Virtual International Seminar on Theoretical Advancements

VISTA

Traveling in a space of approximations for modeling of photoinduced dynamic processes

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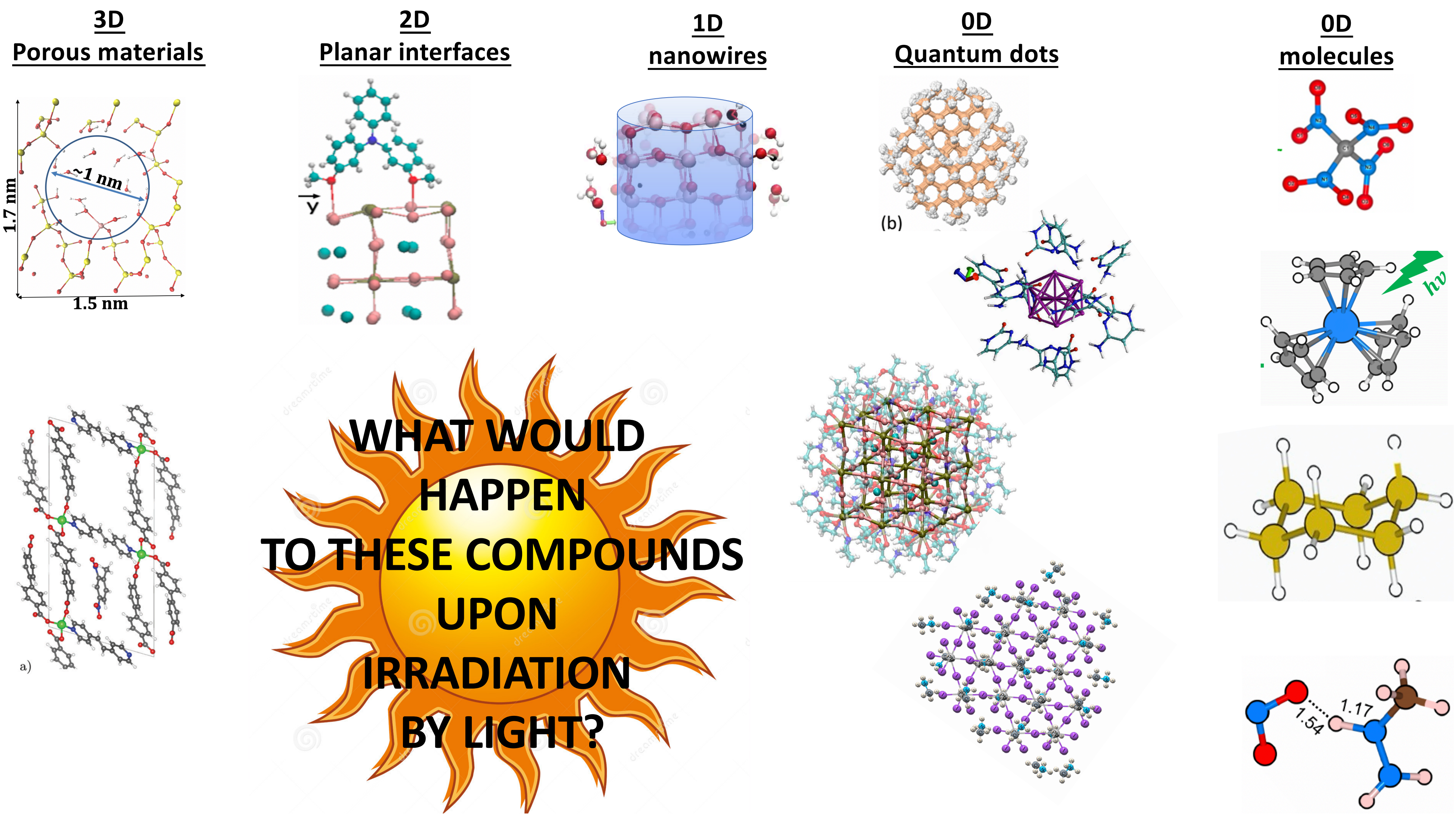
Welcome
to the
ZOO

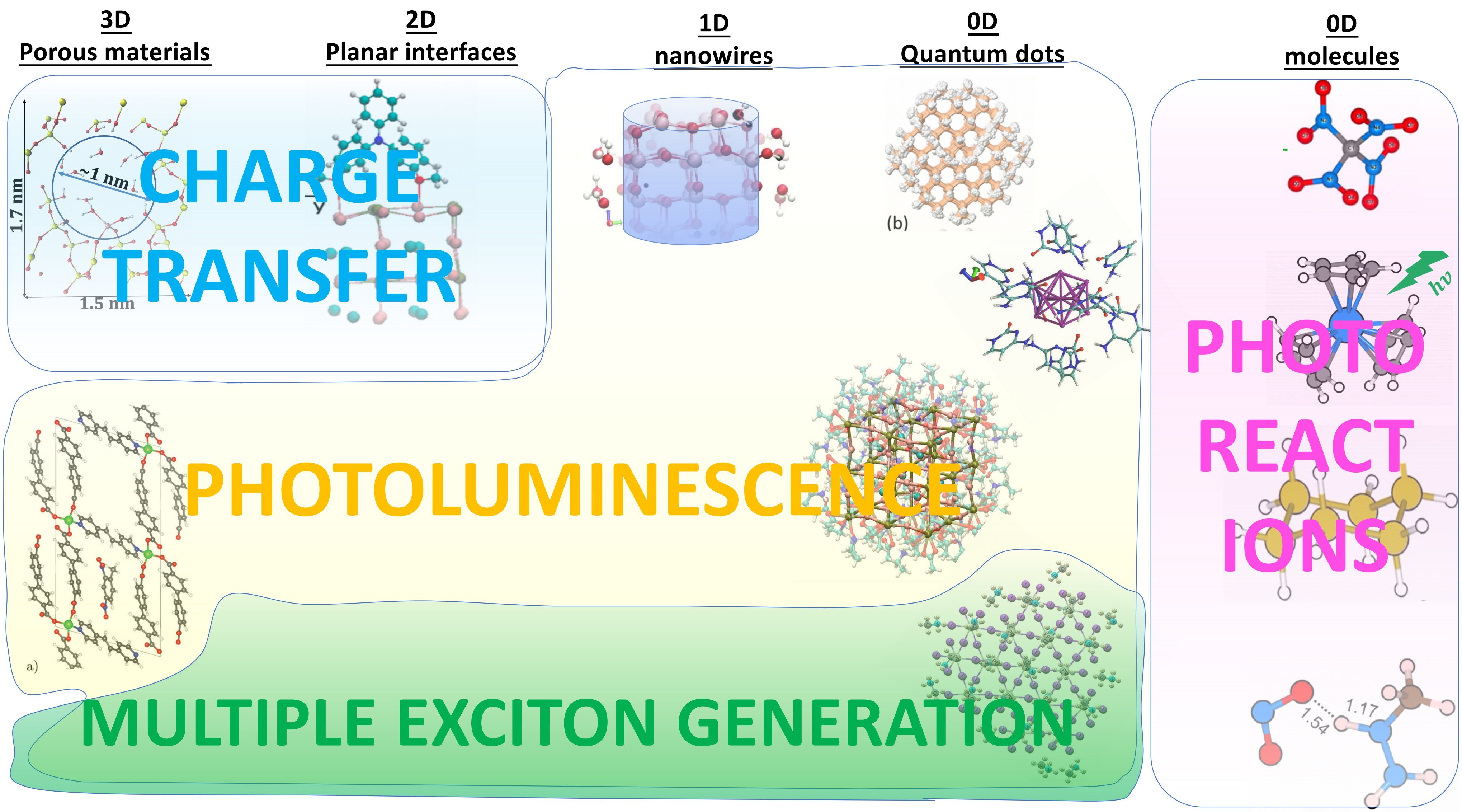
Principles of Research

synthesis

characterization

Study of mechanisms


3D
Porous materials
2D
Planar interfaces
1D
nanowires
0D
Quantum dots
0D
molecules
1.7 nm
~1 nm
1.5 nm
y
(b)
a)
hν
1.17
1.54
WHAT WOULD
HAPPEN
TO THESE COMPOUNDS
UPON
IRRADIATION
BY LIGHT?



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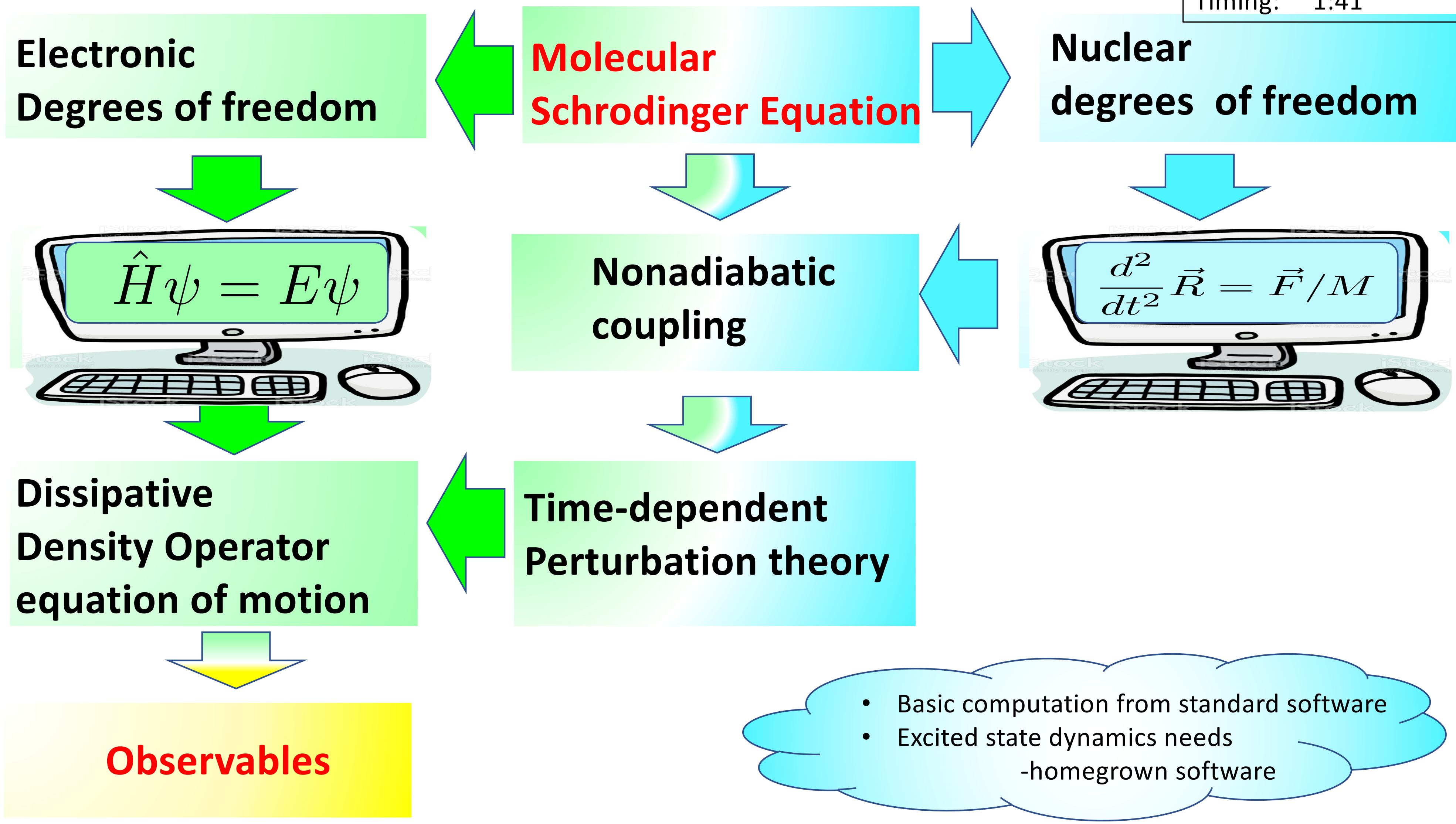
TRANSFER
~1 nm
1.7 nm
1.5 nm
(b)
PHOTOLUMINESCENCE
a)
PHOTO
REACT
IONS
hν
1.17
1.54
MULTIPLE EXCITON GENERATION


WHAT'S MISSING ?

Is there a “ready-to-use” public software to model photoinduced dynamics?

Timing: 1:41

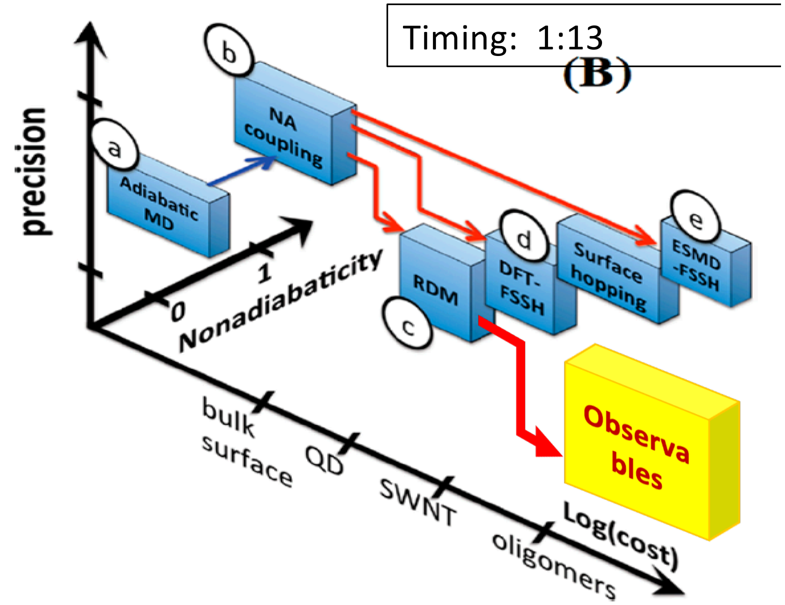


Electronic
Degrees of freedom
Molecular
Schrodinger Equation
Nuclear
degrees of freedom
$\hat{H}\psi = E\psi$
Nonadiabatic
coupling
$\frac{d^2}{dt^2}\vec{R} = \vec{F}/M$
Dissipative
Density Operator
equation of motion
Time-dependent
Perturbation theory
Observables
• Basic computation from standard software
• Excited state dynamics needs
-homegrown software

Adjustments of methodology

- **Independent Orbitals Approximation**
- **Extract probabilities of**
  non-radiative transitions
  from molecular dynamics,
  by "on-the-fly" protocol
- **A very quick original code**
  for dynamics of quantum state
- **Time-independent coefficients in**
  equation of motion
  enable time from 1fs to 1ns

Timing: 1:13



Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$$

density operator

$$\rho = |\psi\rangle\langle\psi|$$

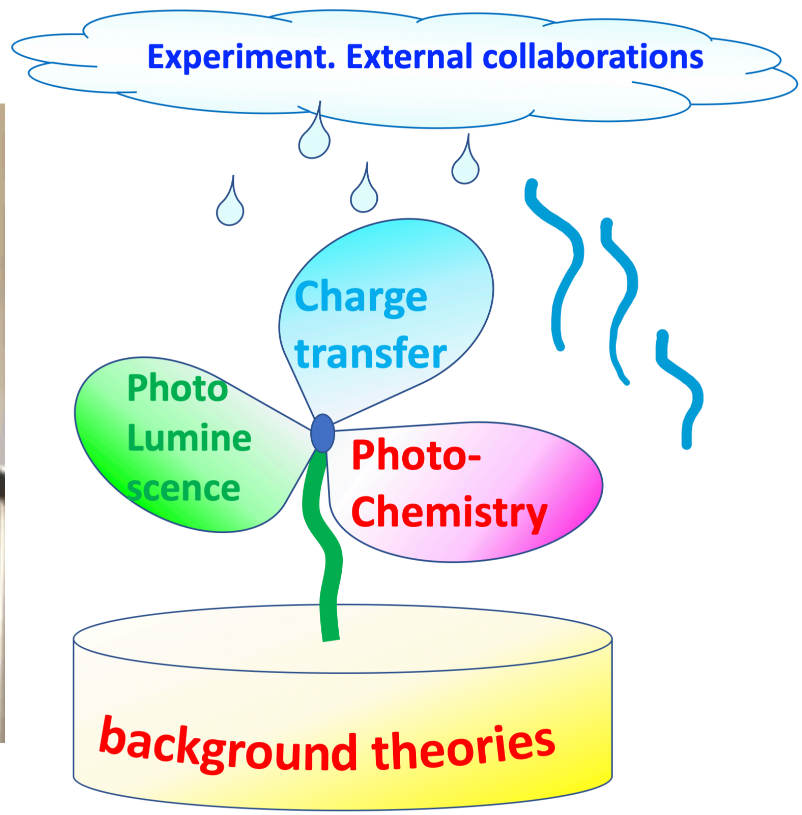
von Neumann equation

$$i\hbar\frac{\partial}{\partial t}\rho = H|\psi\rangle\langle\psi| - |\psi\rangle\langle\psi|H$$

Reference: Kilina, Kilin, Tretiak, *Chemical Reviews* **2015** 115 (12), 5929-5978. *cited 135*

Timing: 1:55

Collaboration between Theory and Experiment



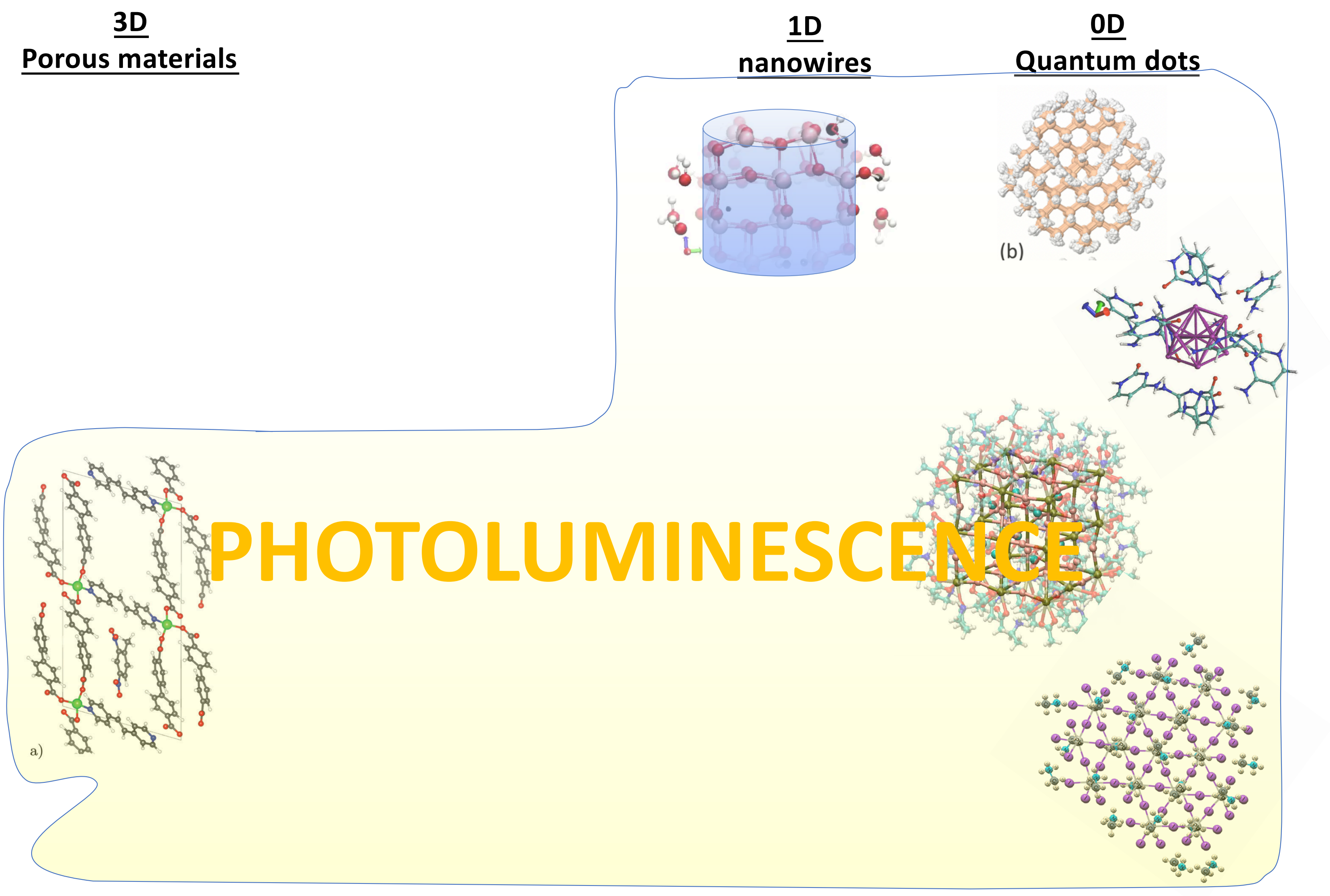
Connection Between Computational Modeling and Experimental Observations

$$\langle \hat{A} \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi \, dx$$

$\langle \hat{A} \rangle$ Expectation value of Experimental observable: An average result for a series of identical experiments

$\Psi(x,t)$ wavefunction of the model

$\hat{A}$ Quantum operator


3D
Porous materials
1D
nanowires
0D
Quantum dots
(b)
PHOTOLUMINESCENCE
a)

PHOTOLUMINESCENCE

-At which wavelength the material emits light?

-Does emission occur at the same wavelength
or in a range of frequencies?

-Does temperature enhance or suppresses emission?

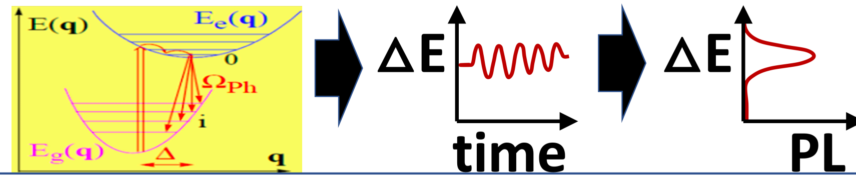
-What is more probable:
to emit light or to convert energy into heat?

-Do surface adsorbates
suppress or enhance photoluminescence?

Specific methods adjustments for modeling of photoluminescence

- sampling
- time integration
- up-/down-conversion
- spinors

FEATURE #1: Approximate Franck-Condon principle by sampling transitions along a trajectory



FEATURE #2: Signals beyond Kasha's rule: Convert electron dynamics into optical transitions

FEATURE #3: Quantitative account for up- and down- conversion processes

up-conversion (Auger Recombination) down-conversion MEG (Multiple Exciton Generation)

FEATURE #4: Quantitative account for spin-flip optical transitions, phosphorescence via implementing concept of spinor

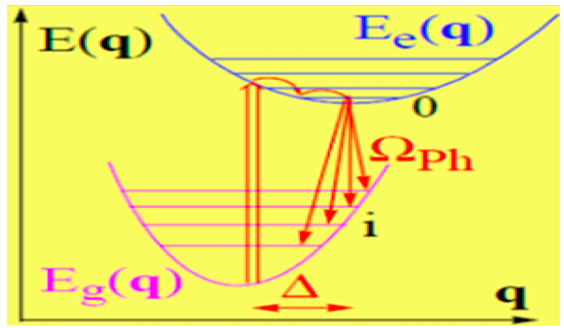
$$\psi_i^{\mathrm{spinor}} = \phi_{i\uparrow}(r)|\uparrow\rangle + \phi_{i\downarrow}(r)|\downarrow\rangle$$

Research Direction: (ii) Photoluminescence

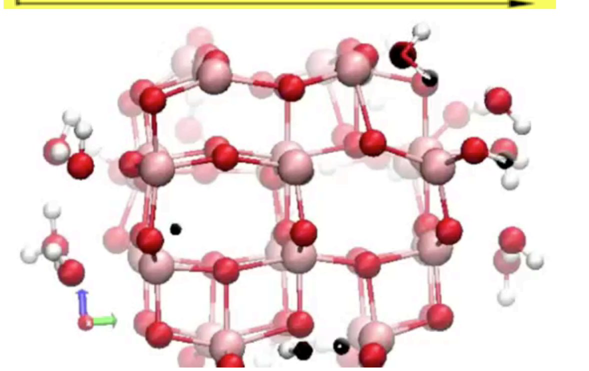
Timing: 2:29

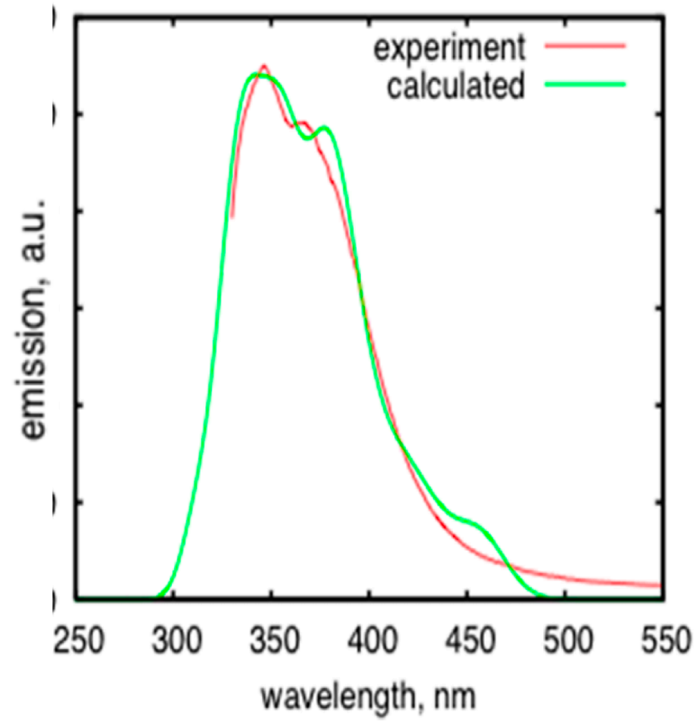
Linewidth thermal broadening of PL signal via MD sampling
Suggested abbreviation:

Molecular **D**ynamics **P**hoto **L**uminescence (**MDPL**)



Wet TiO_2 nanowire





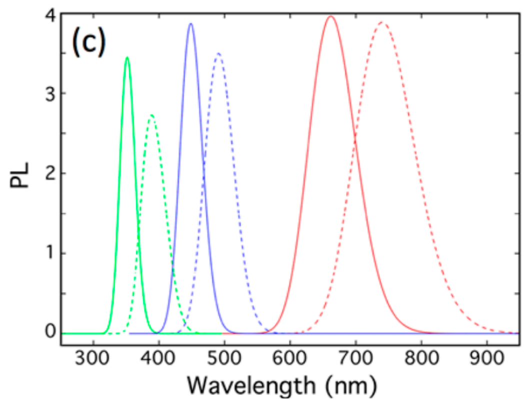
Justification:	quantitatively match experimental data

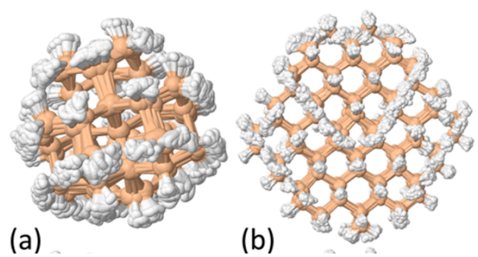
Reference: Vogel, Kilin, *J. Phys. Chem. C* **2015**, 119, 27954–27964

Research Direction: (ii) Photoluminescence

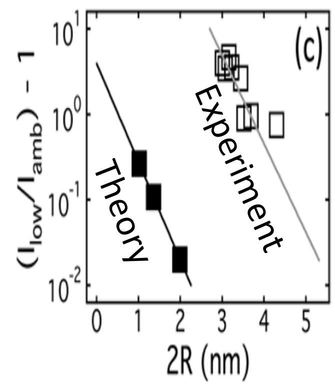
Enhancing photoluminescence in silicon quantum dots by cooling

Theory



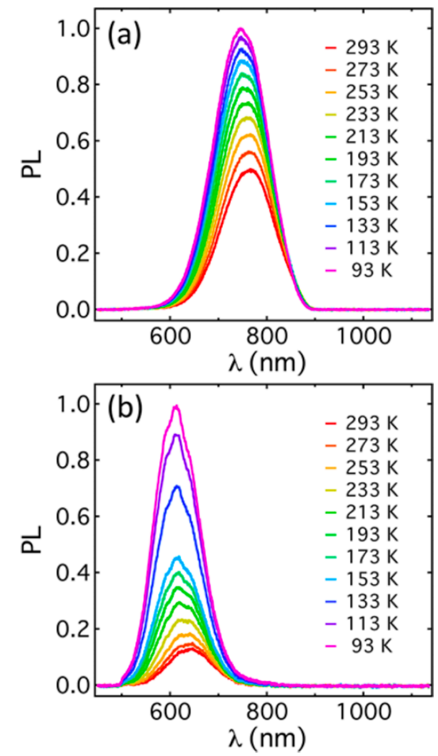


Comparison



Relative increase in PL upon cooling. experiments (open) computation (closed) fit to the same trend.

Experiment

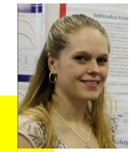


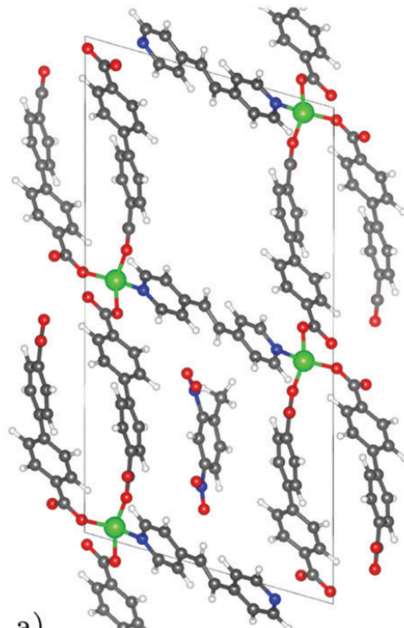
Justification: matches experimental trends

Reference: Brown, Vogel, Miller, Inerbaev, Anthony, Kortshagen, Kilin, Hobbie, *J. Phys. Chem. C* **2016**, 120, 18909

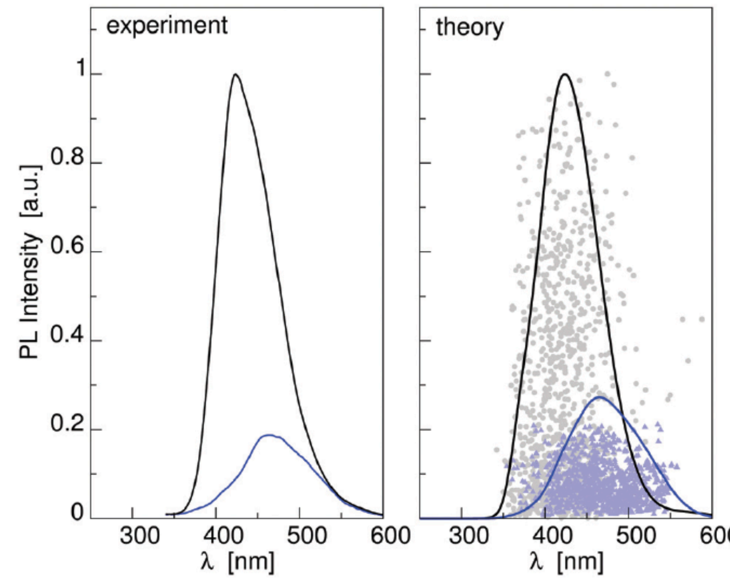
Research Direction: (ii) Photoluminescence

Quenching of photoluminescence in a Zn-MOF sensor by nitroaromatic molecules





a)



RPM3-Zn i.e. $Zn_2(bpdc)_2(bpee)$

bpee = 1,2-bipyridylethene

bpdc = 4,4’-biphenyldicarboxylate

DNT = 2,4-dinitrotoluene

Intensity of PL by RPM3-Zn-MOF decreases with adsorption of explosive dinitro-toluene

Upon photoexcitation $(pbdc)^+(bpee)^-$

electron migrates from (bpee) to (DNT)

Resulting excitations $(pbdc)^+(DNT)^-$

bas CT character and low oscillator strength

Justification: quantitatively matches experimental observables!

Reference: Jensen, Tan, Lustig, Kilin, Li, Chabal, Thonhouser *J. Mater. Chem. C*, **2019**,7, 2625-2632

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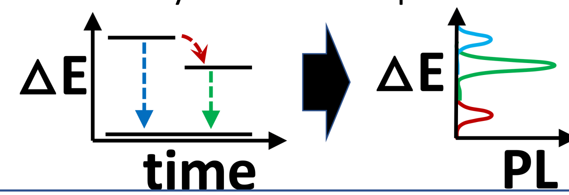

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up-conversion (Auger Recombination) **down-conversion** MEG (Multiple Exciton Generation)

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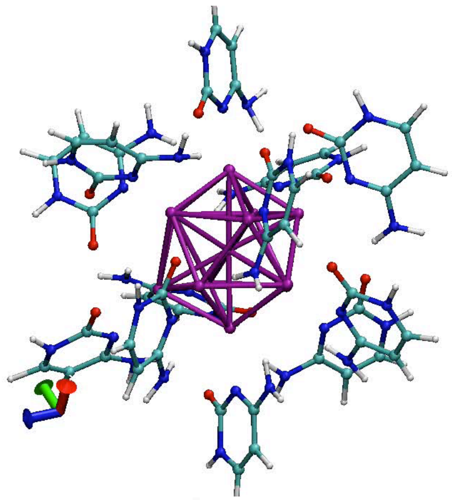
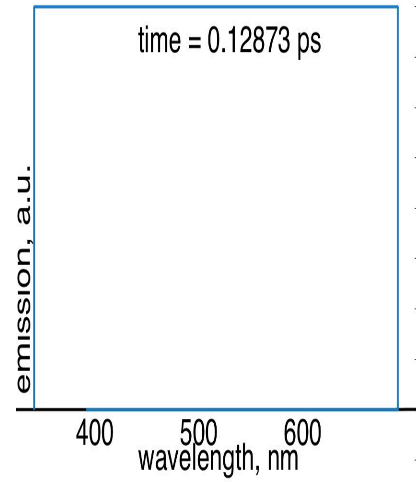
$$\psi_i^{\text{spinor}} = \phi_{i\uparrow}(r)|\uparrow\rangle + \phi_{i\downarrow}(r)|\downarrow\rangle$$

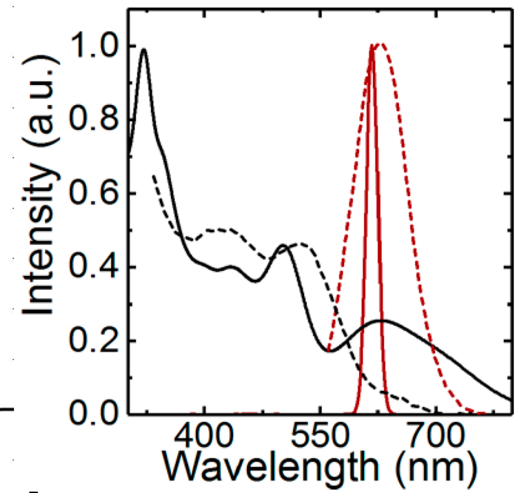
Research Direction: (ii) Photoluminescence

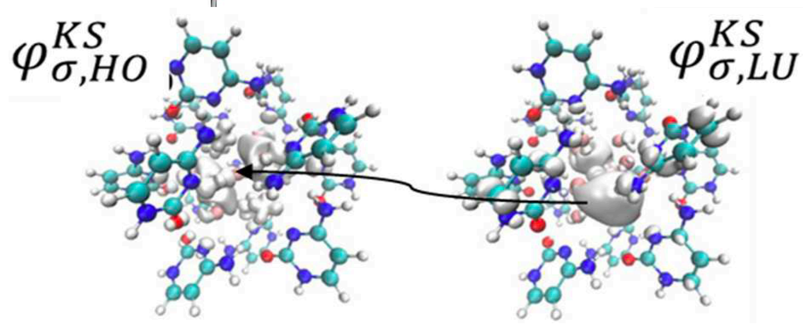
Fluorescence in DNA-protected Silver Nanoclusters

Timing: 4:00









Ag_{13}^{5+} singlet model calculated spectra

PL (solid red)

absorption (solid black)

Experimental spectra

PL (dashed red)

absorption (dashed black)

Justification: matches experimental trends, identified bright charge transfer excitations

Reference: Brown, Hobbie, Tretiak, Kilin, *J. Phys. Chem. C* **2017**, 121, 23875-23885

Specific methods adjustments for modeling of photoluminescence

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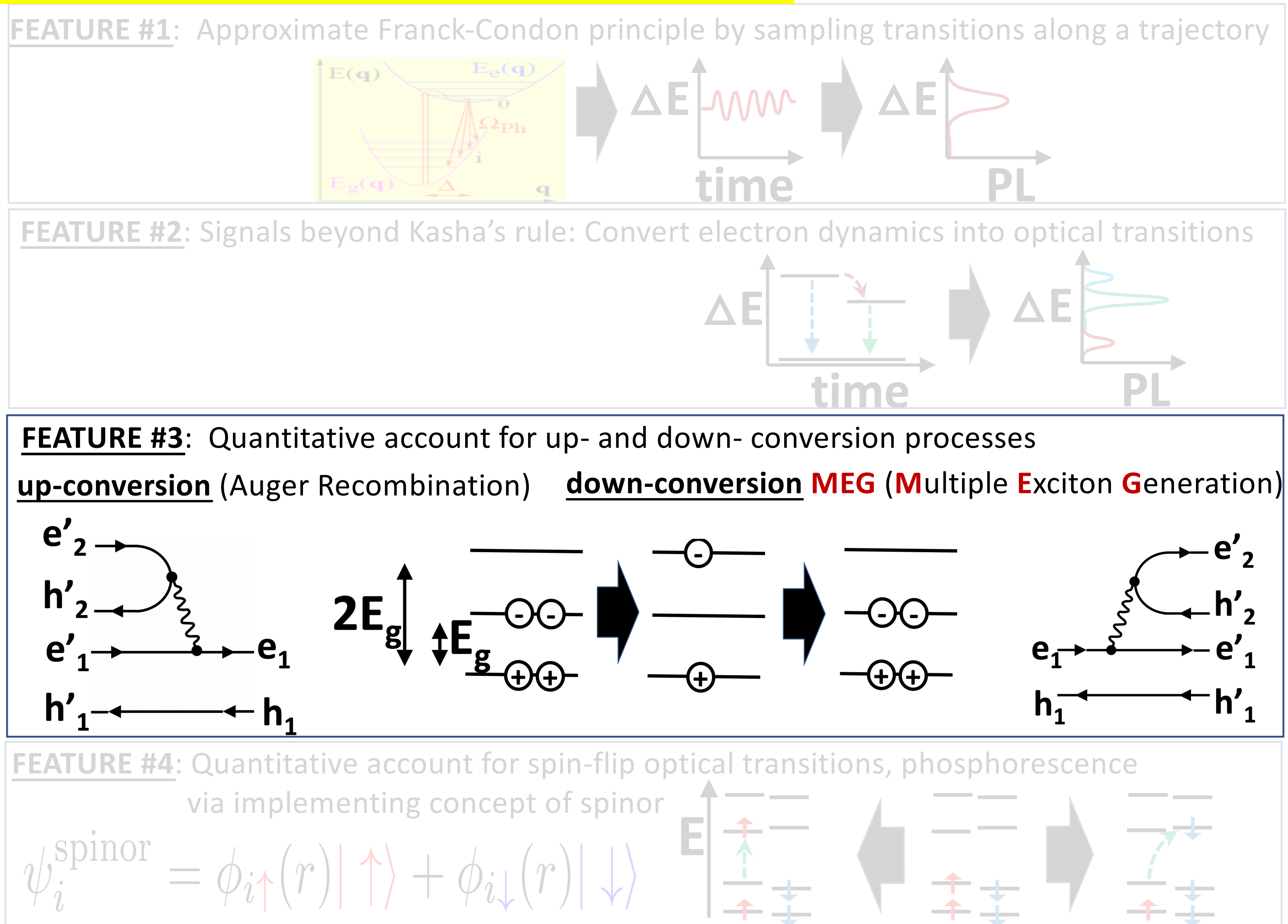
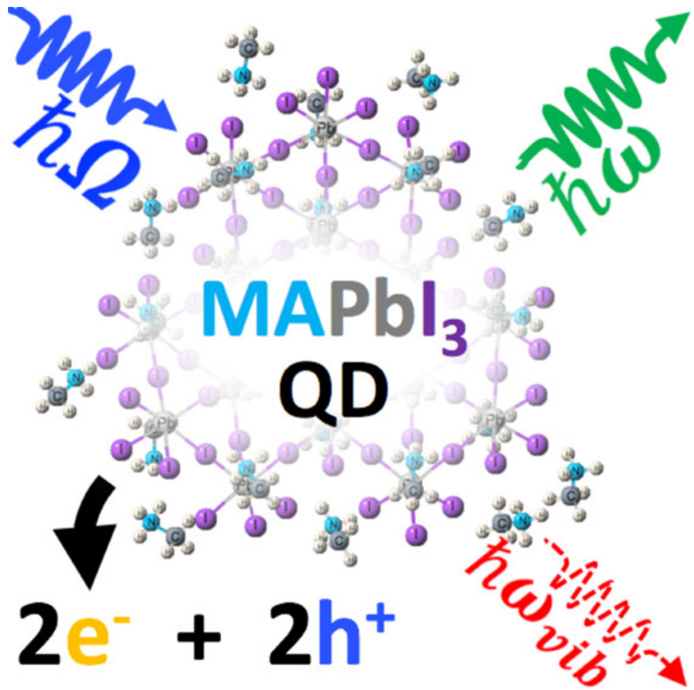
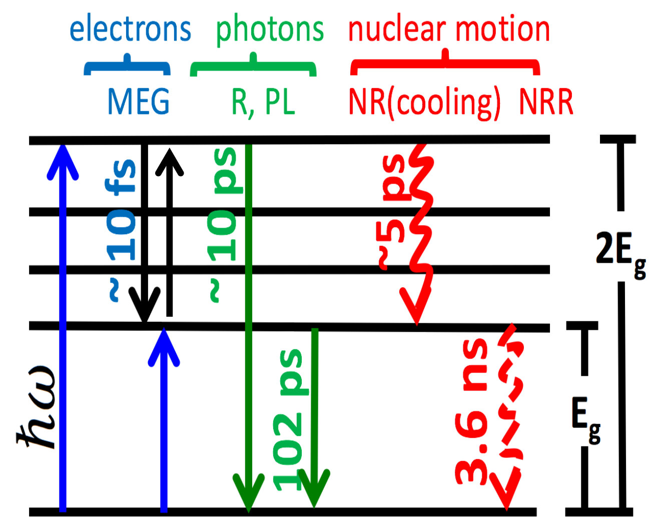


Research Direction: (ii) Photoluminescence

Timing: 2:43

Quantum Confinement in Lead Halide Perovskite Quantum Dots





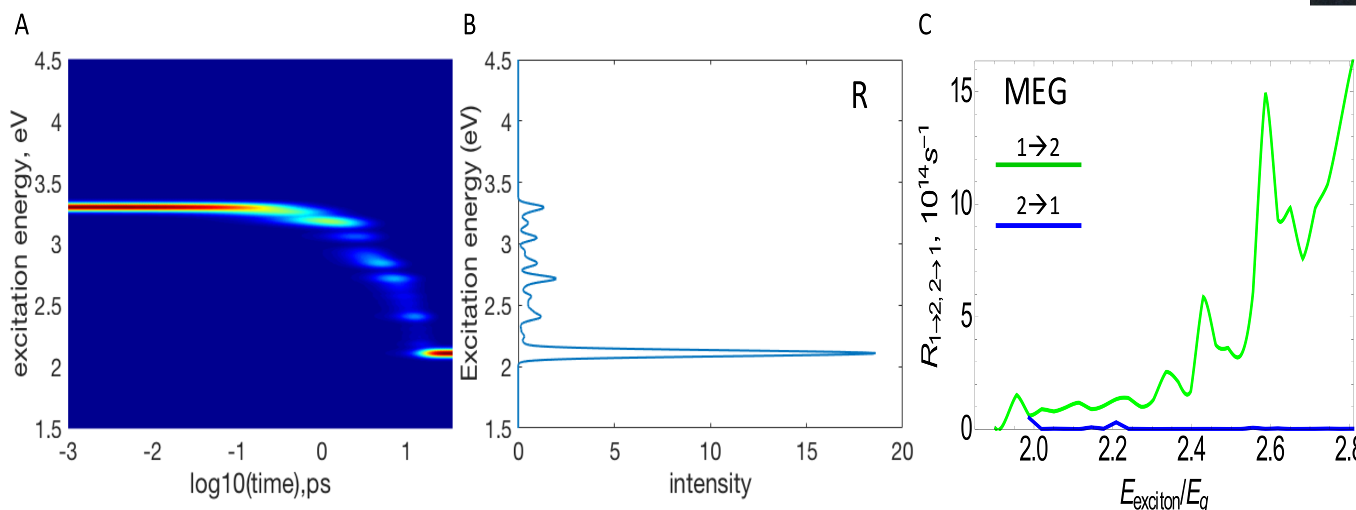
Justification: predict outcome of measurement prior to experimental observarions

Reference: Vogel, Kryjevski, Inerbaev, Kilin *J. Phys. Chem. Lett.* **2017** 8, 3032

Research Direction: (ii) Photoluminescence

Timing: 2:35

Quantum Confinement in Lead Halide Perovskite Quantum Dots



Signatures of size confinement were seen
-- increased spacing of energy states
-- localized electron density

The increased intra-band energy separation
--slows down the nonradiative relaxation
--by requiring multiple phonon modes
to dissipate the hot electron energy.

Multiple **E**xciton **G**eneration (**MEG**)
--is facilitated by confinement
--is beneficial for photovoltaics
--is adverse for light emission

Ultra-small Quantum Dots
--will be less efficient light emitters
--than mid-size ones

Justification: predict outcome of measurement prior to experimental observations

Reference: Vogel, Kryjevski, Inerbaev, Kilin *J. Phys. Chem. Lett.* **2017** 8, 3032

Research Direction: (ii) Photoluminescence

Timing: 0:59

Quantum Confinement in Lead Halide Perovskite Quantum Dots

ACS Editors' Choice

Letter

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-018-06596-1 OPEN

Low threshold and efficient multiple exciton generation in halide perovskite nanocrystals

Mingjie Li[1], Raihana Begum[2], Jianhui Fu[1], Qiang Xu[1], Teck Ming Koh[2], Sjoerd A. Veldhuis[2], Michael Grätzel[3], Nripan Mathews[2,4], Subodh Mhaisalkar[2,4] & Tze Chien Sum[1]

MEG[36,37]. Furthermore, another recent computational work[38] also demonstrated low-threshold MEG (close to $2E_g$) in $MAPbI_3$ NCs. The authors attributed that the stronger Coulomb coupling between the initial single-exciton and final-biexciton states, and the longer hot-carrier cooling of highly excited states were more conducive for MEG. Their calculated MEG process was on a time scale of tens of fs, which agrees well with our measured value of smaller than 90 fs. Although, PbSe or PbS also have similar small

38. Vogel, D. J., Kryjevski, A., Inerbaev, T. & Kilin, D. S. Photoinduced single- and multiple-electron dynamics processes enhanced by quantum confinement in lead halide perovskite quantum dots. *J. Phys. Chem. Lett.* 8, 3032–3039 (2017).

Justification: predict outcome of measurement prior to experimental observations

Reference: Vogel, Kryjevski, Inerbaev, Kilin *J. Phys. Chem. Lett.* **2017** 8, 3032-3039. *cited 39 times*

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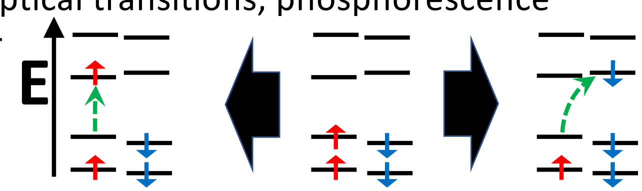
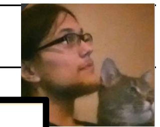
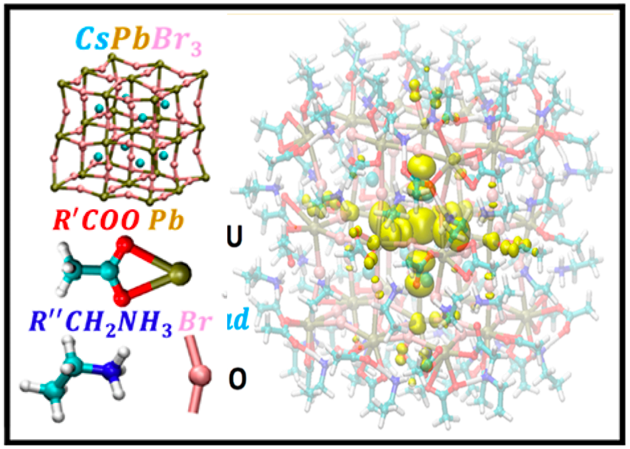
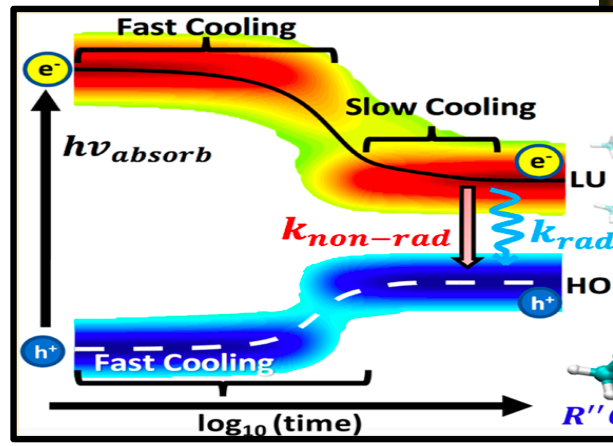


Research Direction: (ii) Photoluminescence

Timing: 4:11







Hot electron cooling

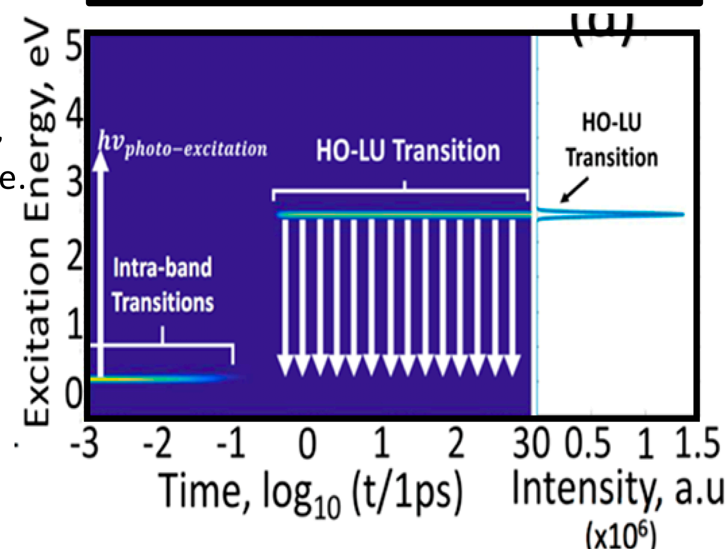
--slows down at the band edge, due to large SOC and strong confinement, which gives sub-gaps above the band edge.

Strong confined nanocrystals

--are better for photovoltaics

Weak confined nanocrystals

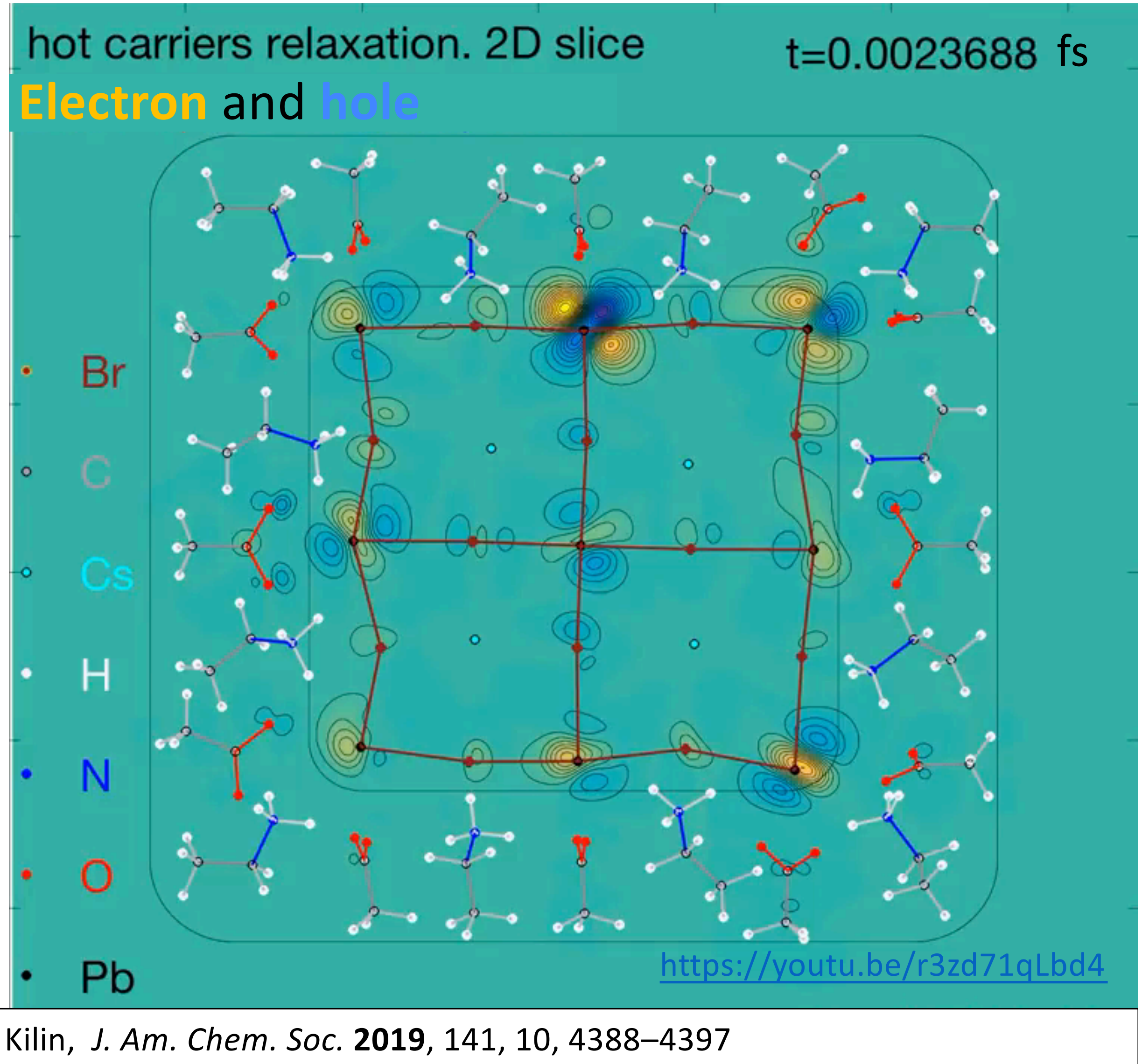
--are better for light-emitting



Justification: PLQY=53% matches experiment

Reference: Forde, Inerbaev, Hobbie, Kilin, *J. Am. Chem. Soc.* **2019**, 141, 10, 4388–4397

Research Direction: (ii) Photoluminescence

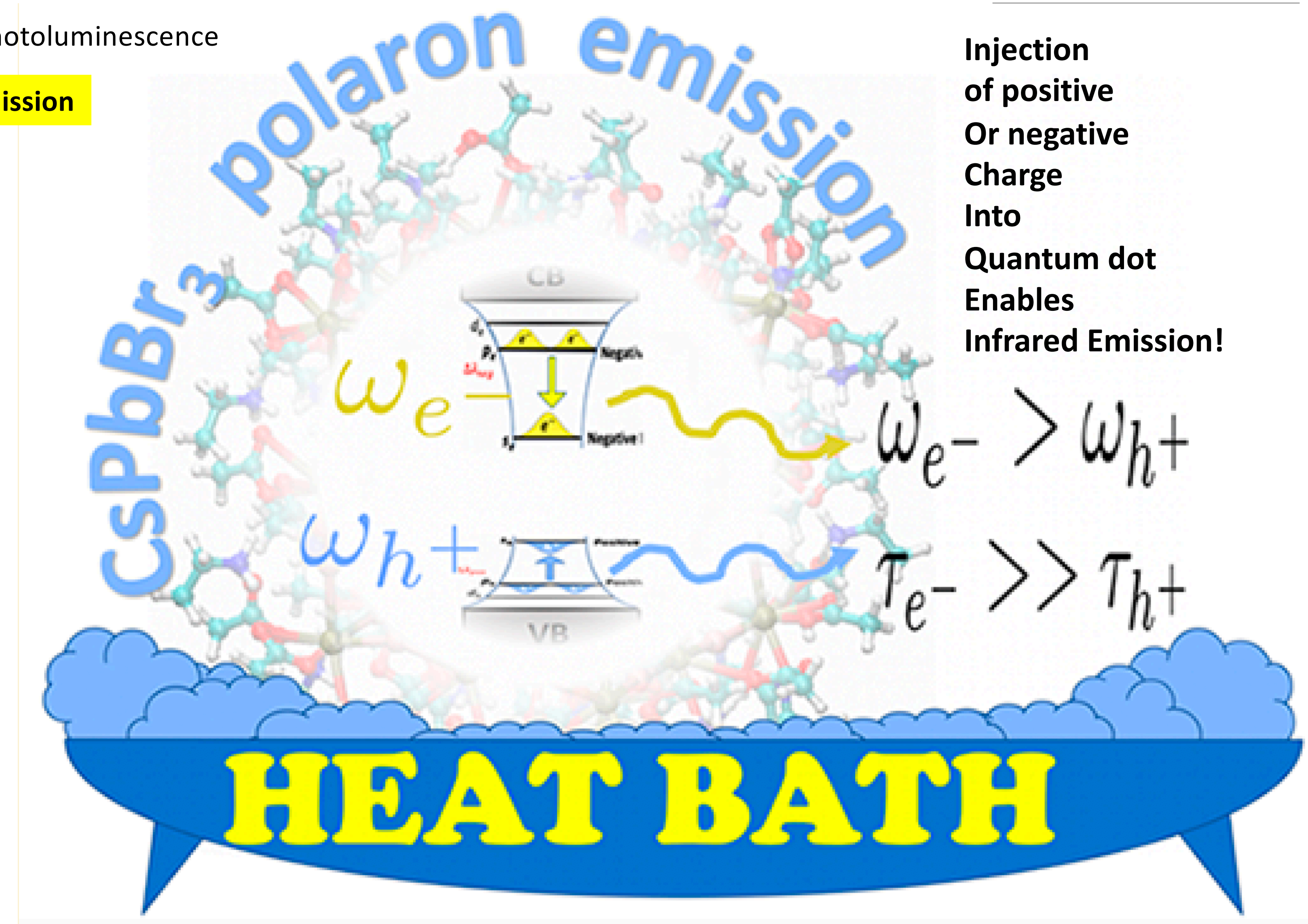


Reference: Forde, Inerbaev, Hobbie, Kilin, *J. Am. Chem. Soc.* **2019**, 141, 10, 4388–4397

Research Direction: (ii) Photoluminescence

Hot polaron Infrared emission

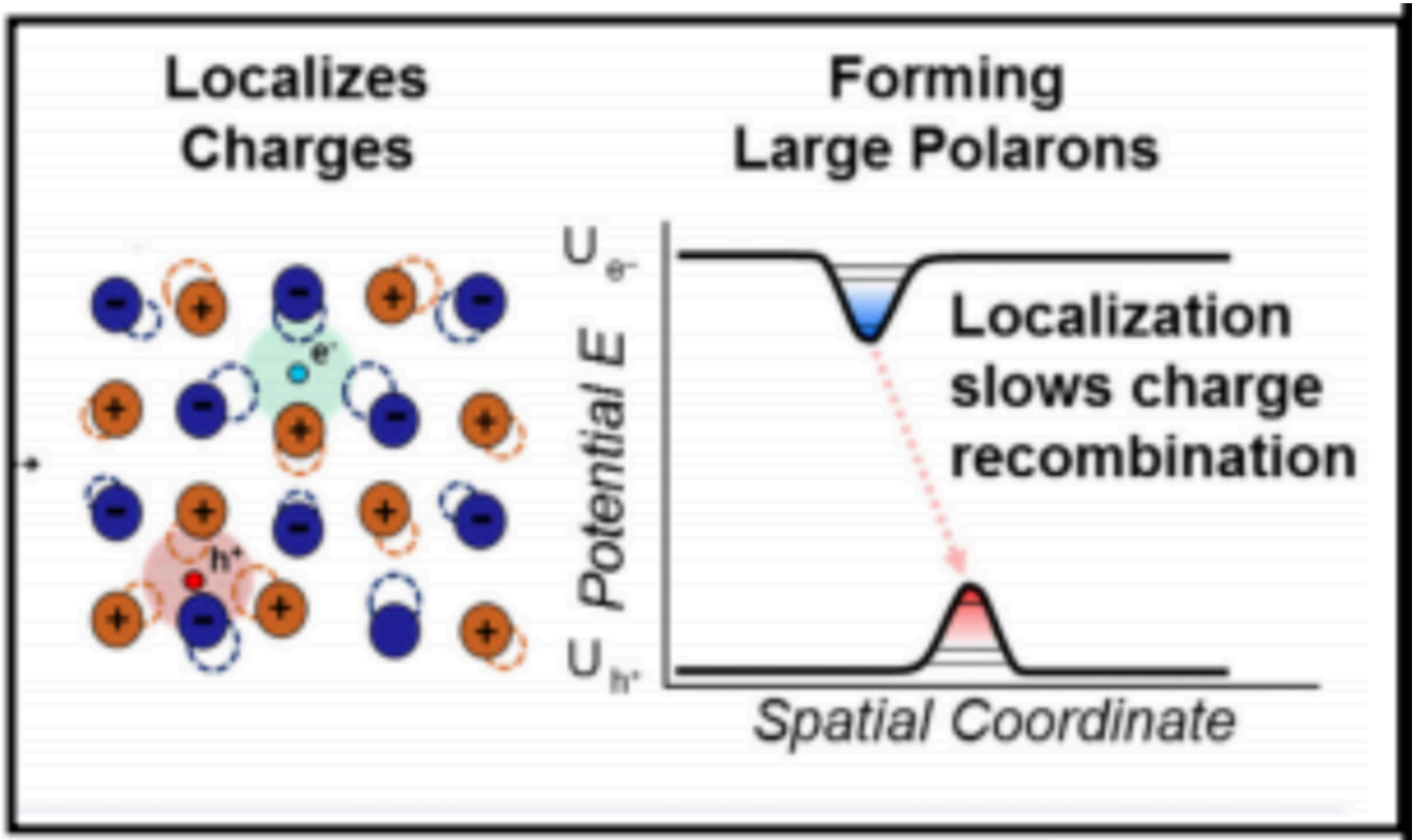
Injection of positive Or negative Charge Into Quantum dot Enables Infrared Emission!



Research Direction: (ii) Photoluminescence

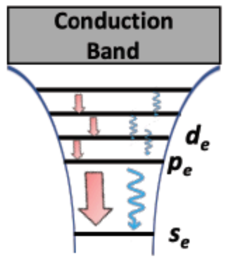
Timing: 0:36

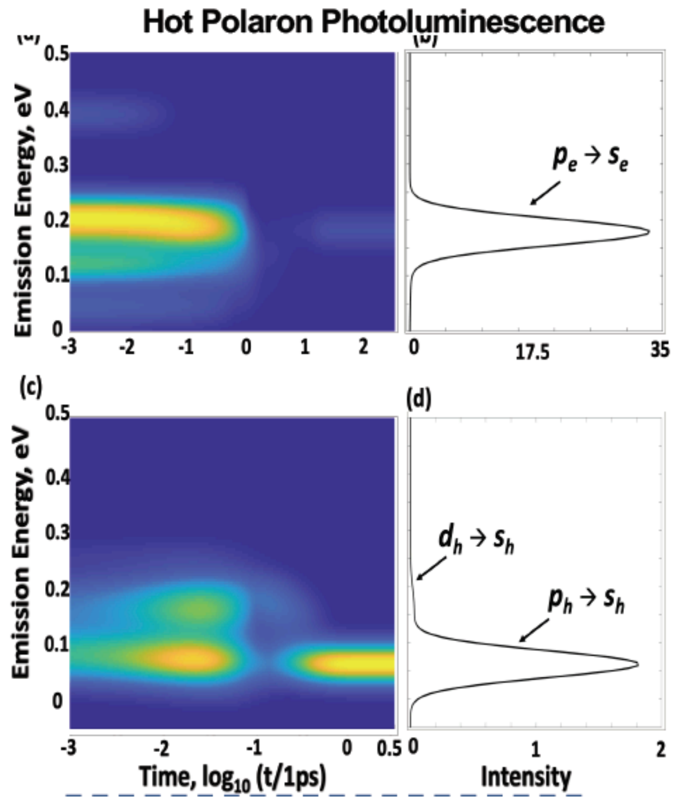
Hot polaron Infrared emission

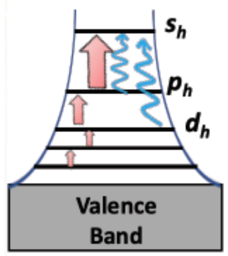


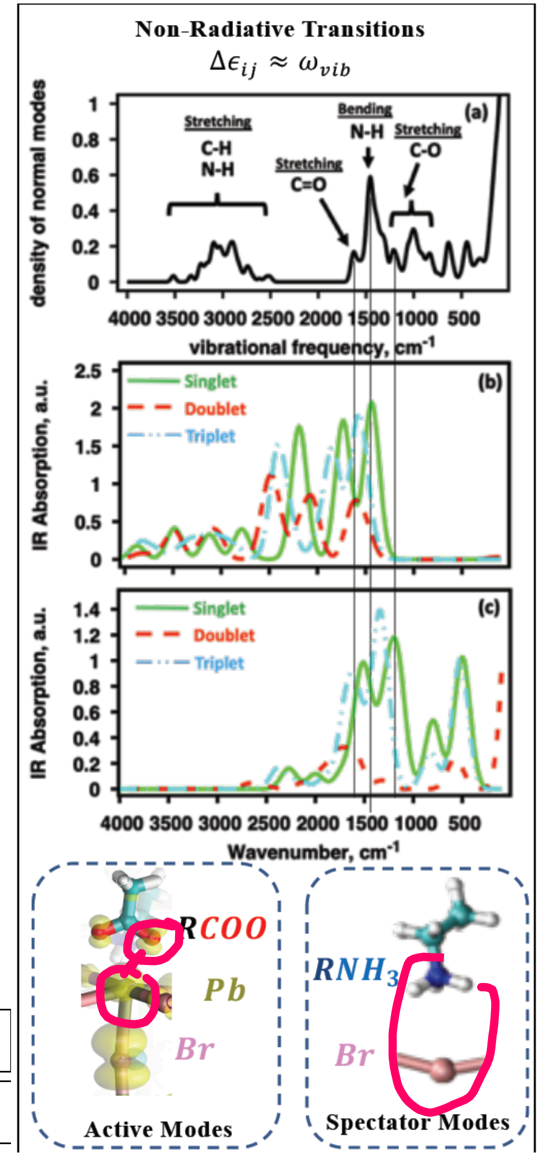
Research Direction: (ii) Photoluminescence

Hot polaron Infrared emission





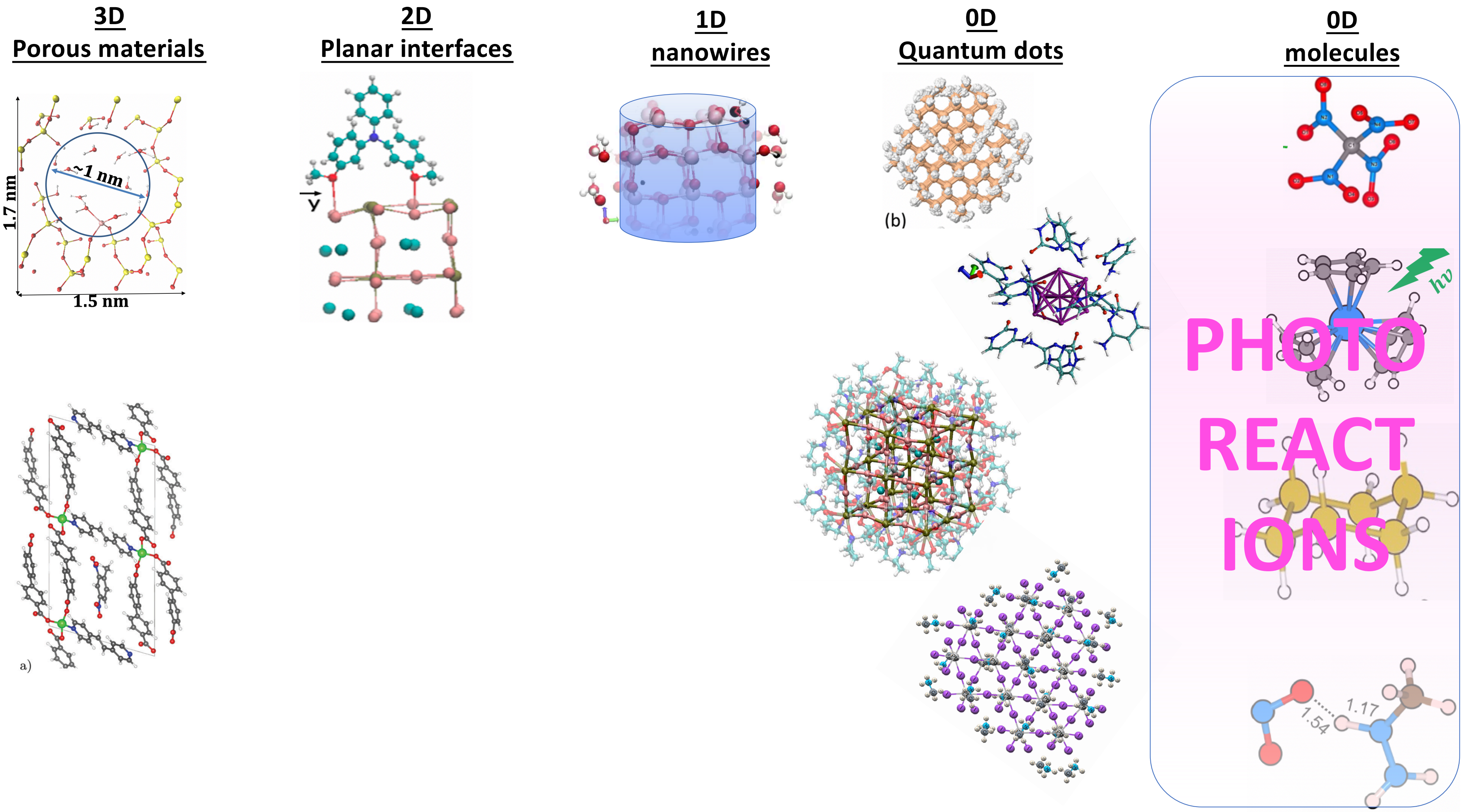




Model	$f_{PGS-RES}$	k_r [1/ns]	k_{nr} [1/ns]	PLQY	log(PLQY)
Positive-Singlet	0.14	2.81x10^{-4}	2.08x10^{3}	1.35x10^{-7}	-7
Negative-Singlet	0.29	5.10x10^{-3}	1.64x10^{1}	3.11x10^{-4}	-4

Justification: Prediction of a property ahead of experimental measurement

Reference: Forde, Inerbaev, Kilin, *J. Phys. Chem. C* **2020**, 124, 1, 1027–1041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REACT
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1.17
1.54

PHOTOREACTIONS

-does light change a molecule?

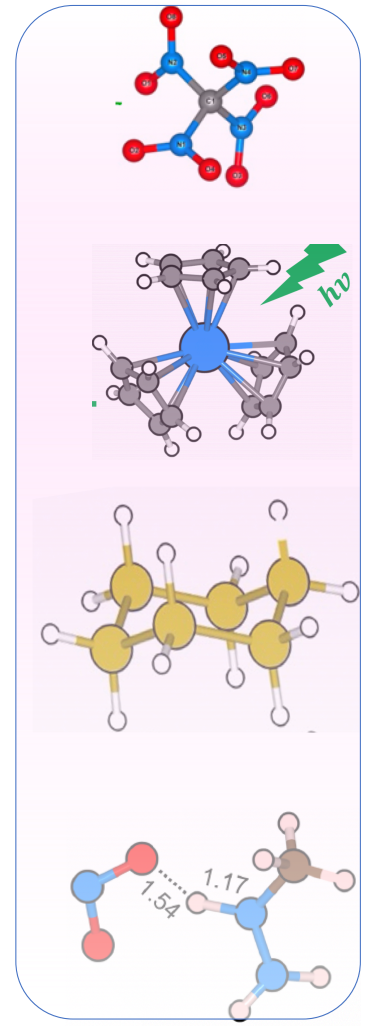
-which frequency / intensity of light
facilitate most vivid reaction?

-which molecules are produced
by a photoreaction?

-what is relative proportion of different
product molecules?

-what would be a mass-spectrum for
distribution of photoreaction' products?

0D molecules



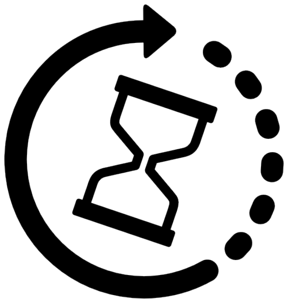
PHOTOREACTIONS

- ”fork road”
  ambiguity of reaction pathways
  originating from the same precursor

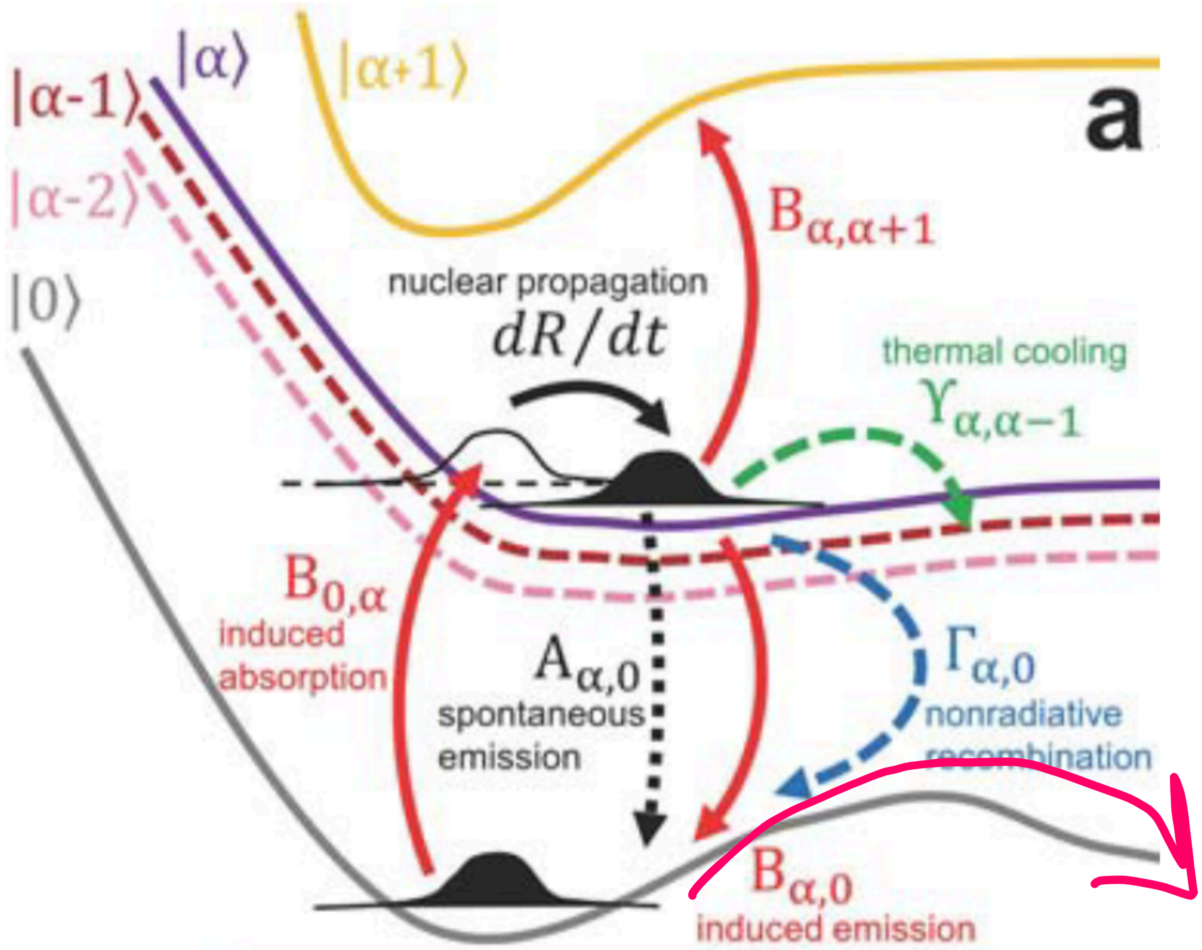
- Many isomers!

- A need to choose pathway/target isomer
  by tuning laser light parameters

- Very long time-scales, hard to simulate



Timing: 1:13



$|\alpha-1\rangle$
$|\alpha\rangle$
$|\alpha+1\rangle$
a
$|\alpha-2\rangle$
$B_{\alpha,\alpha+1}$
$|0\rangle$
nuclear propagation
dR/dt
thermal cooling
$\Upsilon_{\alpha,\alpha-1}$
$B_{0,\alpha}$
induced absorption
$A_{\alpha,0}$
spontaneous emission
$\Gamma_{\alpha,0}$
nonradiative recombination
$B_{\alpha,0}$
induced emission

Specific methods adjustments for modeling of photoreactions

Timing: 2:09

FEATURE #1: Substantially shorten computational resources/simulation time by

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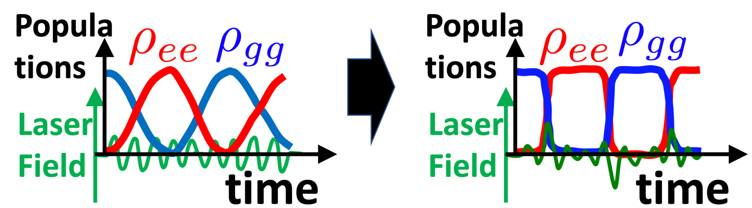
*replacing continuous change of state' population by instantaneous hops

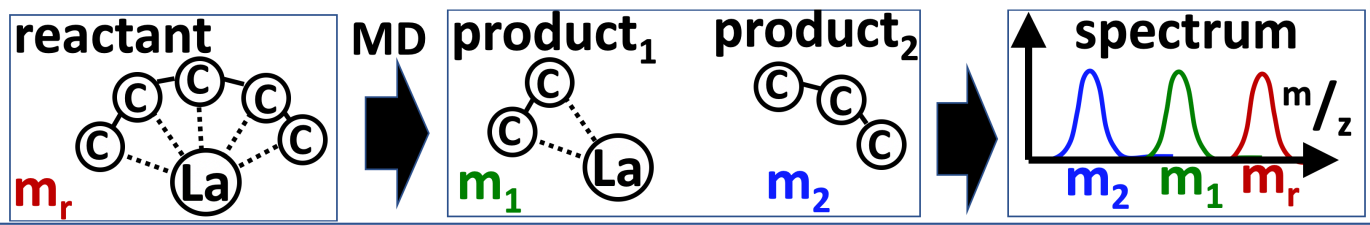
*use of "pulse-area theorem"



FEATURE #2: developed method which models irradiation of the model with

*more than two photons

FEATURE #3: mass-spectra became available via unique computational procedure



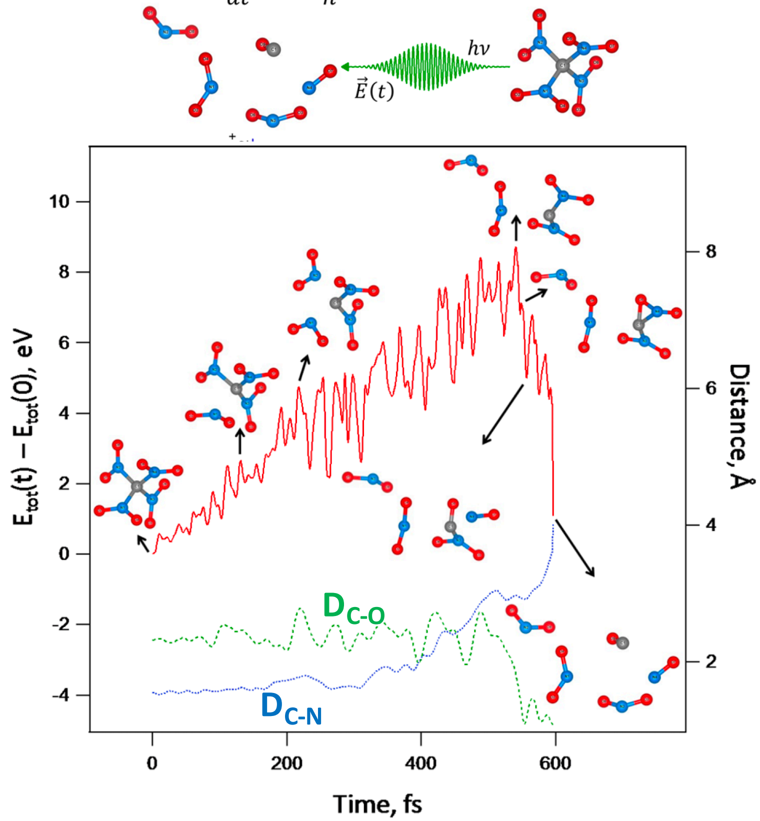
FEATURE #4: activation energies of reactions are computed more accurately

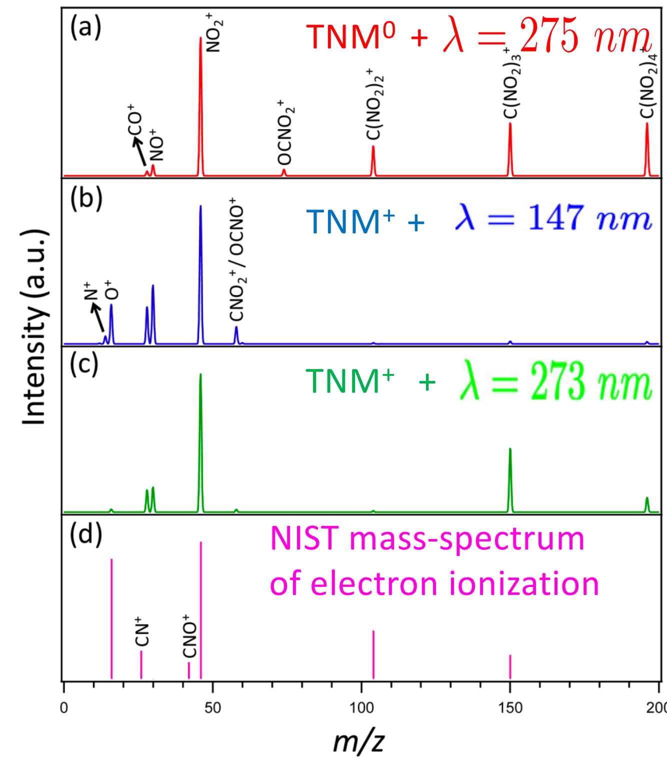
* via quantum tunneling of quantized nuclei

Research Direction: (iii) Light-induced Reactions

Photofragmentation of Tetranitromethane

$$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}[H(\vec{R}) - \vec{M}\cdot\vec{E}(t), \hat{\rho}]$$





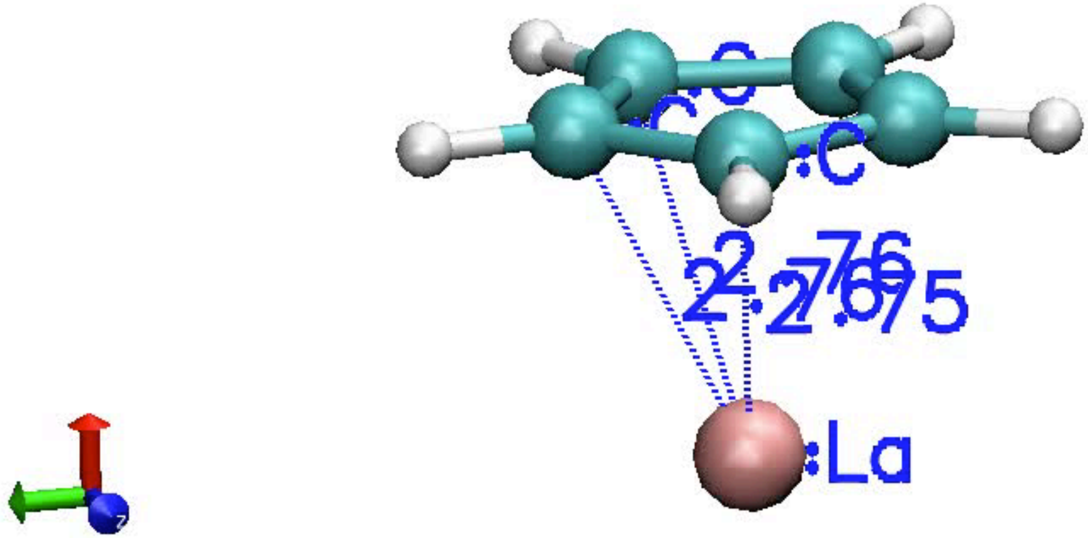
Justification: matches experimental trends, control of reaction outcome by light wavelength and charge

Reference: Han, Rasulev, Kilin, *J. Phys. Chem. Lett*. **2017**, 8, 3185–3192

Research Direction: (iii) Light-induced Reactions

Timing:	0:51

ALL STAGES OF PHOTOREACTION



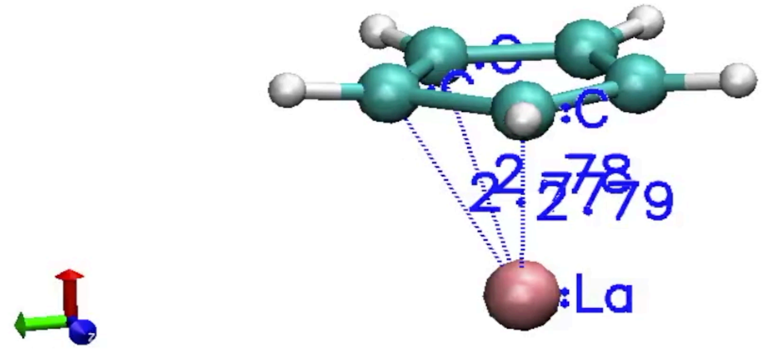
Justification: Quantitatively matches experiment: mass and intensity in the mass-spectra

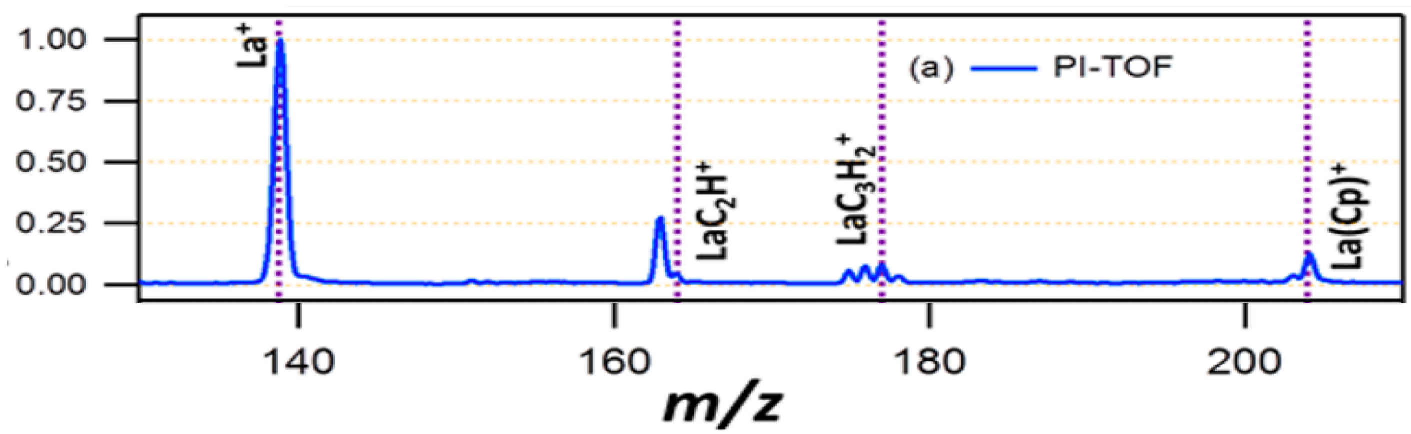
Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281−4296

Research Direction: (iii) Light-induced Reactions

STAGE 1: LaCp → $LaC_3H_2^+$

Timing: 0:29



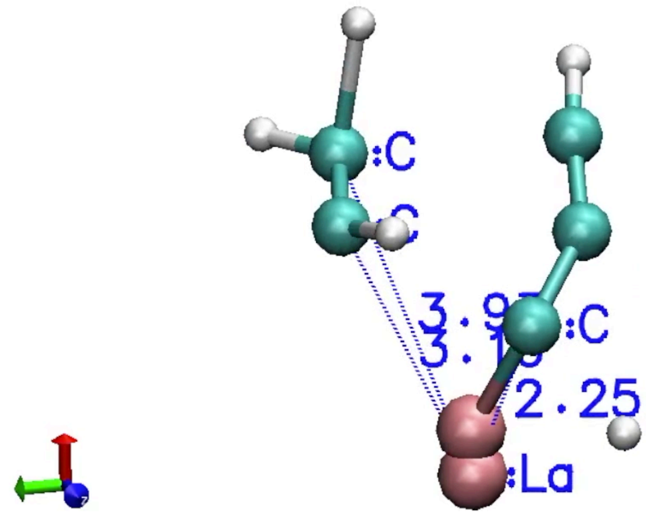


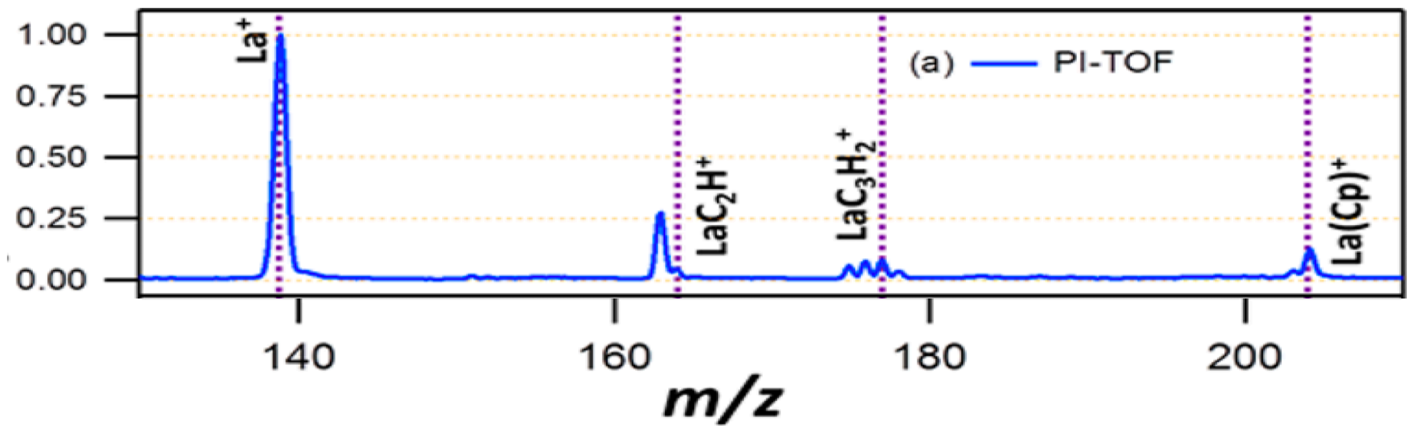
Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281−4296

Research Direction: (iii) Light-induced Reactions

STAGE 2: LaCp → $LaC_2H_3^+$

Timing: 0:12



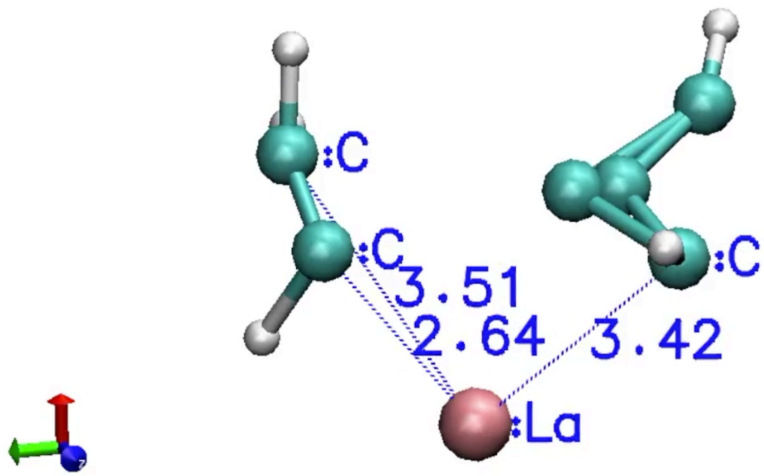


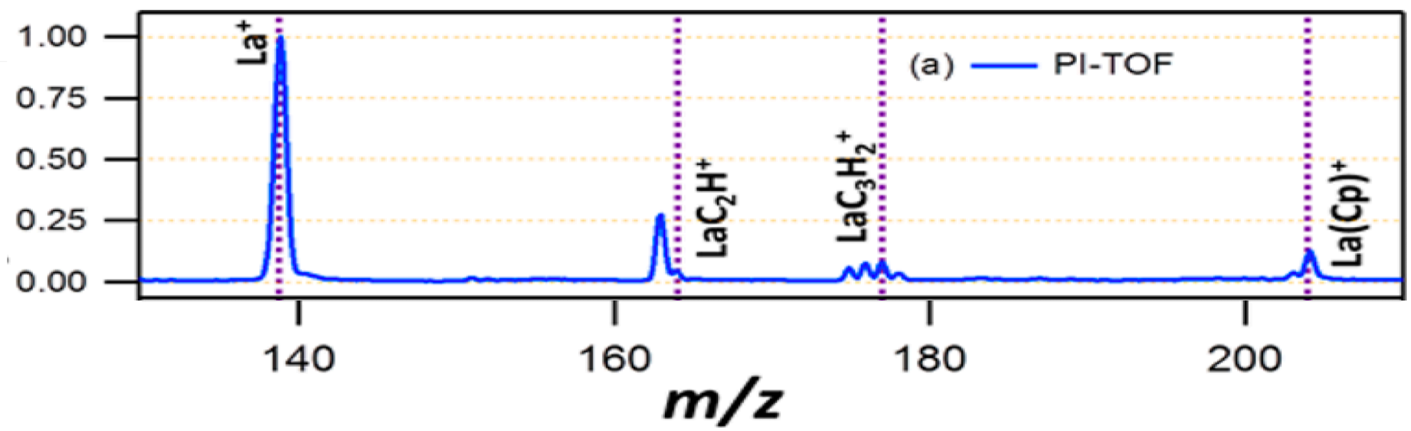
Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281–4296

Research Direction: (iii) Light-induced Reactions

STAGE 3: LaCp → La^+

Timing: 0:11

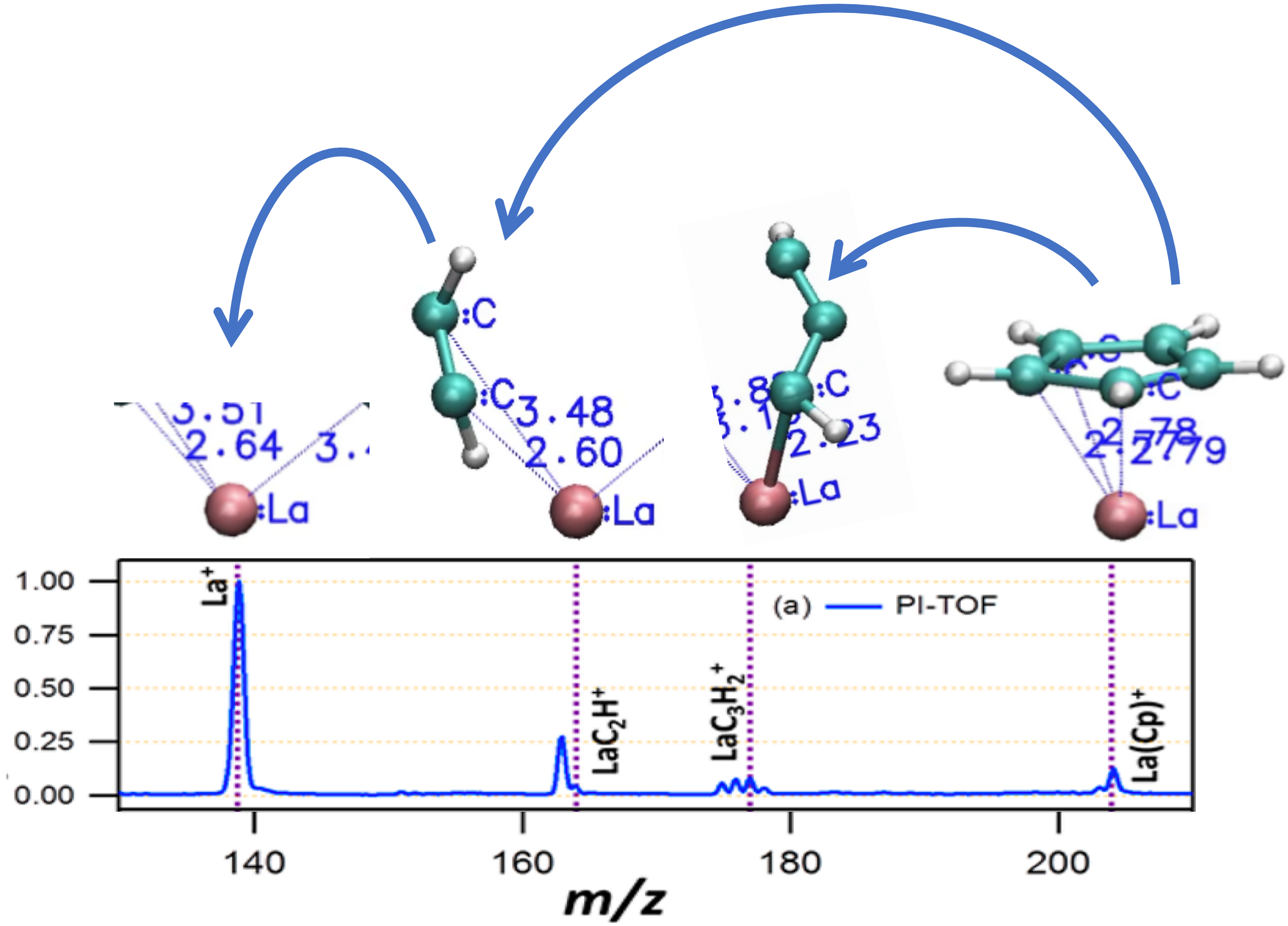




Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281–4296

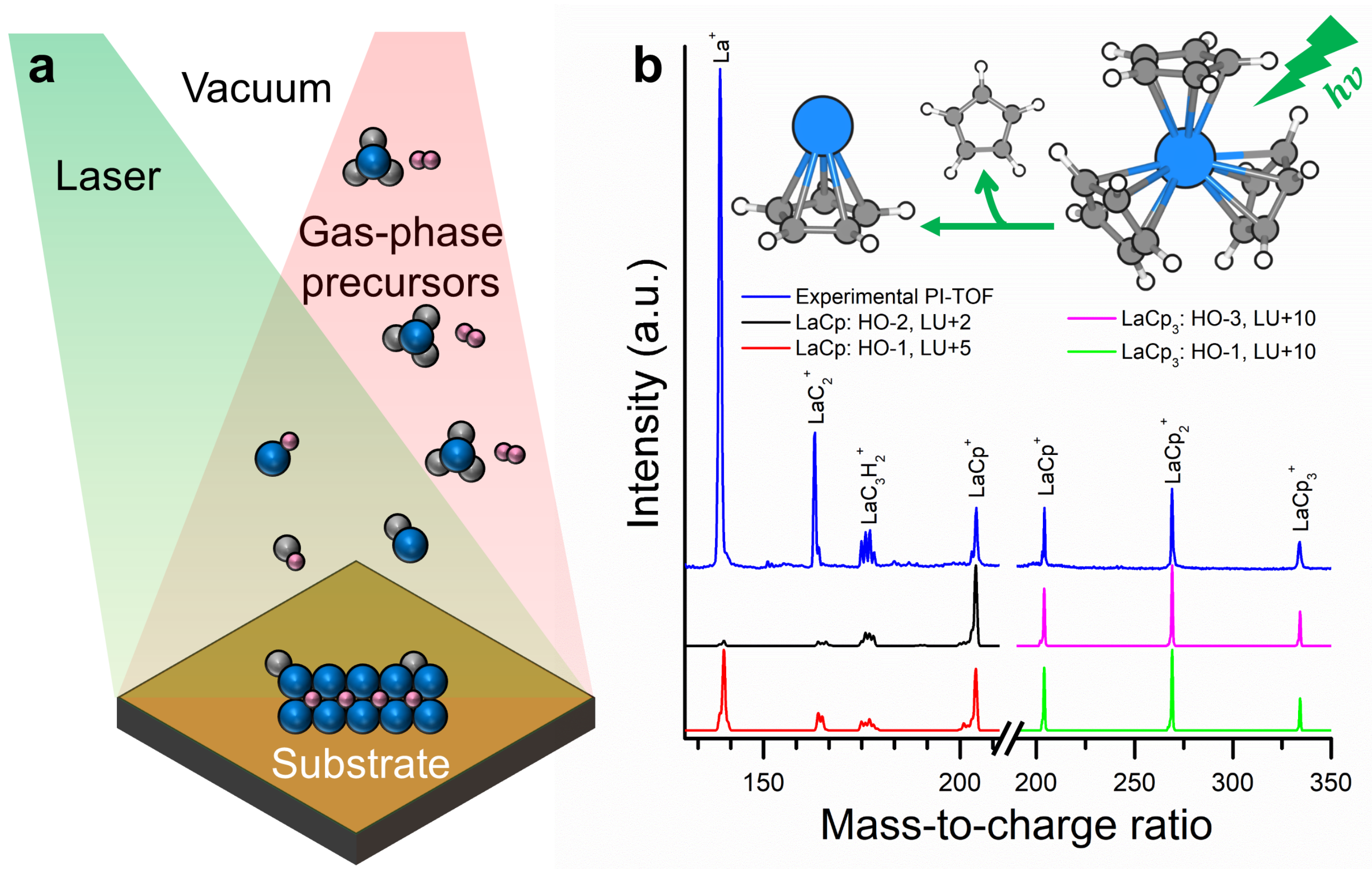
Research Direction: (iii) Light-induced Reactions

Timing: 0:17



Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281–4296

Research Direction: (iii) Light-induced Reactions



Justification: Quantitatively matches experiment: mass and intensity in the mass-spectra

Reference: Han, Meng, Rasulev, May, Berry, Kilin, *J. Chem. Theory Comput*. **2017**, 13, 4281–4296

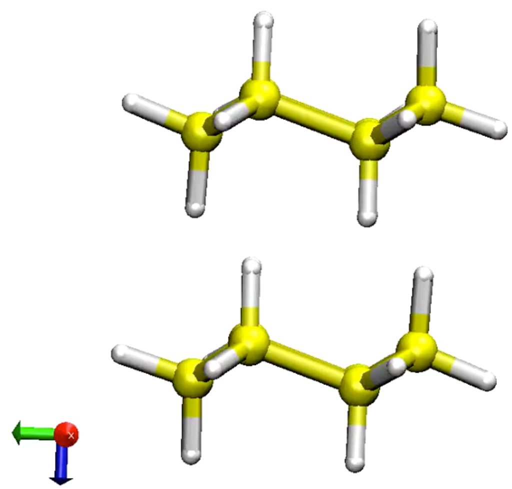
Research Direction: (iii) Light-induced Reactions

Timing: 1:56

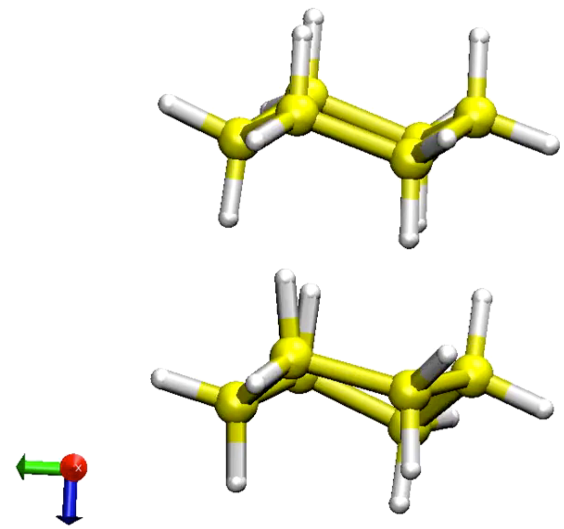
https://youtu.be/5JmGb5vx-dE

https://youtu.be/V-whfiCBRg8

Molecular Dynamics



Optimized Intermediates

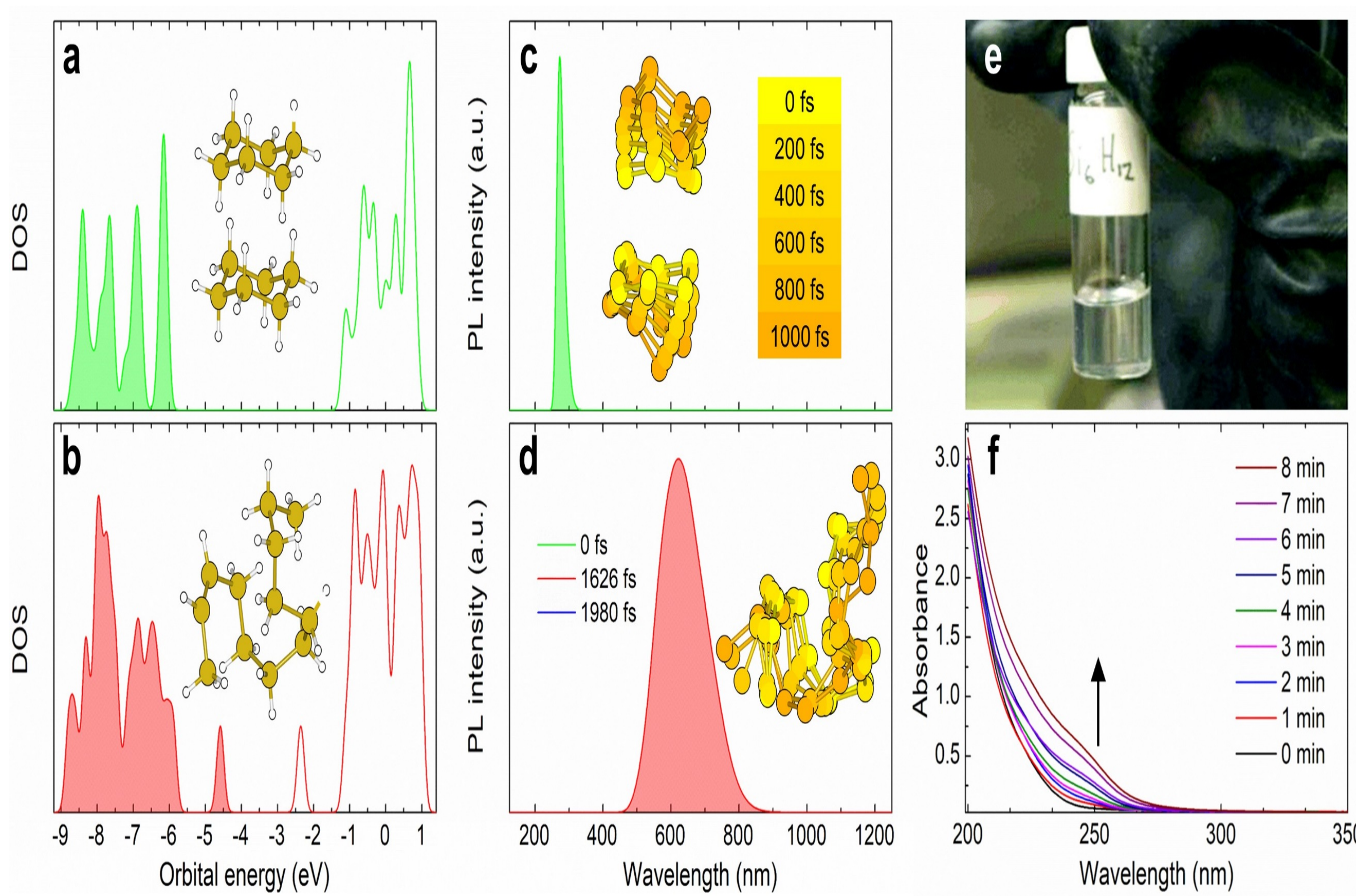


Justification: matches experimental trends

Reference: Han, Anderson, Hobbie, Boudjouk, Kilin, *J. Phys. Chem. Lett*. **2018**, 9, 4349−4354

Research Direction: (iii) Light-induced Reactions

Timing: 1:11

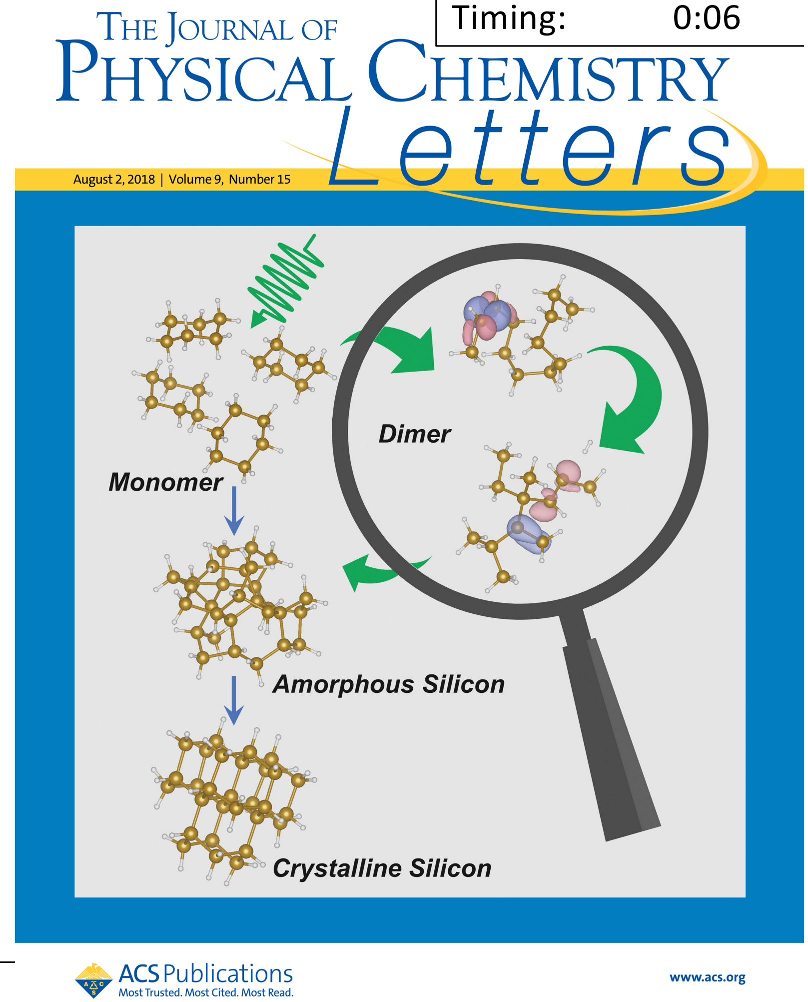


Justification: matches experimental trends

Reference: Han, Anderson, Hobbie, Boudjouk, Kilin, *J. Phys. Chem. Lett*. **2018**, 9, 4349–4354

Research Direction: (iii) Light-induced Reactions

Timing: 0:06



Justification: matches experimental trends

Reference: Han, Anderson, Hobbie, Boudjouk, Kilin, *J. Phys. Chem. Lett.* **2018**, 9, 4349–4354

Specific methods adjustments for modeling of photoreactions

Timing: 2:09

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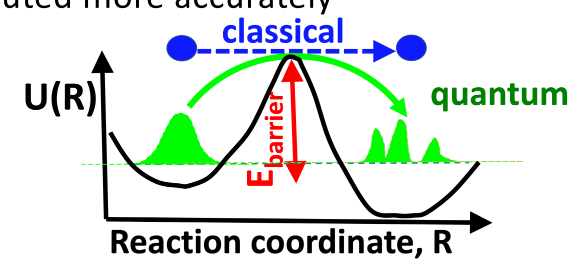
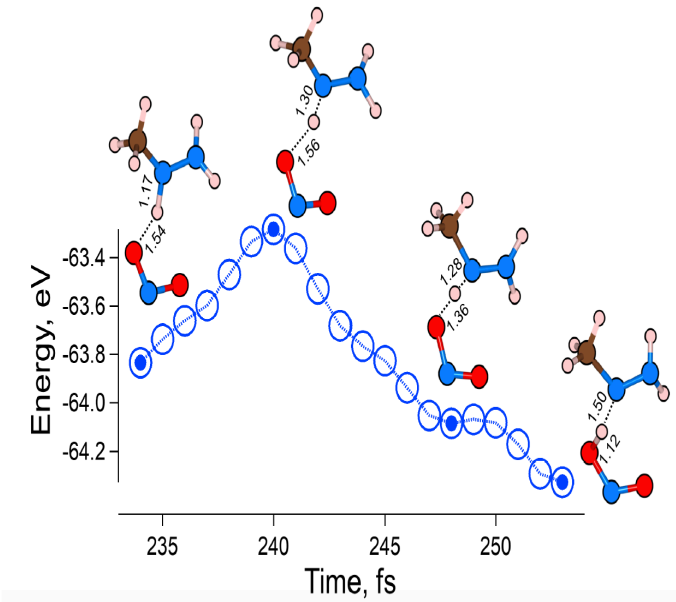
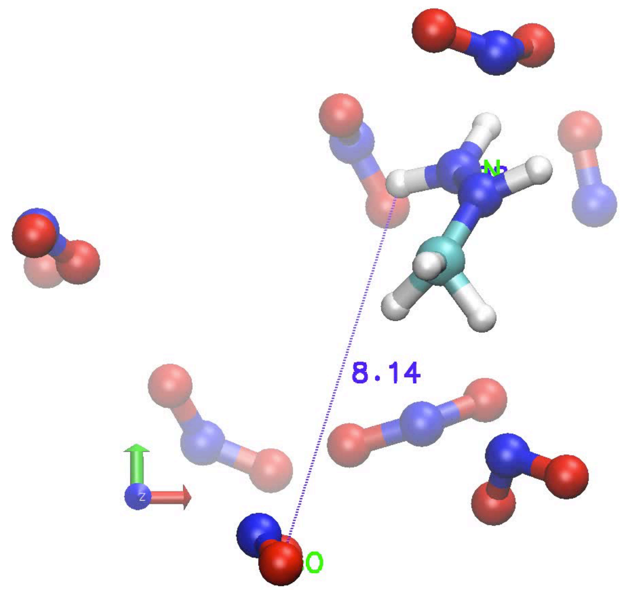


Research Direction: (iii) Light-induced Reactions

Timing: 2.38

Role of Quantum Tunneling for Proton Transfer: Case Study of Monomethylhydrazine and Nitrogen Dioxide Inition





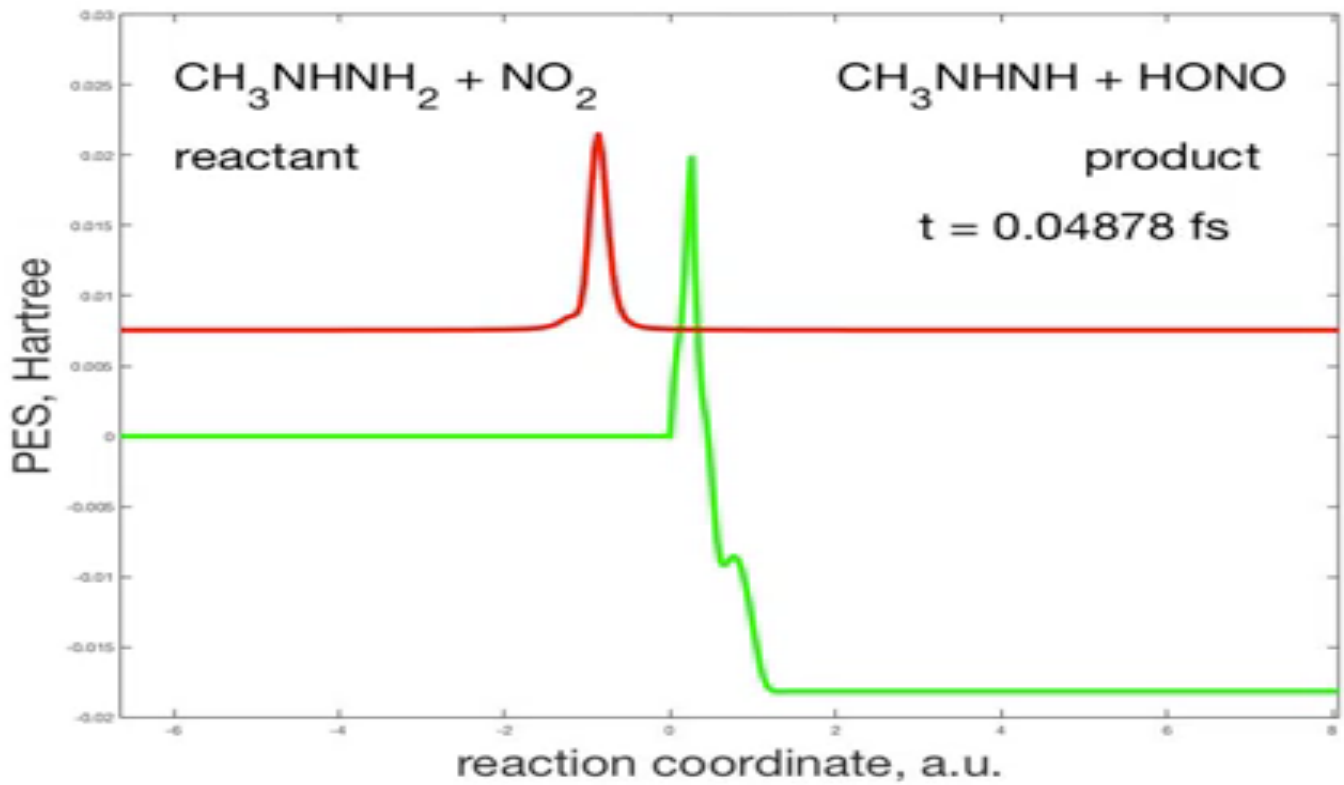
Justification: matches experimental trends

Reference: Han, Hobbie, Kilin *J. Phys. Chem. Lett*. **2019**, 10, 2394–2399

Research Direction: (iii) Light-induced Reactions

Timing: 1.06

Role of Quantum Tunneling for Proton Transfer:
Case Study of Monomethylhydrazine and Nitrogen Dioxide Ignition



Justification: matches experimental trends

Reference: Han, Hobbie, Kilin *J. Phys. Chem. Lett*. **2019**, 10, 2394–2399

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Timing: 2:09

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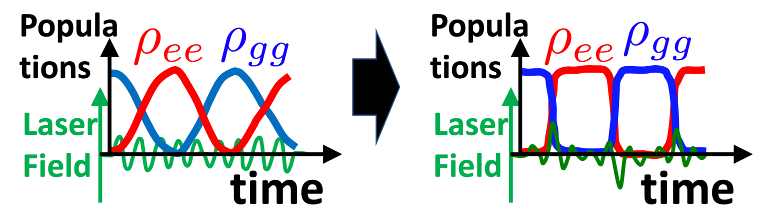

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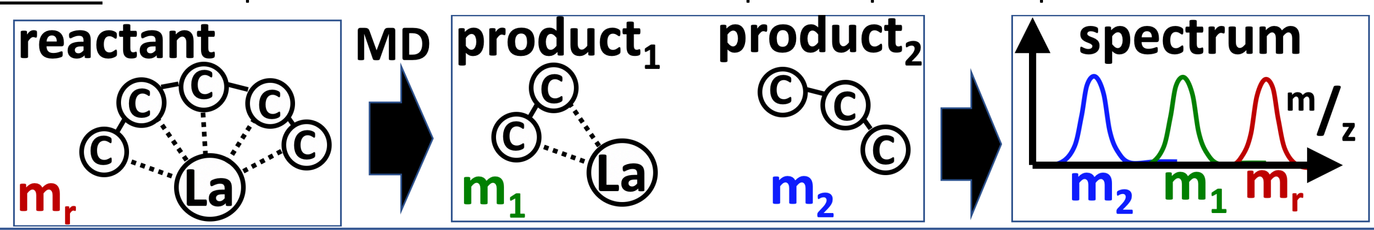

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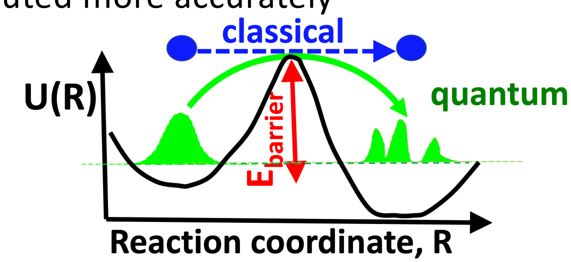
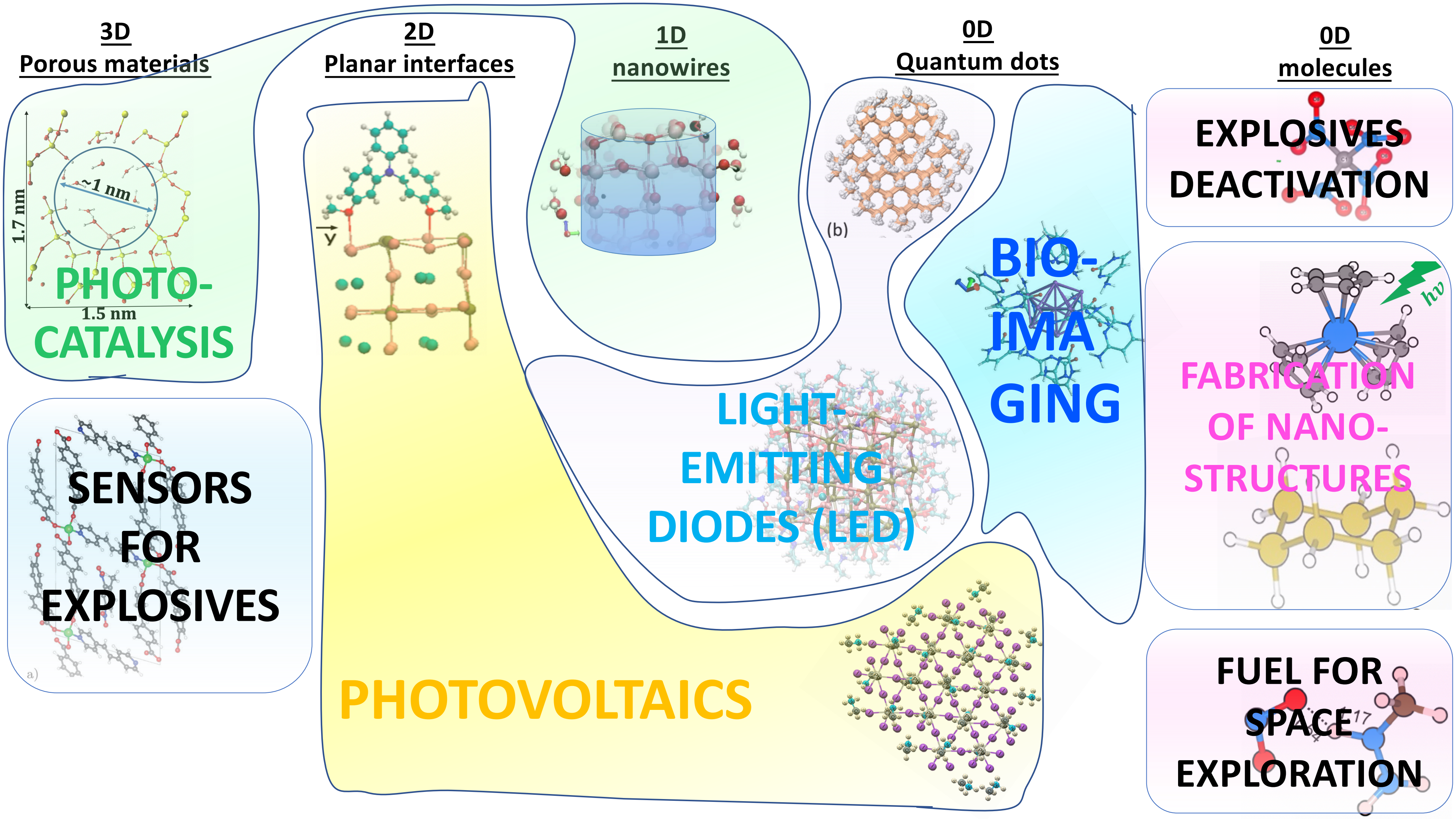
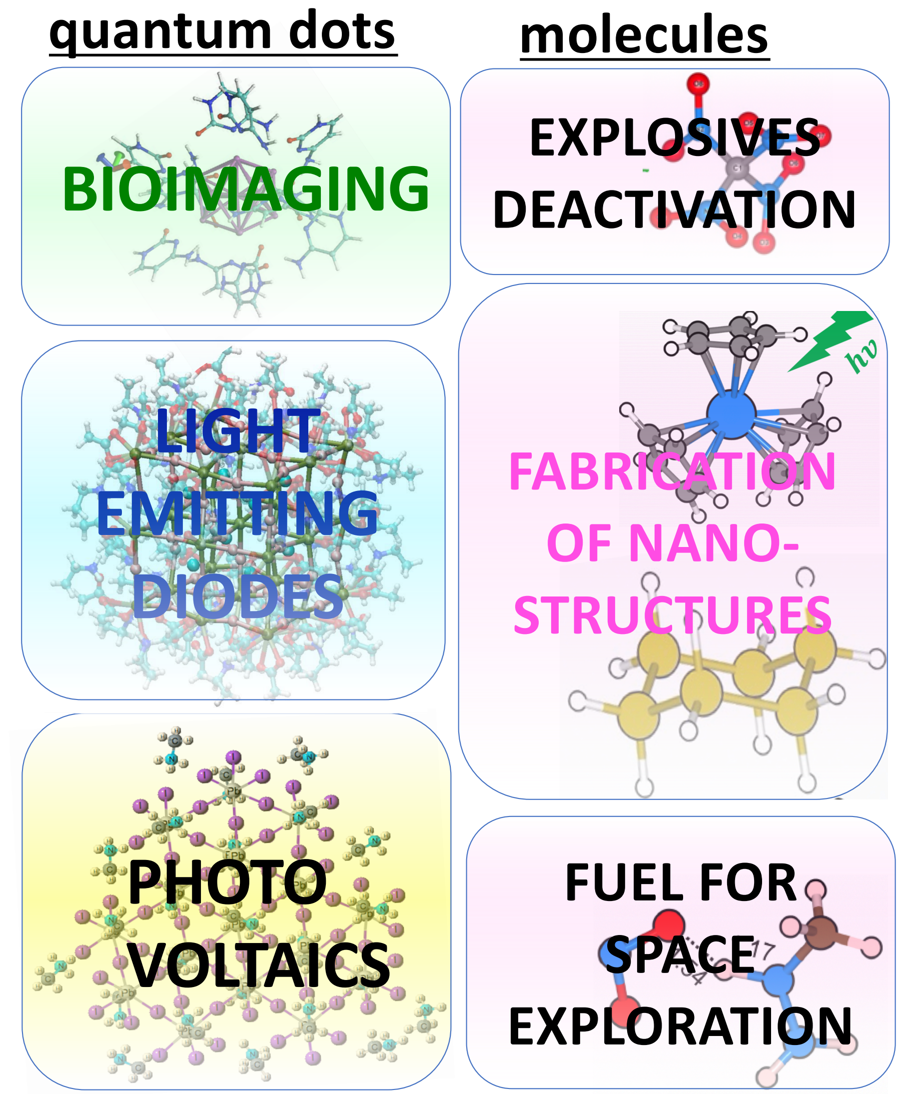



3D
Porous materials
1.7 nm
~1 nm
1.5 nm
PHOTO-
CATALYSIS
2D
Planar interfaces
y
1D
nanowires
0D
Quantum dots
(b)
0D
molecules
EXPLOSIVES
DEACTIVATION
BIO-
IMA
GING
LIGHT-
EMITTING
DIODES (LED)
FABRICATION
OF NANO-
STRUCTURES
hν
SENSORS
FOR
EXPLOSIVES
a)
PHOTOVOLTAICS
FUEL FOR
SPACE
EXPLORATION


quantum dots
molecules
BIOIMAGING
EXPLOSIVES DEACTIVATION
LIGHT EMITTING DIODES
FABRICATION OF NANO-STRUCTURES
hν
PHOTO VOLTAICS
FUEL FOR SPACE EXPLORATION

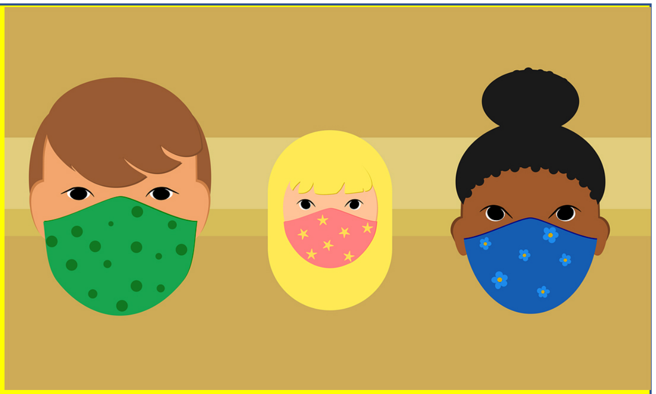
Acknowledgement

(i) Charge transfer NSF CHE-2004197
“Modeling of Charge Transfer Processes in Heterostructured Nanocomposites”
ND EPSCOR seed
DOE NERSC facility DE-AC02-05CH11231
"*Computational Modeling of Photo-catalysis and Photo-induced Charge Transfer Dynamics on Surfaces*”

(ii) Photoluminescence NSF CHE-1800476
*“D3SC: Integrated Studies on Designing Organometallic Complexes with Nonlinear Absorption and Near-Infrared Emissio*n’
LANL CINT facility visit

(iii) Photoreactions NSF CHE-1944921
”CAREER: Investigation of laser-driven chemical reactions by molecular dynamics”
local DOE CCAST seed

All projects: Department and College startup



Special Thank you to all attendees of this seminar: face-to-face and online!