Reaching ultimate perovskite quantum dot (QD) optical properties with a new synthetic approach

NanoGe NSM22

Tan Nguyen
Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR - UMR 6226

PoLLoC

Work Package WP2

Acknowledgements

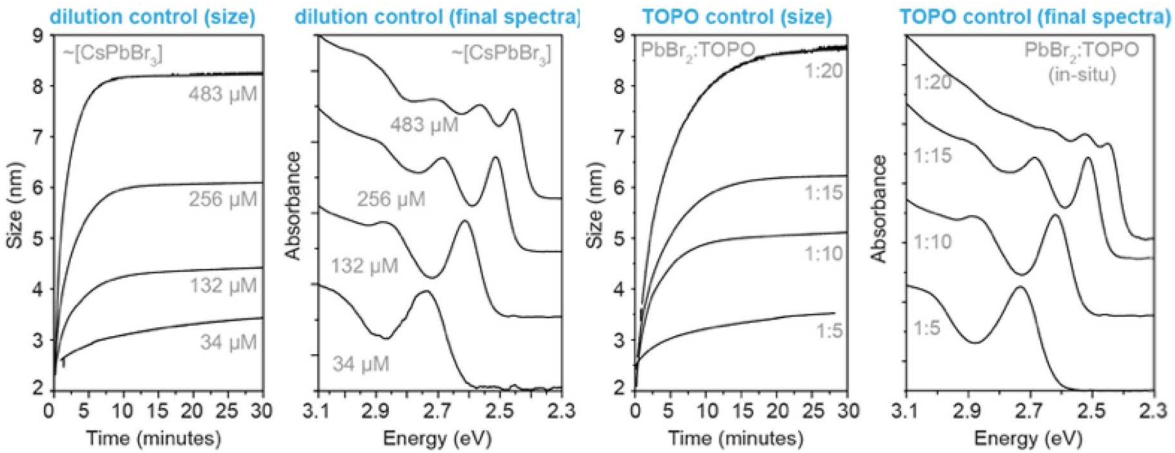
Collaborators

CNRS & INSA Rennes
- Claudine KATAN
- Jacky EVEN

Kovalenko's group, Zurich
- Quinten A. Akkerman (LMU)
- Simon C. Boehme
- Federico Montanarella
- Dmitry N. Dirin
- Philipp Wechsler
- Finn Beiglböck
- Rolf Erni
- Gabrielle Raino
- Maksym V. Kovalenko

This project has received funding from the European Union's Horizon 2020 program, through a FET Open research and innovation action under the grant agreement No 899141 (POLLOC).

New synthetic approach for colloidal perovskite QDs



New approach to colloidal synthesis

◊ Nucleation and growth decoupled temporally

◊ Slow reaction time

→ In-situ characterization (abundance of data)

◊ Ex-situ characterization possible with strongly binding zwitterionic ligand

reaction mechanism

Precursors:

2Cs-DOPA + 3PbBr$_2$[TOPO]

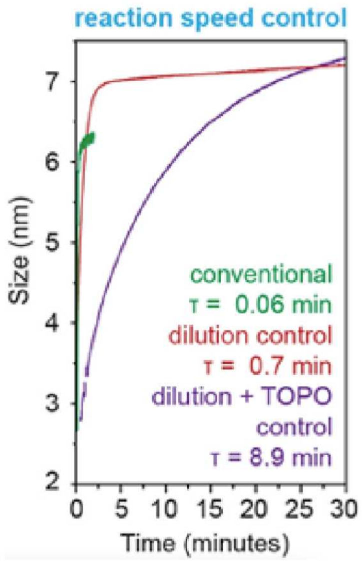
⇅

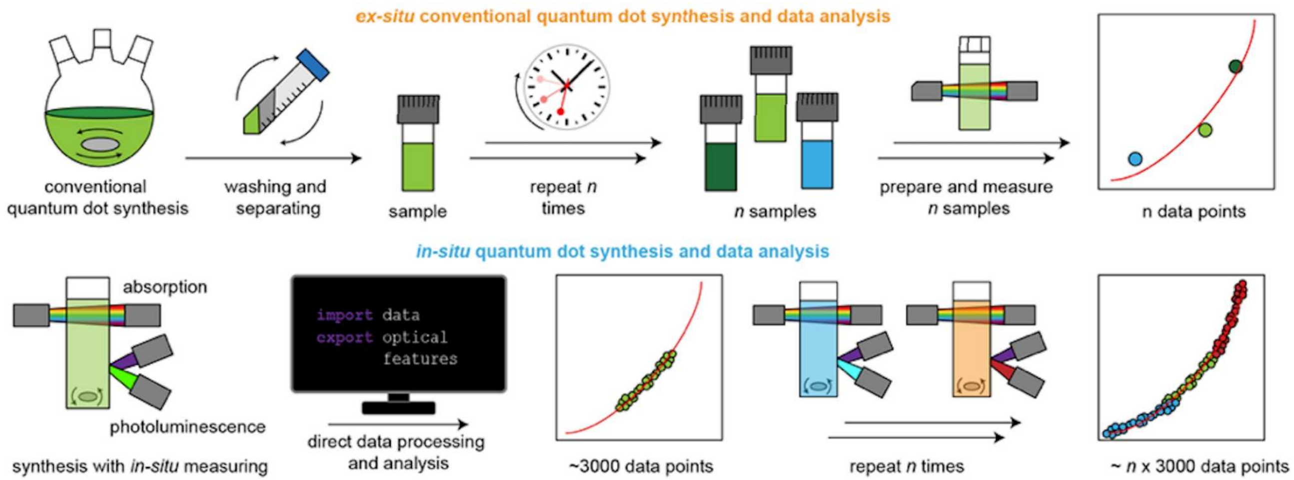
Intermediate:

2Cs[PbBr$_3$][TOPO] + PbDOPA$_2$ + TOPO

↓

2 CsPbBr$_3$ (Quantum dots)

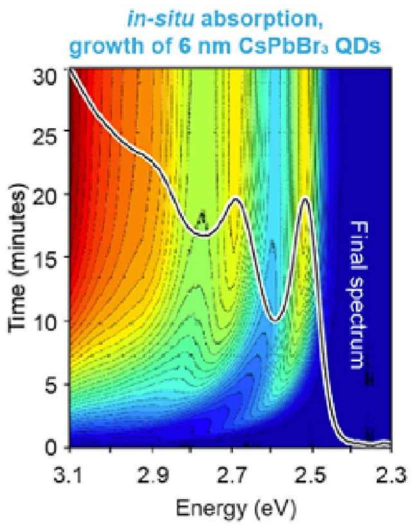


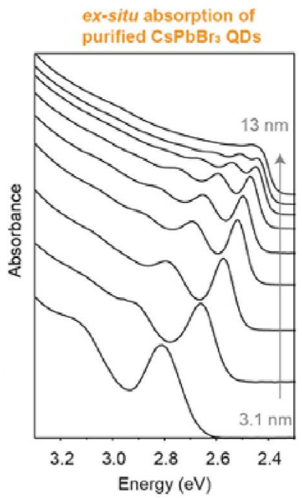


Almeida, G. et al., ACS Nano 12, 1704-1711 (2018)
Hui, J. et al., Chem. Mater. 32, 4574-4583 (2020)

Akkerman, Q. et al., *submitted*, Research Square (2022)
DOI: 10.21203/rs.3.rs-1236393/v1

Size and shape of the resulting perovskite QDs



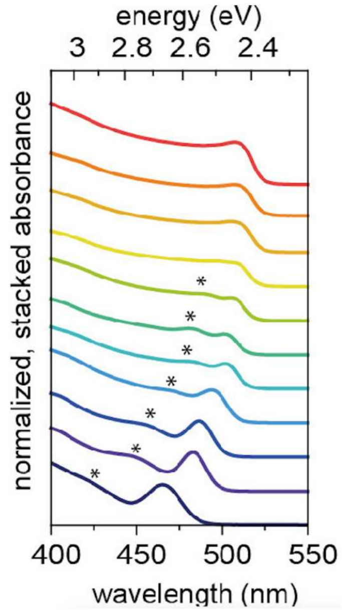


Newly synthesized QDs

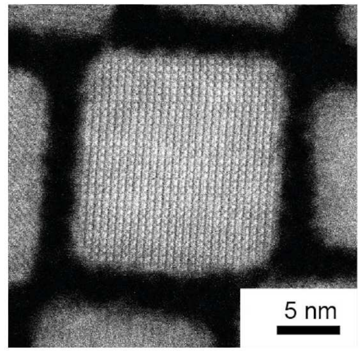
◊ Size tunable in the range 3-13 nm

◊ Rhombicuboctahedral or spheroidal shape

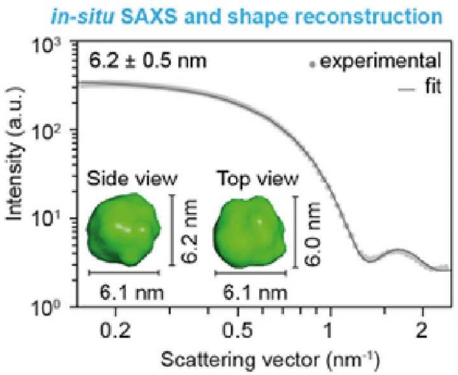
◊ Different absorption compared to cuboidal QDs

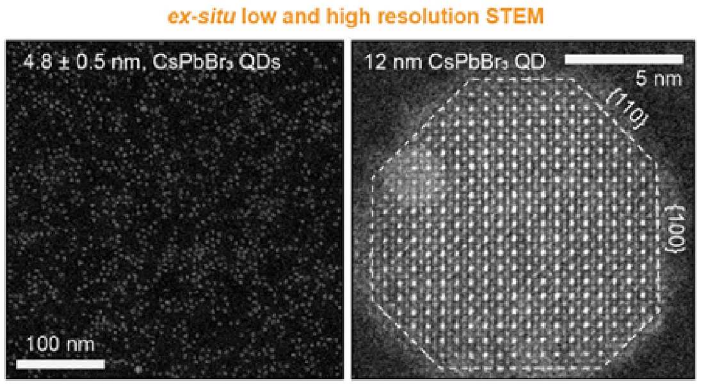


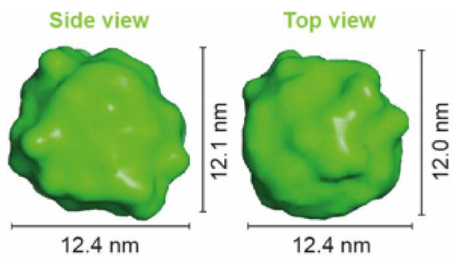
Cuboidal QDs

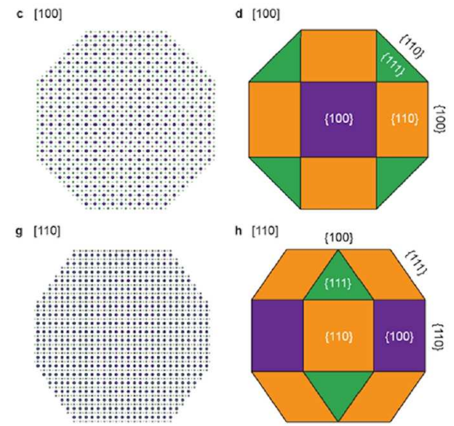


Rhombicuboctahedral/spheroidal QDs









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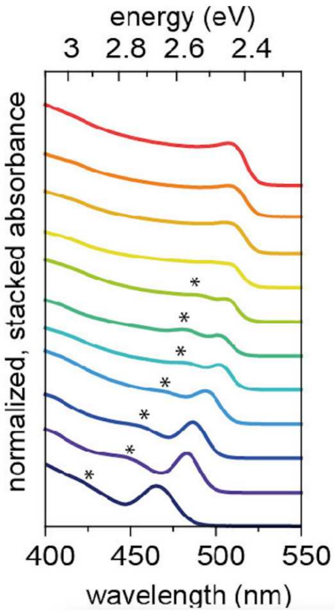
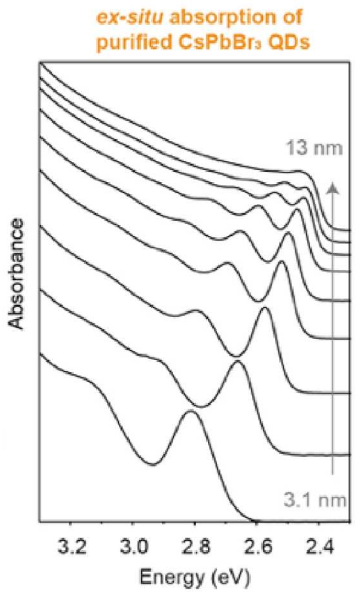
Krieg, F. et al., ACS Cent. Sci. 7, 135-144 (2021)

Optical spectra of the newly synthesized QDs

Absorption spectra of $CsPbBr_3$ for various sizes

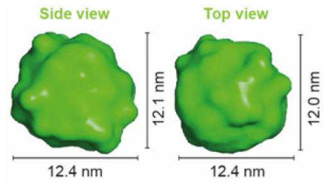


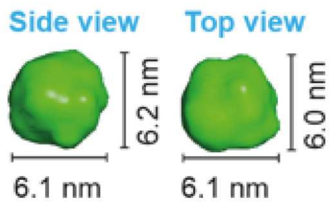


QDs from previous syntheses

◊ Cuboidal shape

◊ **Similar level of size dispersion**





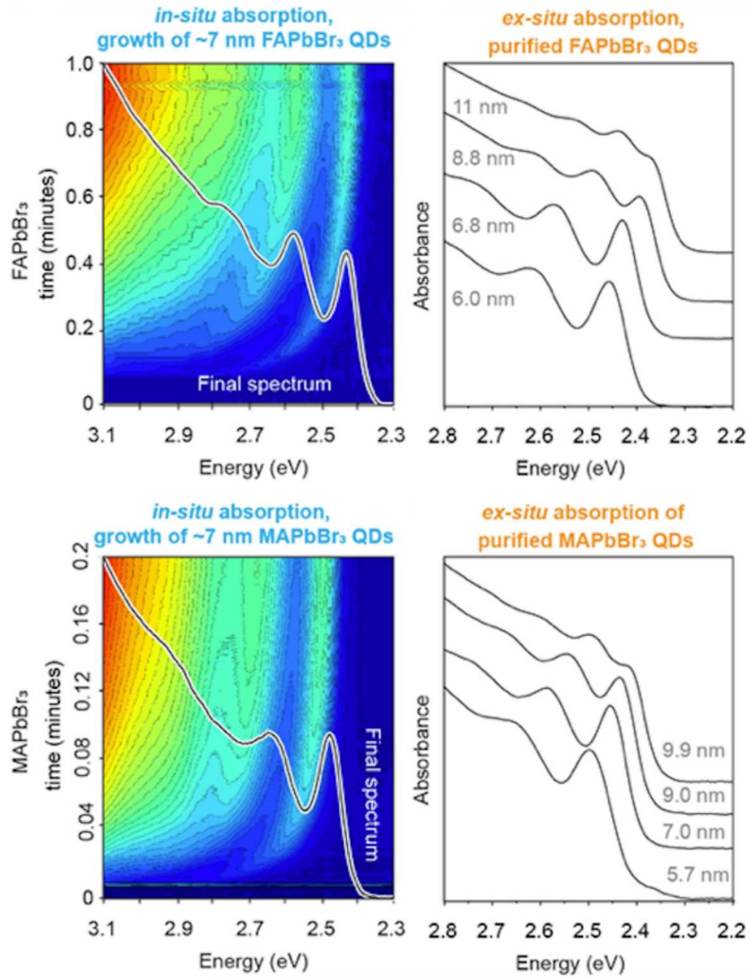
QDs from **new approach**

◊ Spheroidal shape

◊ High monodispersity

◊ **Exceptionally well-resolved higher excitonic transitions**

$FAPbBr_3$ and $MAPbBr_3$



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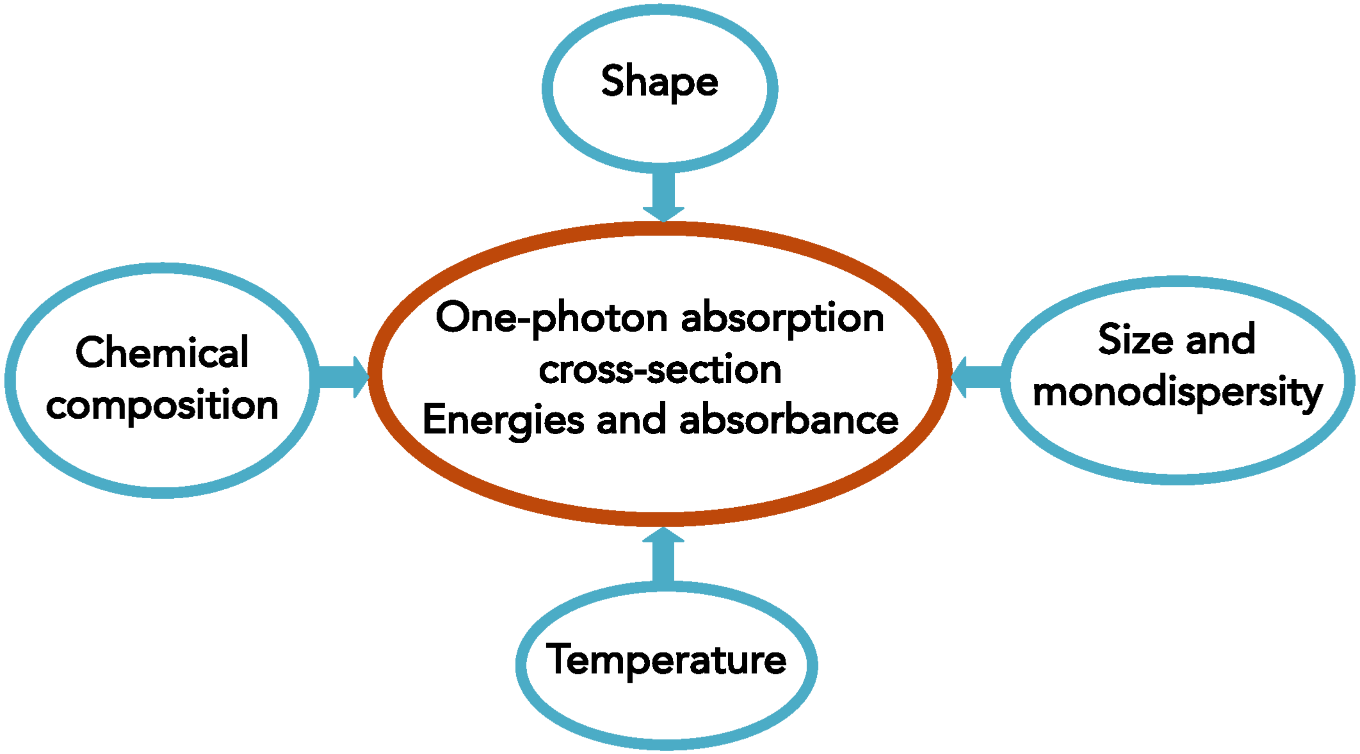
Diagrammatic view of optical properties



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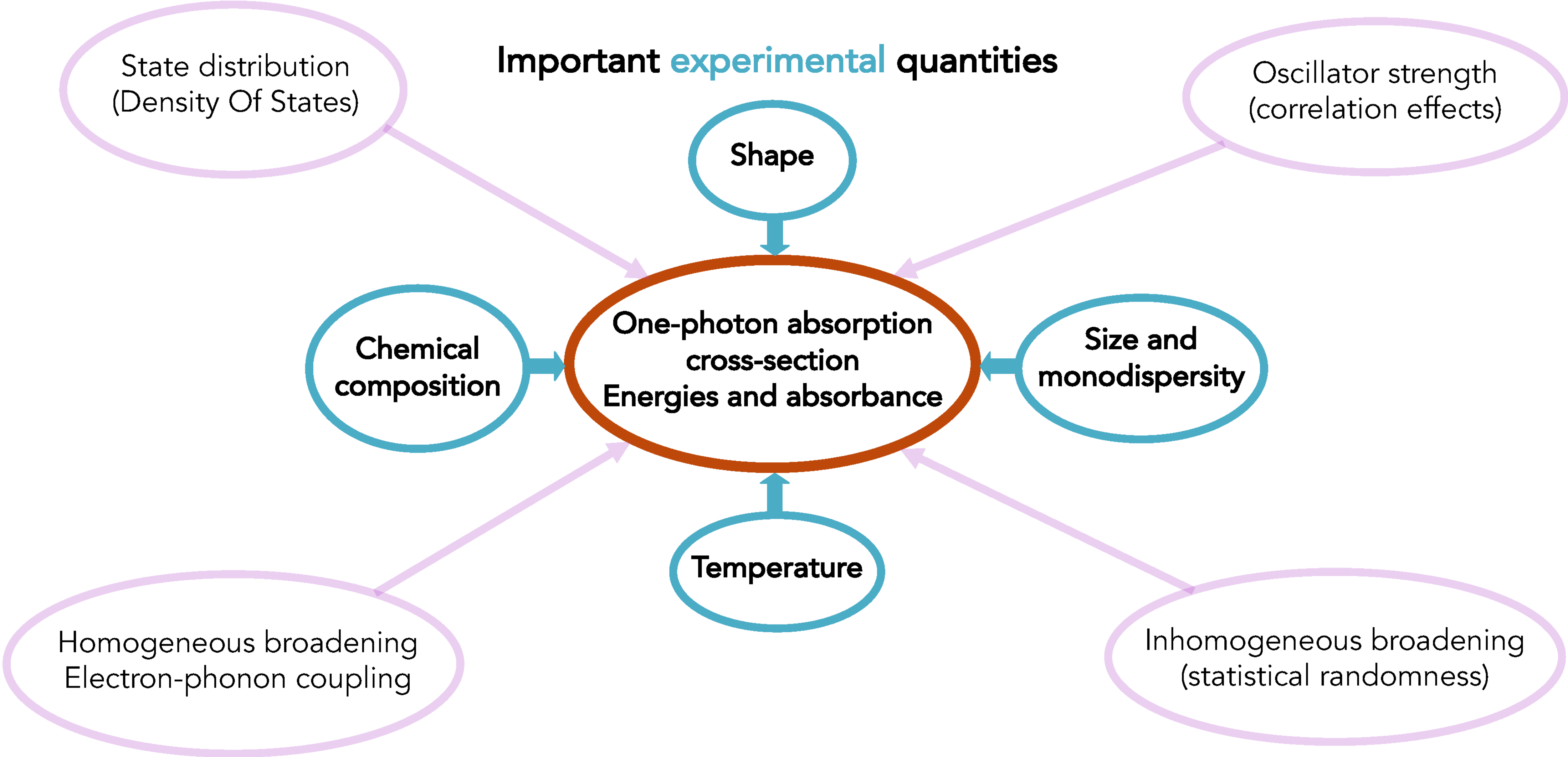

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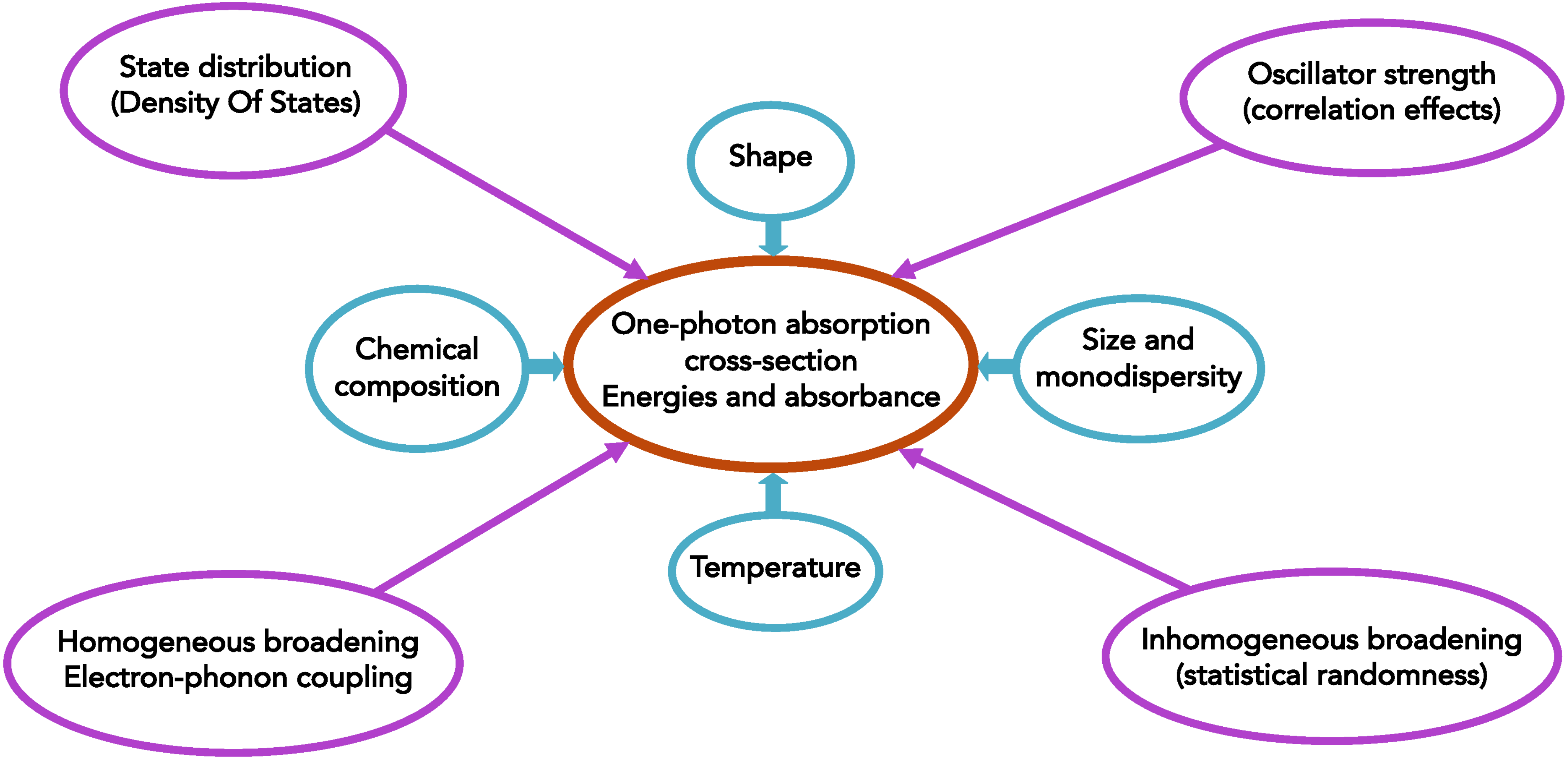

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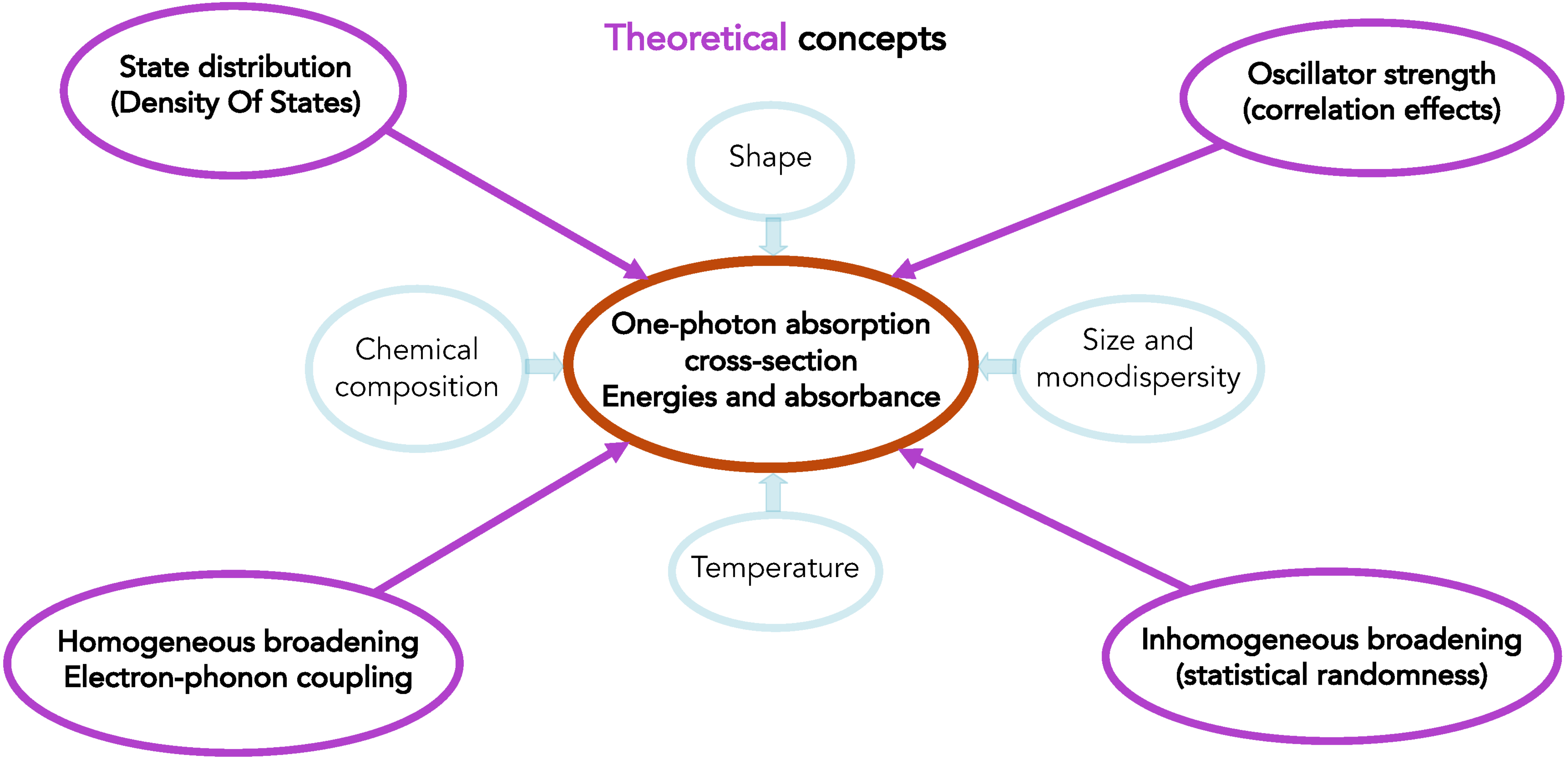

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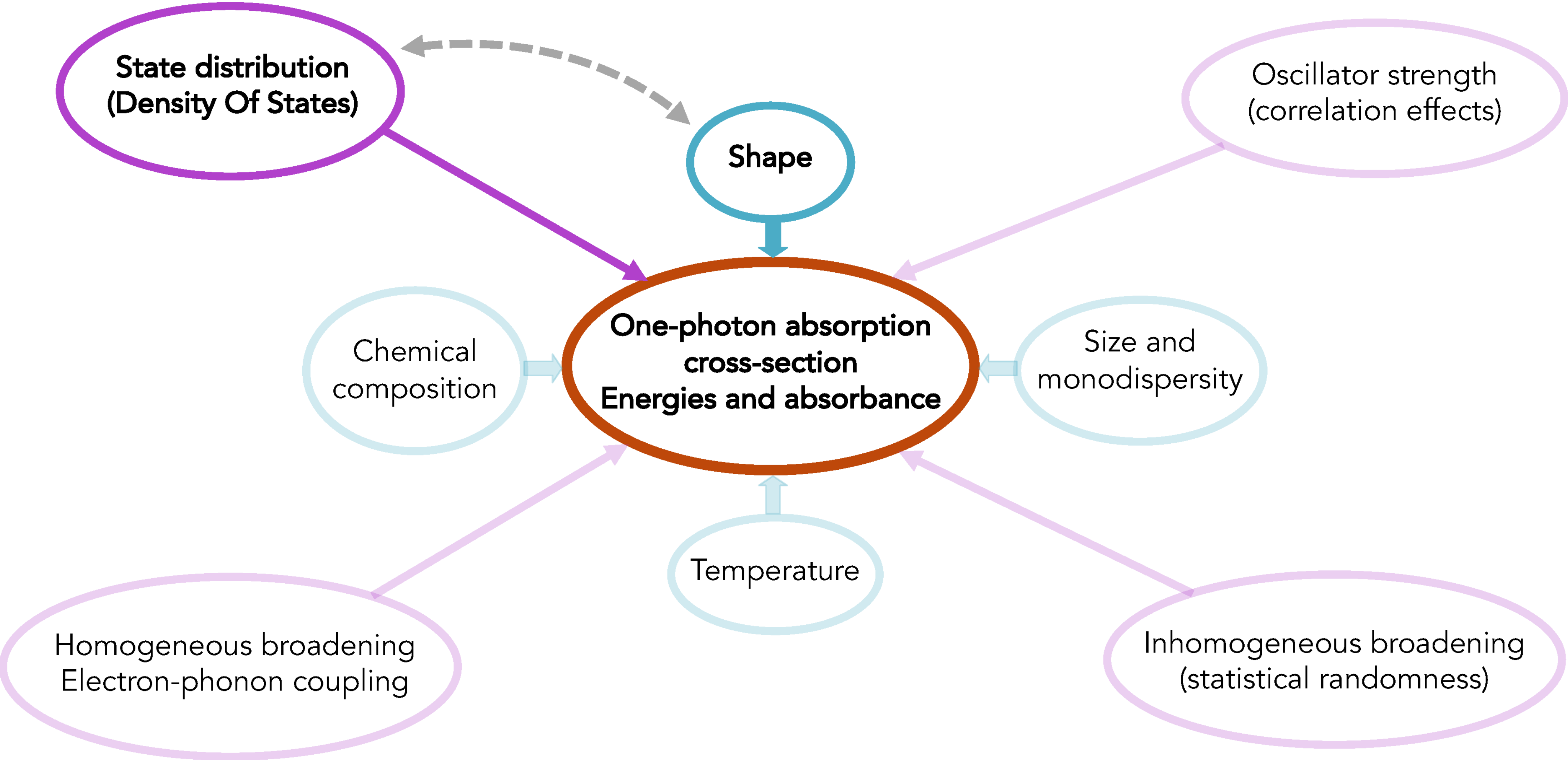
Diagrammatic view of optical properties – SHAPE



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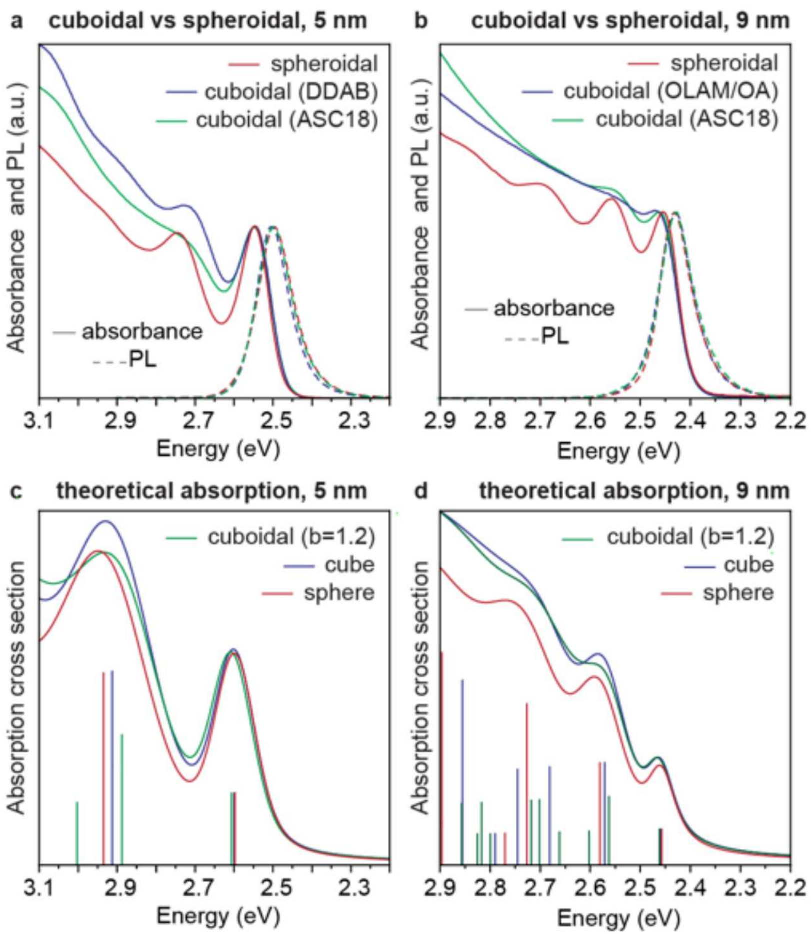
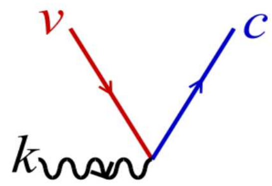
Theoretical approach to understand the effect of shape



One-photon absorption cross-section

◊ Effective Mass Approximation

◊ First-order perturbation, no self-consistency



$$\sigma^{(1)}(E) = \sum_{eh} \Xi_{eh}\, g_{eh}(E - E_{eh})$$

Broadening line shape

Oscillator strength $$\Xi_{eh} = \frac{4\pi^2}{3} \frac{f_\varepsilon^2}{\sqrt{\varepsilon_{\text{out}}} c_0} \frac{1}{E_{eh}} |M_{eh}|^2$$

$$f_\varepsilon = \frac{3\varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + 2\varepsilon_{\text{out}}}$$

Spherical factor for dielectric screening

$$|M_{eh}|^2 = E_P\, \delta_{v,c}$$

Optical matrix element

Akkerman, Q. et al., *submitted*, Research Square (2022)
DOI: 10.21203/rs.3.rs-1236393/v1

Krieg, F. et al., ACS Energy Lett. 3, 641-646 (2018)
Cherniukh, I. et al., Nature 593, 535-542 (2021)

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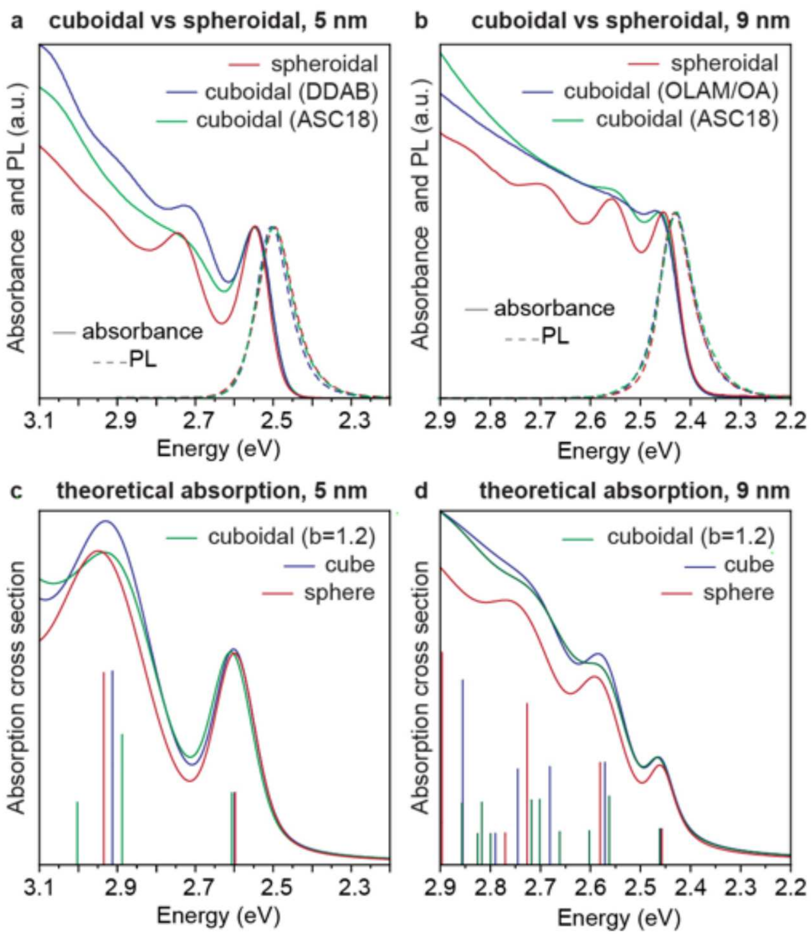

One-photon absorption cross-section

◊ Effective Mass Approximation

◊ First-order perturbation, no self-consistency

Influenced by QD shape

$$\sigma^{(1)}(E) = \sum_{eh} \Xi_{eh}\, g_{eh}(E - E_{eh})$$

Broadening line shape

$$\Xi_{eh} = \frac{4\pi^2}{3} \frac{f_\varepsilon^2}{\sqrt{\varepsilon_{\text{out}}}c_0} \frac{1}{E_{eh}} |M_{eh}|^2$$

Spherical factor for dielectric screening

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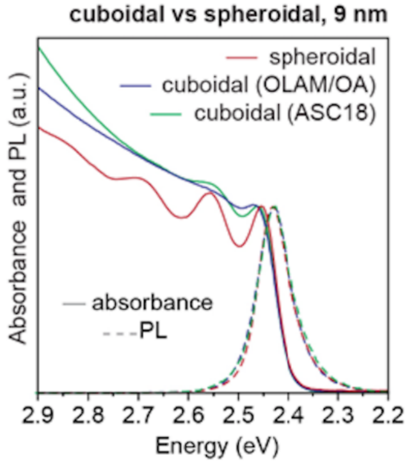
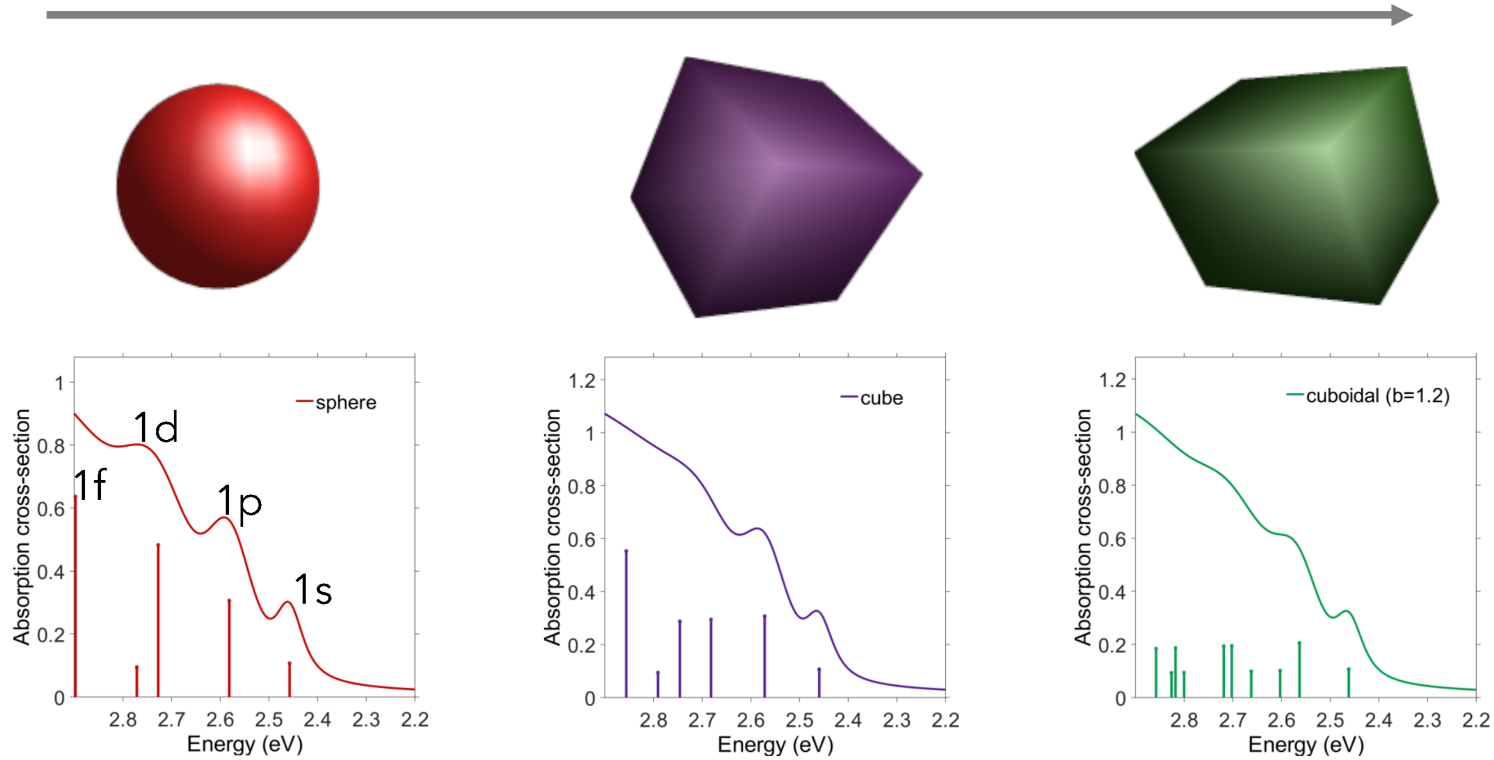
The effect of symmetry on the QD optical spectra

All QDs have similar level of size dispersion



Descending symmetry
of QD shape



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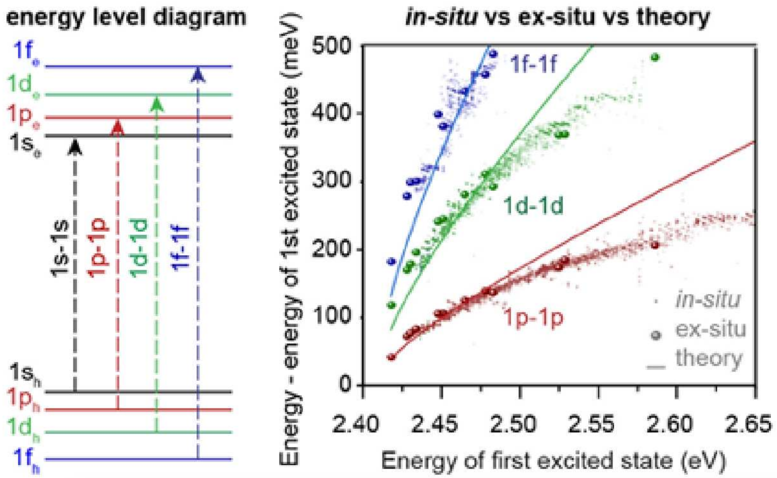
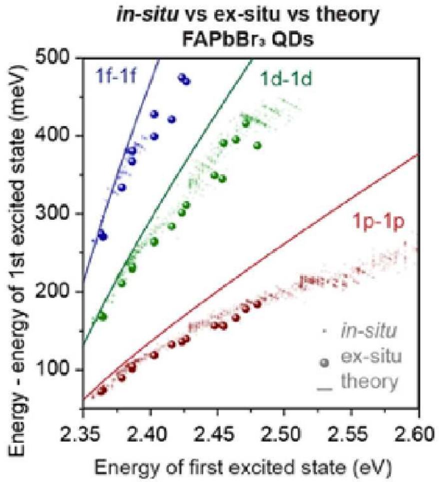
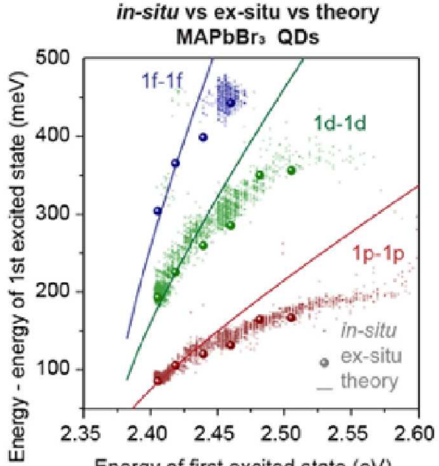
Cherniukh, I. et al., Nature 593, 535-542 (2021)
Yang et al., ACS Energy Letters, 2(7):1621–1627 (2017)

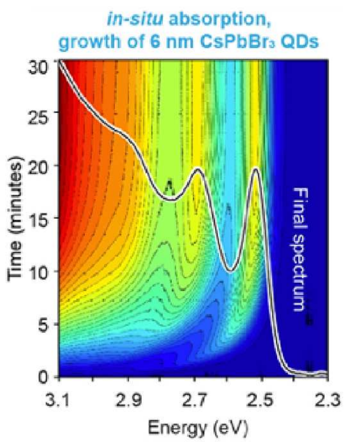
Optical absorption of excited states of exciton

Copious data from in-situ measurements!









$$(H_{k.p} + V_{\text{conf}} + V_{\text{HF}})|a\rangle = E_a|a\rangle \qquad |a\rangle = R_s(r)|(s,1/2)Fm_F\rangle + R_p(r)|(p,1/2)Fm_F\rangle$$

$$(H_{k.p} + V_{\text{conf}} + V^a_{\text{HF}})|i\rangle = E_i|i\rangle \qquad E_{\text{HF}} = E_{\text{gap}} + E_{\text{conf}} + E^{\text{HF}}_{\text{Coul}}$$

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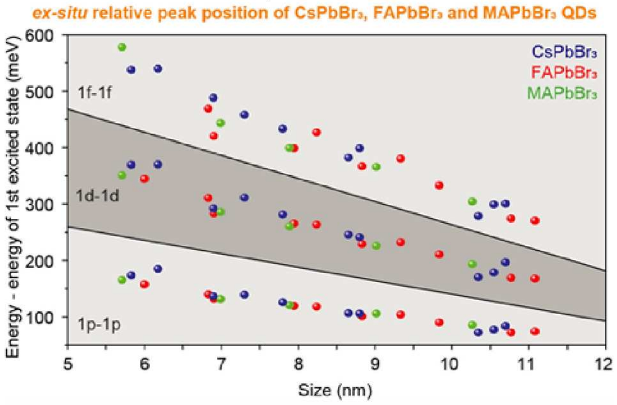
Yang et al., ACS Energy Letters, 2(7):1621–1627 (2017)
Galkowski et al., Energy Environ. Sci. 9, 962-970 (2016)

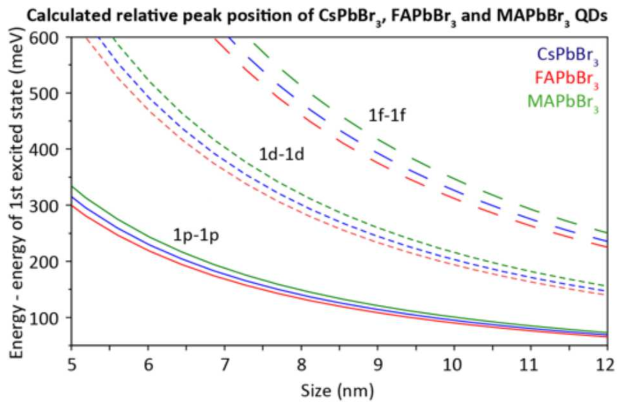
Optical absorption of excited states of exciton

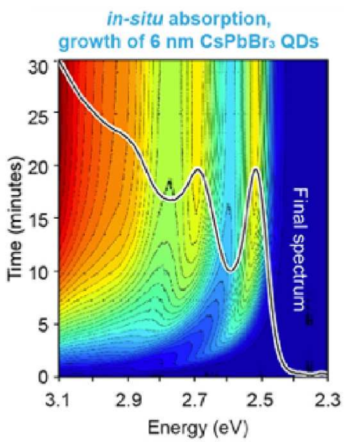
Optical properties relatively independent of A-site cations (Cs, FA, MFA)

Experiments



Theory





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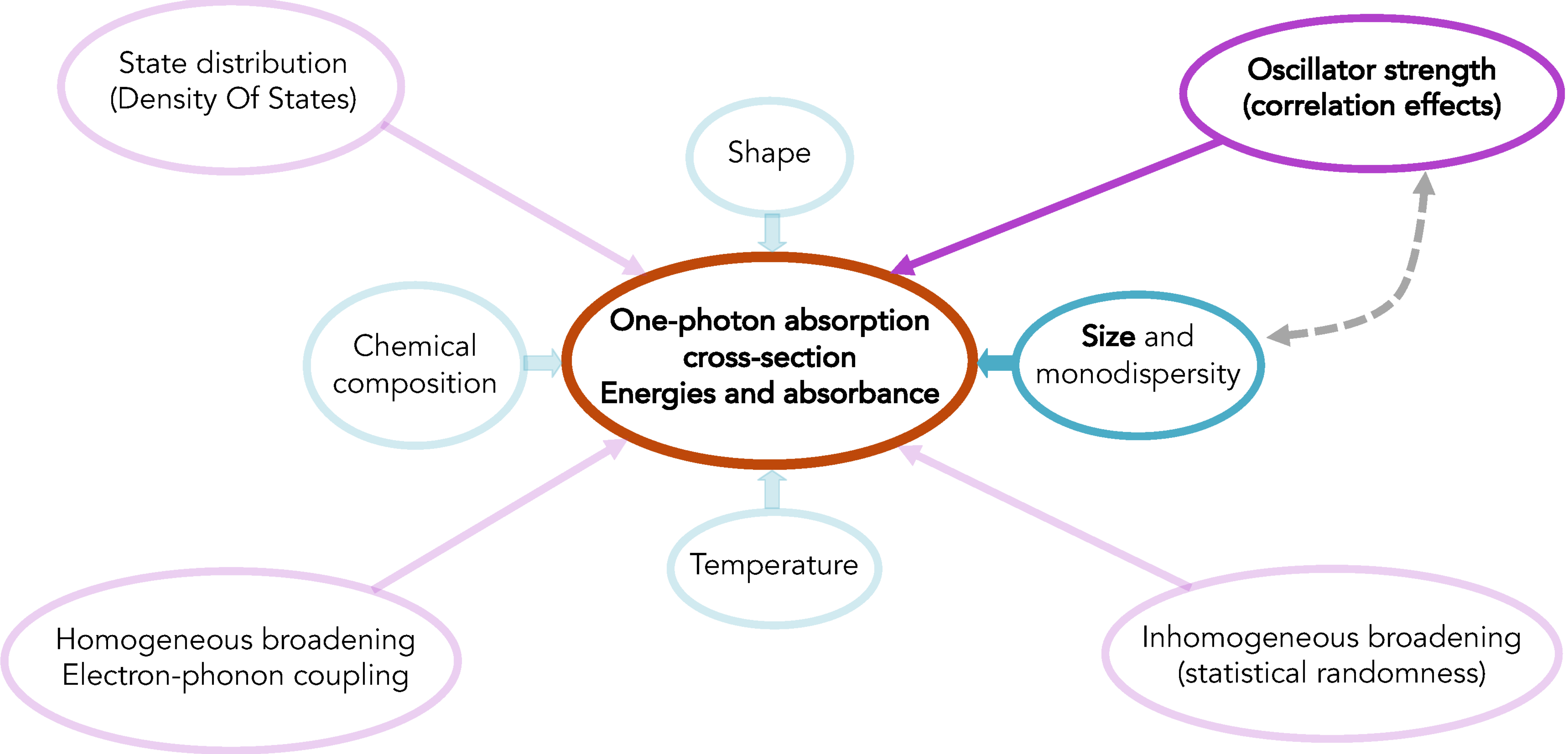
Diagrammatic view of optical properties – SIZE (correlation)



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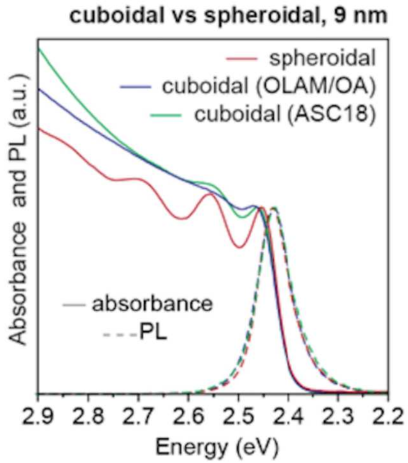
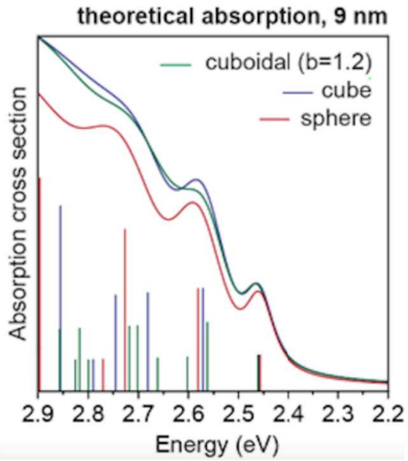
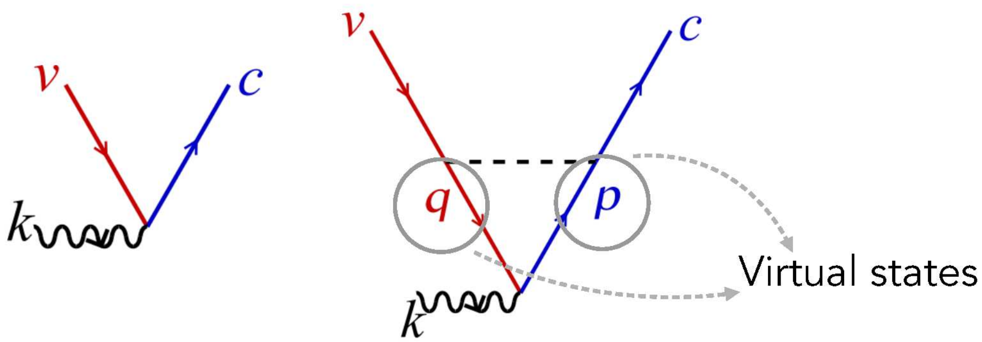
Blundell, S.A., Guet, C., arXiv:2202.09596v1 (2022)

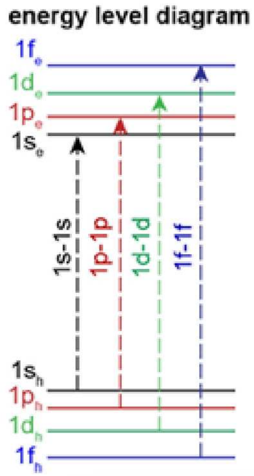
Correlation effect in the optical absorption spectrum

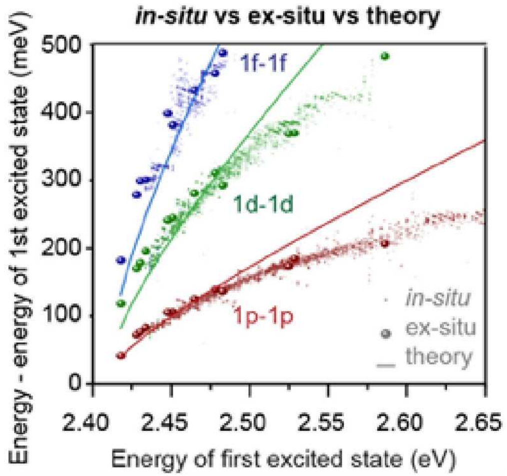


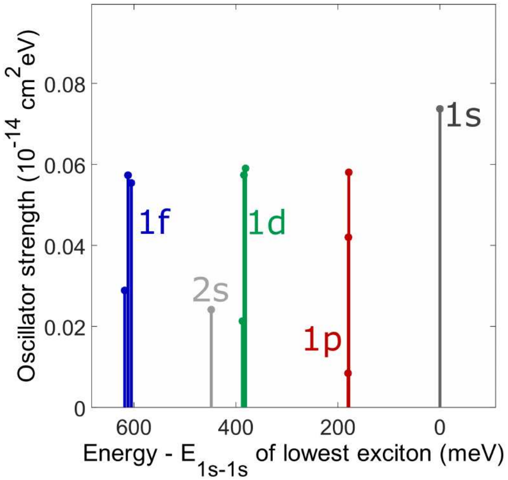


Correlation correction to
electron-photon interaction









Theoretical transition energies and oscillator strength of L=7.0 nm QD

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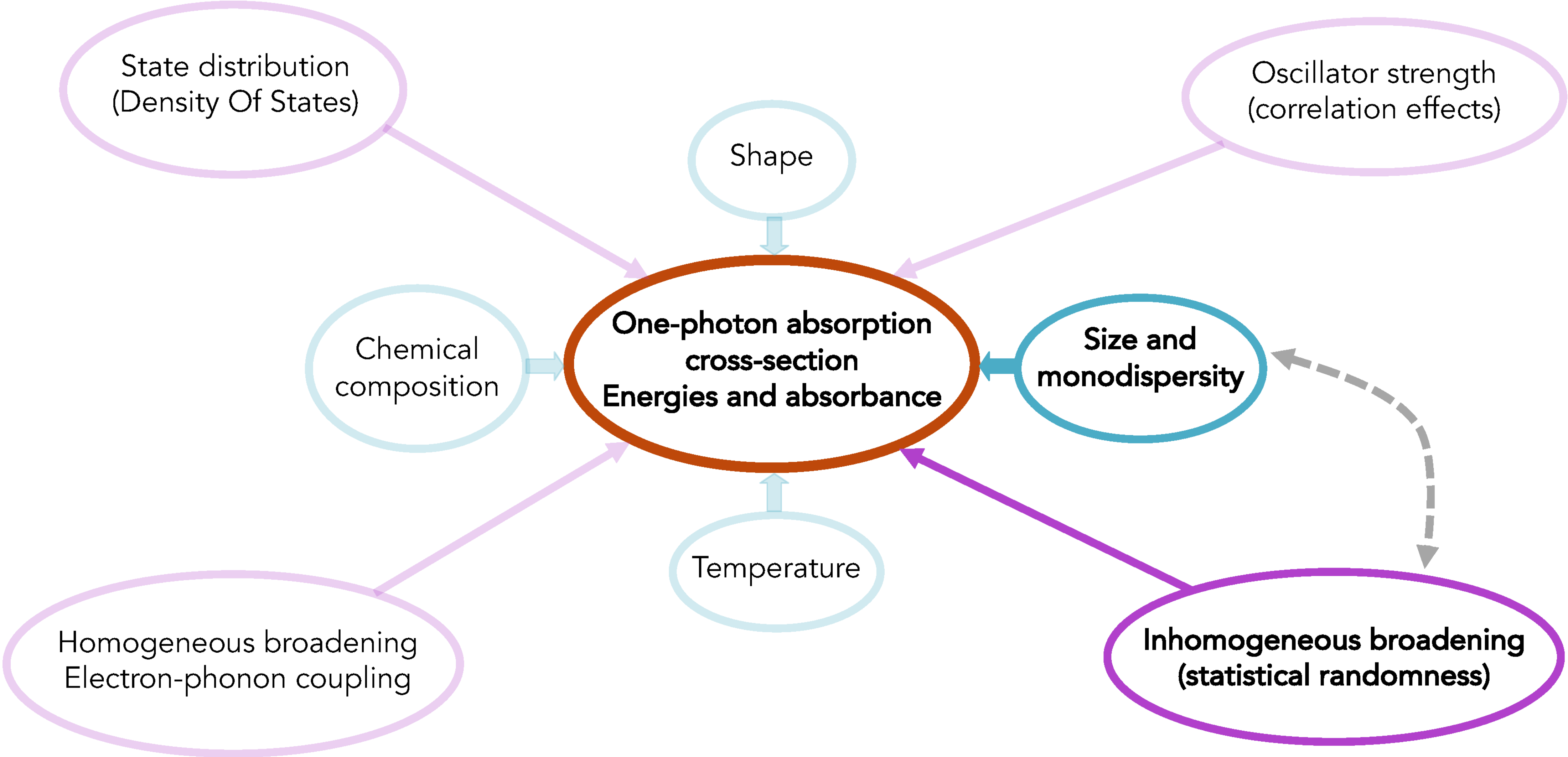
Diagrammatic view of optical properties – SIZE dispersion



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Inhomogeneous broadening in QD absorption spectra

PoLLoC

$$\sigma^{(1)}(E) = \sum_{eh} \Xi_{eh}\, g_{eh}(E - E_{eh})$$

Broadening line shape

$$g_{eh}(\sigma, \Gamma, u) = \int G(\sigma, u')\, L(\Gamma, u - u')\, du'$$

Gaussian standard deviation
statistical randomness in size

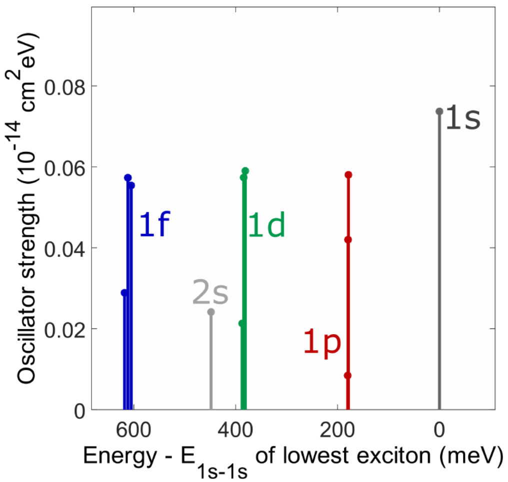
$$\sigma = \sum_i \sigma^{(i)} (\delta_{size})^i$$

size dispersion

$$\sigma^{(i)} = (-1)^i [(i+1) E_{\text{conf}} + E_{\text{coul}}]$$

Taylor-series coefficients

Theoretical transition energies and oscillator strength of L=7.0 nm QD



◊ **Experimental** full width at half maximum (FWHM) = **43.8 meV** at T = 14 K

◊ Using $\boldsymbol{\delta_{size}}$ **= 10%, estimated FWHM = 44.5 meV** at low-T

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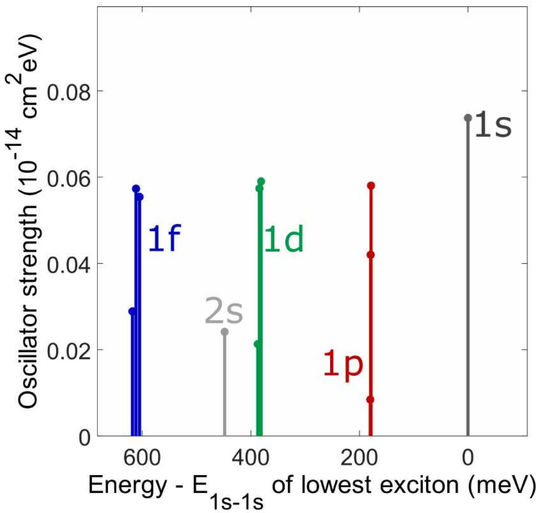
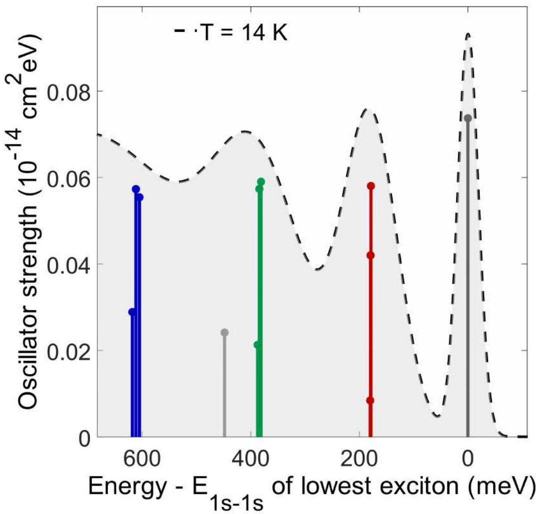
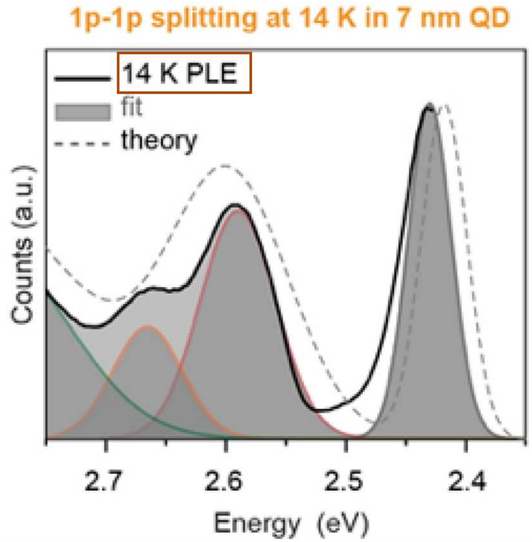


Broadening line shape Gaussian at low T



Theory versus experimental PLE



At high(er) temperature?

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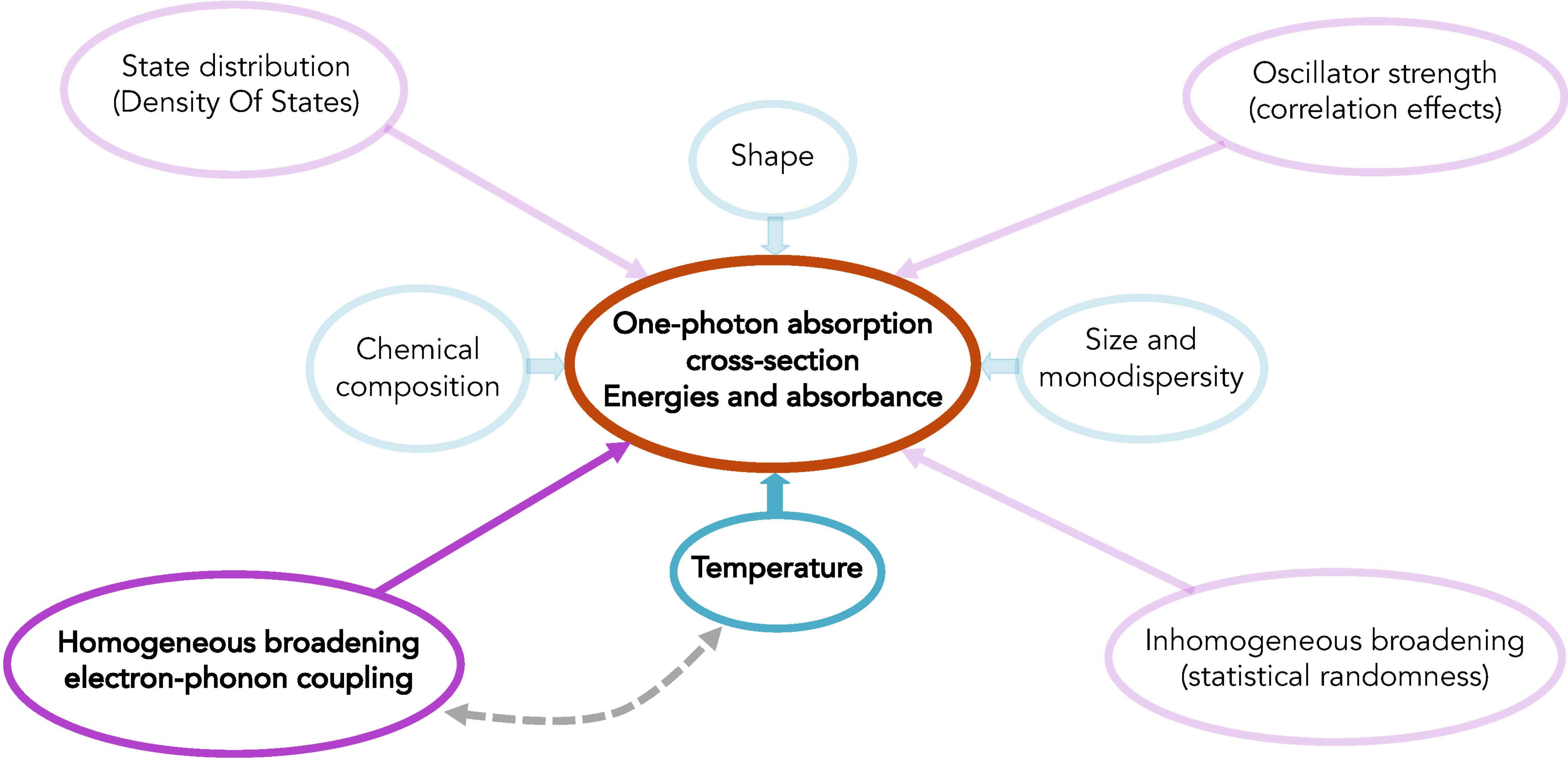
Diagrammatic "view" of optical properties – TEMPERATURE



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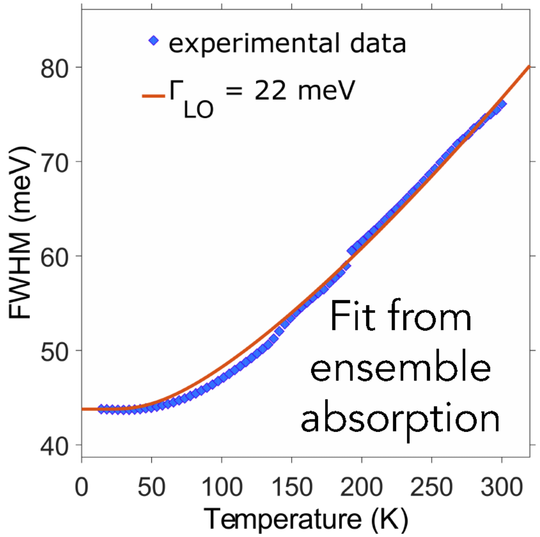
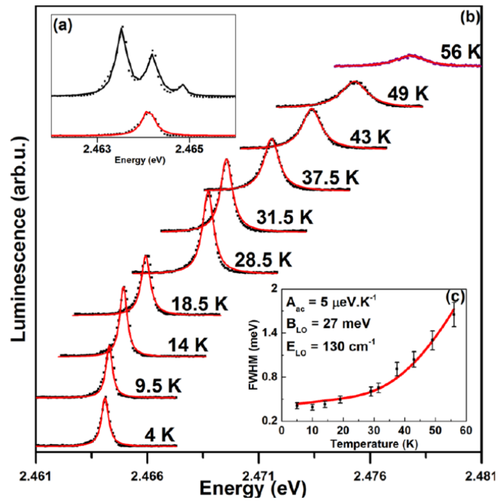
DOI: [10.21203/rs.3.rs-1236393/v1](10.21203/rs.3.rs-1236393/v1)

Shcherbakov-Wu, W. et al., J. Phys. Chem. Lett. 12, 33, 8088-8095 (2021)

Temperature-dependent homogeneous broadening

PoLLoC





$$\sigma^{(1)}(E) = \sum_{eh} \Xi_{eh}\, g_{eh}(E - E_{eh})$$

Broadening line shape

$$g_{eh}(\sigma, \Gamma, u) = \int G(\sigma, u')\, L(\Gamma, u - u')\, du'$$

$$\Gamma(T) = \Gamma_0 + \sigma_{\mathrm{Ac}} T + \Gamma_{\mathrm{LO}} N_{\mathrm{LO}}$$

Lorentzian line width

Acoustic phonon coupling

LO phonon coupling

Phonon occupation number

$$N_{\mathrm{LO}} = \frac{1}{\exp\left(\hbar\omega_{\mathrm{LO}}/k_B T\right) - 1}$$

$\Gamma_{\mathrm{LO}} = 42$ meV from single dot PL

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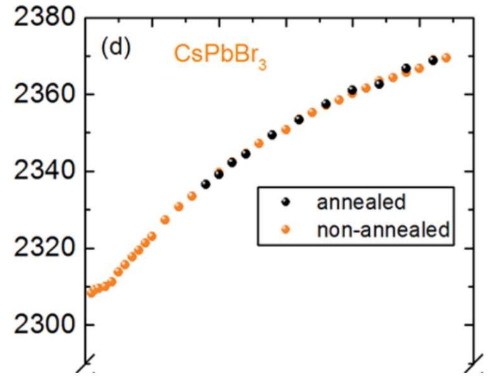
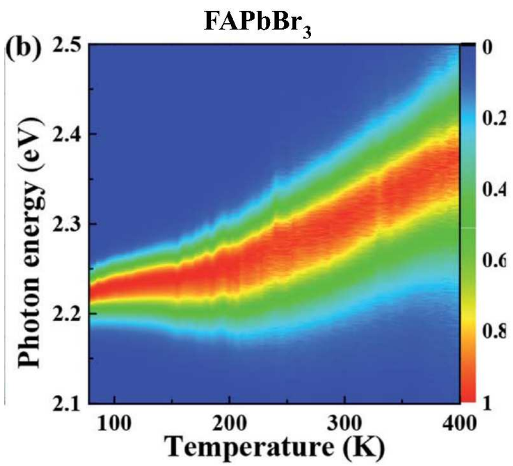
Temperature-dependent absorption spectra



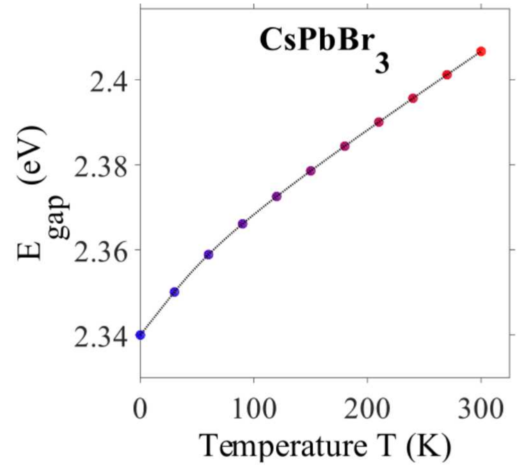


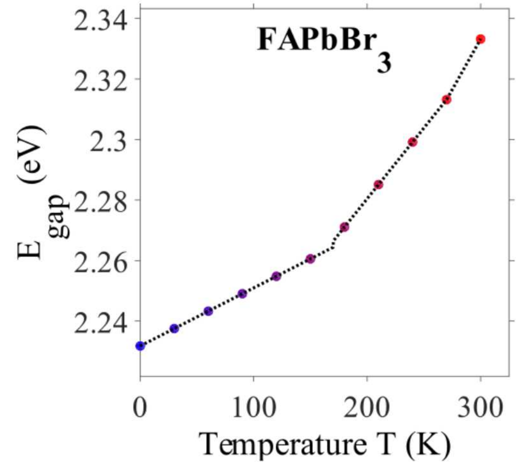
Temperature-dependent band gap $E_{gap}(T)$

$$E_{\text{gap}}(T) = E_{\text{gap}}(T=0) + A_{\text{linear}}T - A_{\text{e-LO phonon}}N_{\text{LO}}$$

Volume expansion

e-LO phonon coupling band gap renormalization





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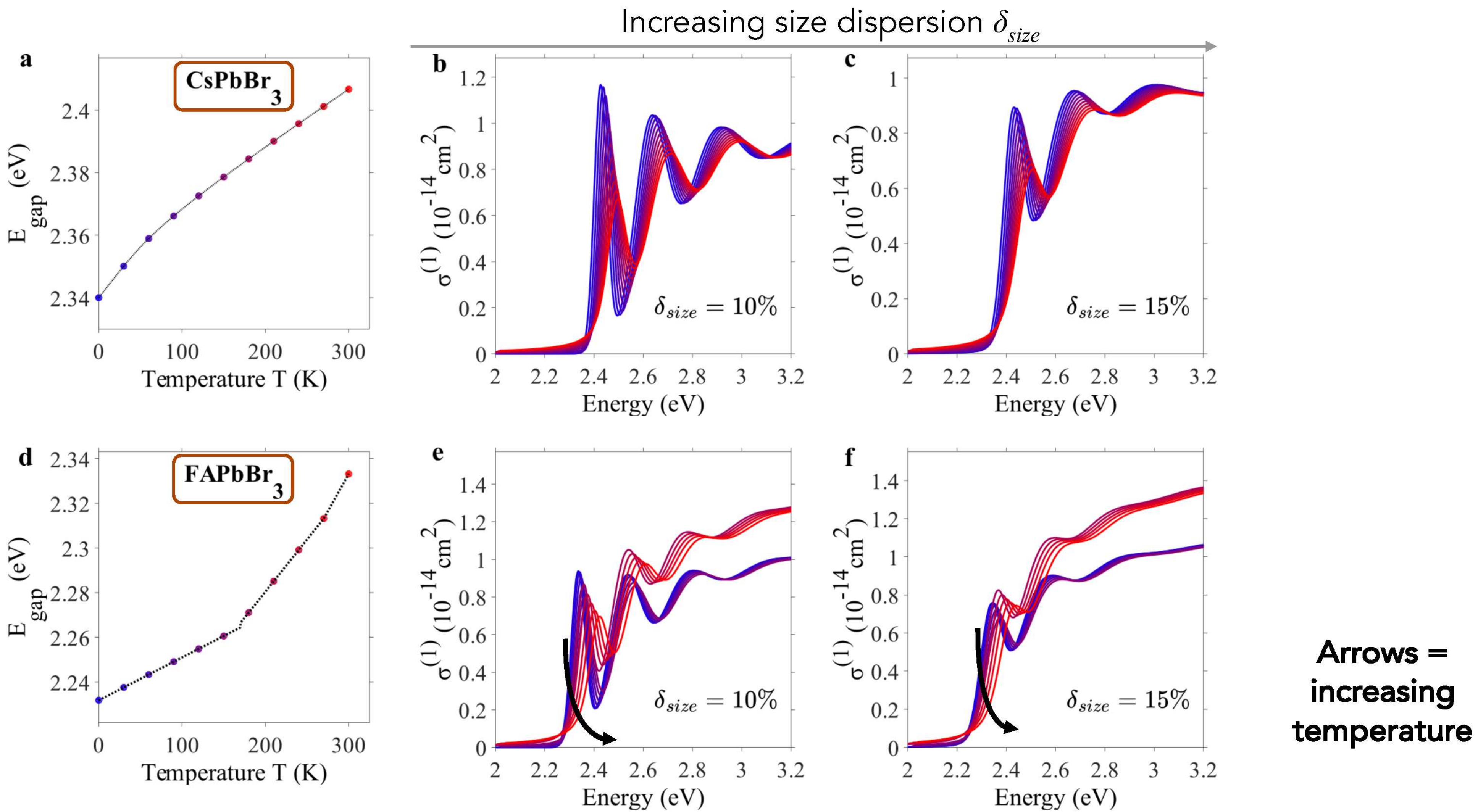
Temperature-dependent absorption spectra



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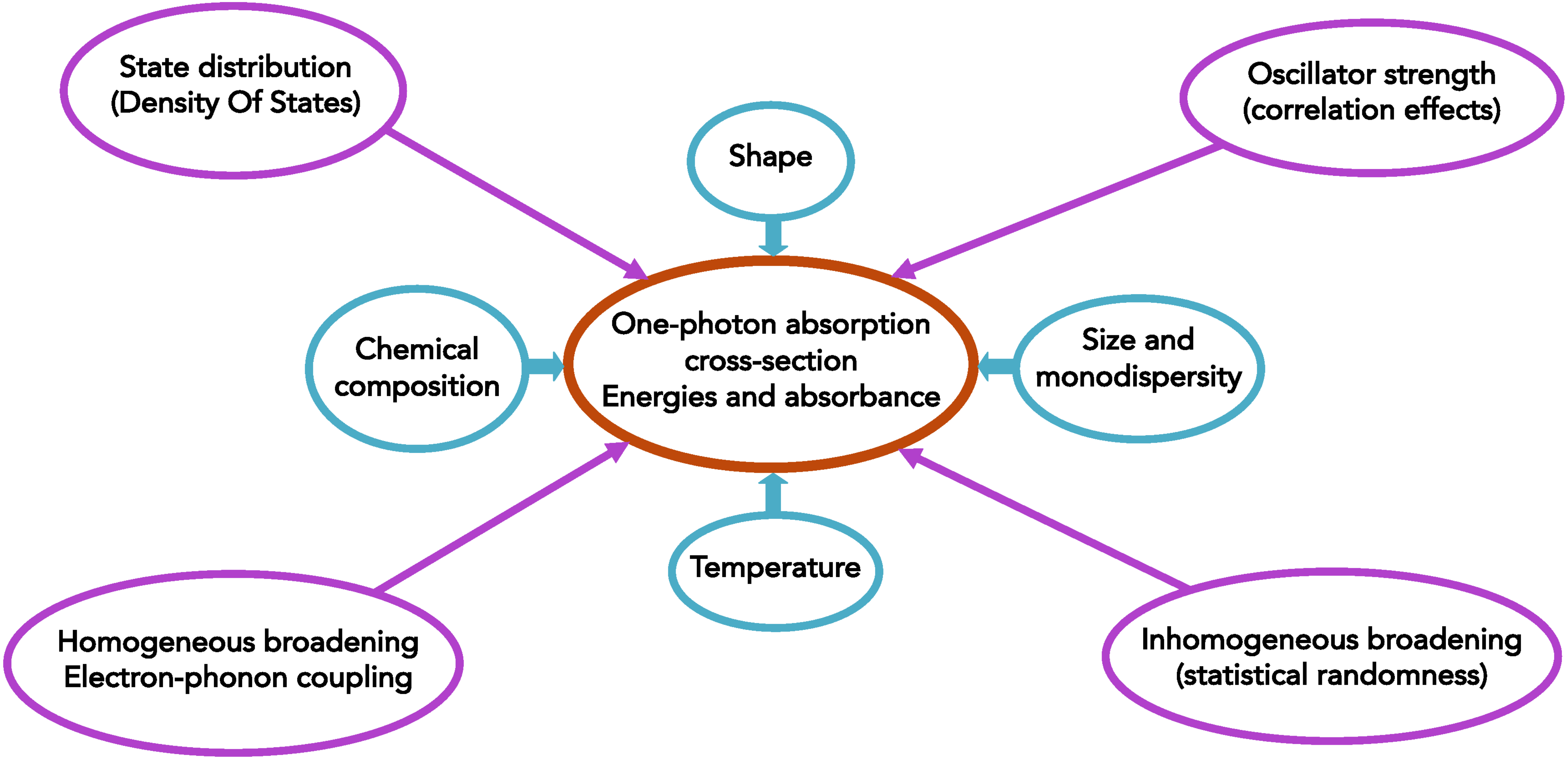
Final remarks and outlook



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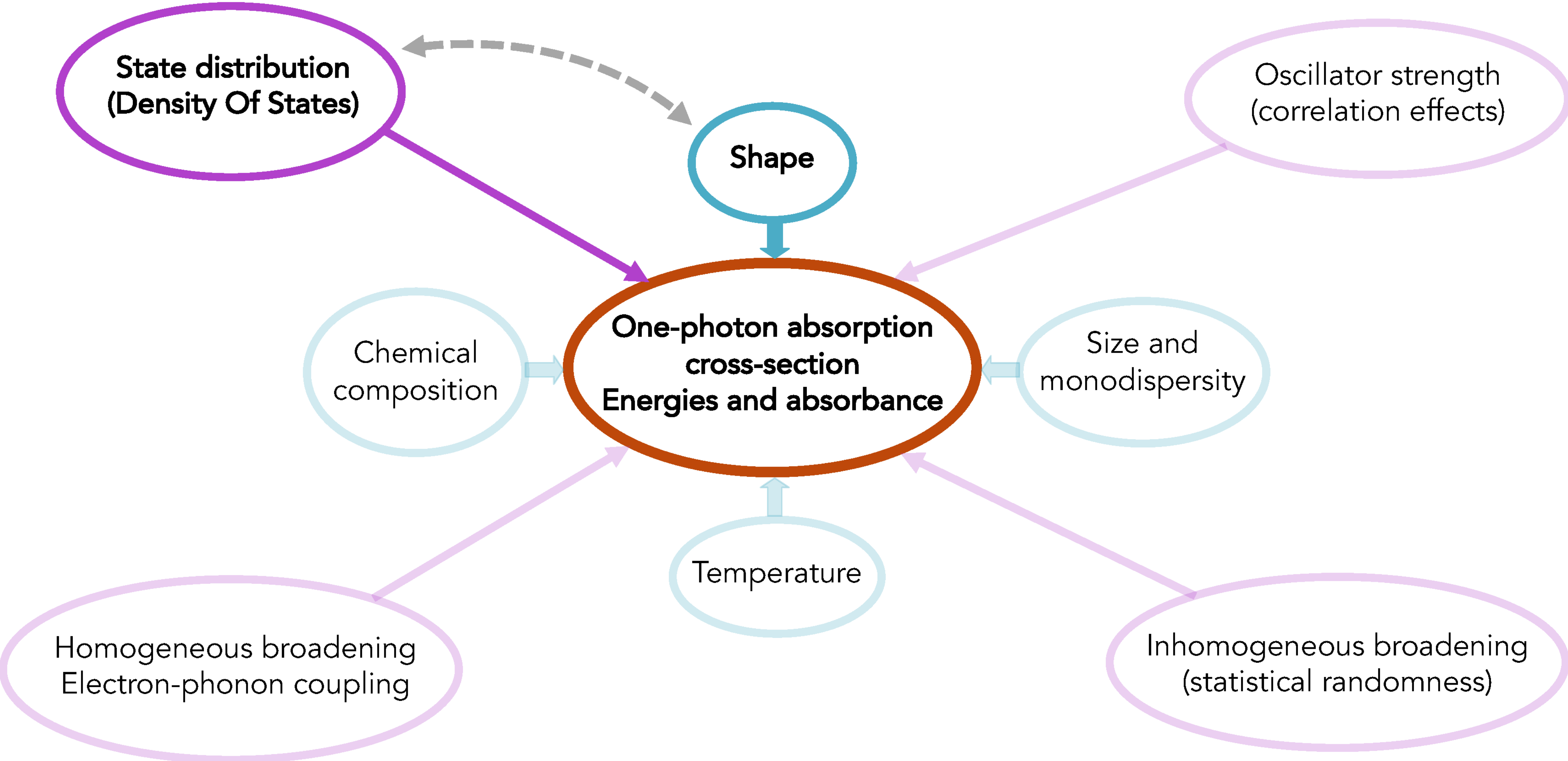
Final remarks and outlook



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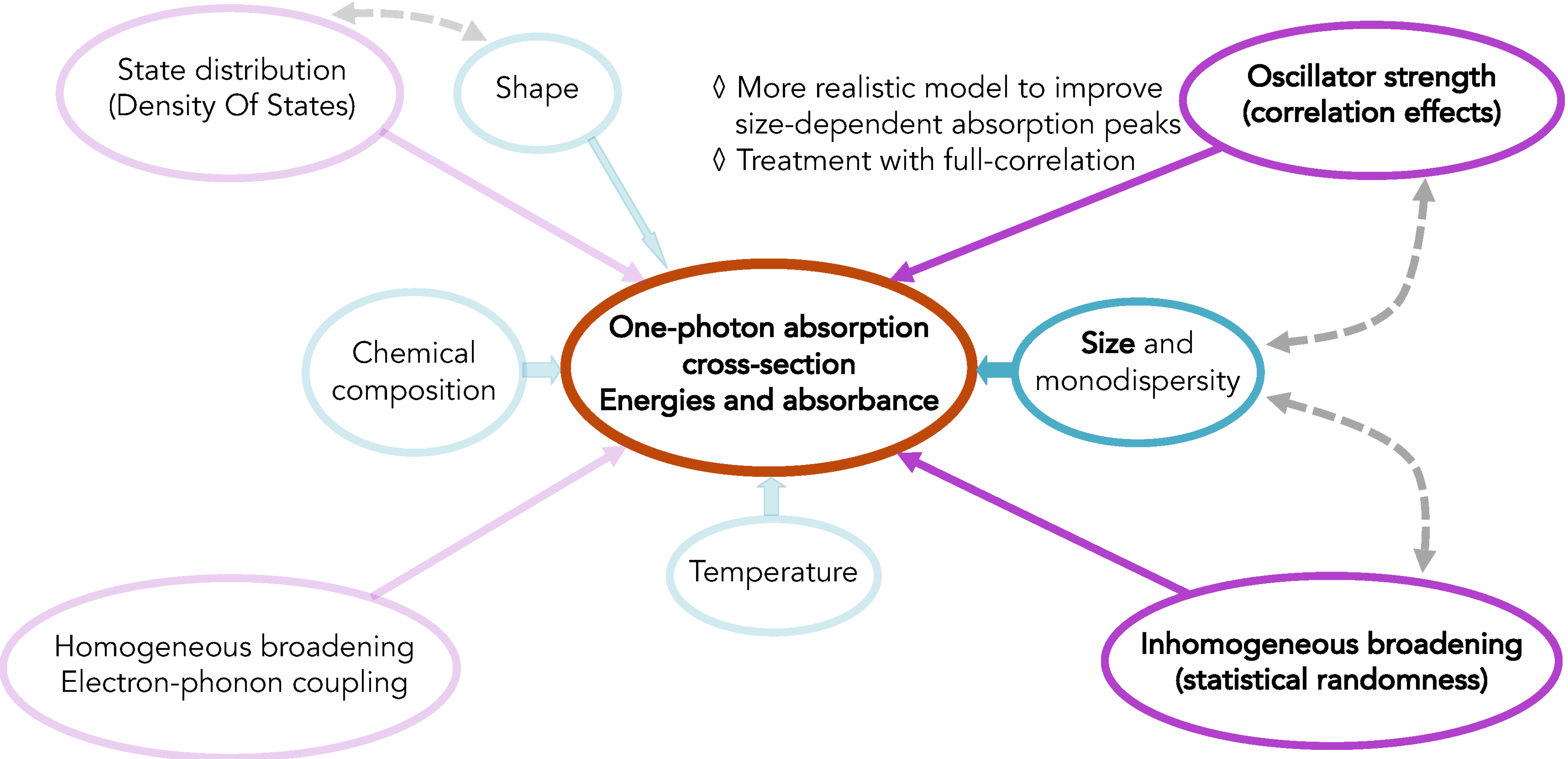
Final remarks and outlook

◊ More realistic model to improve size-dependent absorption peaks
◊ Treatment with full-correlation



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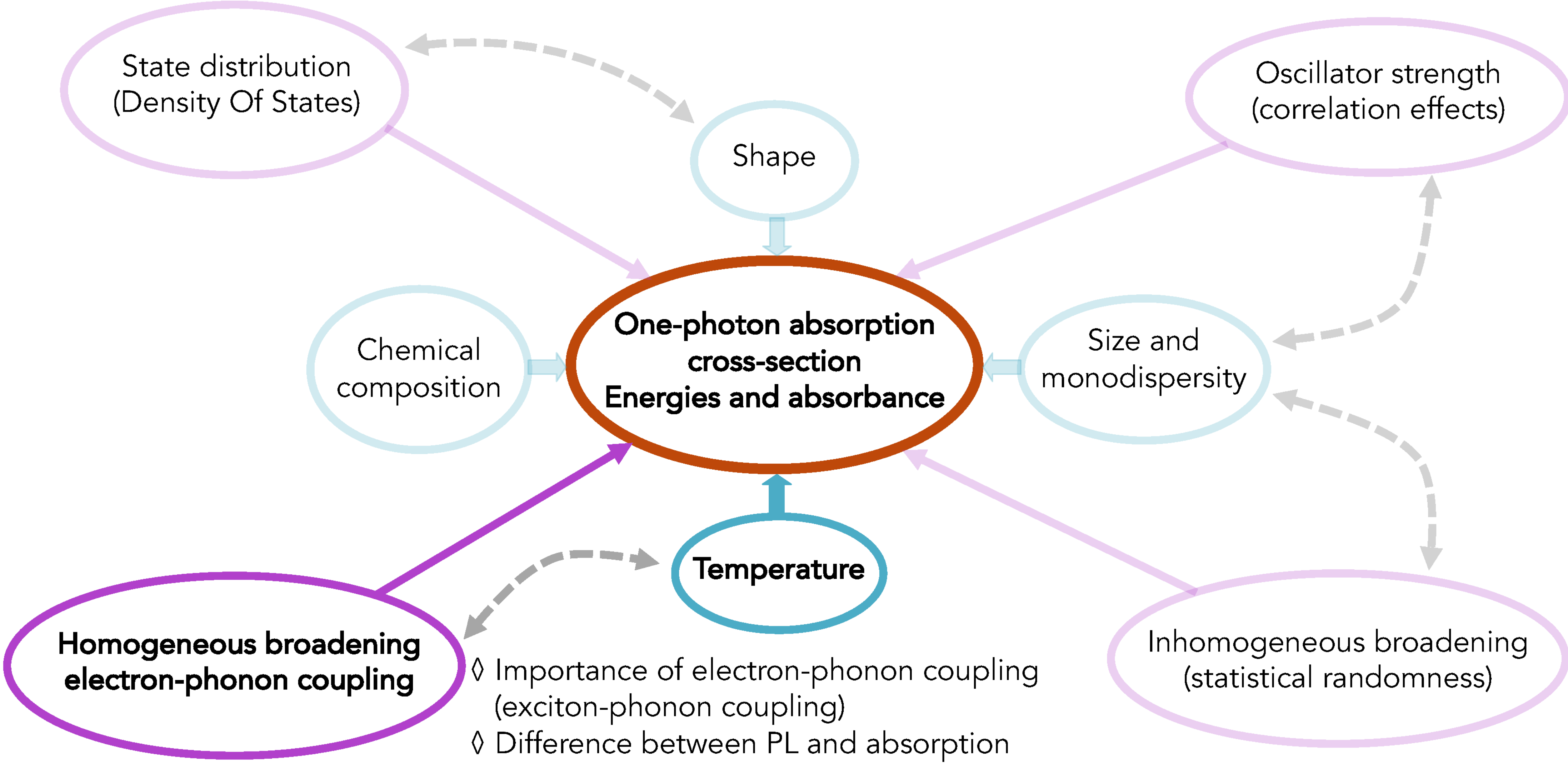
Final remarks and outlook



◊ Importance of electron-phonon coupling (exciton-phonon coupling)

◊ Difference between PL and absorption

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Shcherbakov-Wu, W. et al., J. Phys. Chem. Lett. 12, 33, 8088-8095 (2021)

THANK YOU FOR YOUR ATTENTION!

CNRS & INSA Rennes

- Claudine KATAN
- Jacky EVEN

Kovalenko's group, Zurich

- Quinten A. Akkerman (LMU)
- Simon C. Boehme
- Federico Montanarella
- Dmitry N. Dirin
- Philipp Wechsler
- Finn Beiglböck
- Rolf Erni
- Gabrielle Raino
- Maksym V. Kovalenko

This project has received funding from the European Union's Horizon 2020 program, through a FET Open research and innovation action under the grant agreement No 899141 (POLLOC).