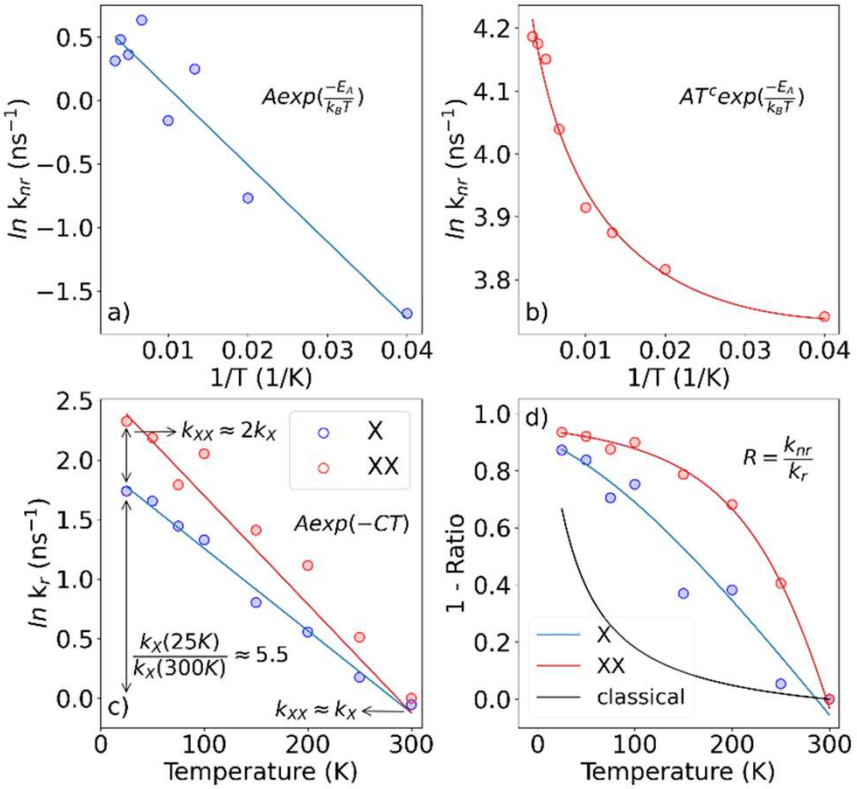
[Light Emission from $CsPbBr_3$ Metal Halide Perovskite Nanocrystals Arises from Dual Emitting States with Distinct Lattice Couplings]
Nano Letters 23 (23), 11330-11336

Deconstructing PL into radiative and non-radiative recombination paths and the implications upon spatial delocalization.



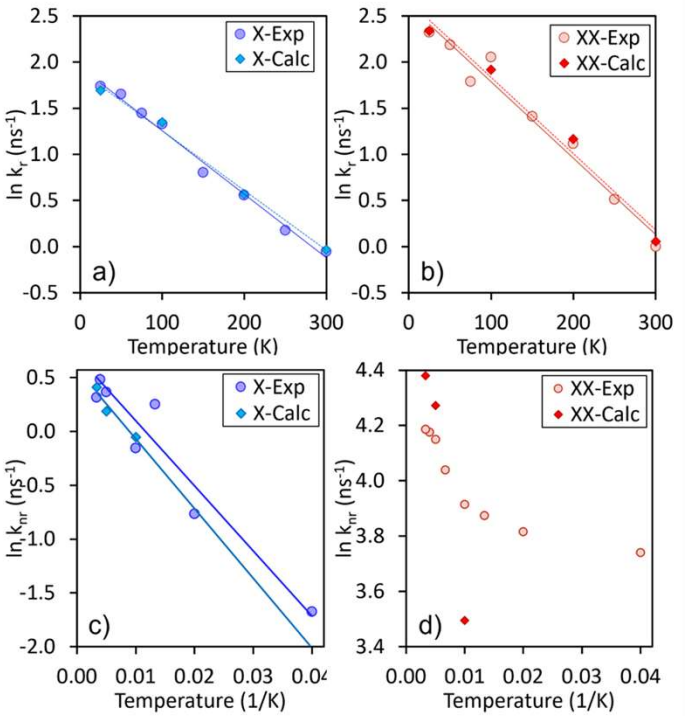
Excitonic Quantum Coherence in Light Emission from $CsPbBr_3$ Metal-Halide Perovskite Nanocrystals
Nano Letters 24 (1), 61-66

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

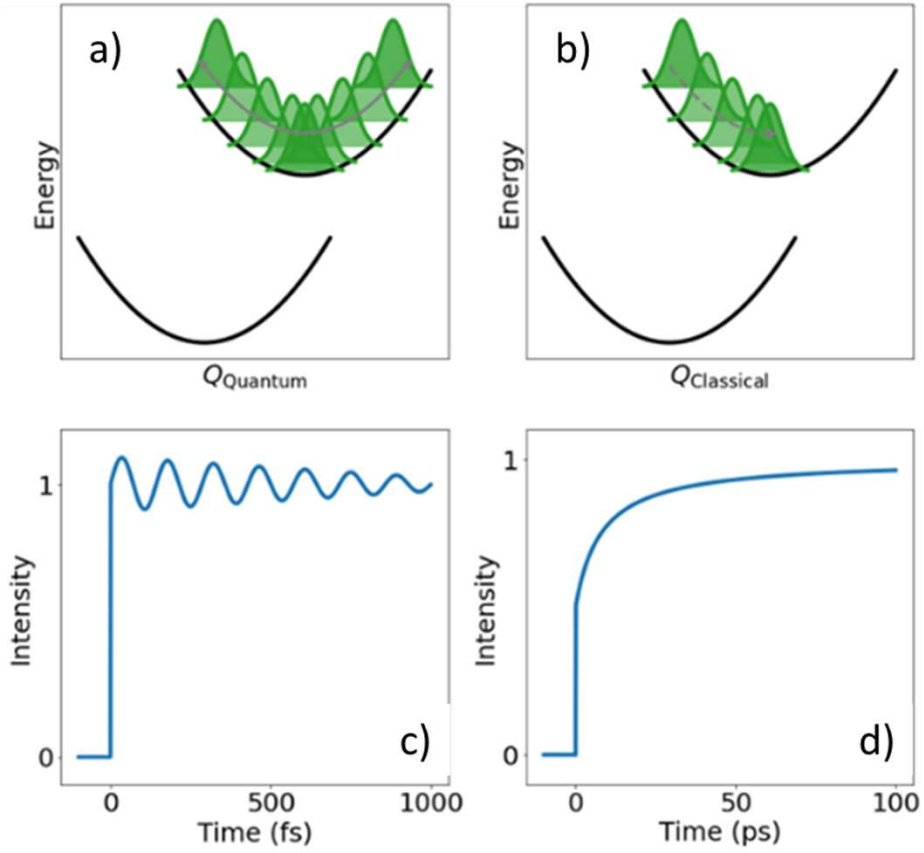
AIMD theory (O Prezhdo, USC) reproduces experiment quantitatively



Excitonic Quantum Coherence in Light Emission from $CsPbBr_3$ Metal-Halide Perovskite Nanocrystals

Nano Letters 24 (1), 61-66

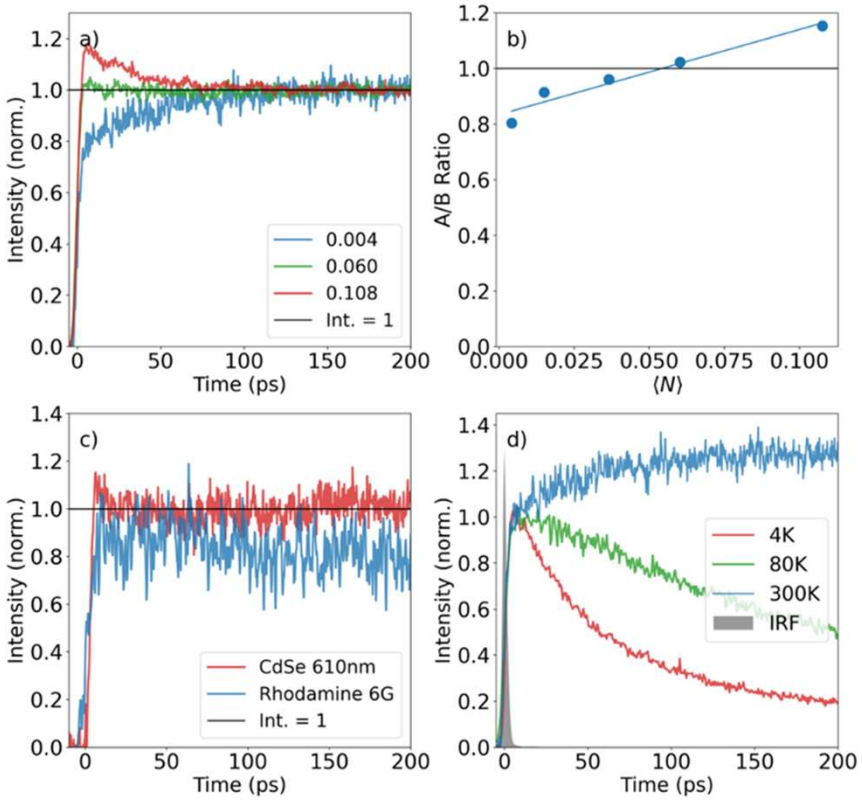
Ultrafast measurements enable moving from measurements of kinetics to dynamics.



Breaking the Condon Approximation for Light Emission from Metal Halide Perovskite Nanocrystals

The Journal of Physical Chemistry Letters 14 (50), 11281-11285

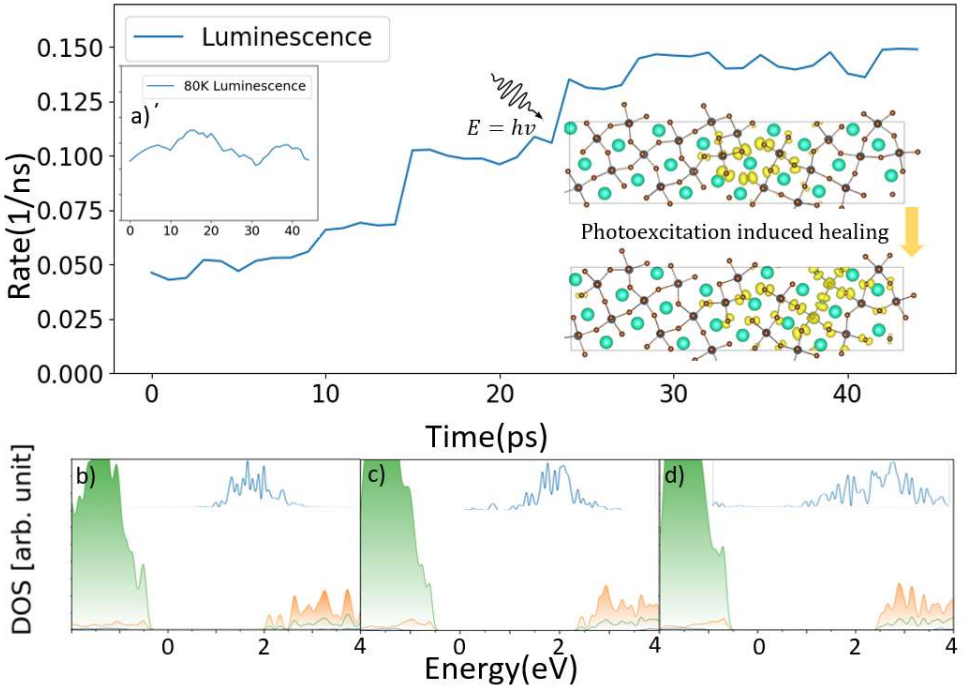
Experimental observation of t-PL dynamics.



[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