北京大學
PEKING UNIVERSITY

二维卤素钙钛矿ns²孤对电子效应对光物理性质的影响探究

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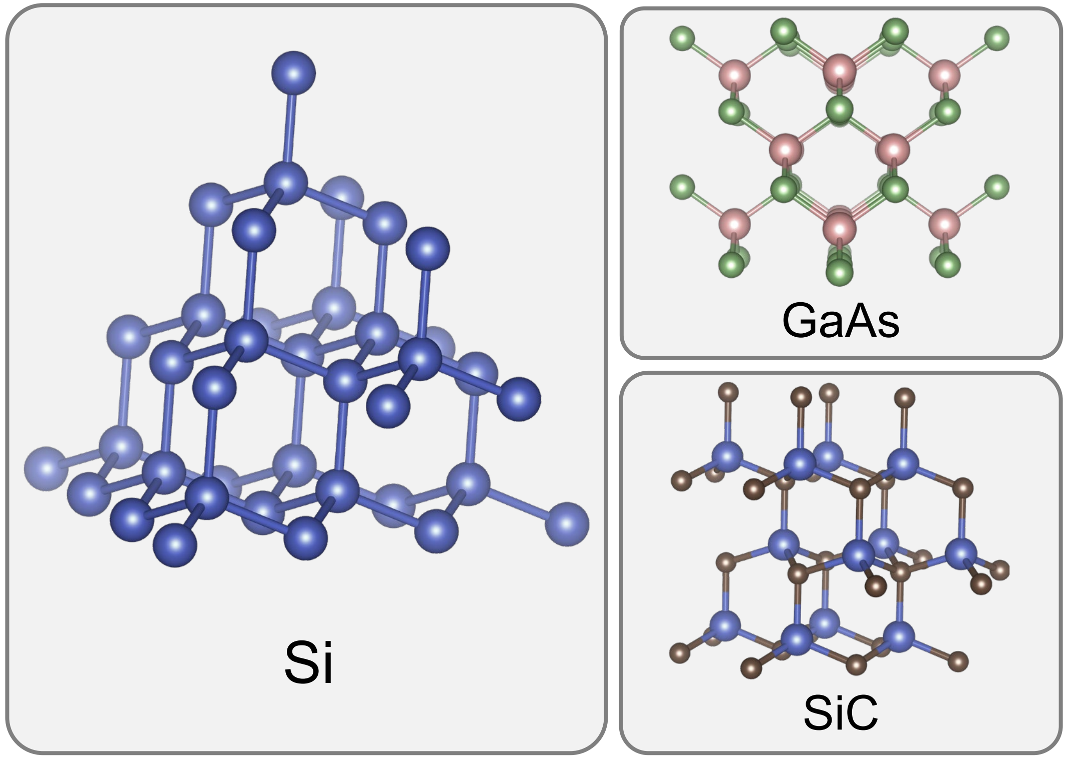
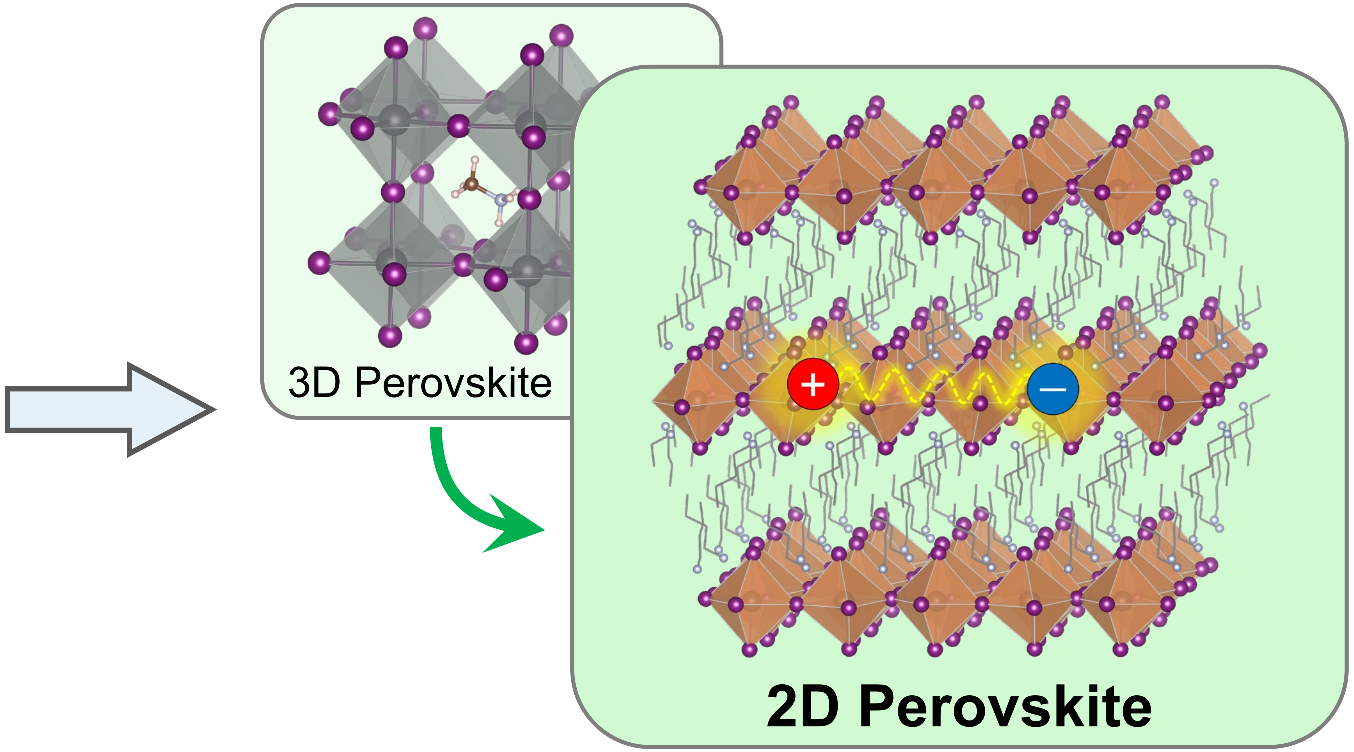
2023.09.16

Contents

1.1 Why 2D Halide Perovskite?





Inorganic Semiconductors:

- Rigid;
- Static;
- Harmonic lattice;

Well-Studied

Hybrid Halide Perovskites:

- Soft;
- Dynamic;
- Strong anharmonicity;

New Properties of Anharmonic SCs?

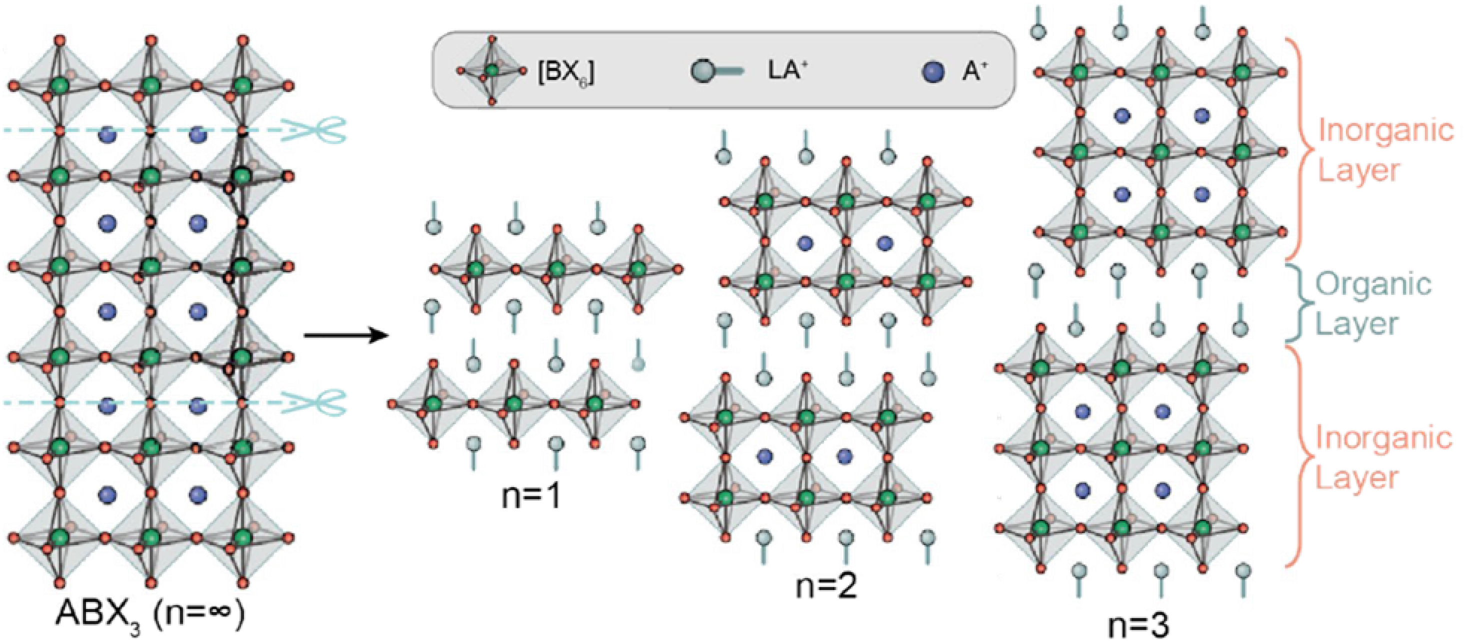
1.2 2D Halide Perovskites

Formula

$(LA)_2(A)_{n-1}B_nX_{3n+1}$

for n=1:

$(LA)_2BX_4$ $(B^{2+} = \mathbf{Pb^{2+}}, Sn^{2+}, Ge^{2+}...)$



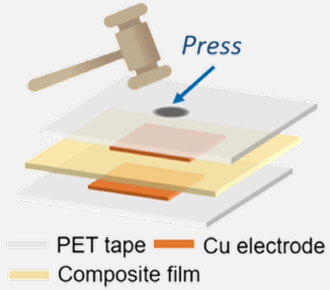
Crystal Structure

"Slicing 3D perovskite ABX_3 lattice"

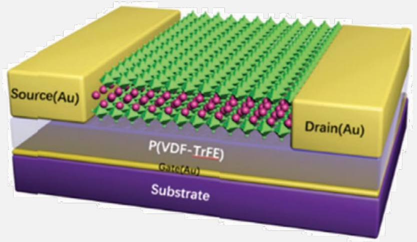
Various LA ==> **Great tunability**

Heterogeneity ==> **Nano-devices**

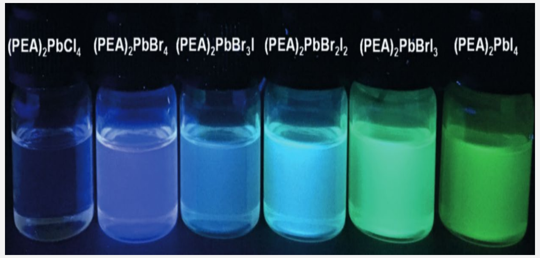
Layered structure ==> **Excitonic nature**



Ferroelectrics



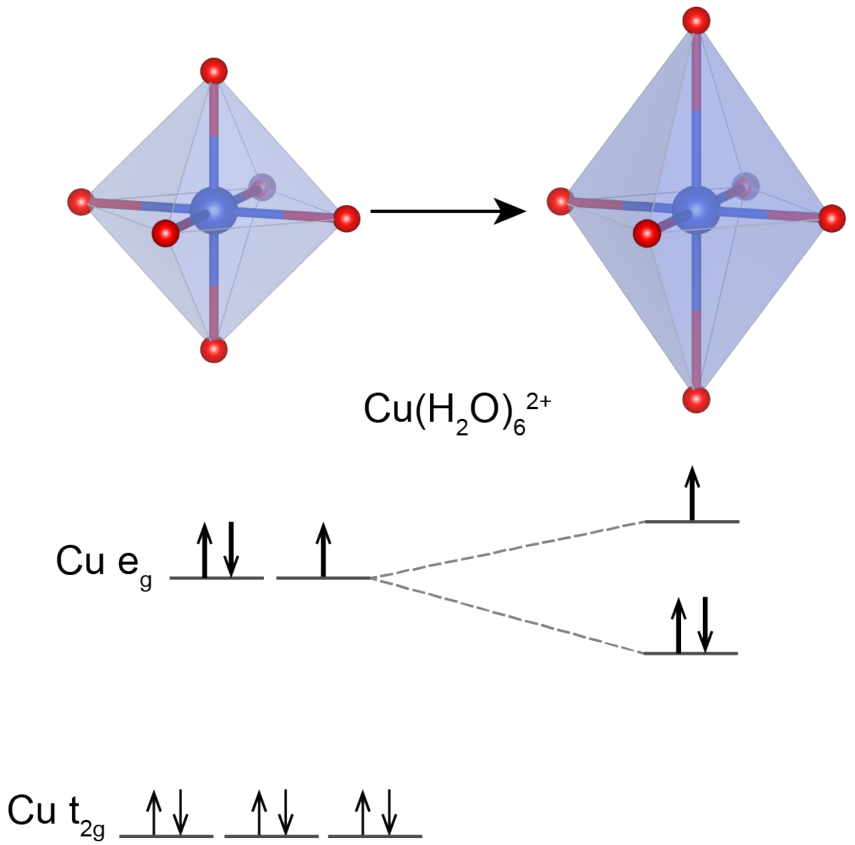
Nanoelectronics



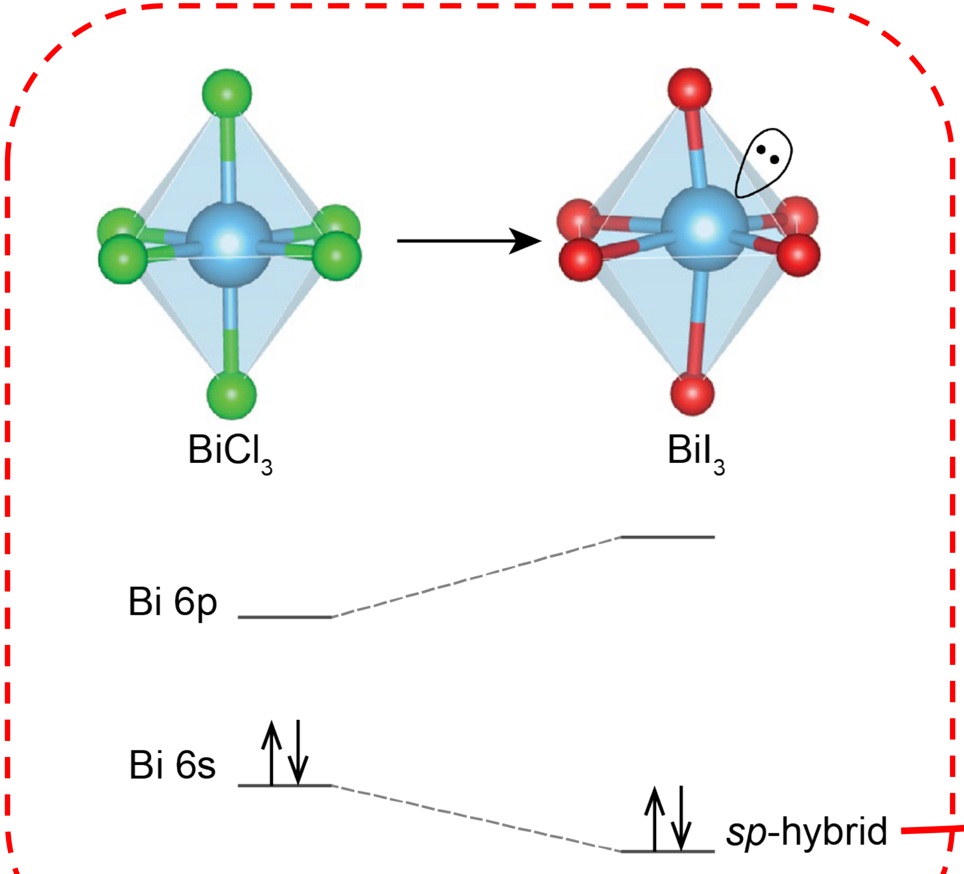
Light-emitters

1.3 ns^2 Lone Pair Effect (LPE)

Second-order Jahn-Teller (SOJT) Effect

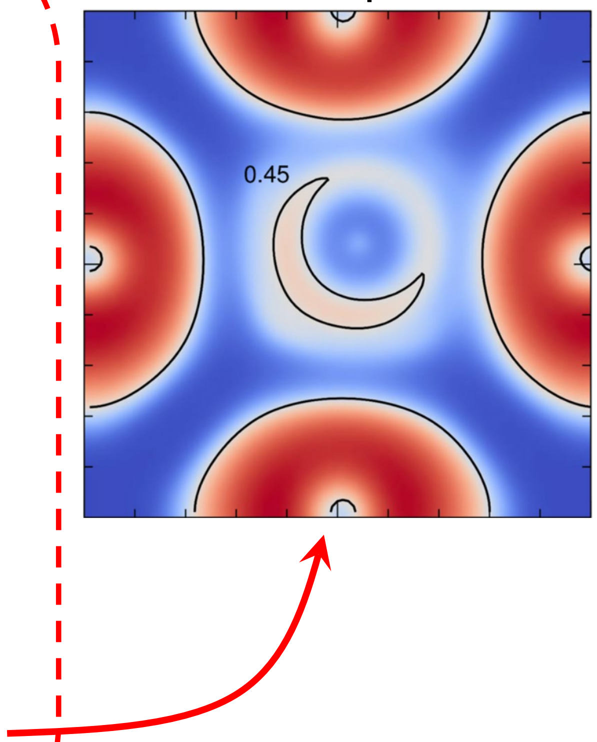


1st-order Jahn-Teller Effect



2nd-order Jahn-Teller Effect

ns^2 lone pair effect & off-center displacement



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Nat. Rev. Chem. **2021**, 5, 838. *JACS*, **2016**, 138, 11820.

1.3 ns^2 Lone Pair Effect (LPE)

Lattice Anharmonicity

Harmonic oscillator:

$$E_p = \frac{1}{2}kx^2 \text{ (Parabola)}$$

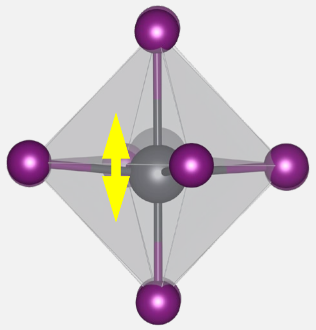
With ns^2 LPE:

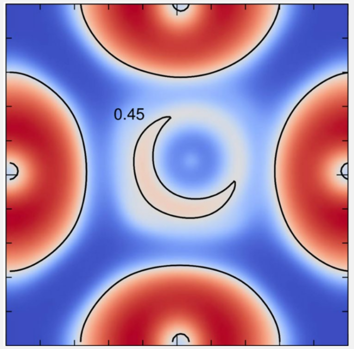
Double-well potential curve

=> Strong anharmonicity

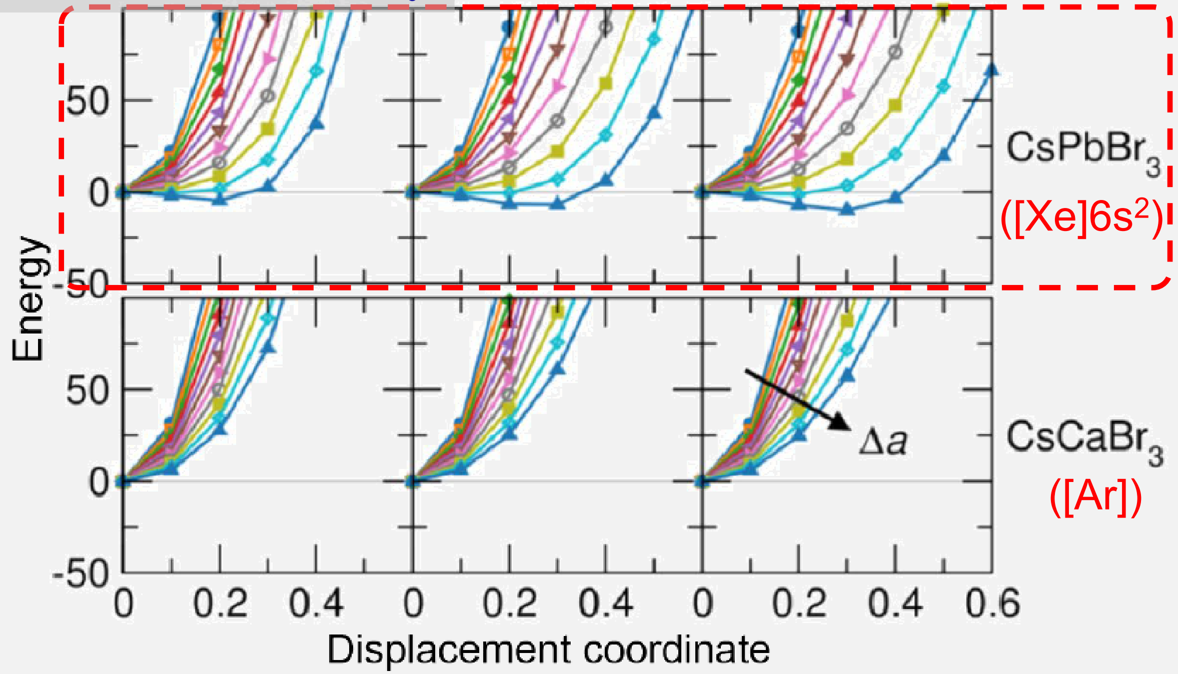
=> Exciton-phonon coupling ↑

Pb^{2+} $6s^2$ LPE

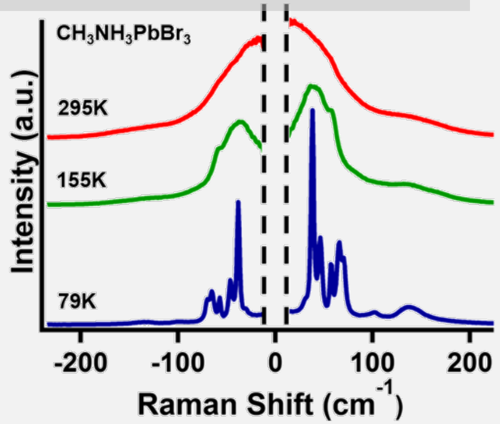


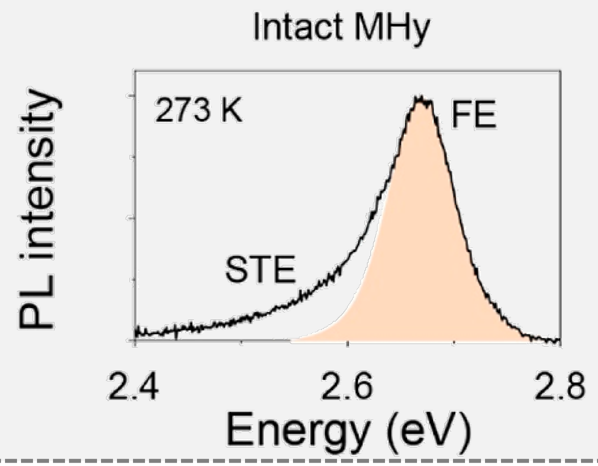


Lattice Anharmonicity



Exciton-Phonon Coupling





Nat. Rev. Chem. **2021**, 5, 838. *JACS*, **2016**, 138, 11820. *Phys. Rev. Lett.* **2017**, 118, 136001. *JACS*. **2022**, 144, 27, 12247

1.3 ns^2 Lone Pair Effect (LPE)

Effects on Excited States

Ground State:

$ns^2 \rightarrow (sp)^2$

$\Delta G = -2\Delta E_{LPE}$

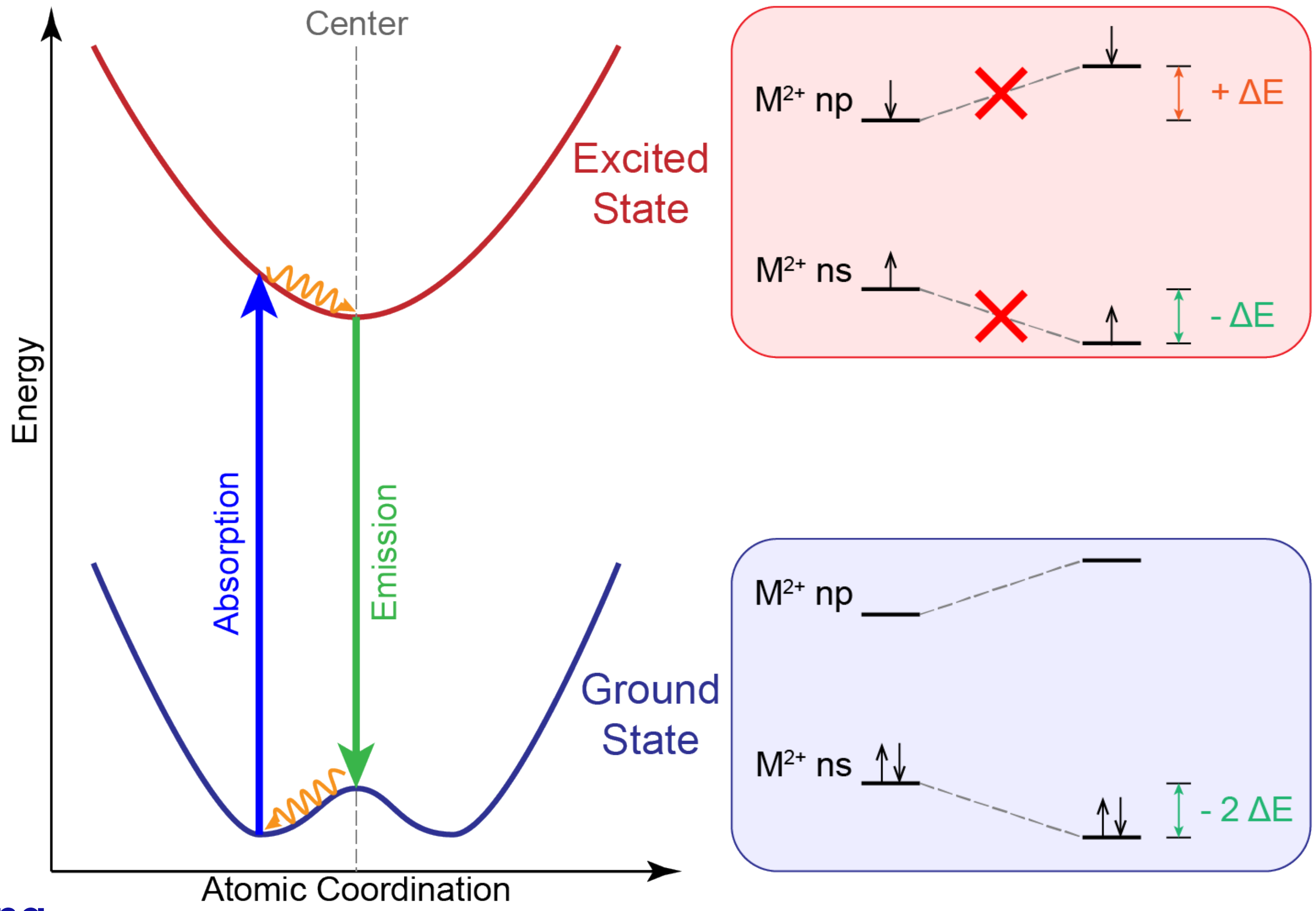
LPE active

Excited State:

$ns^1np^1 \rightarrow (sp)^1(sp^*)^1$

$\Delta G = 0$

LPE inactive



LPE enhances exciton-phonon coupling.

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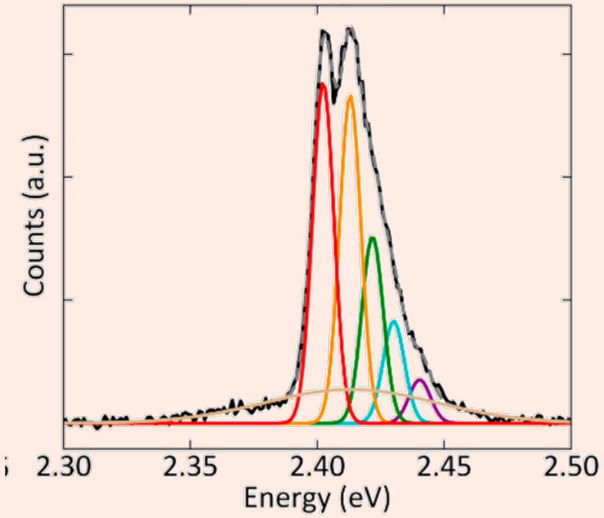
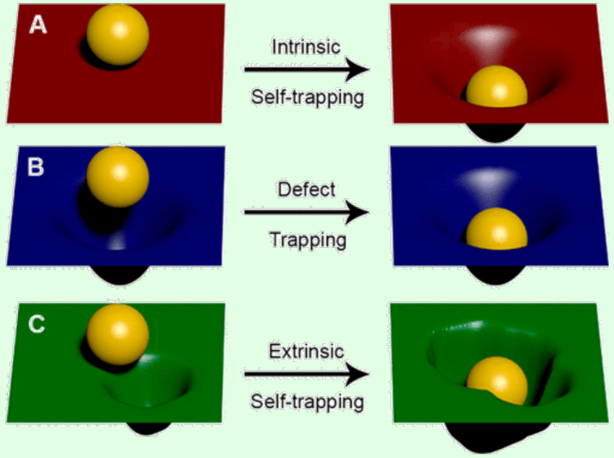
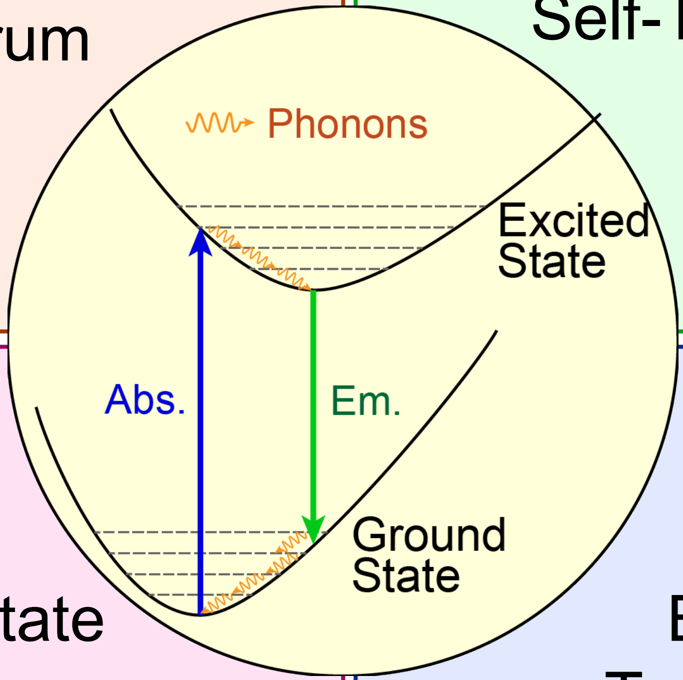
1.4 Exciton-Phonon Coupling (EPC)

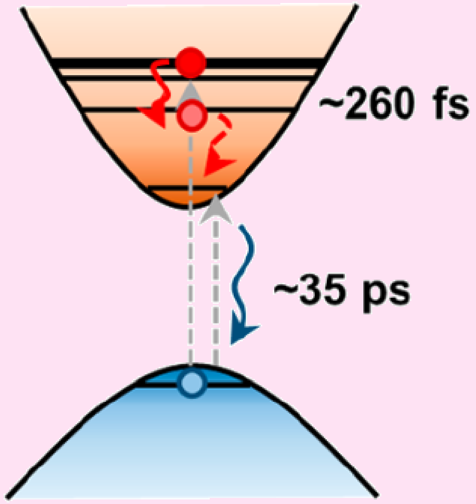


Emission Spectrum

Carrier Self-Trapping

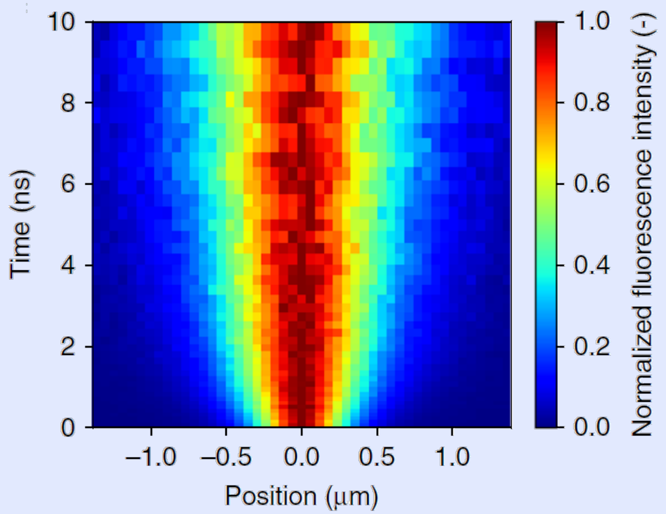






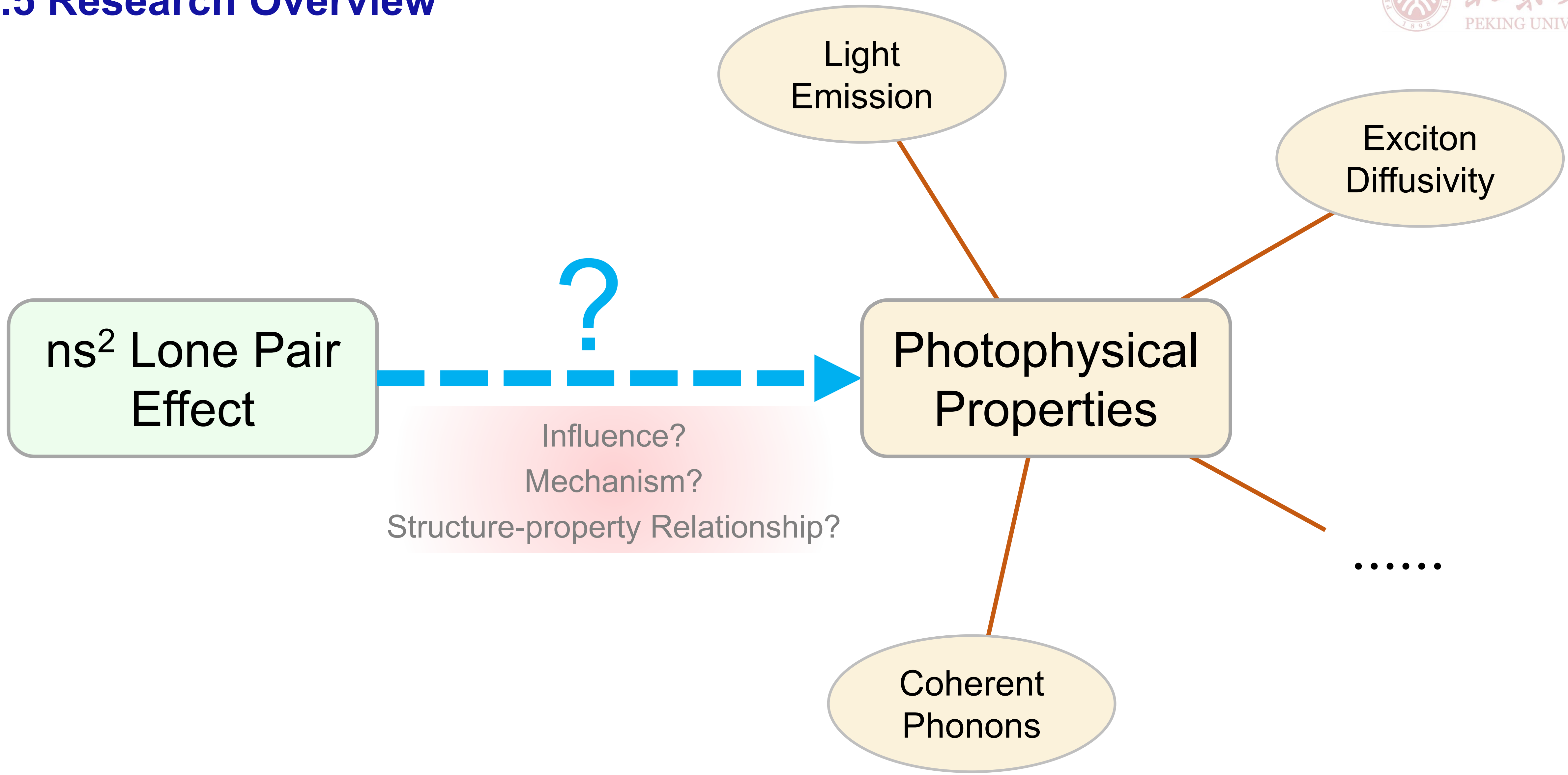
Excited State Dynamics

Exciton Transport



ACS Nano **2020**, 14, 3, 3621. *Acc. Chem. Res.* **2018**, 51, 3, 619. *Nat. Comm.* **2020**, 11, 2035. *ACS Nano* **2019**, 13, 11, 12621–12629

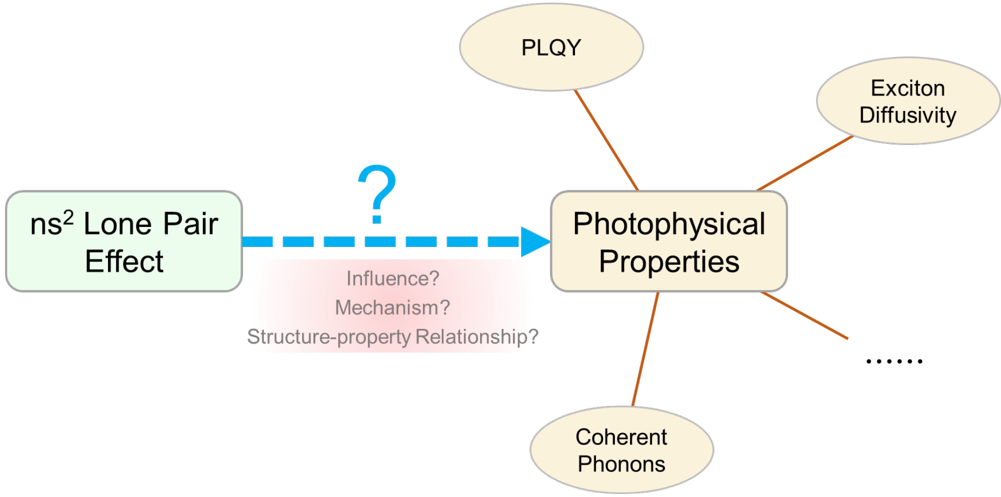
1.5 Research Overview



1.5 Research Overview

Part. 1: Origin of ns^2 LPE & tuning PLQY (**Done**)

- Large LA elongates Pb-I bond length and induces ns^2 LPE;
- ns^2 LPE enhances EPC and quenches PL;



Part. 2: ns^2 LPE tuning exciton diffusivity (**On-going**)

- ns^2 LPE enhances exciton scattering;
- Strong LPE will decrease exciton diffusivity (expected)

Part. 3: Excited-state properties upon ns^2 LPE phase transition (**Scheduled**)

- Use coherent phonon spectrum to evaluate EPC upon LPE transition.

Part. 2
Current Progress

LPE tuning structural distortion

LPE tuning PLQY

LPE tuning exciton diffusivity

2.1 Origin of ns^2 LPE

LA Size

- Undersized LA --> Octahedral tilting

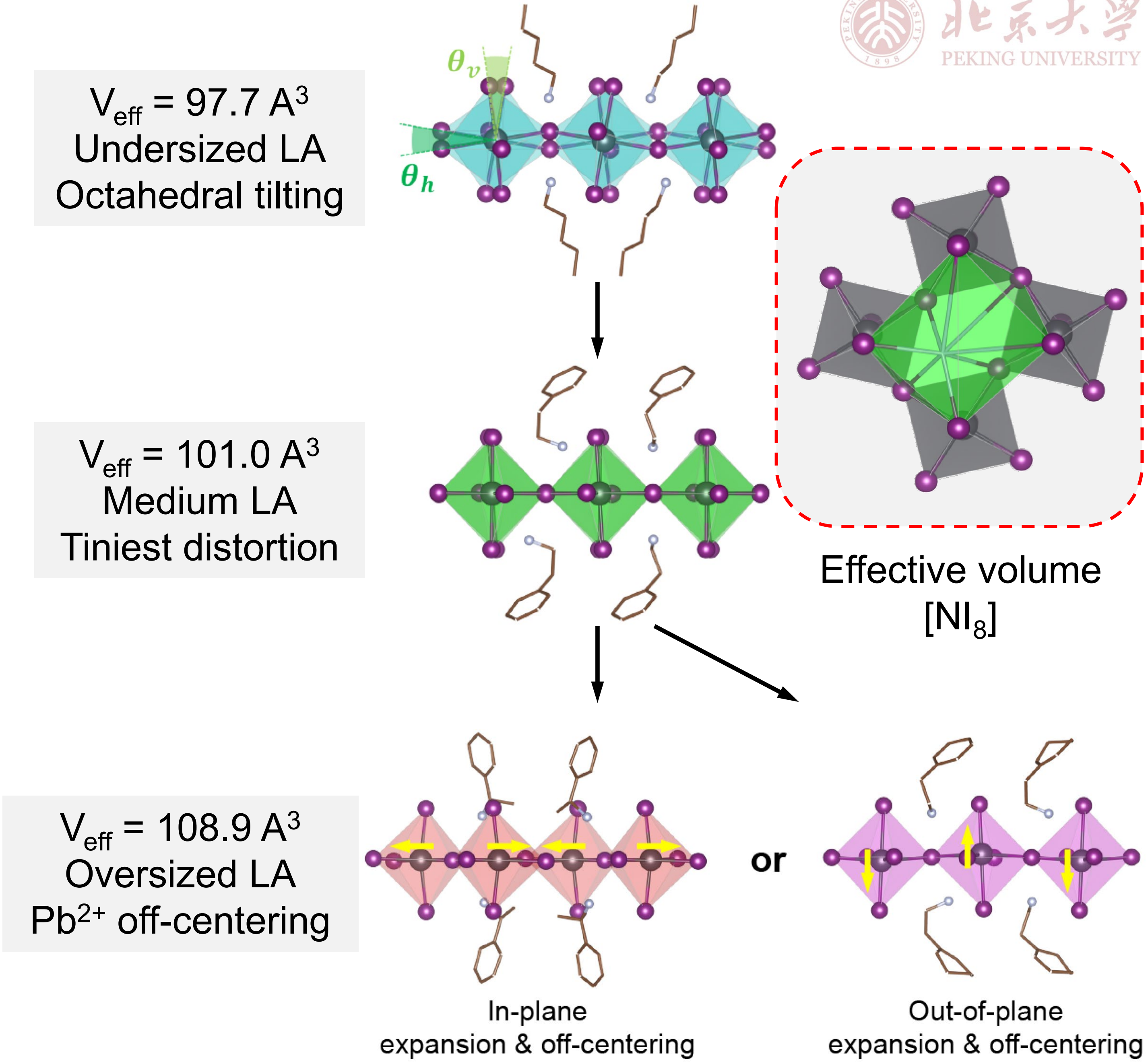
- Oversized LA ----> Pb off-centering

Off-centering Heterogeneity

R-MBA: in-plane off-centered

CHEA: out-of-plane off-centered

also validated in **18 other samples**.



Angew. Chem. Int. Ed. **2023**, 62, e202304515.

2.1 Origin of ns^2 LPE

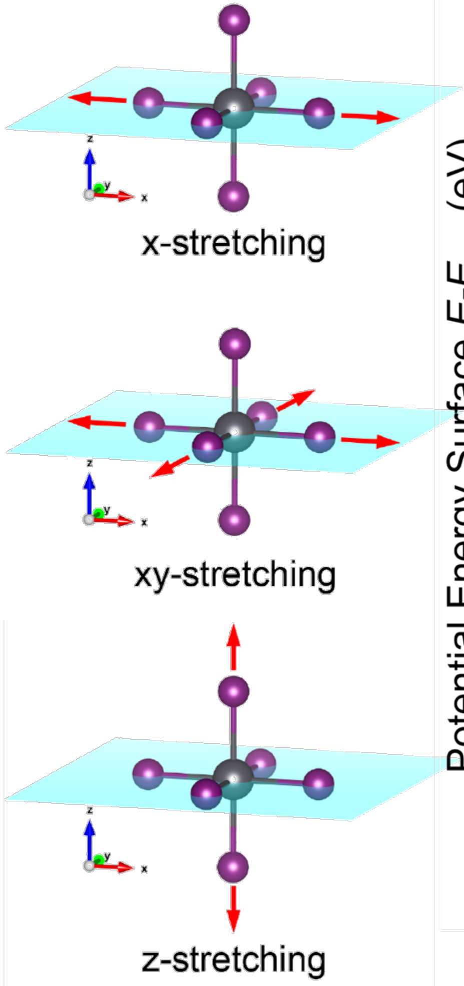
DFT Calculation Results

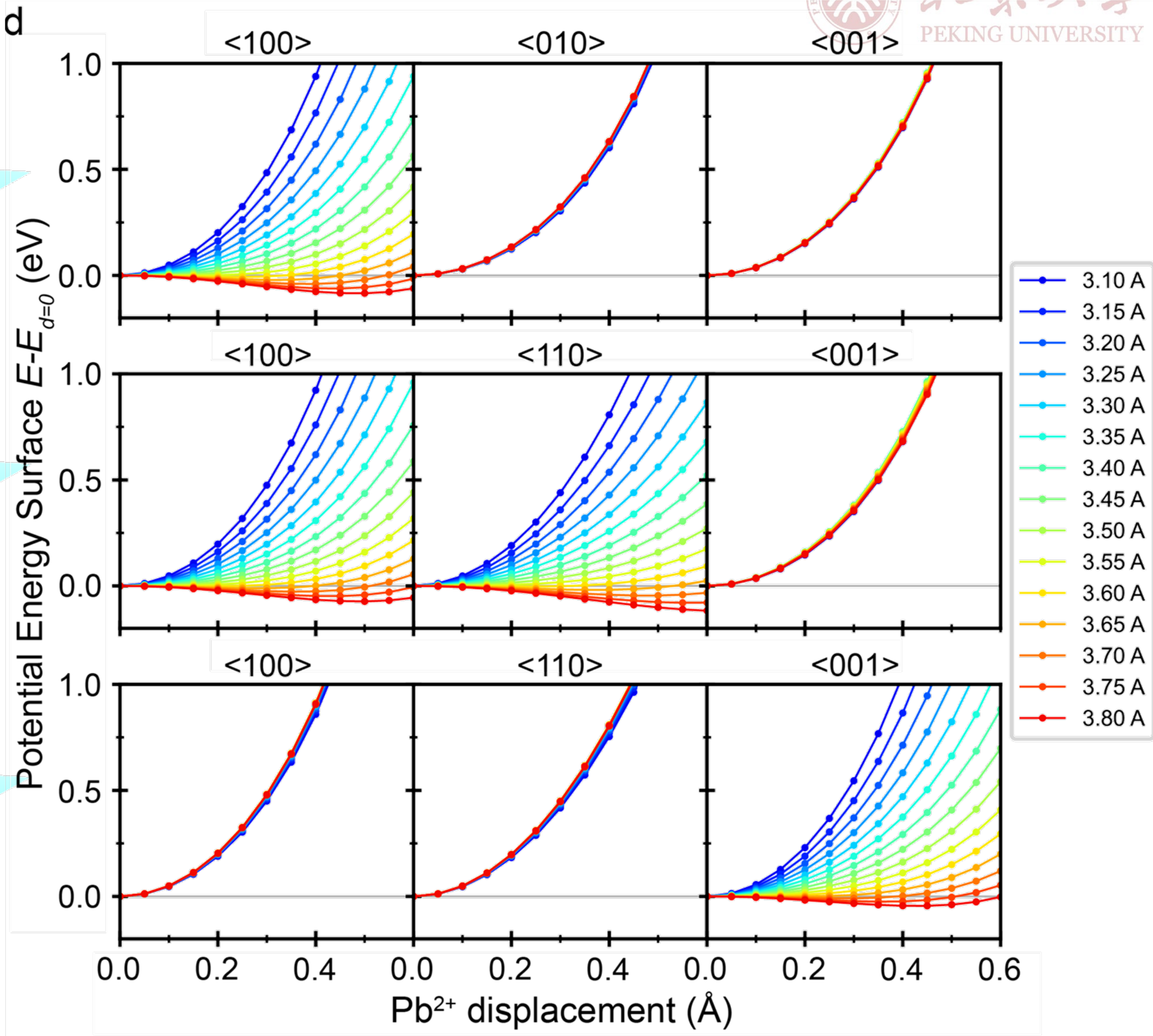
Model: Cs_2PbI_4

Stretched Axis → Anharmonic Double-well

Unstretched Axis → Harmonic Parabola

Pb-I elongation induces $6s^2$ LPE





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2.2 Correlating ns^2 LPE with PLQY

Urbach Tail & Asymmetry Factor (AF)

Both reflect the exciton-phonon coupling (EPC) strength;

Urbach tail: low-energy tailing of PL peak

$$\alpha(E) = \alpha_0 \exp\left(\frac{E - E_0}{\boldsymbol{E_U}}\right)$$

E_U: Urbach energy

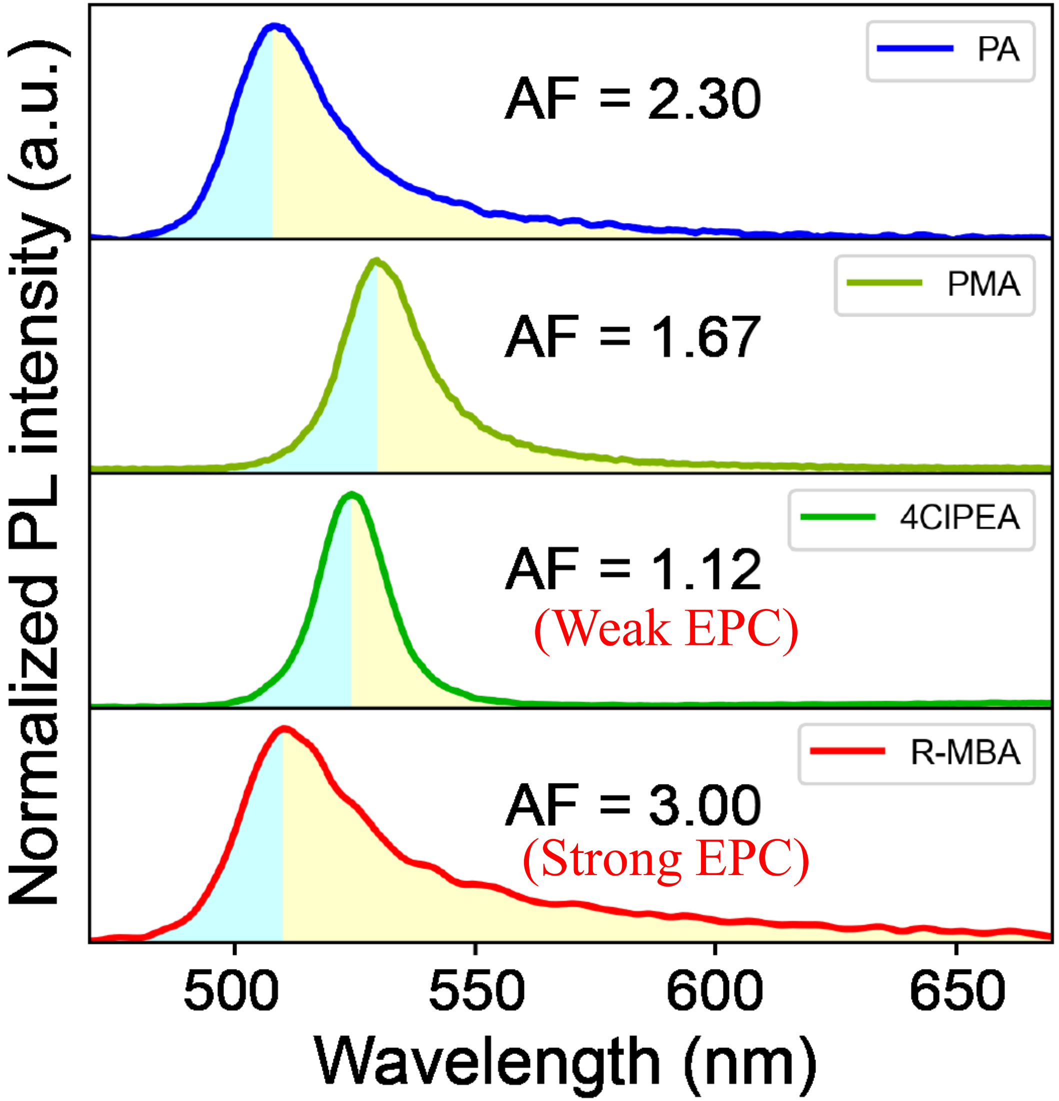
$$\boldsymbol{E_U} = \frac{\hbar\boldsymbol{\omega_{ph}}}{2\sigma_0}\left[\coth\left(\frac{\hbar\boldsymbol{\omega_{ph}}}{2k_B T}\right) + X\right]$$

Asymmetry Factor (AF):

An easier way to quantize E_U.

Stronger EPC → Larger E_U → Longer Tail

→ Larger AF



J. Phys. D: Appl. Phys. **2021**, 54, 383001. *Angew. Chem. Int. Ed.* **2023**, 62, e202304515.

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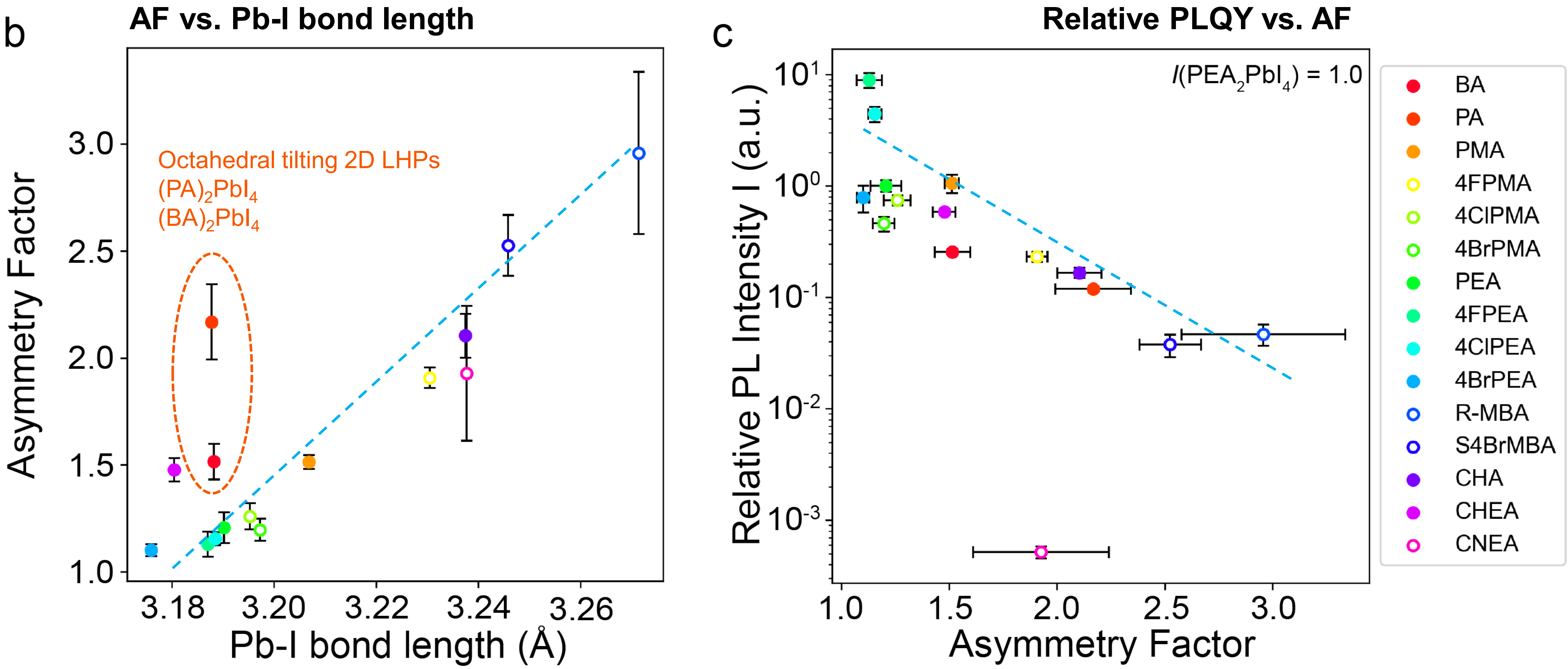
2.2 Correlating ns^2 LPE with PLQY



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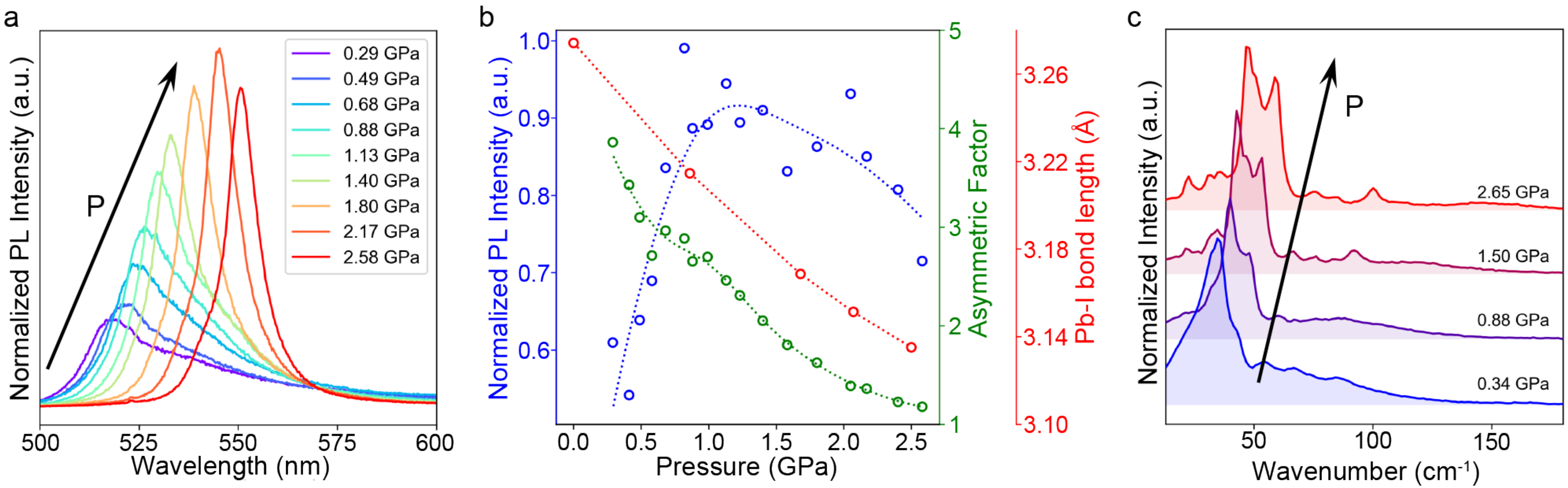
2.2 Correlating ns^2 LPE with PLQY



Shortening Pb-I bond Length by Pressure

As P increases:

- Pb-I bond length ↓;
- PL intensity ↑ then ↓;
- AF ↓;
- Raman peak frequency ↑;
- Raman central peak ↓;

All indicate **less tendency of $6s^2$ LPE** because of the **shortening** of Pb-I bond length.

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Details of this work are available online:

GDCh

Research Articles

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Perovskites *Hot Paper*

Correlating Photophysical Properties with Stereochemical Expression of $6s^2$ Lone Pairs in Two-dimensional Lead Halide Perovskites

*Jiazhen Gu, Yu Tao, Tonghuan Fu, Songhao Guo, Xiaofan Jiang, Yan Guan, Xiaotong Li, Chen Li, Xujie Lü, and Yongping Fu**

2.3 Measuring Exciton Diffusivity

Exciton Diffusion Dynamics

Classic diffusion model & PL:

$$\frac{\partial n}{\partial t} = -D\frac{\partial^2 n}{\partial x^2} - k_f n$$

solution:

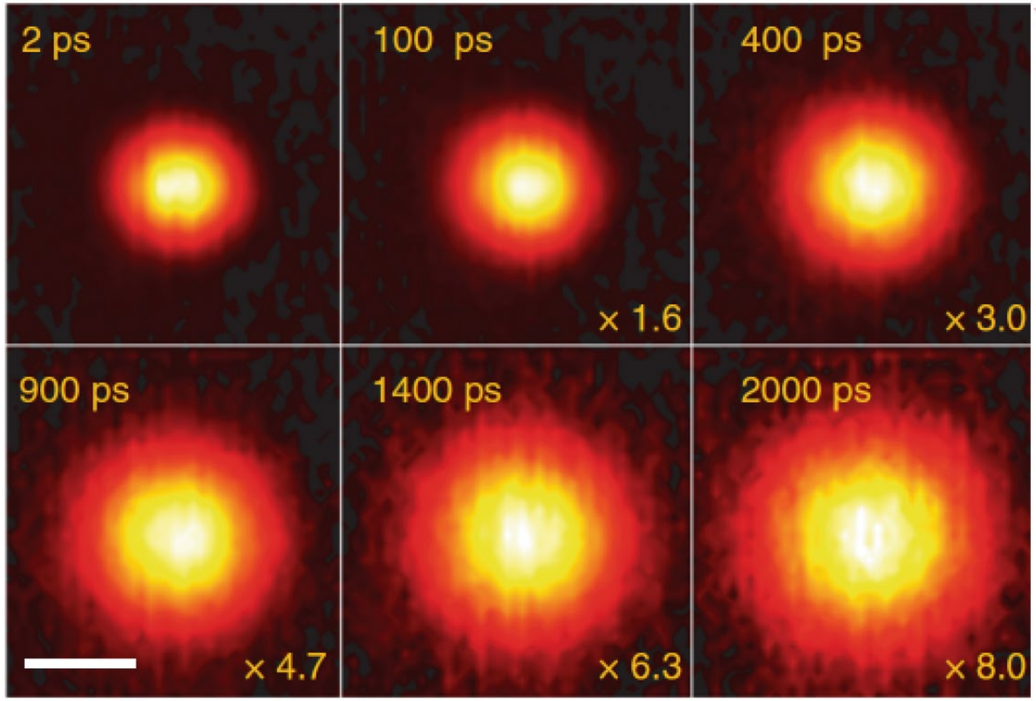
$$n(x,t) = \exp(-kt)\frac{1}{\sqrt{4\pi Dt}}\int_{-\infty}^{\infty} n(x_0,0)\exp\left[-\frac{(x-x_0)^2}{4Dt}\right]dx_0$$

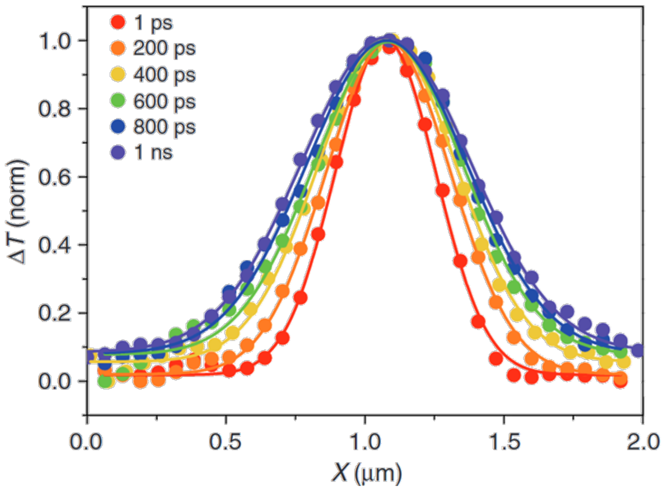
or $\quad n(x,t) \propto n(x_0,0) * G(x,t)$

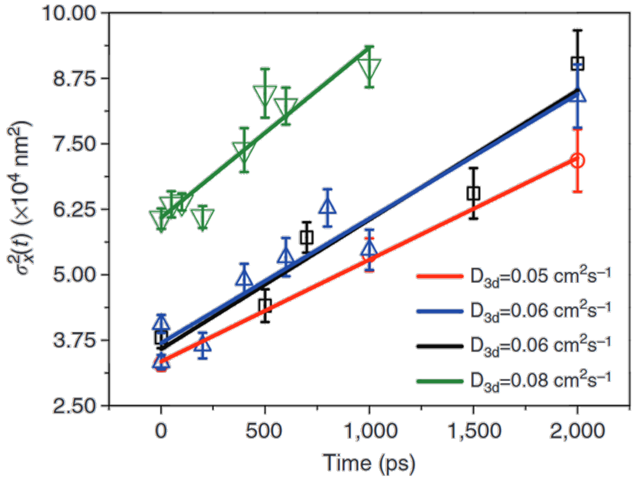
Exciton concentration follows **Gaussian** shape $G(x,t)$.

Exciton diffusivity D is calculated from:

$$\boldsymbol{\sigma_G^2 = 2Dt}$$







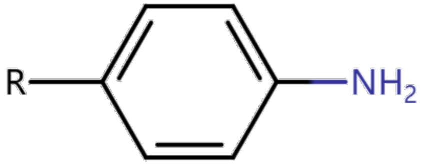
Nat. Comm. **2020**, 11, 664. *Adv. Energy Mater.* **2020**, 10, 1903781.

2.3 Measuring Exciton Diffusivity

Exciton Diffusivity of 2D LHPs

1. Rigidity dominates

4RAn series:



Rigid LA suppresses EPC, despite tilting

2. Distortion dominates

Tilting & ns^2 LPE enhance **EPC**;

Exciton scattering ↑, diffusivity ↓

Rigidity dominating: 4tFMPMA, 4ClAn, 4BrAn, 4BuAn

EPC dominating: 4FPEA, PEA, R-MBA, 4DFCHA, PA

LA Cation	Structural Distortion Type	Diffusivity (cm^2s^{-1})
4tFMPMA	Tilting	4.730
4ClAn	Tilting	2.174
4BrAn	Tilting	1.458
4BuAn	Minor Tilting	0.640
4FPEA	Intermediate	0.613
PEA	Intermediate	0.204
R-MBA	Off-center	0.168
4DFCHA	Off-center	0.020
PA	Tilting	0.016

Part. 3
Future Plan

Enhancing LPE in other systems

LPE tuning exciton diffusivity

LPE tuning excited-state properties

3.1 ns^2 LPE in Other Halide Perovskites

n=1 2D LHP:

$$(LA)_2PbX_4$$

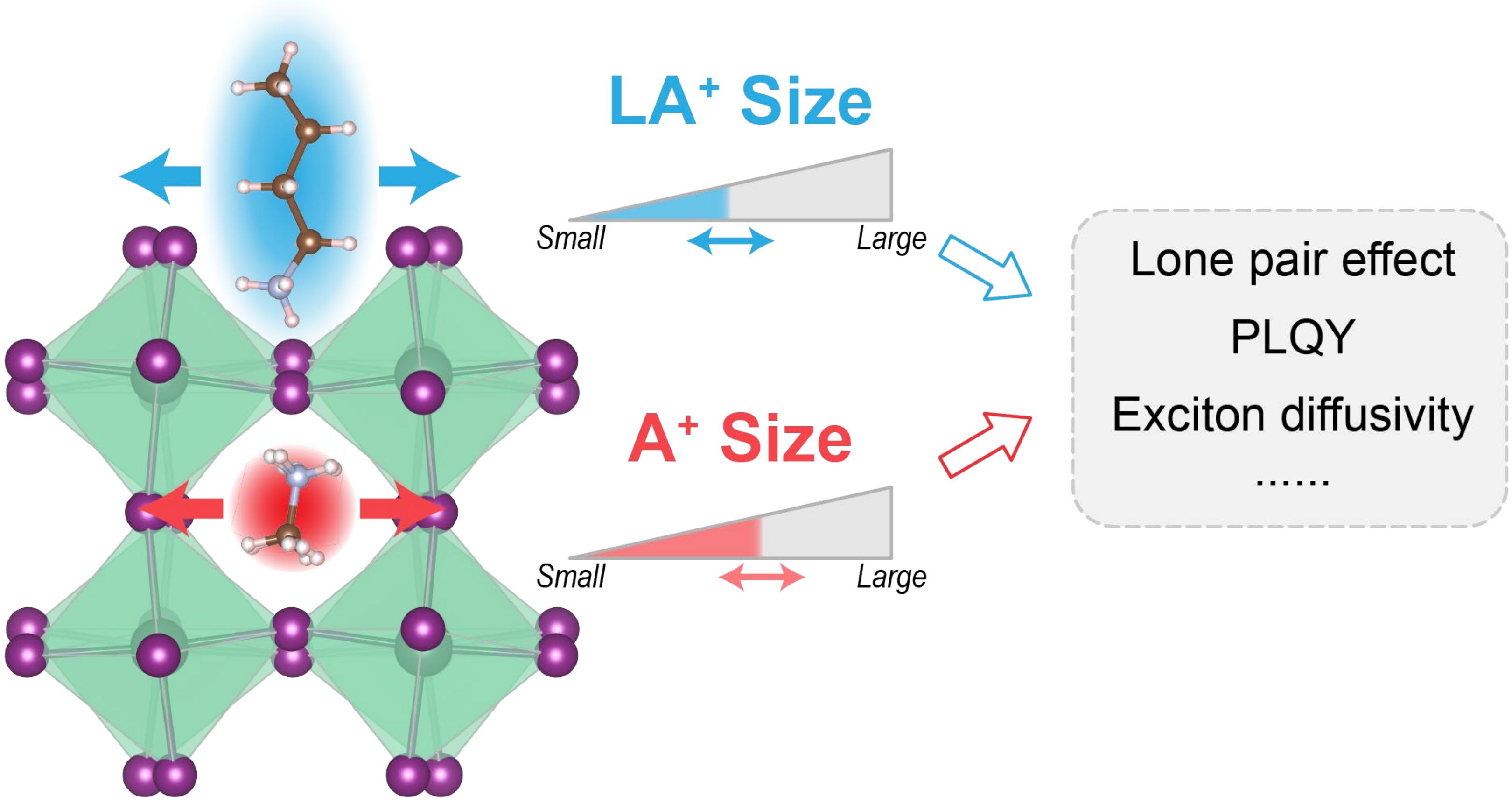
n>1 Quasi-2D LHP:

$$(LA)_2(A)_{n-1}Pb_nX_{3n+1}$$

Introducing A cation

New dimension of tuning

Achieve **higher ns^2 LPE extent**

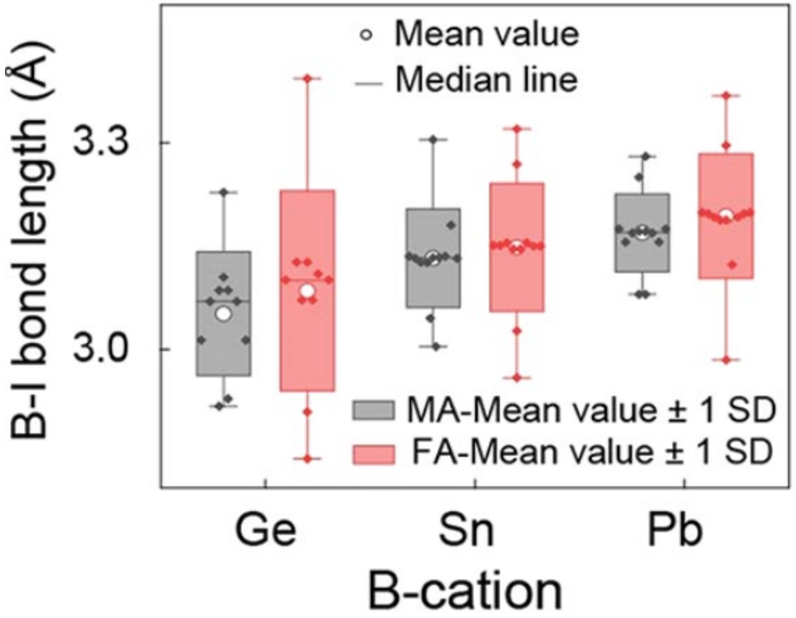


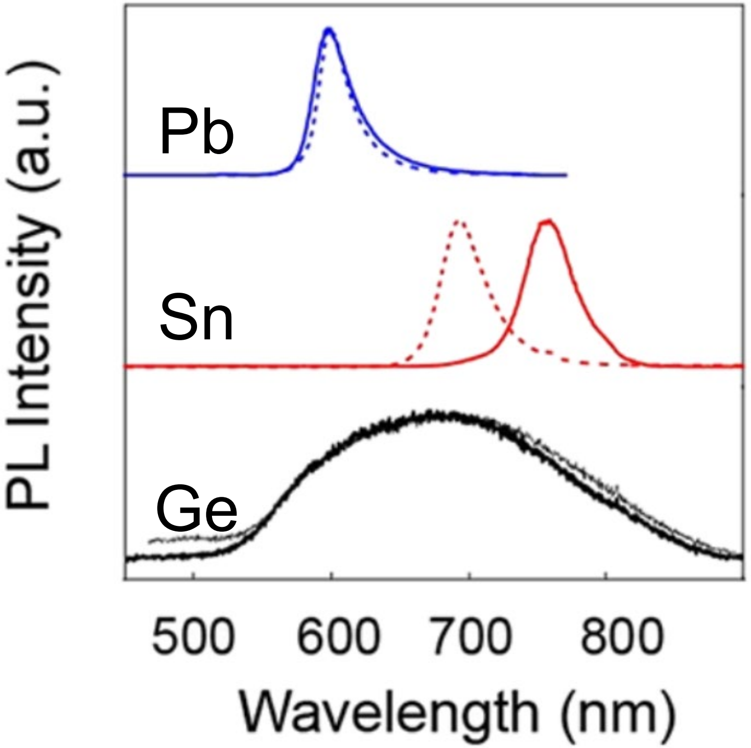
3.1 ns^2 LPE in Other Halide Perovskites

2D Sn/Ge Perovskites

ns^2 LPE tendency: $Pb^{2+} < Sn^{2+} < Ge^{2+}$

Stronger LPE, larger difference





Challenges

1. Oxidation

$$\varphi_{PbO_2/Pb^{2+}} = 1.455\ V$$
$$\varphi_{Sn^{4+}/Sn^{2+}} = 0.151\ V$$
$$\varphi_{Ge^{4+}/Ge^{2+}} = 0.00\ V$$

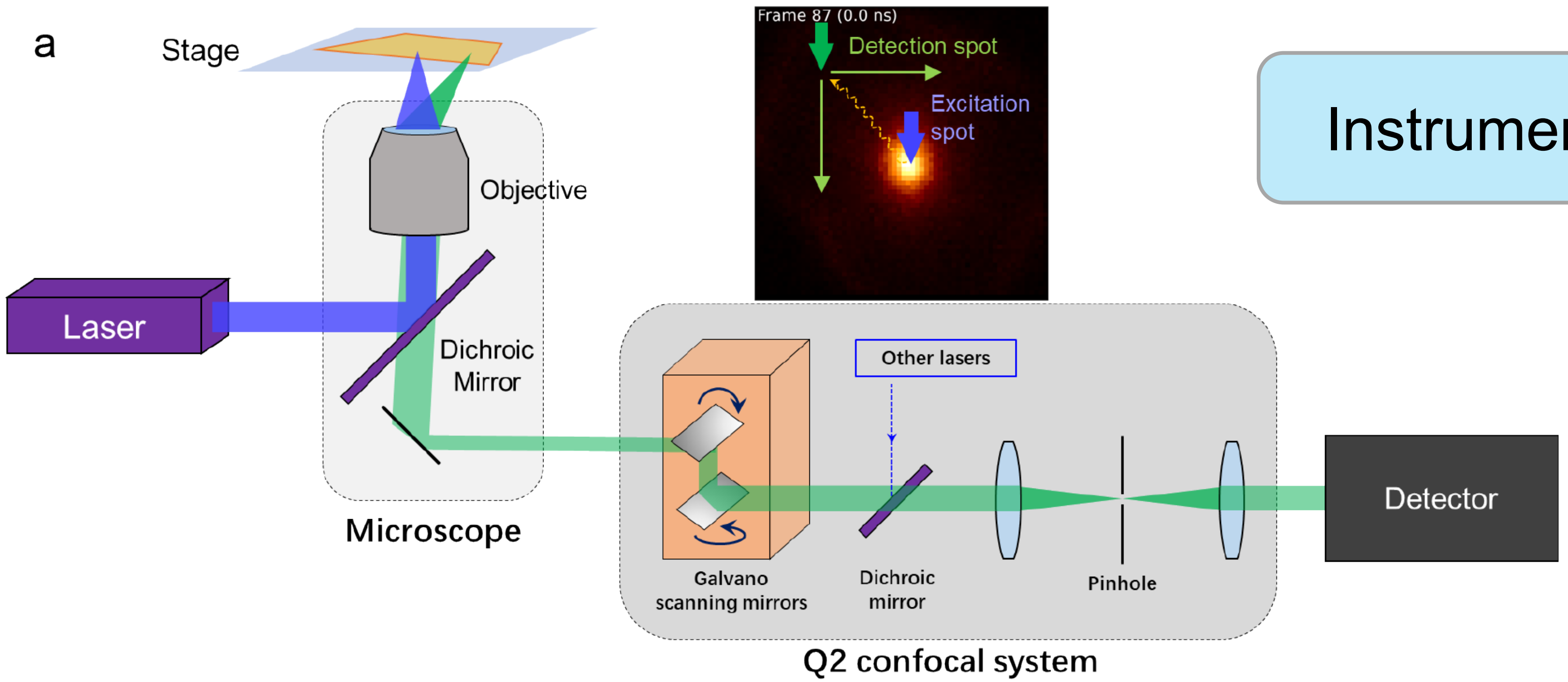
2. Lower PLQY

High LPE tendency, EPC ↑, PLQY ↓.

Low **S/N ratio** in some tests

JACS, **2022**, 144, 18030.

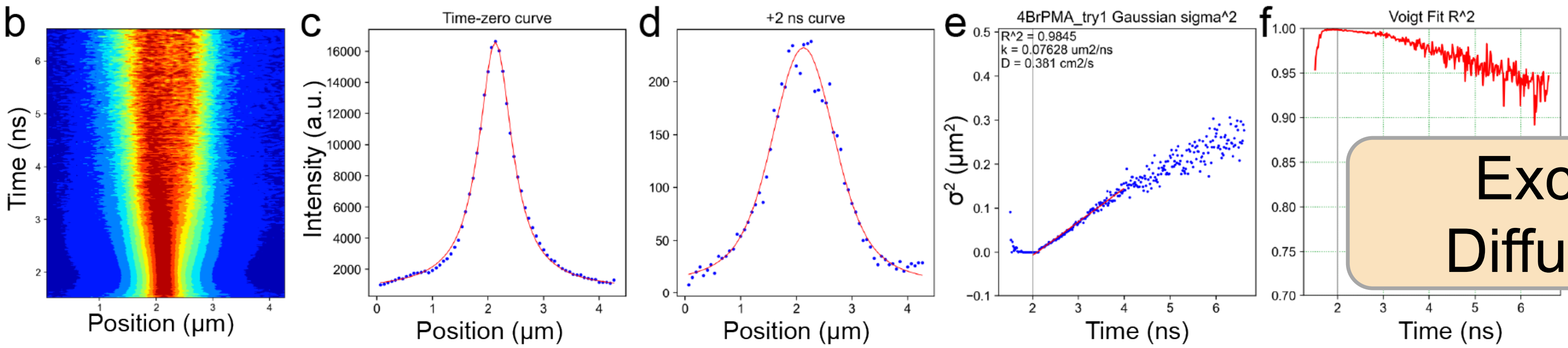
3.2 Measuring Exciton Diffusivity



Instruments

Data Analysis

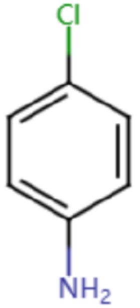
Exciton Diffusivity



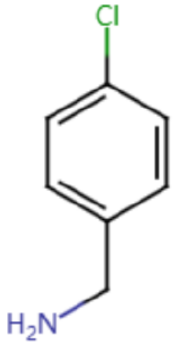
LPE
Temperature
Excitation Power
Trap State

3.2 Measuring Exciton Diffusivity

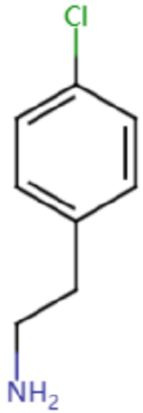
New LA Series



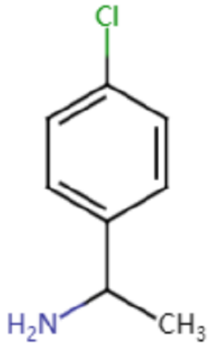
4ClAn
(Strong Tilting)



4ClPMA
(Minor Tilting)

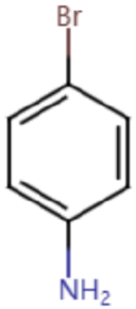


4ClPEA
(Intermediate)

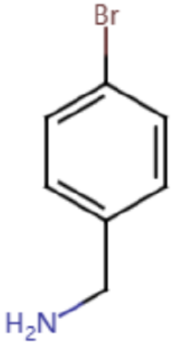


4ClMBA
(Off-centered)

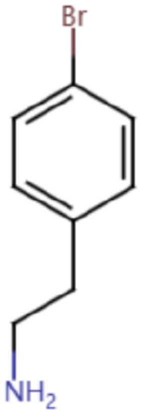
Octahedral Tilting → Off-center Displacement / LPE → Diffusivity ?



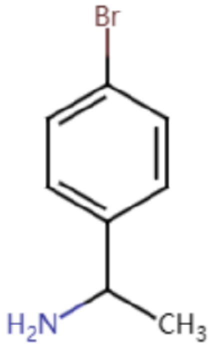
4BrAn
(Strong Tilting)



4BrPMA
(Minor Tilting)



4BrPEA
(Intermediate)



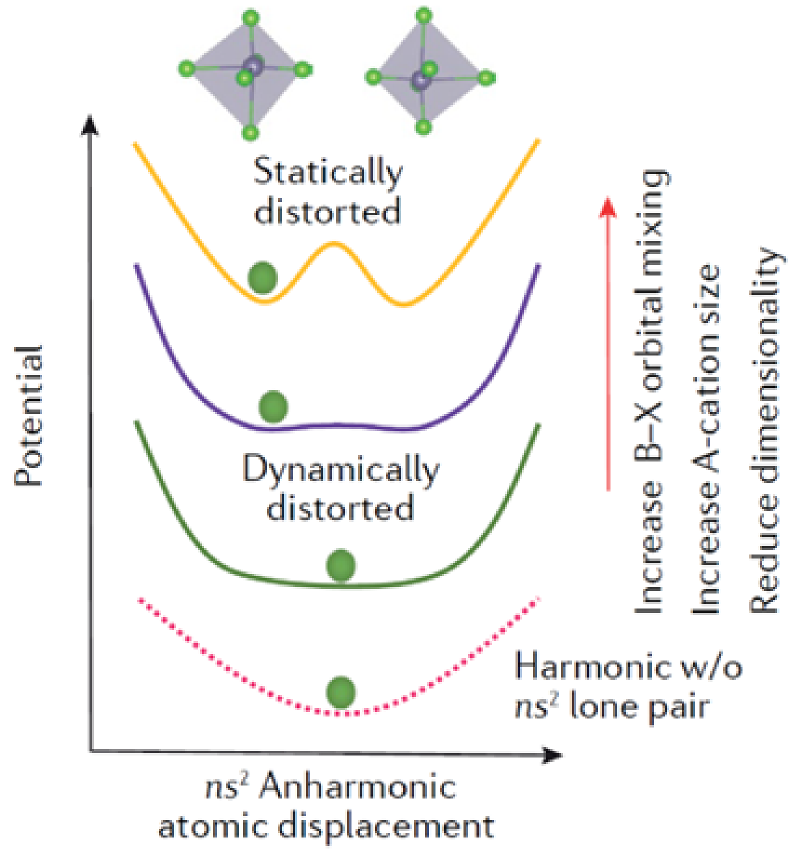
4BrMBA
(Off-centered)

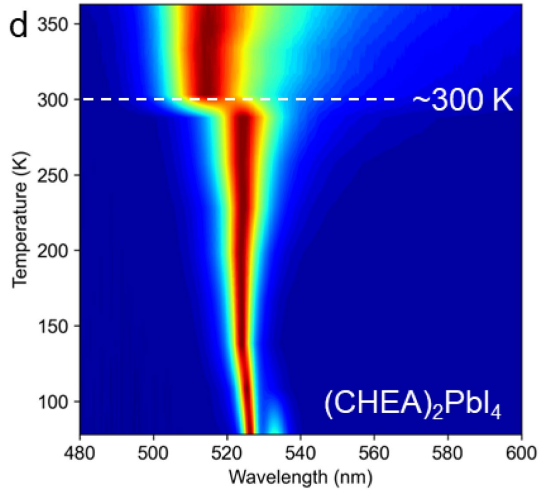
3.3 LPE-related Phase Transition

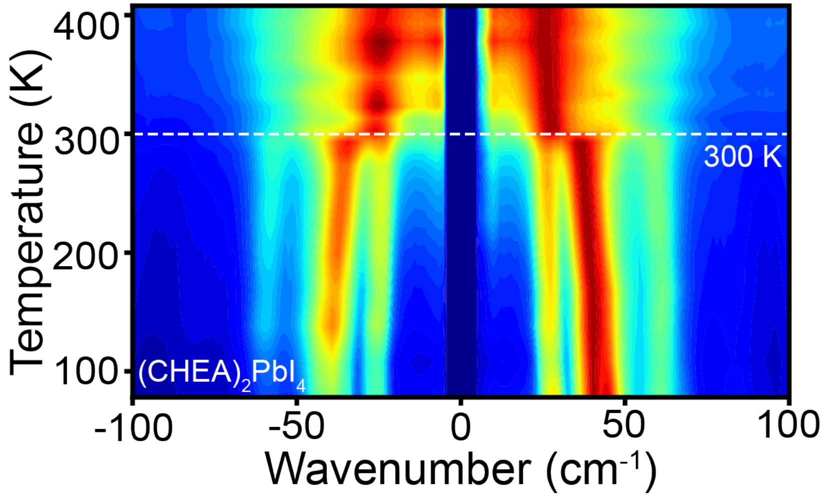
For double-well potential curve:

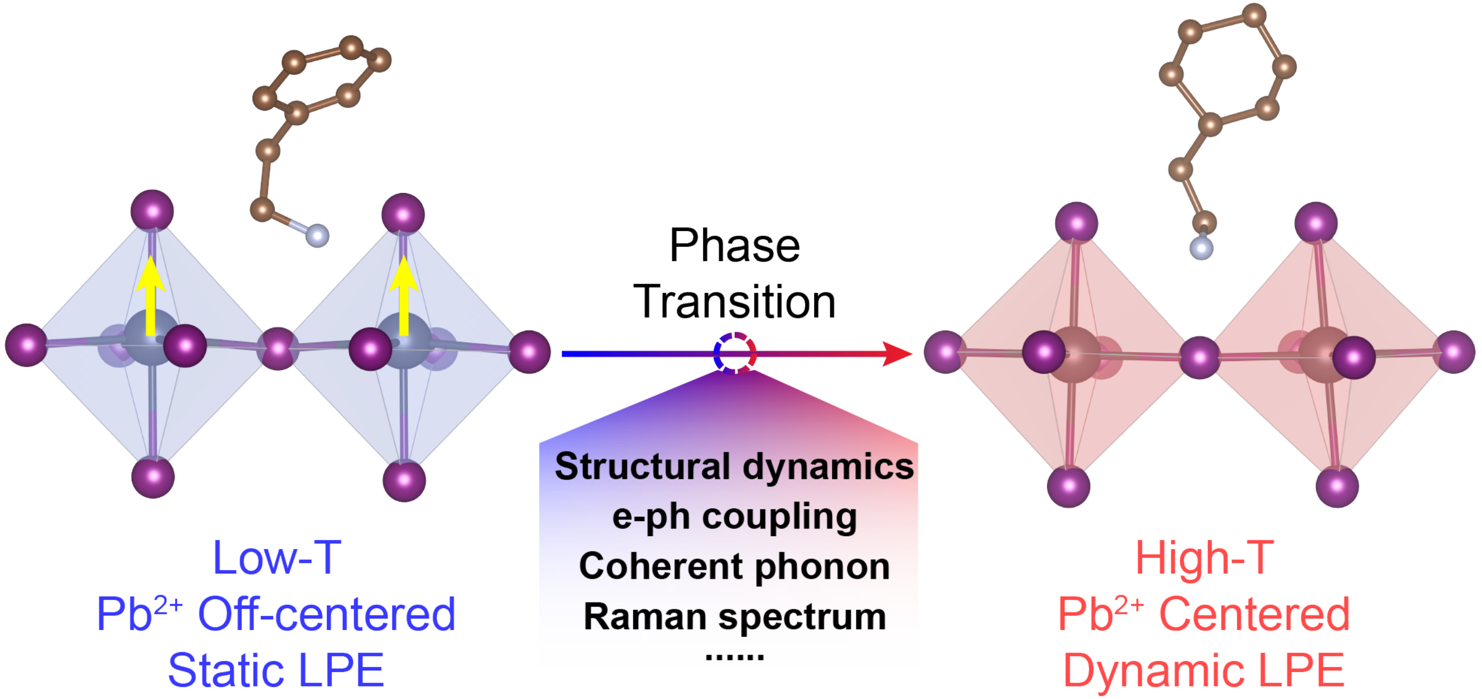
$k_B T < E_a$: Static LPE

$k_B T > E_a$: Dynamic LPE









Nat. Rev. Chem. **2021**, 5, 838.

3.3 LPE-related Phase Transition

Coherent Phonon Spectrum

Lattice vibration frequency:

$\tilde{\nu} = 33\ cm^{-1}$ $\qquad f = 1\ THz = 10^{12} Hz$

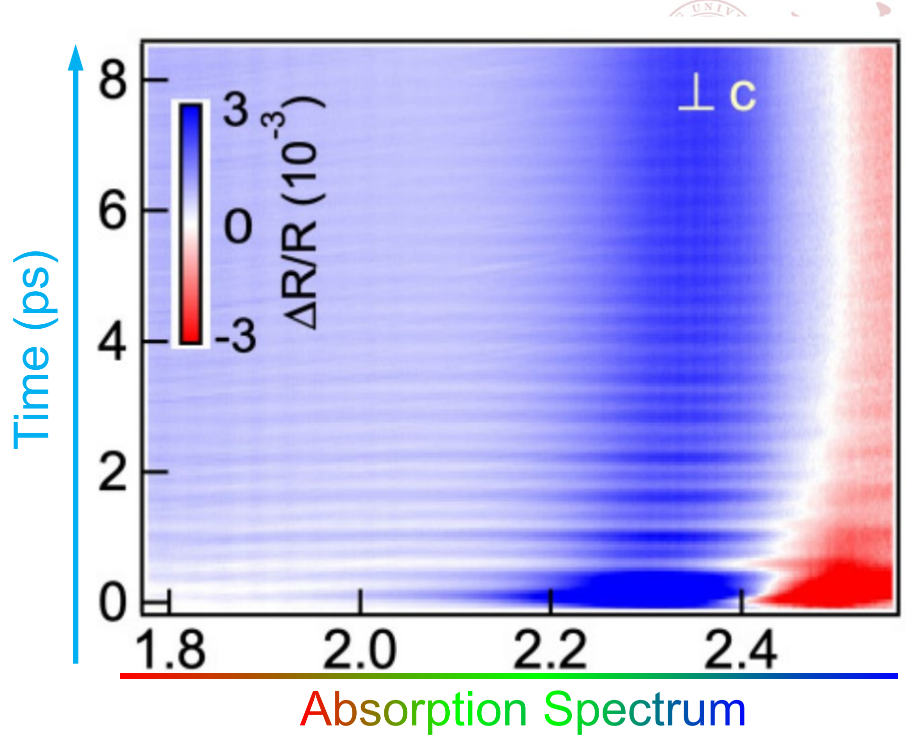
$T = 1/f = 10^{-12} s = 1\ ps$

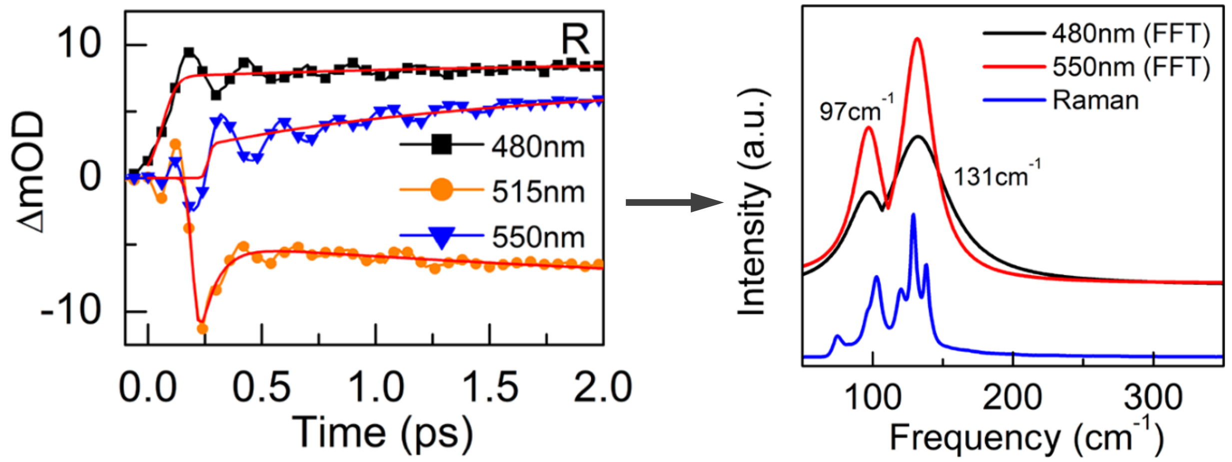
Lattice vibration timescale ≈ detection timescale

Upon vibration:

- dielectric constant ε;
- Refraction index n;
- Reflection R;
- Absorption A; ......

Signal Oscillation $S(t)$ → Fourier Transformation → Coherent Phonon Frequency ν





Phys. Rev. Mater. **2022**, 6, 095401. *J. Phys. Chem. Lett*. **2022**, 13, 4073.

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Thanks for your attention!

1.1 2D Halide Perovskites

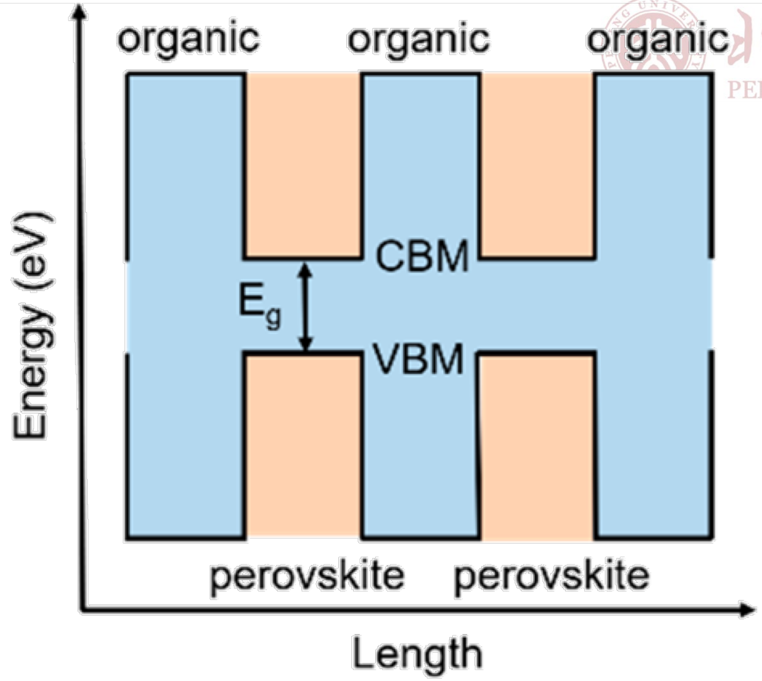
Electronic Structure

Organic layer: HOMO - LUMO gap E_{org}

Inorganic layer: VBM - CBM bandgap E_g

In general, $E_g < E_{org}$ ==> **Quantum Confinement**

e^- and h^+ trapped in inorganic layer, forming **exciton**

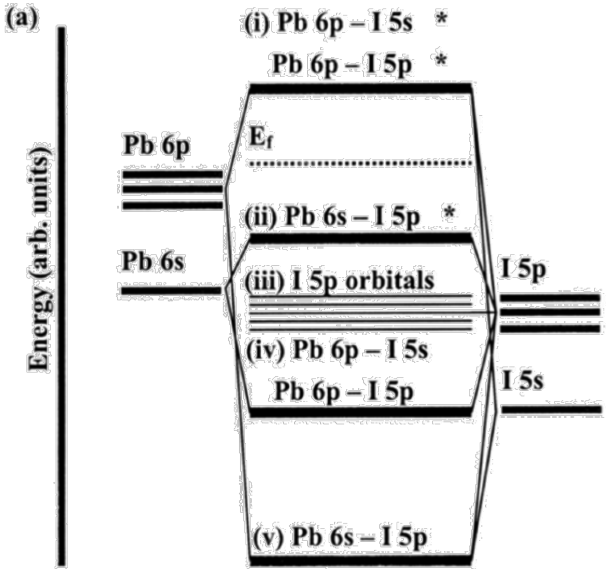


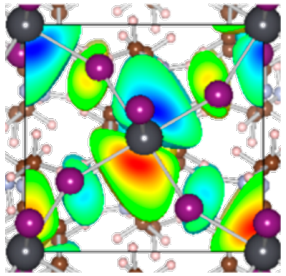
In inorganic layer:

VBM: (B^{2+} ns + X np)*

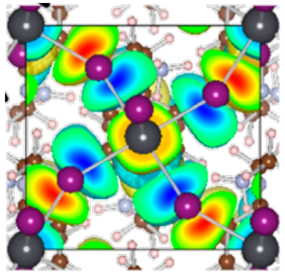
CBM: (B^{2+} np + X ns&np)*

Inorganic lattice dominates the **excitonic** properties.





CBM: (Pb np + I ns&np)*



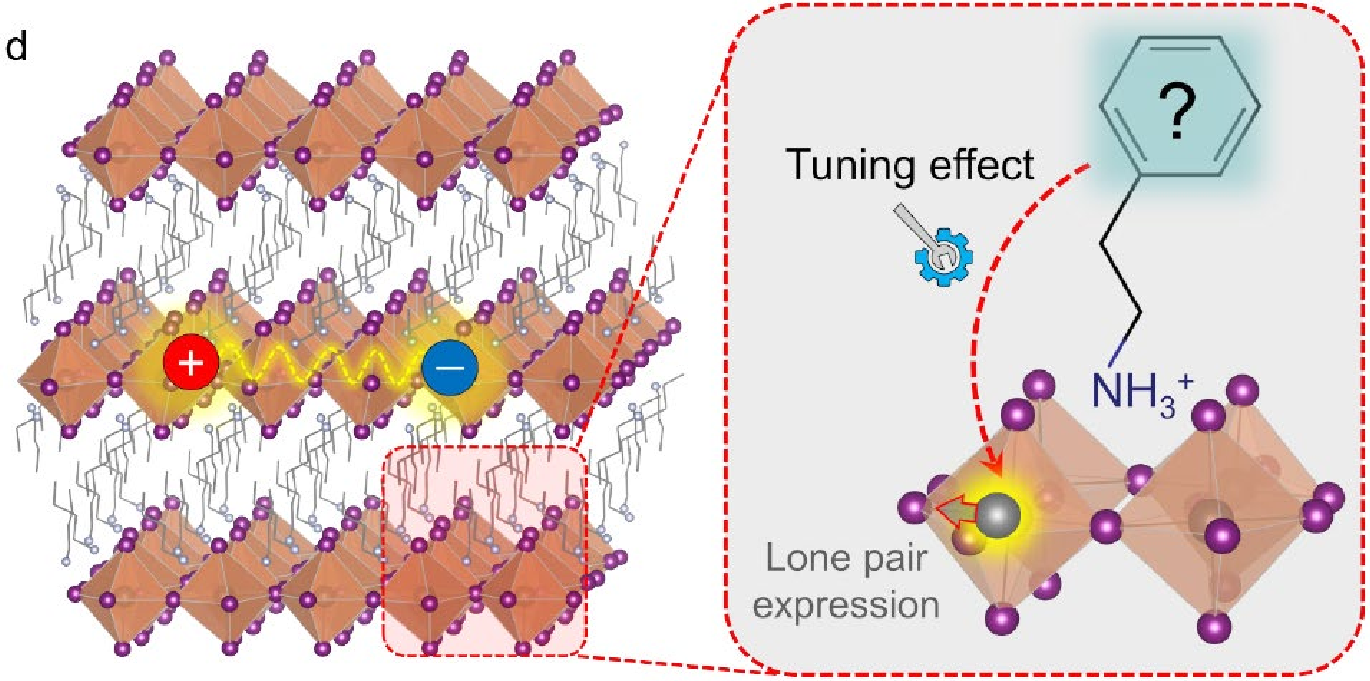
VBM: (Pb ns + I np)*

Chem. Rev. **2019**, 119, 3140. *JACS*, **2019**, 141, 1171.

1.1 2D Halide Perovskites

Tuning the Properties

d



LA⁺ chemical engineering

ns² lone pair effect ⇄ Inorganic layer distortion

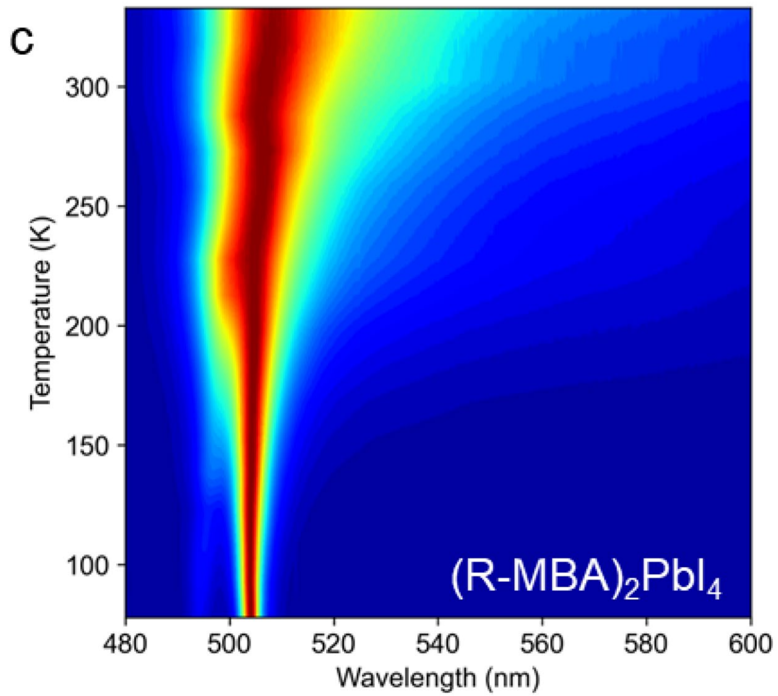
Exciton-phonon coupling

Emission wavelength | Carrier mobility | PLQY | ......

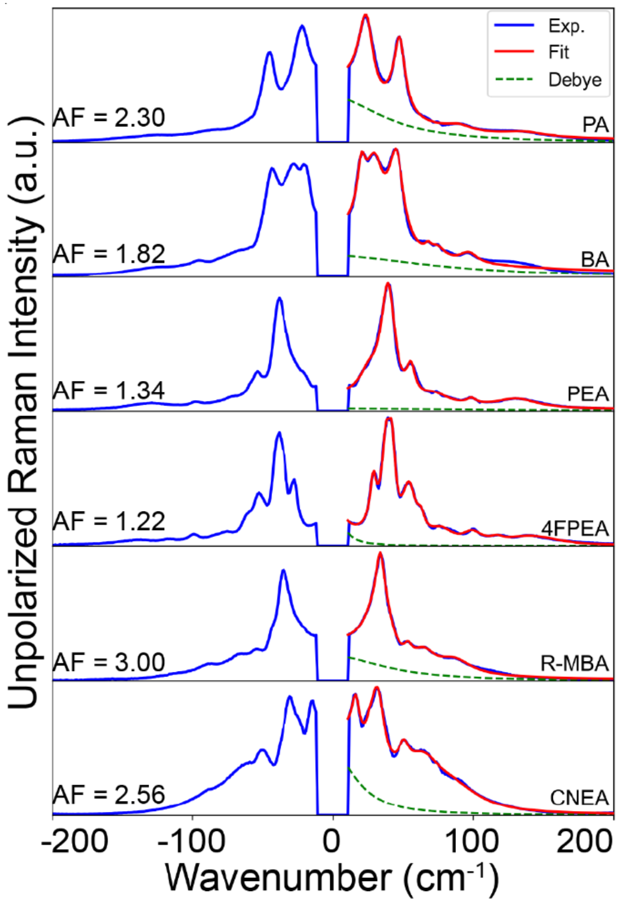
.

1.3 Exciton-Phonon Coupling (EPC)

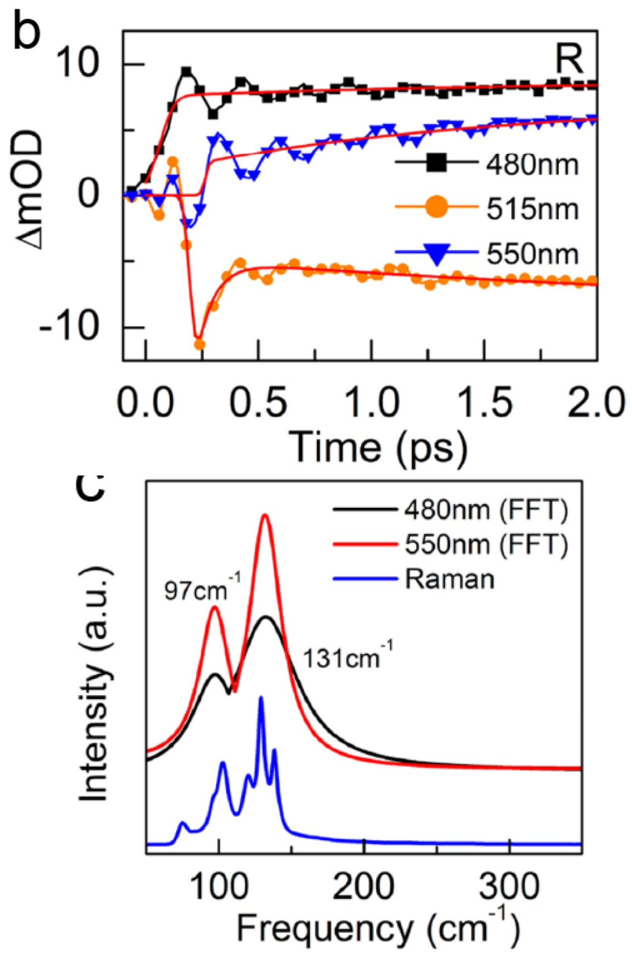
How to Measure EPC Strength



Temperature-dependent Photoluminescence (TDPL)



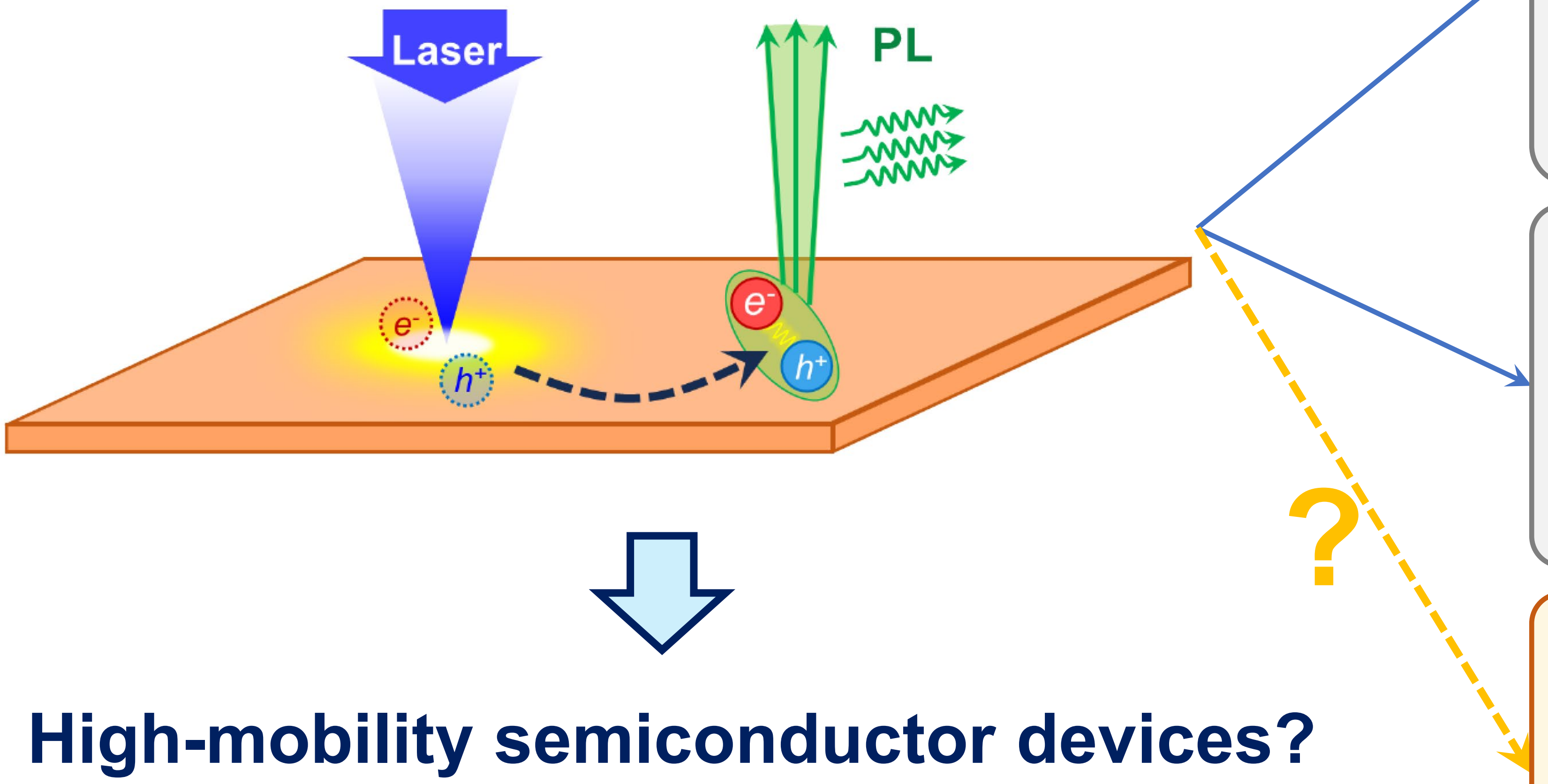
Raman central peak



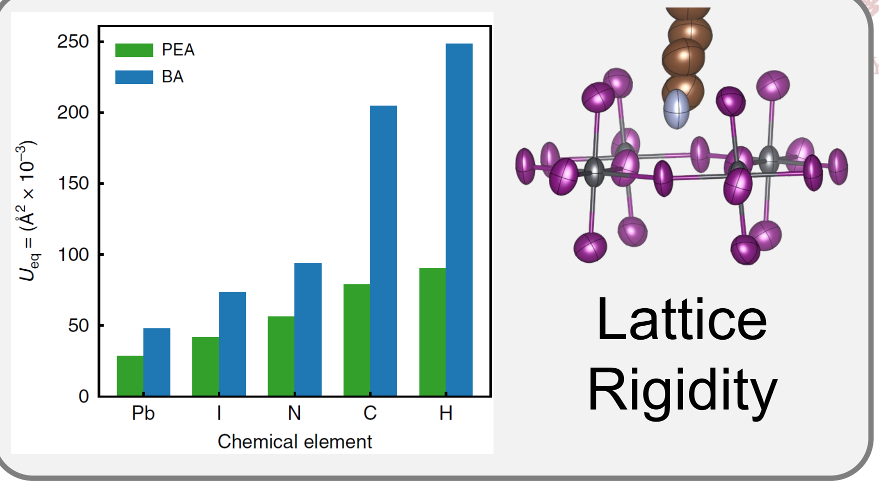
Transient absorption & Coherent phonon spectrum

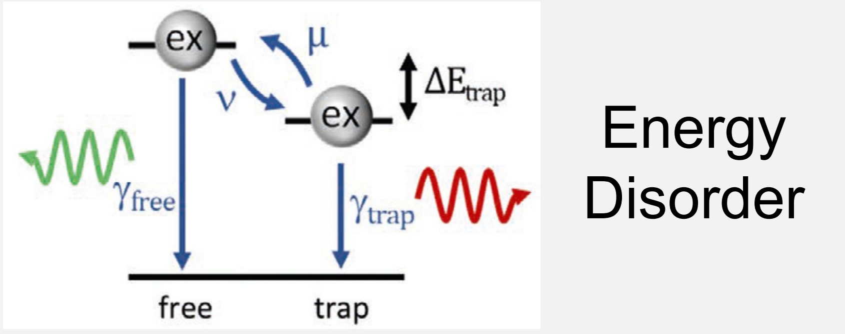
J. Phys. Chem. Lett. **2022**, 13, 4073.

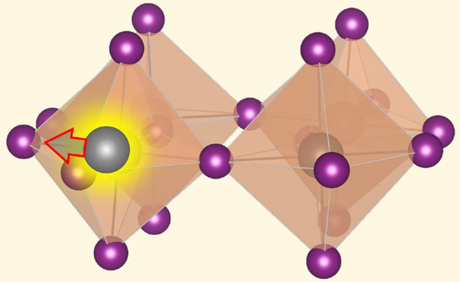
1.5 Exciton Diffusion



High-mobility semiconductor devices?



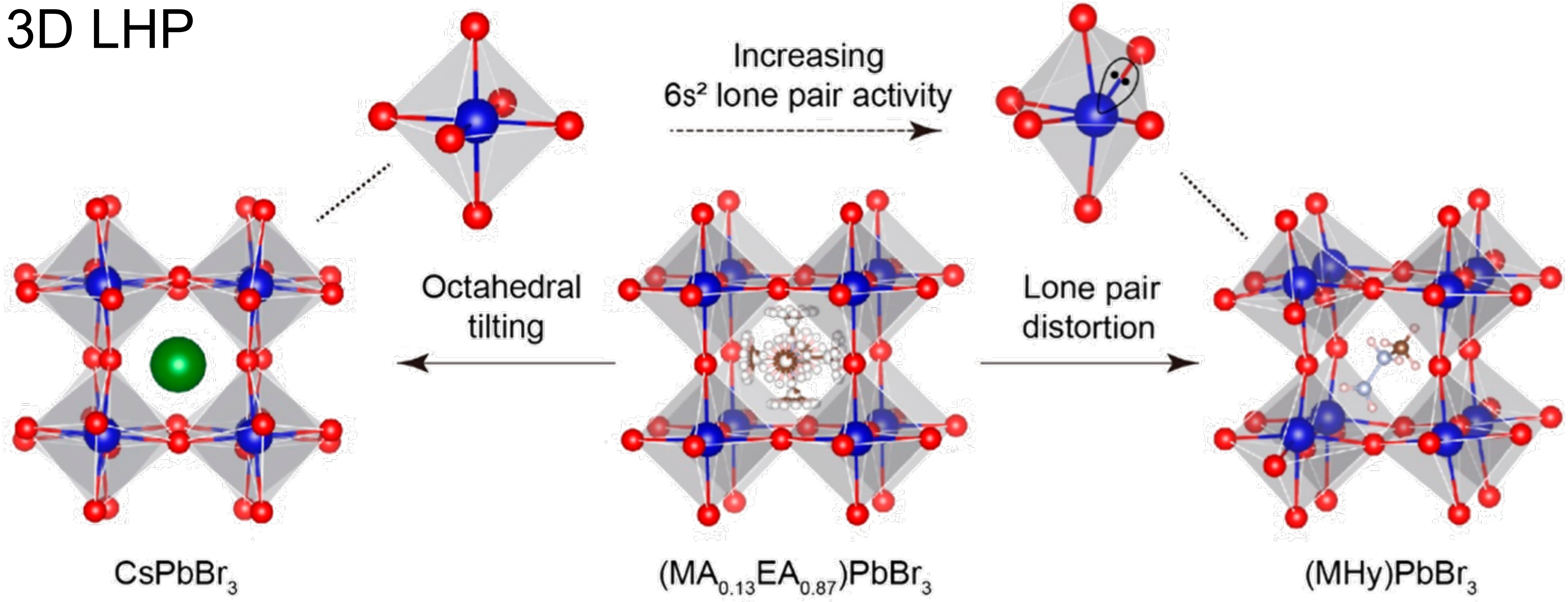




Nat. Comm. **2020**, 11, 2035. *Adv. Optical Mater.* **2021**, 9, 2001875

2.1 Structural Distortions in 2D LHP

ns^2 LPE in 3D LHP



$t < 1$	Undersized A^+	**Octahedral tilting**
$t \approx 1$	Intermediate A^+	Tiniest distortion
$t > 1$	Oversized A^+	**Pb^{2+} off-center displacement**

Tolerance factor:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

JACS, **2022**, 144, 12247.

2.1 Structural Distortions in 2D LHP

ns^2 LPE in 2D LHP

*"2. Pb off-centering is **orientational**:*

R-MBA: in-plane off-centered

CHEA: out-of-plane off-centered"

LPE is correlated with the Pb-I elongation direction;

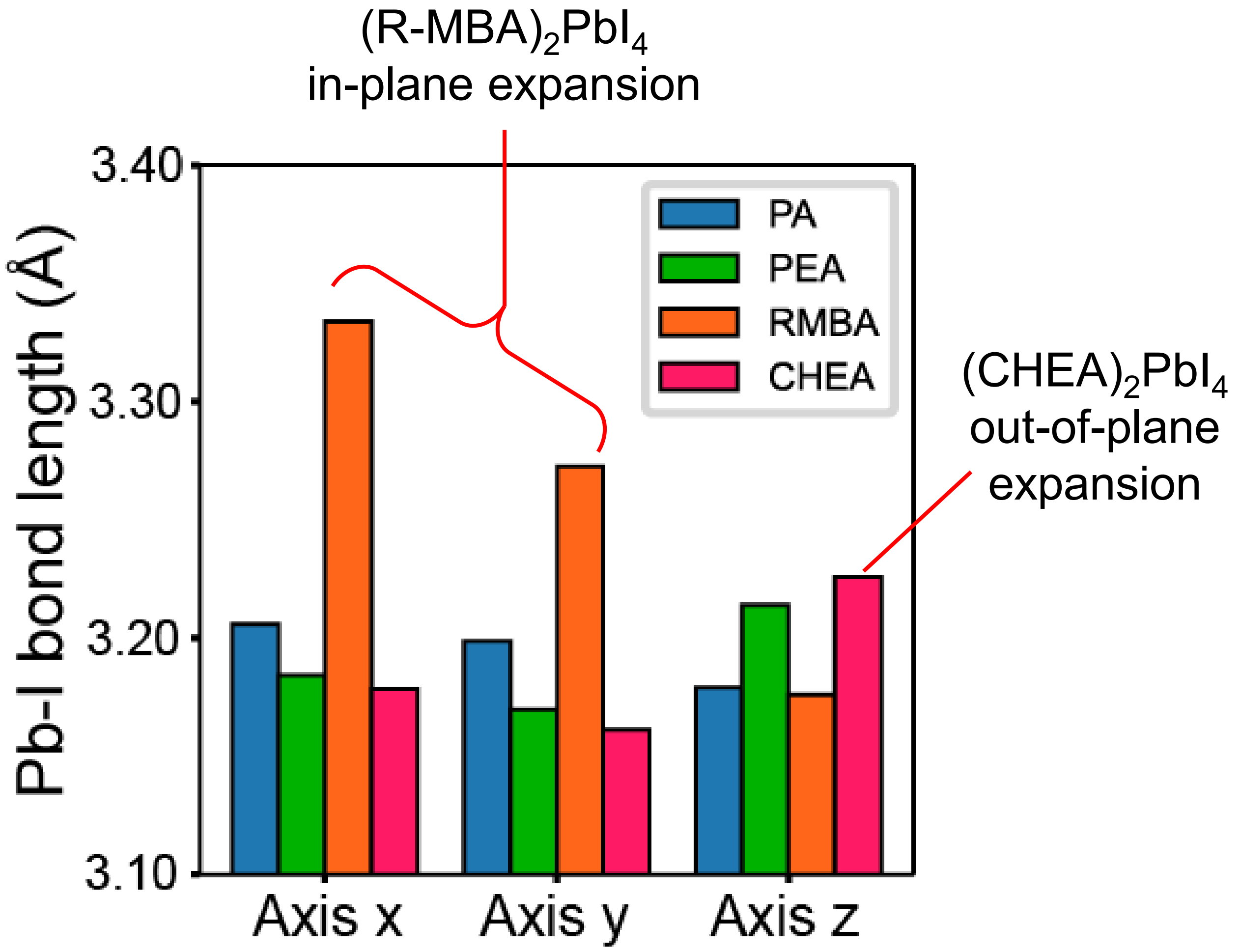
R-MBA (108.9 A^3) expands horizontal Pb-I;

=> **in-plane** expansion & off-centering

CHEA (99.5 A^3) expands vertical Pb-I;

=> **out-of-plane** expansion & off-centering

Such correlation is valid across **18 other samples**.



Angew. Chem. Int. Ed. **2023**, 62, e202304515.

2.2 Origin of ns² LPE

Off-centering Vector

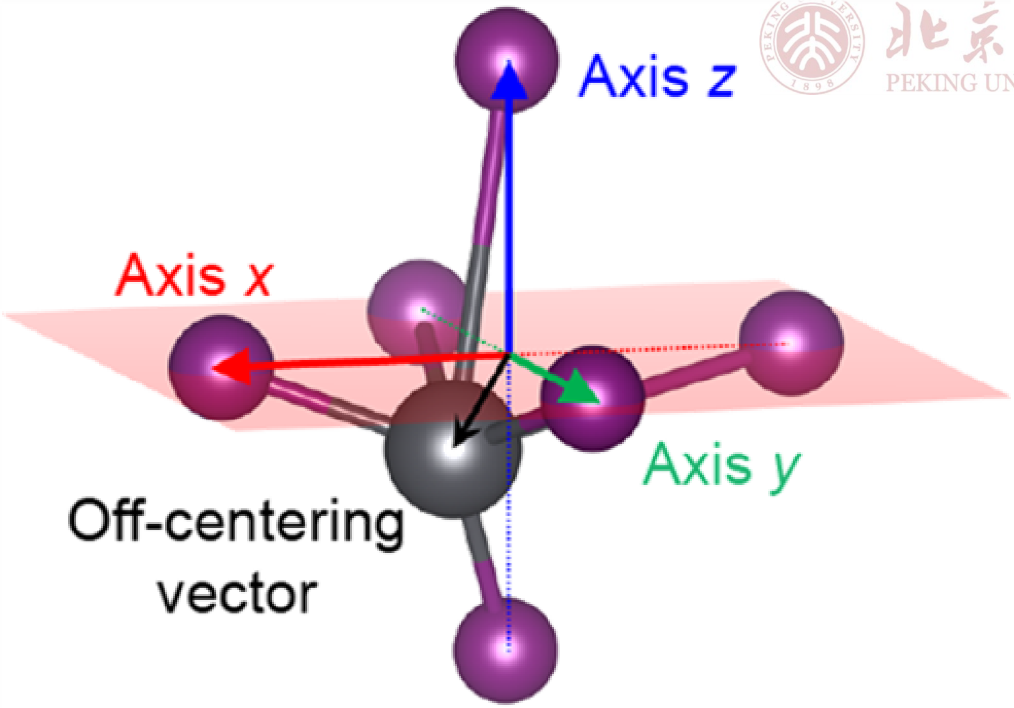
$$\boldsymbol{l} = \boldsymbol{r}(Pb) - \frac{1}{6}\sum_{i=1}^{6} \boldsymbol{r}(I_i)$$

Octahedral Coordinates

X axis: in-plane longer $\frac{1}{2}I - I$

Y axis: in-plane shorter $\frac{1}{2}I - I$

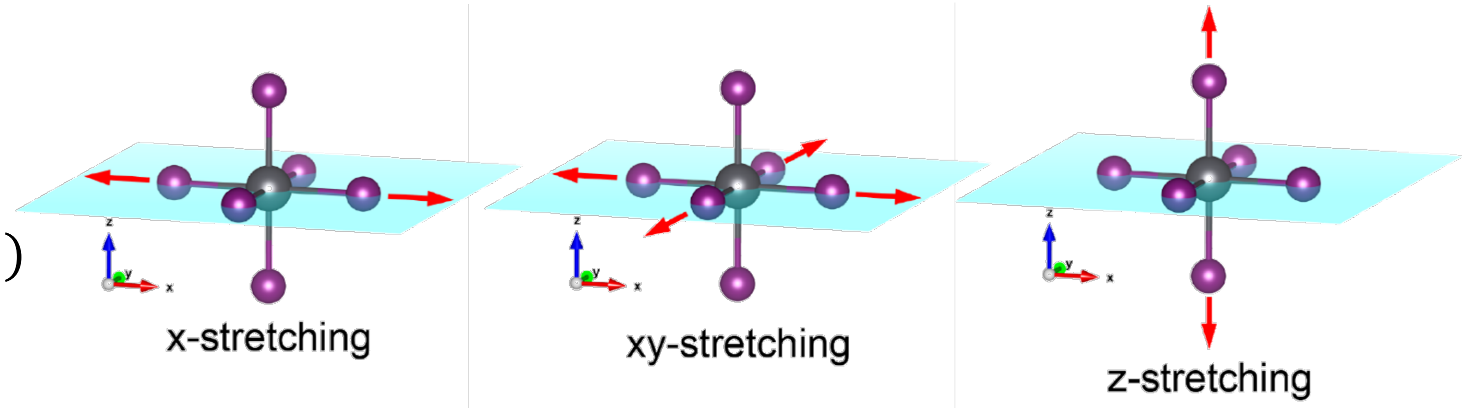
Z axis: out-of-plane $\frac{1}{2}I - I$



Projected Off-centering Vector

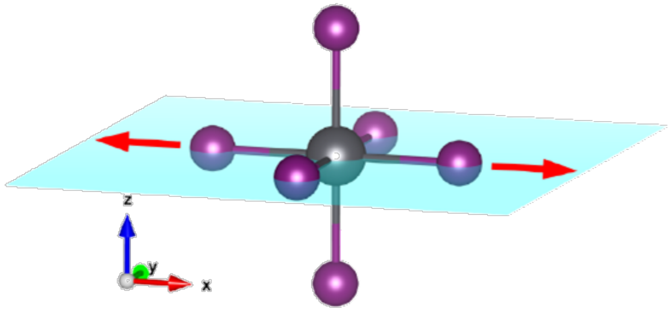
$$\boldsymbol{l} = k_x \boldsymbol{e_x} + k_y \boldsymbol{e_y} + k_z \boldsymbol{e_z} \qquad \boldsymbol{l}: (k_x, k_y, k_z)$$

$$\boldsymbol{e_i} = \frac{1}{2}[\boldsymbol{r}(I_{i+}) - \boldsymbol{r}(I_{i-})]$$

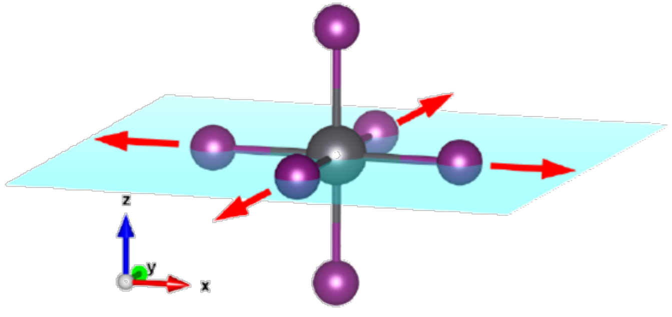


Angew. Chem. Int. Ed. **2023**, 62, e202304515.

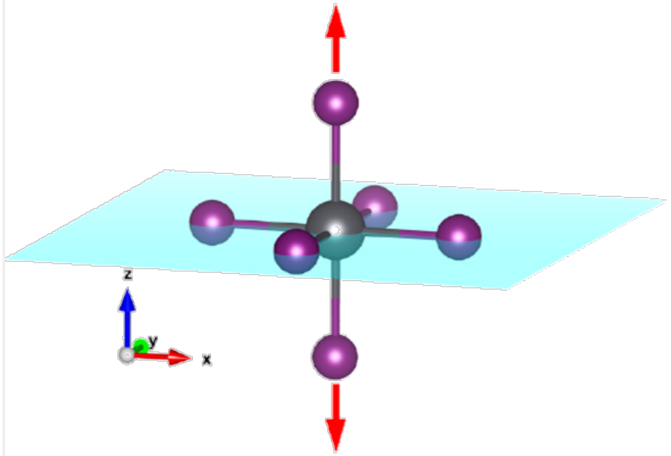
2.2 Electron Localization Function (ELF)



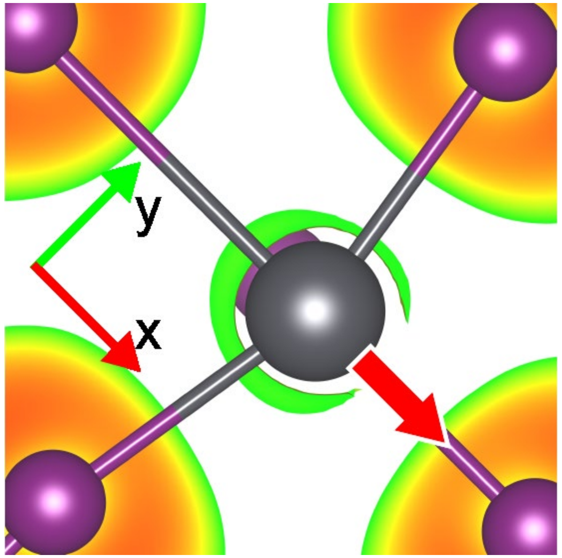
x-stretching

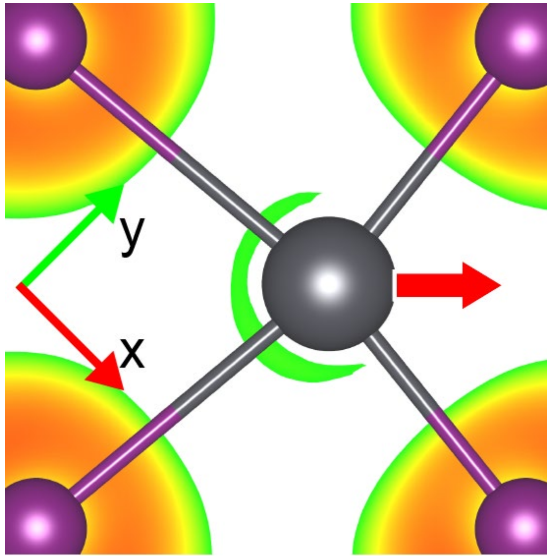


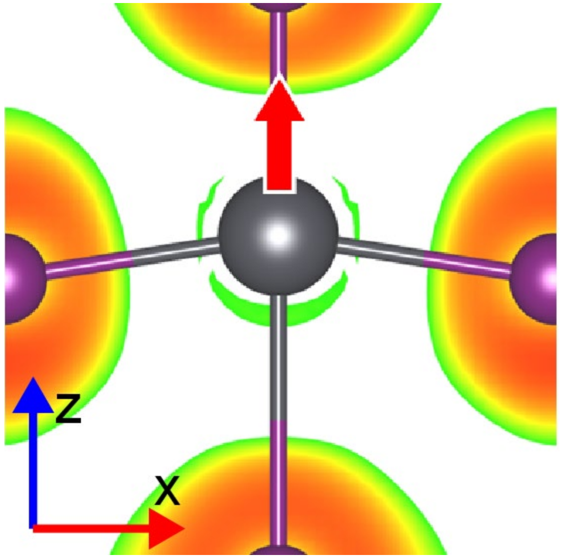
xy-stretching



z-stretching







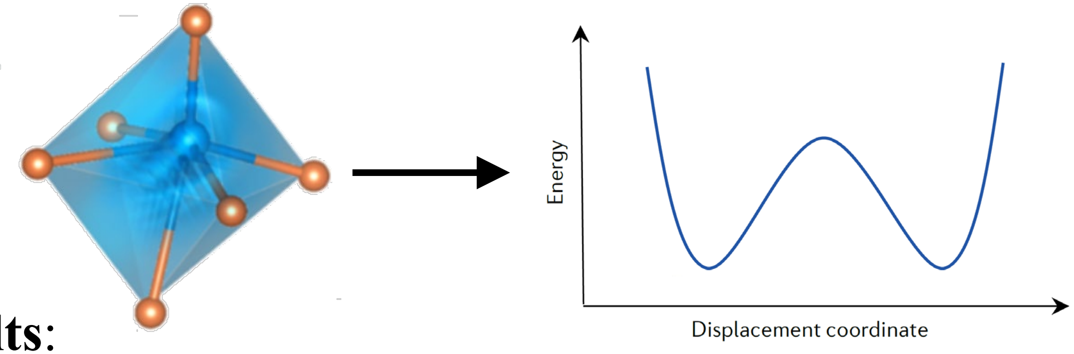
2.4 ns^2 LPE and Exciton-Phonon Coupling

Raman Central Peak

Pb^{2+} hopping causes **polar fluctuation**

enhancing lattice anharmonicity & EPC

=> 0 cm^{-1}, broadband background

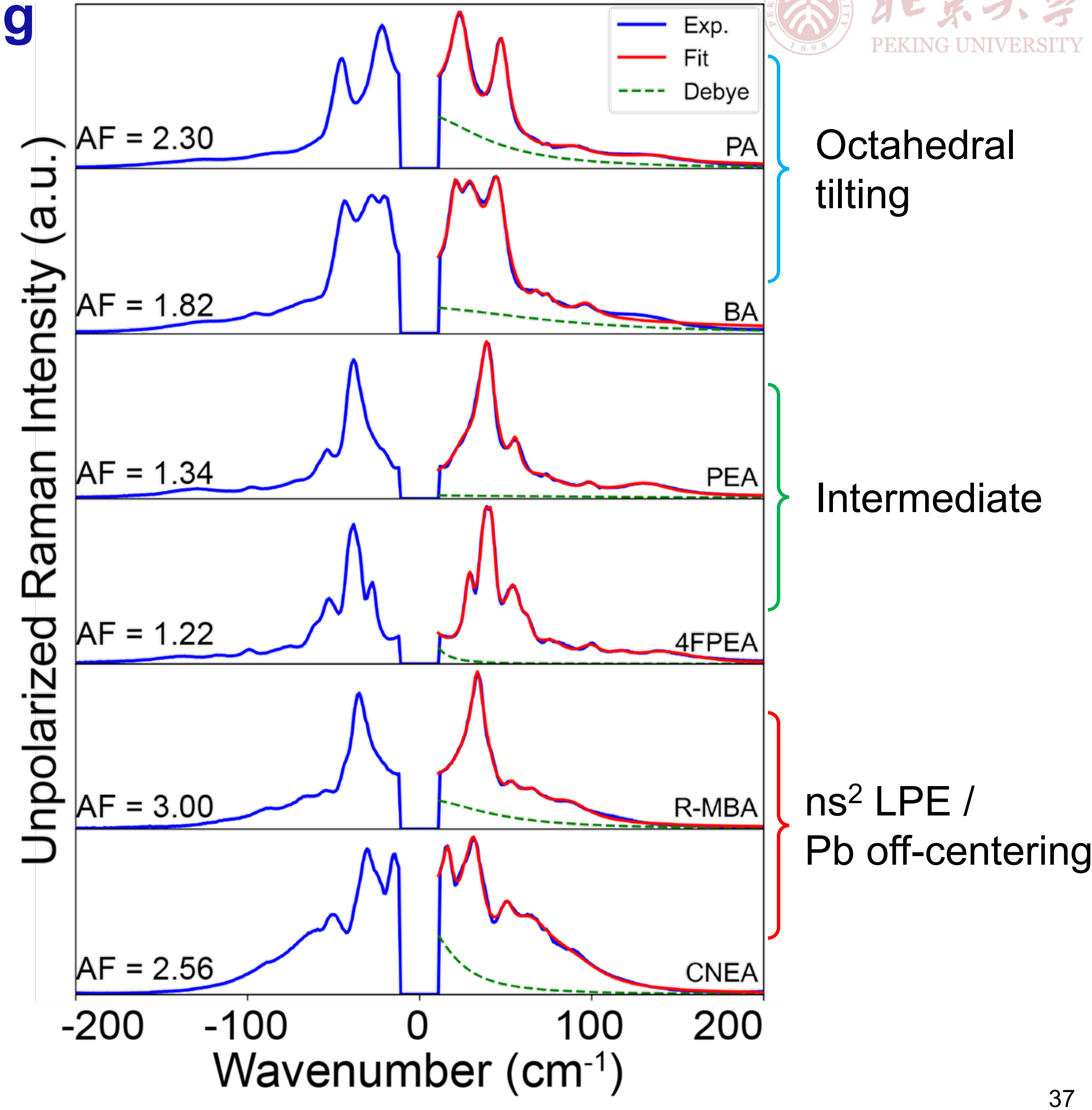


Results:

Octahedral tilting ---- Strong central peak

Intermediate ---------- Weak central peak

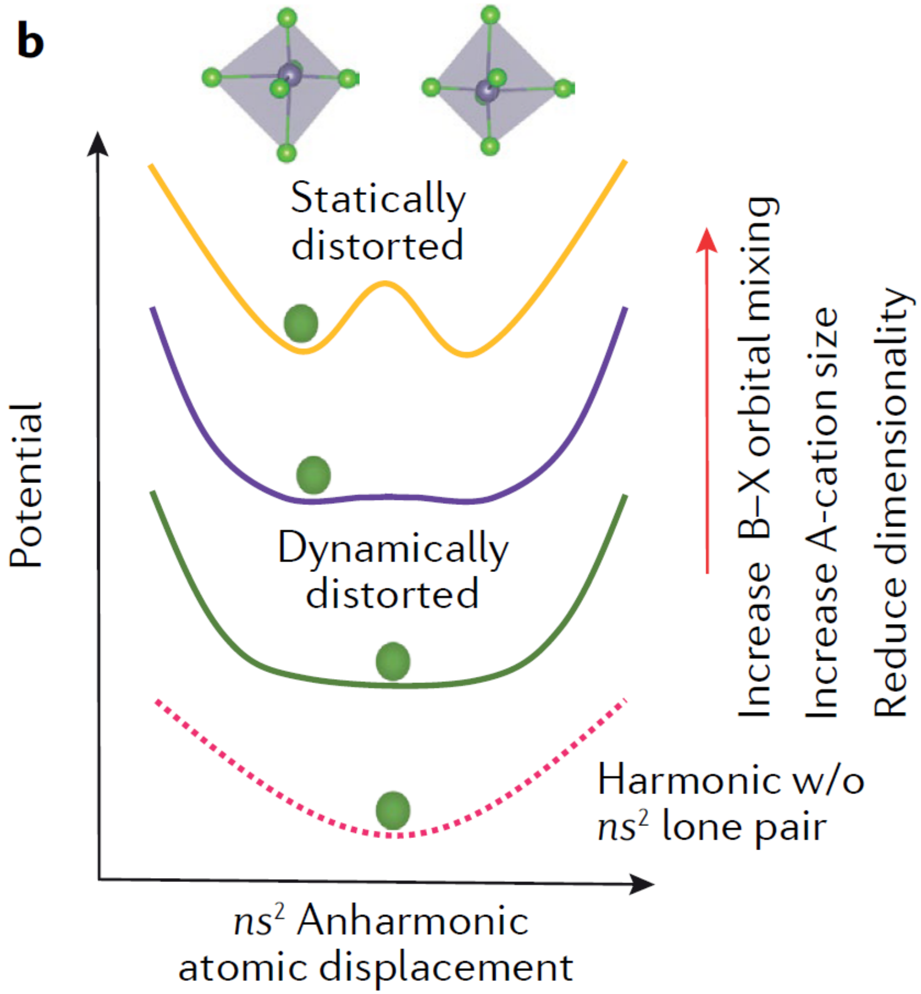
ns^2 LPE --------------- Strong central peak

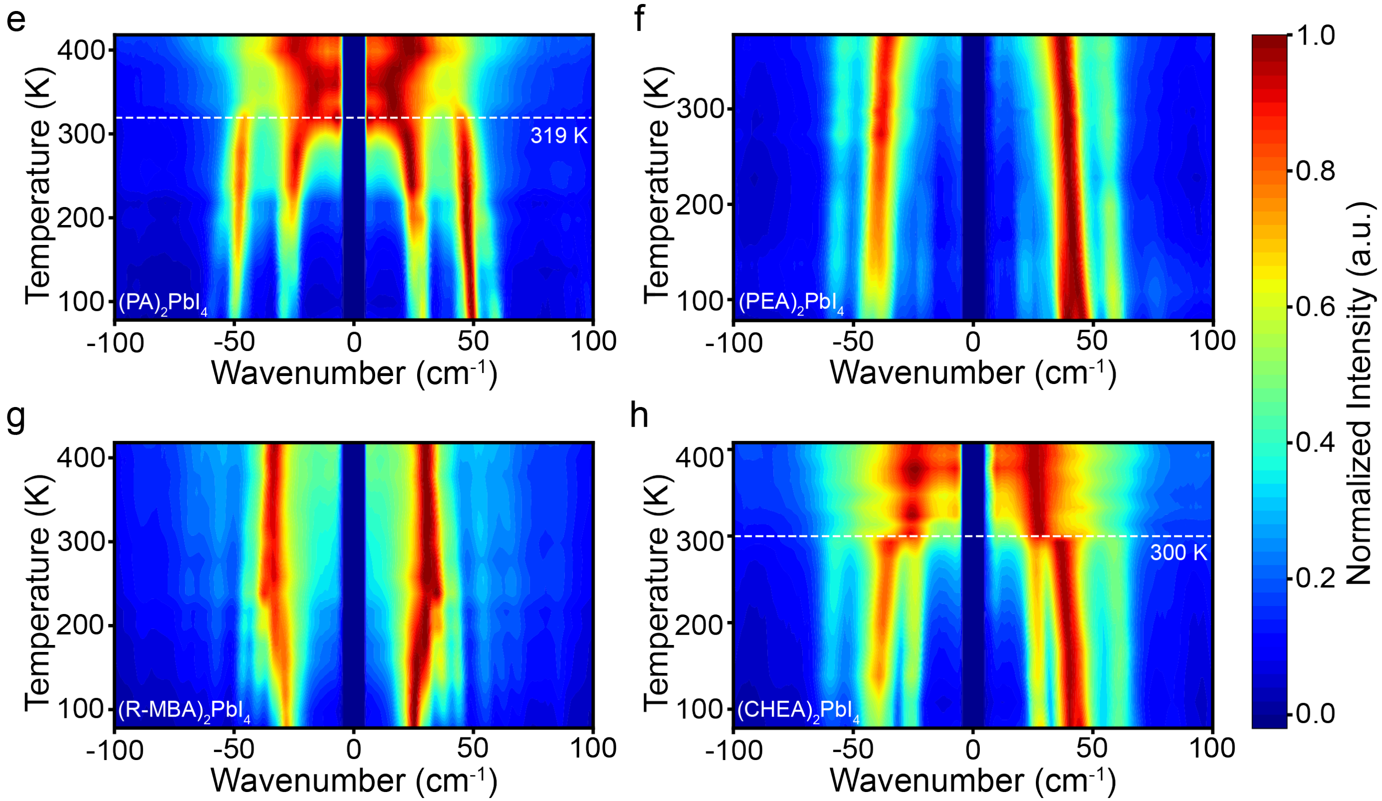


Angew. Chem. Int. Ed. **2023**, 62, e202304515.

2.4 ns^2 LPE and Exciton-Phonon Coupling

Dynamic & Static Distortion





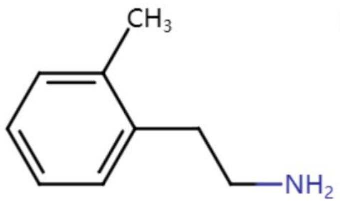
Nat. Rev. Chem. **2021**, 5, 838. *Angew. Chem. Int. Ed.* **2023**, 62, e202304515.

2.3 Measuring Exciton Diffusivity

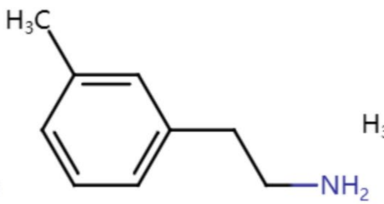
Impact of Structural Distortion Type

We designed **chemically similar** LAs;

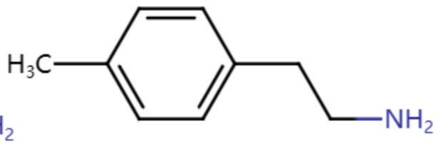
Diffusivity shows no trend due to **trap-state emission**.



2MePEA

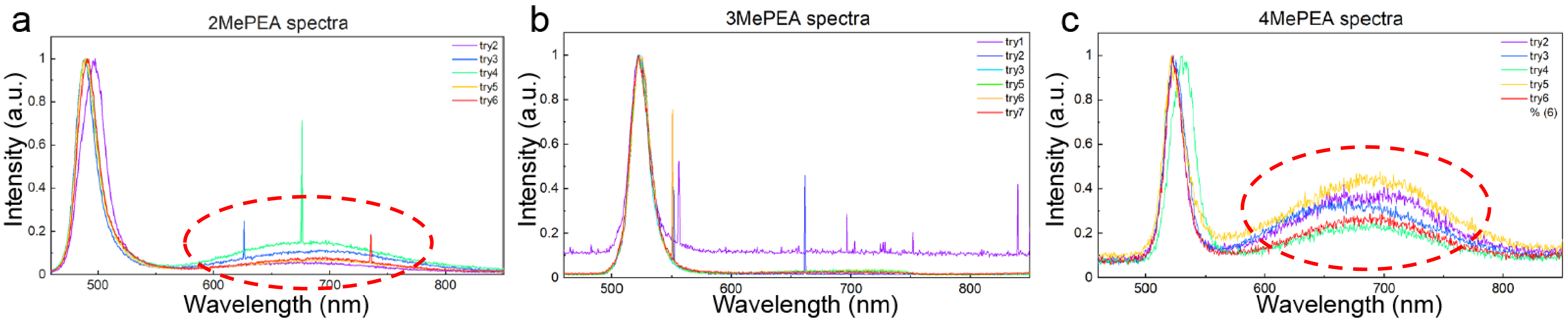


3MePEA



4MePEA

LA Cation	Structural Distortion Type	Diffusivity (cm^2s^{-1})
2MePEA	Tilting	0.262 ± 0.087
3MePEA	Off-center	0.303 ± 0.107
4MePEA	Intermediate	0.174 ± 0.051



2.7 Impact of Trap States

Free & Trapped Exciton Diffusion

*Free Exciton (**FE**)* *Trapped Exciton (**TE**)*

$(4BrAn)_2PbI_4$ shows strong TE emission;

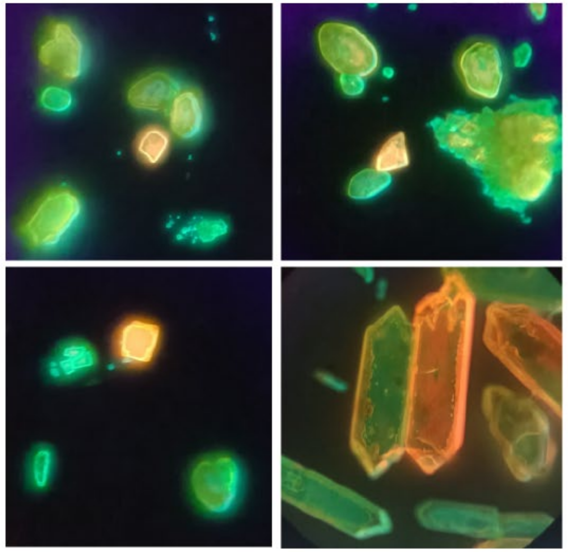
FE and TE emissions can be separated by filters;

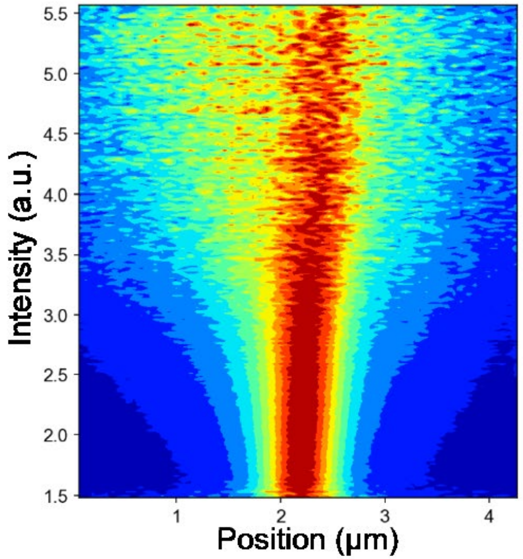
FE diffusion:

- Narrow Voigt distribution;
- "Accelerating" diffusion;

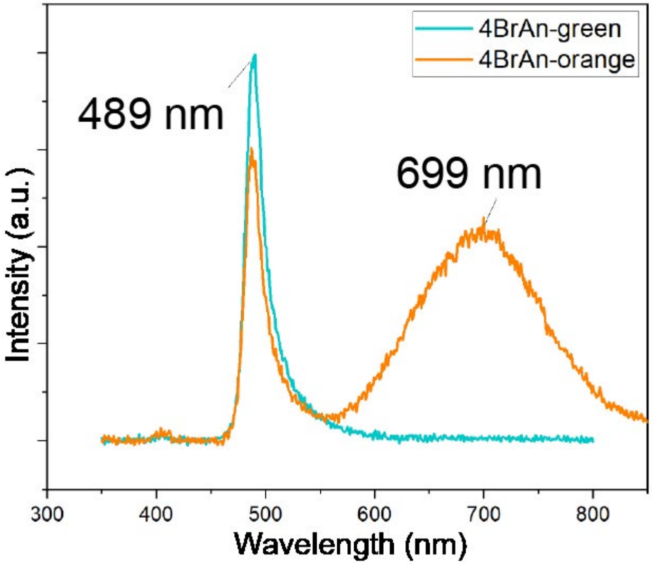
TE diffusion:

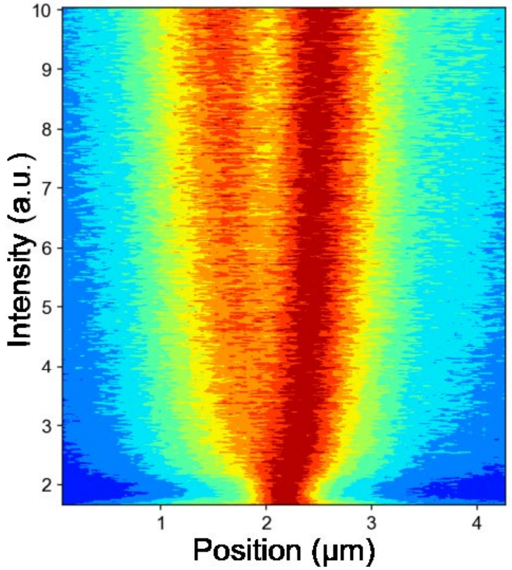
- Broad irregular distribution;
- "Decelerating" diffusion;





FE

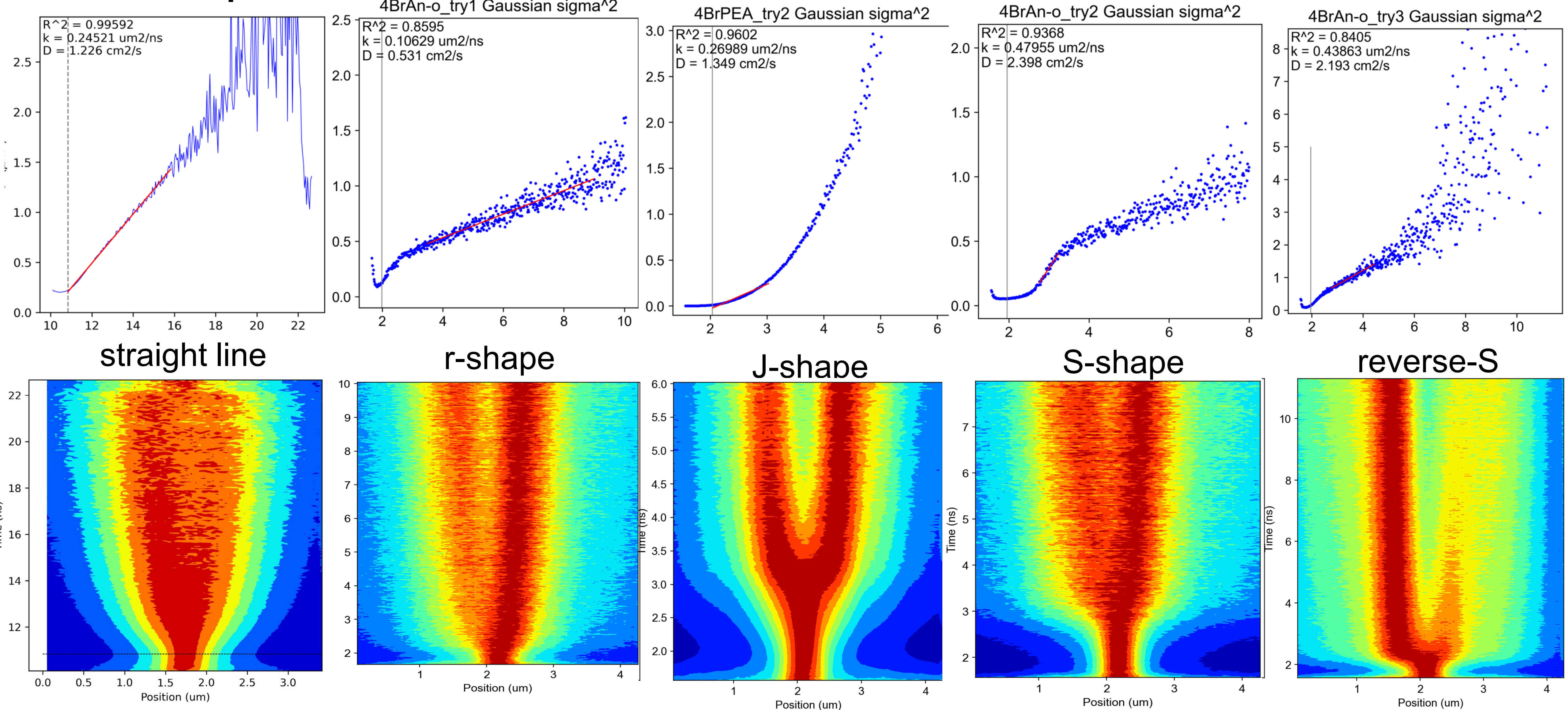




TE

2.8 Exciton Diffusion Dynamics

Different shapes of σ^2-t curve



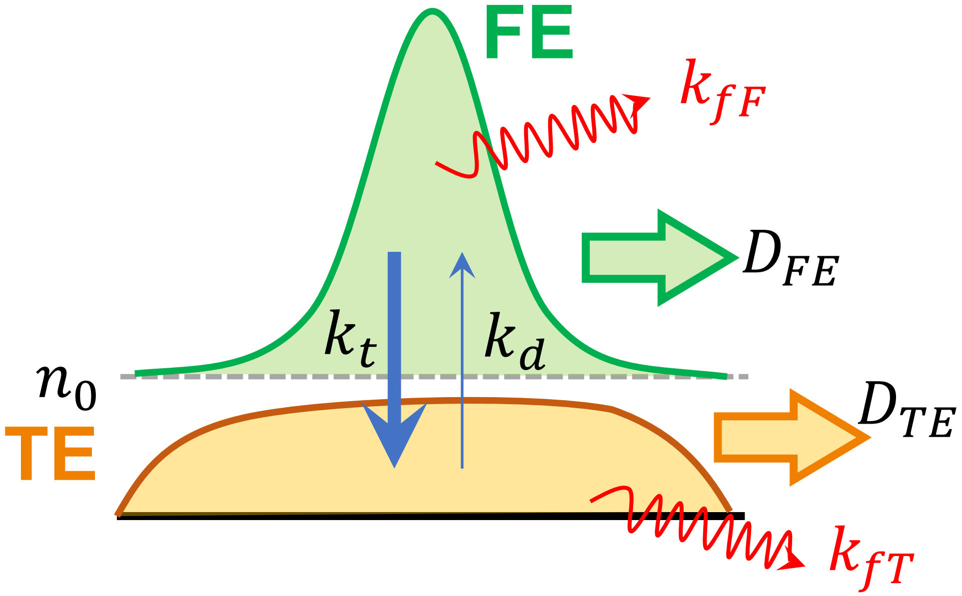
3.4 Hypothesis of Trapped Exciton Diffusion

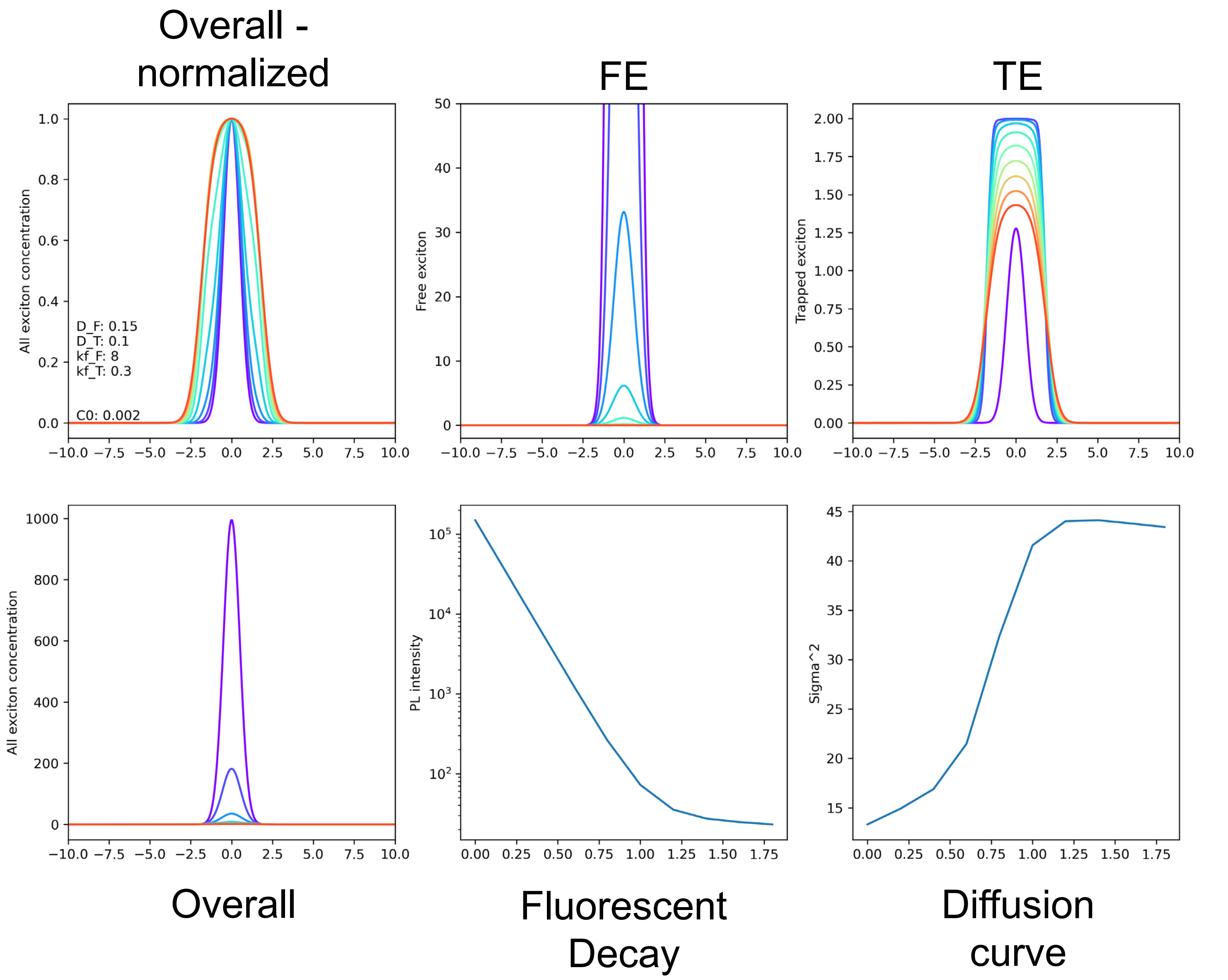
A possible model

1. There's a defect saturation level n_0;
2. FE traps fast, while TE detraps slow;

   $(k_t \gg k_d)$
3. FE has shorter lifetime than TE;

   $(\tau_{FE} \ll \tau_{TE})$





3.4 Hypothesis of Trapped Exciton Diffusion