ab initio colors

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talk given at *ES12: The 24th Annual Workshop on Recent Developments in Electronic Structure Theory*
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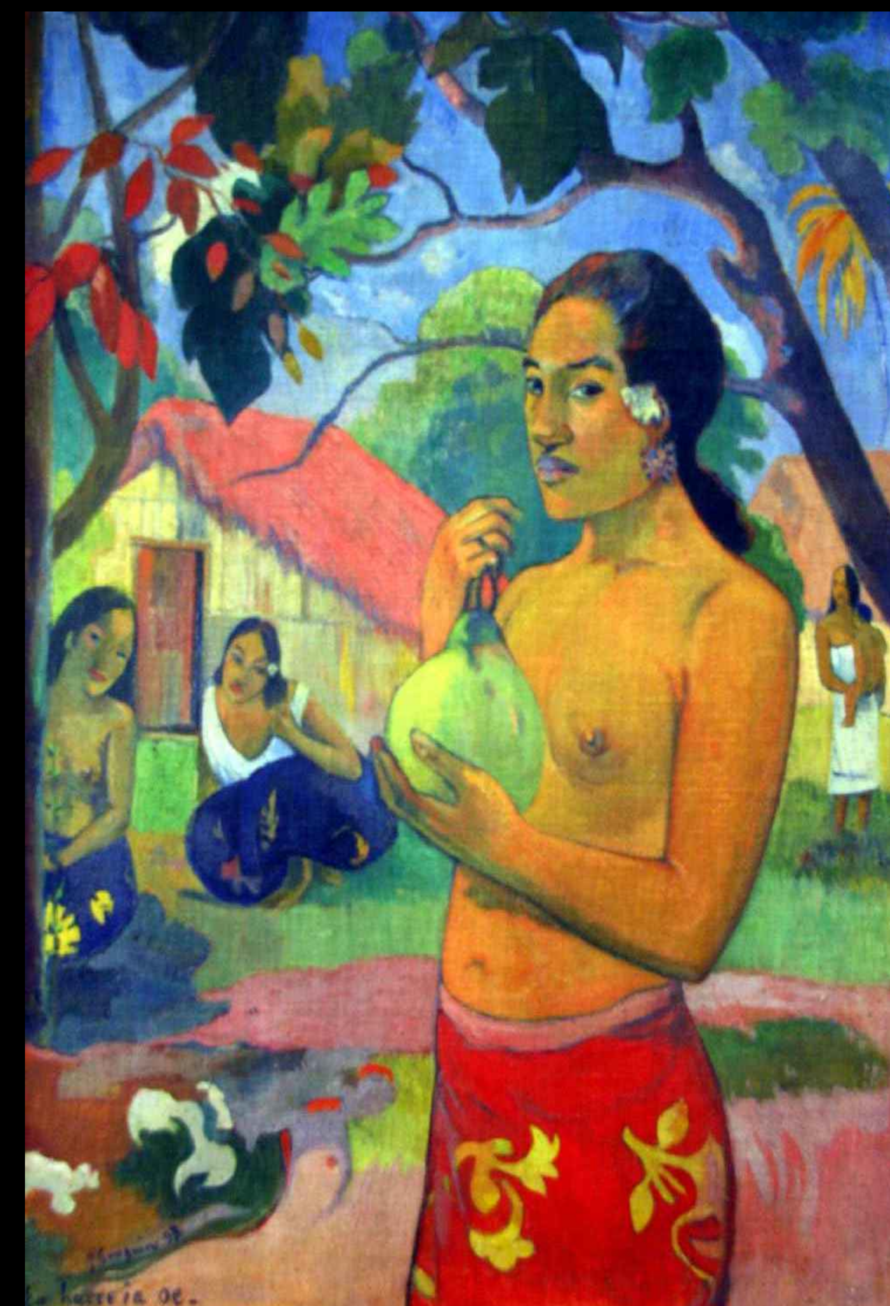
what color is all about



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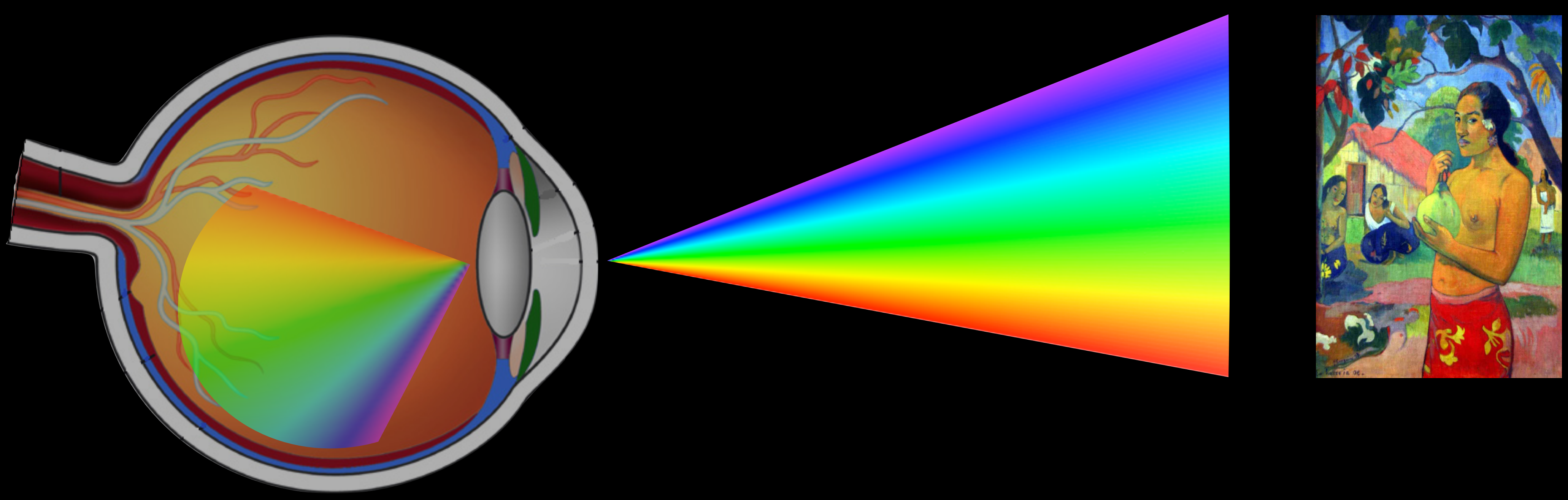

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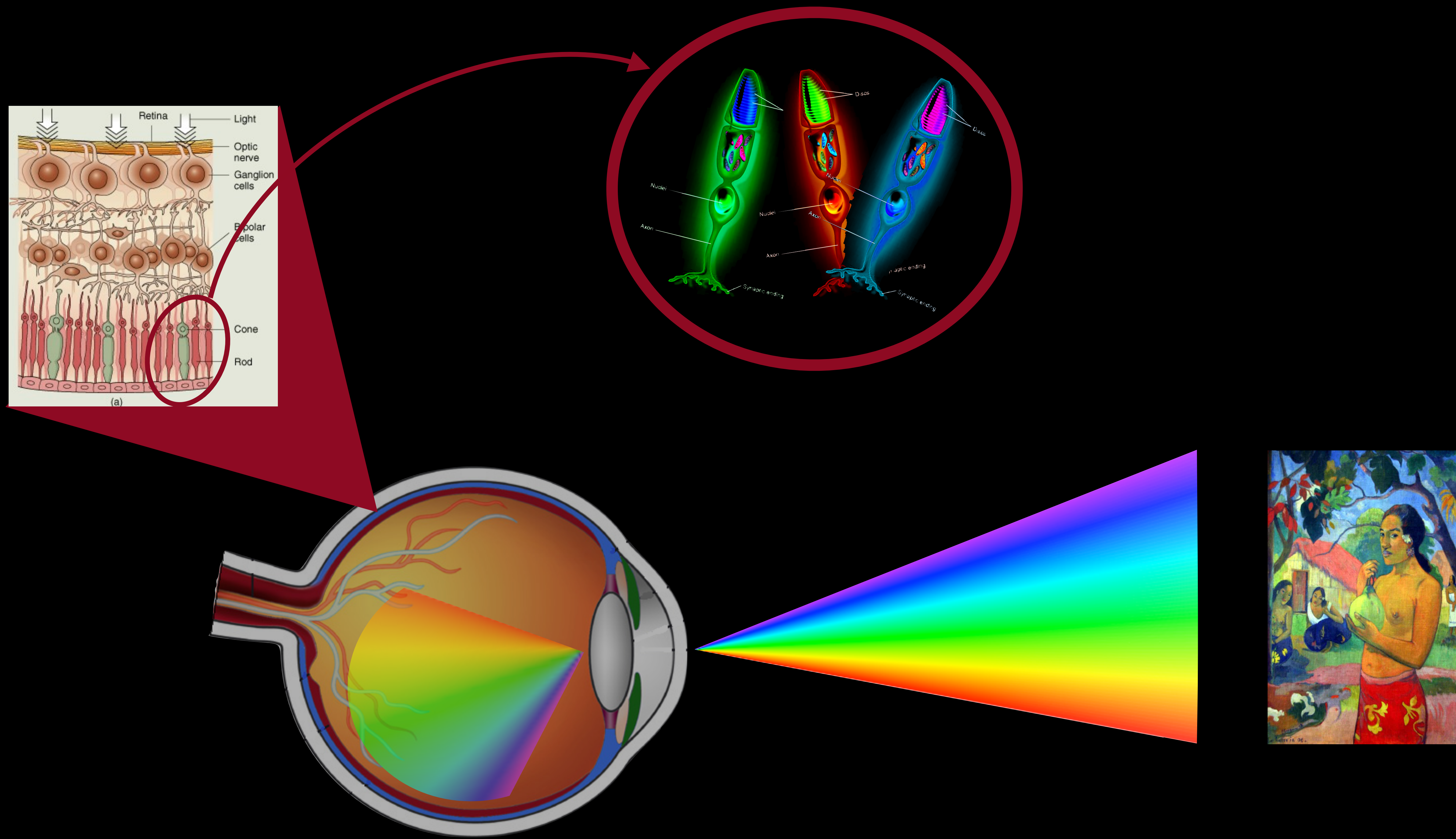

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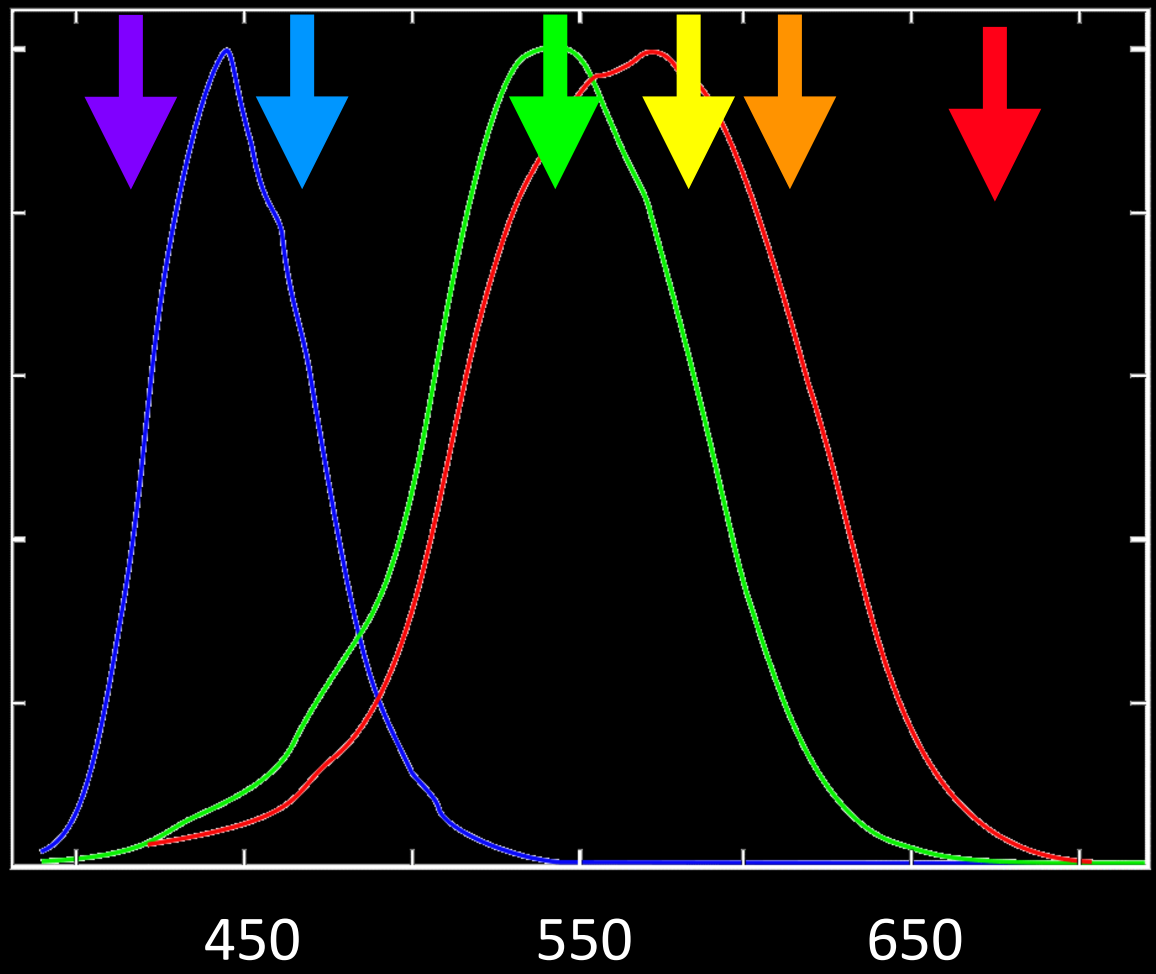
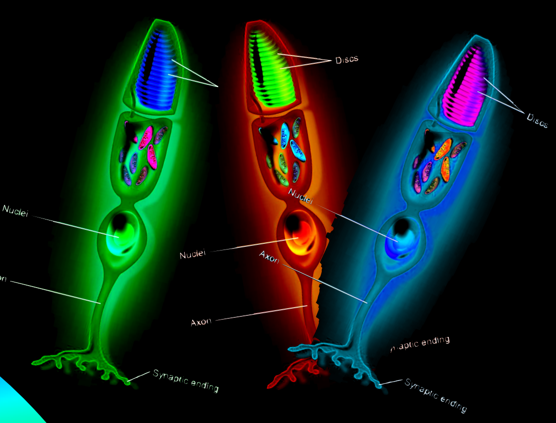
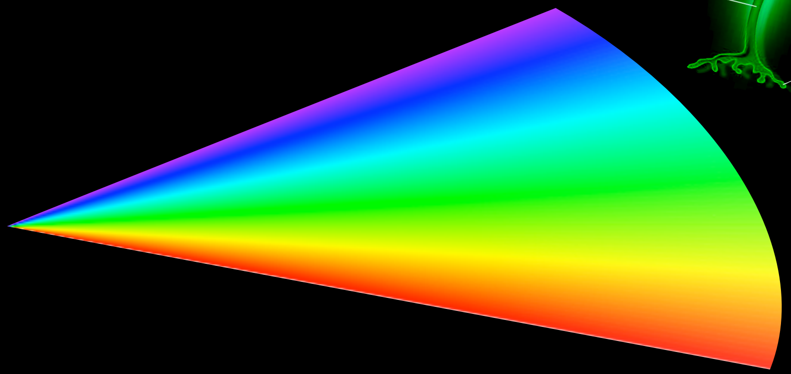




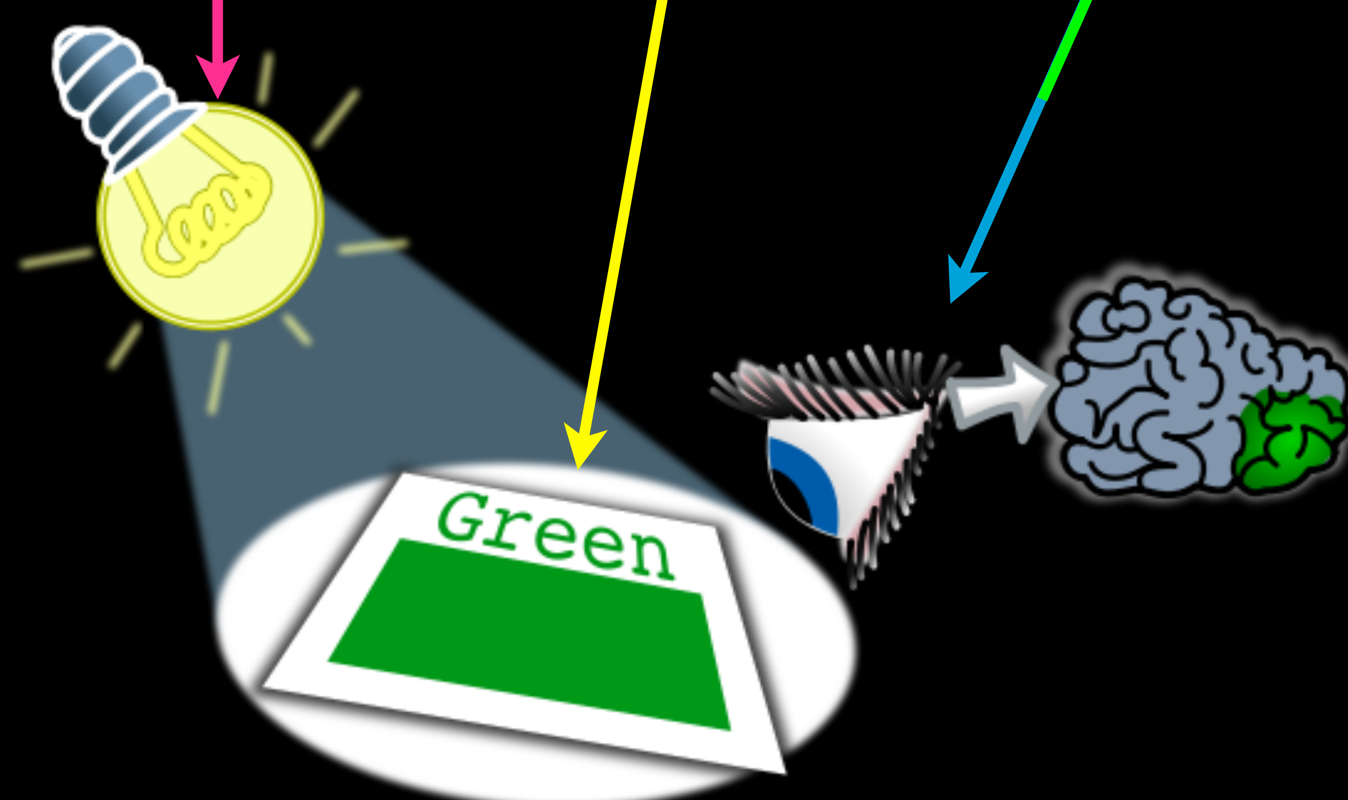


$$\text{anycolor}(\lambda) = r(\lambda) + g(\lambda) + b(\lambda)$$

what makes things glitter the way they do

stimulus =

illuminant × trasmission × sensitivity



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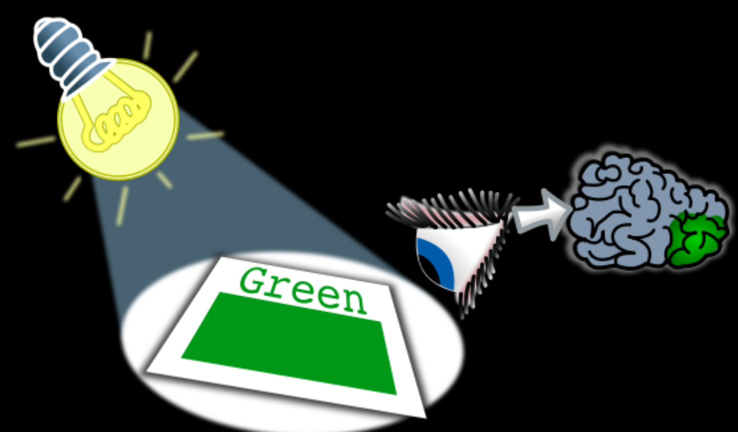

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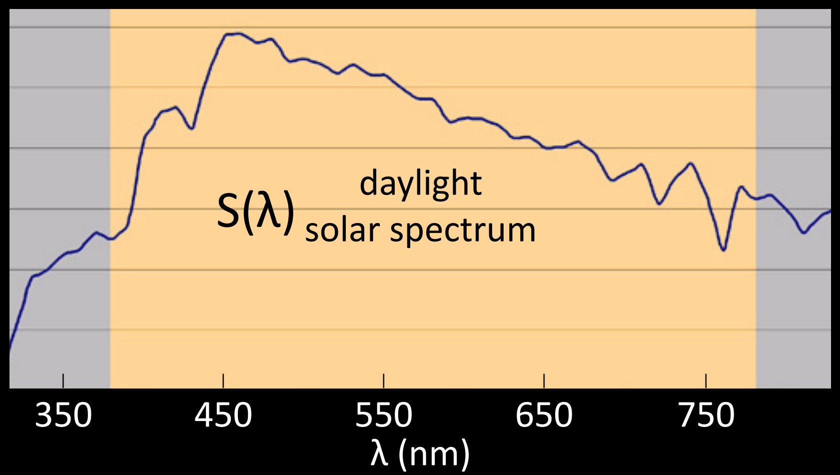
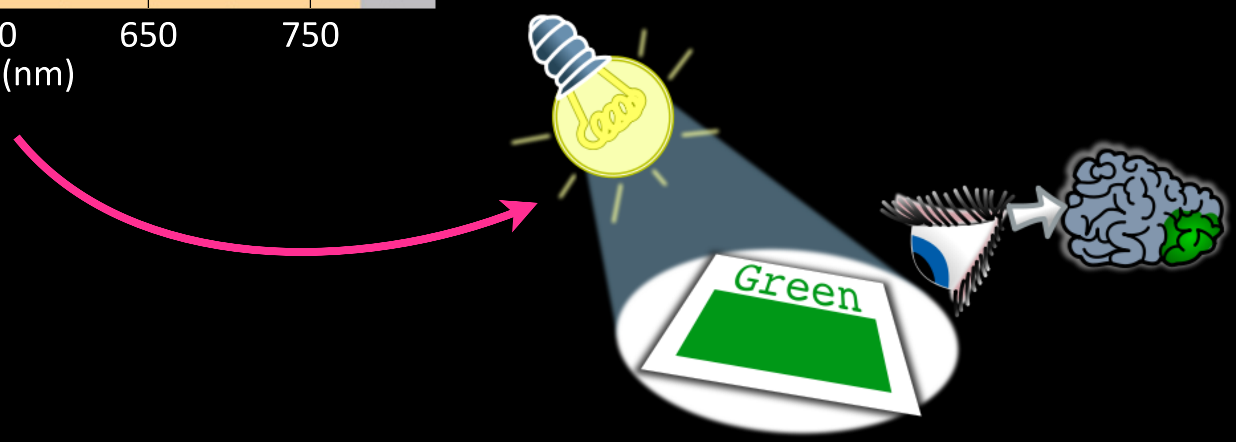
what makes things glitter the way they do



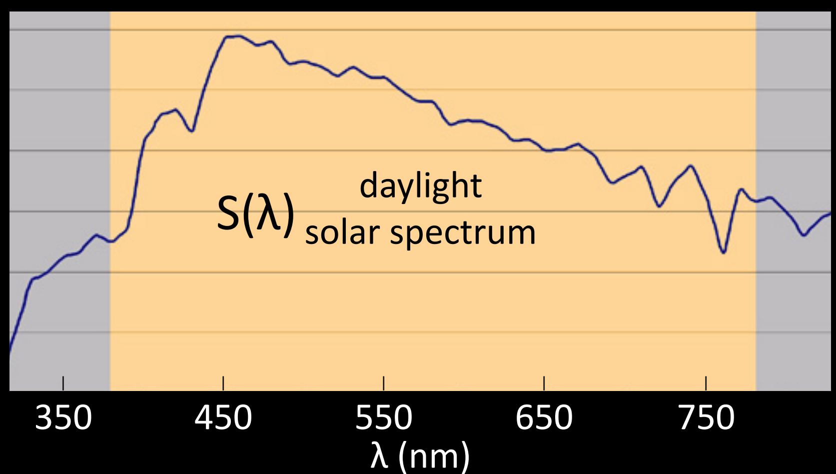


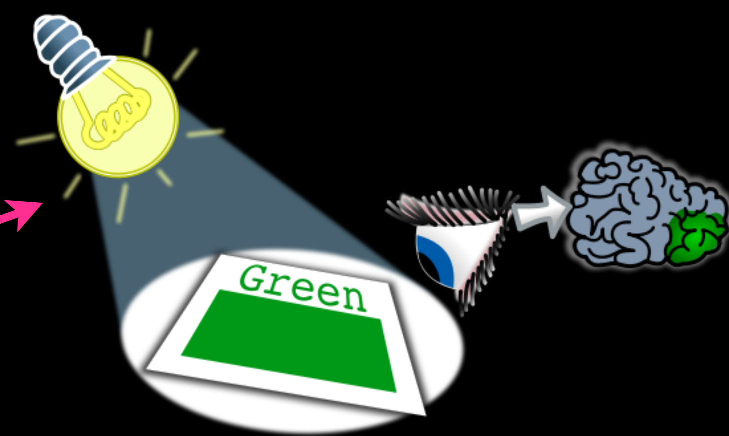
stimulus =

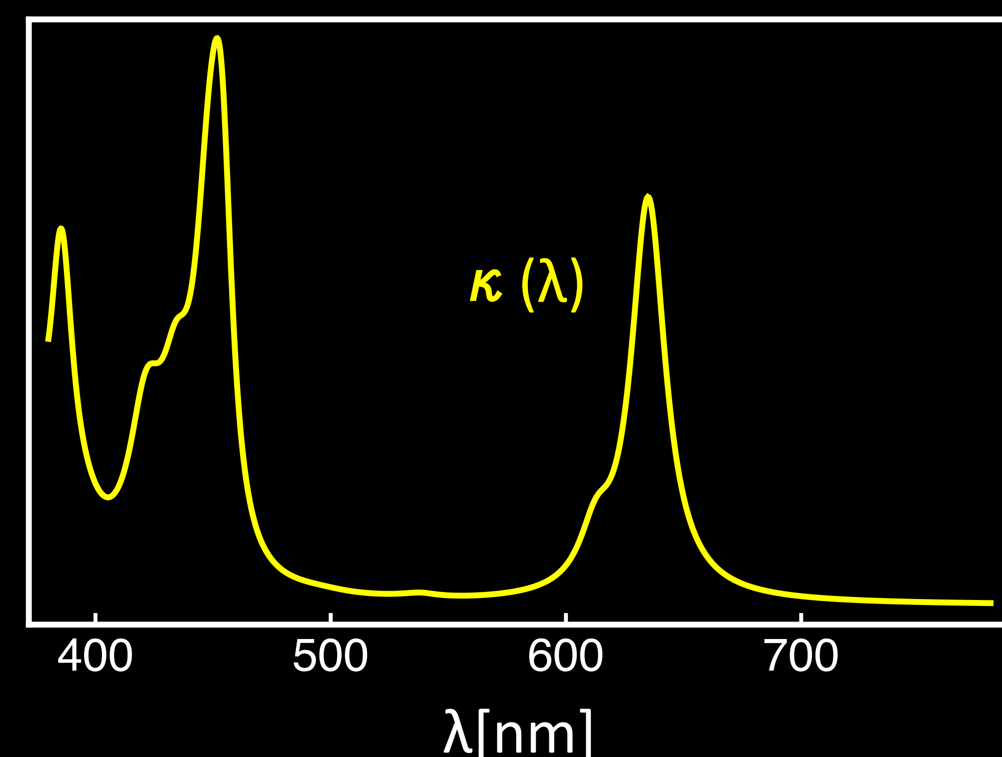
illuminant × trasmission × sensitivity

$S(\lambda)$

what makes things glitter the way they do





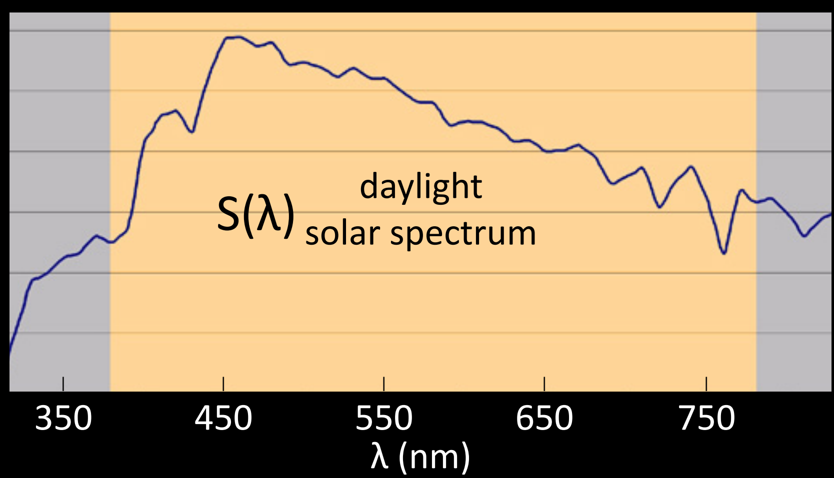


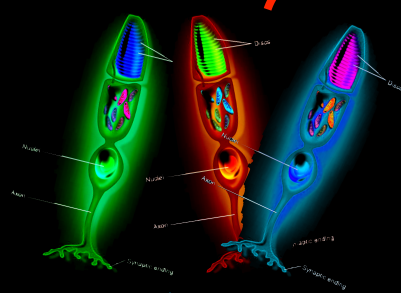
stimulus =

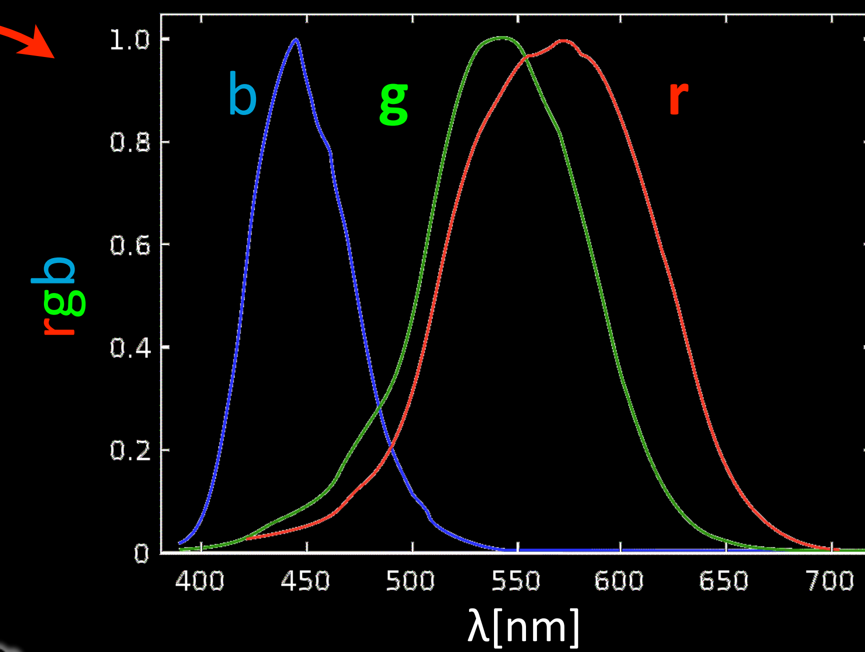
illuminant × trasmission × sensitivity

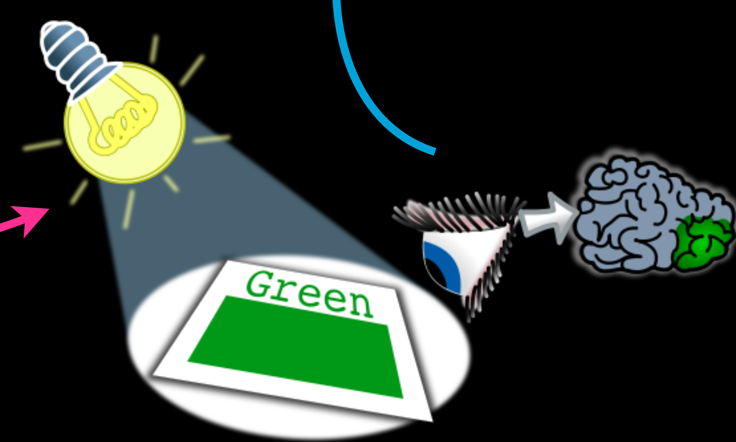
$$S(\lambda) \times e^{-\kappa(\lambda)x}$$

what makes things glitter the way they do





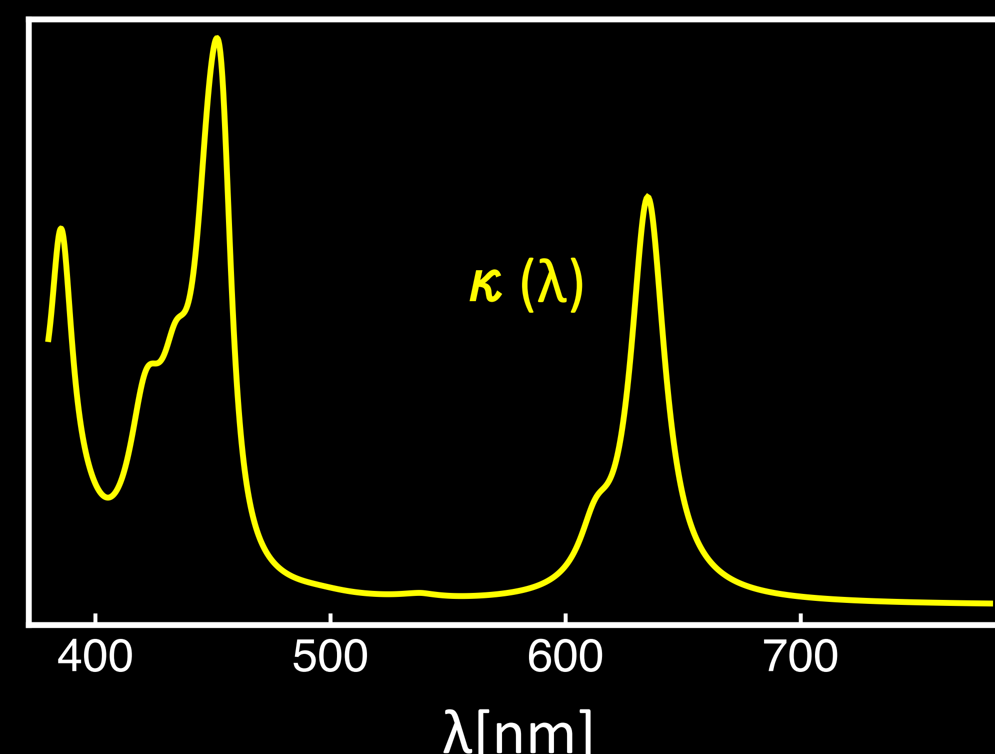




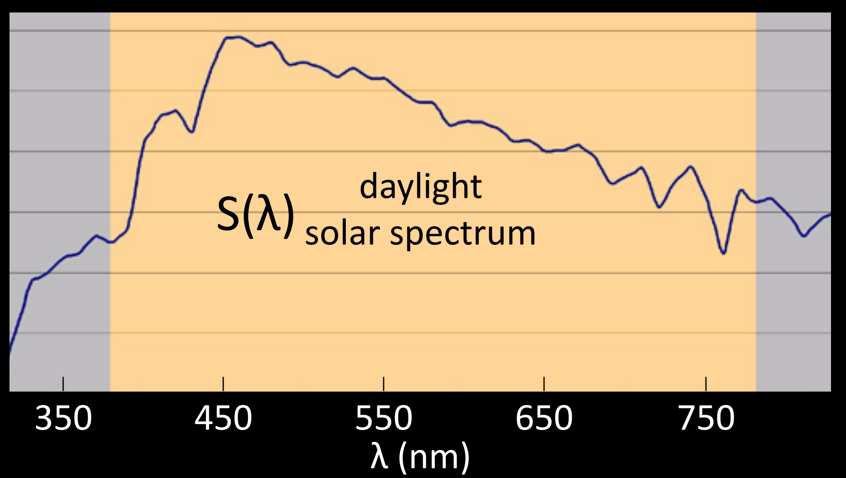
stimulus =

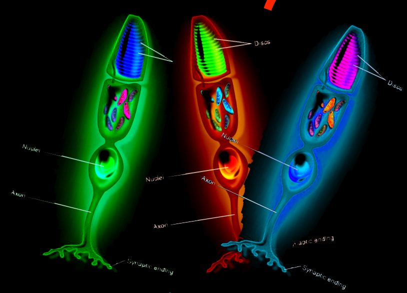
illuminant × trasmission × sensitivity

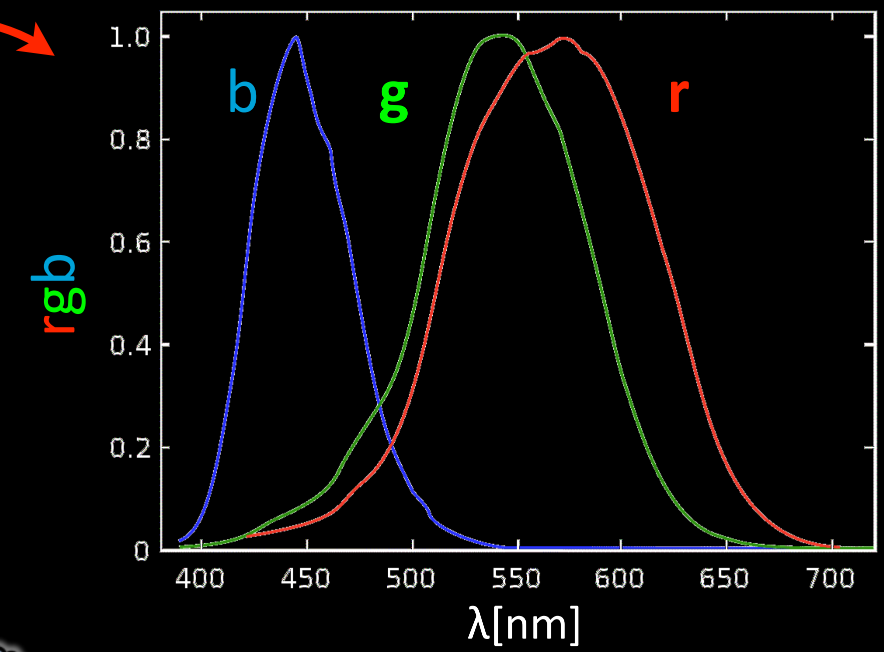
$$S(\lambda) \times e^{-\kappa(\lambda)x} \times rgb(\lambda)$$

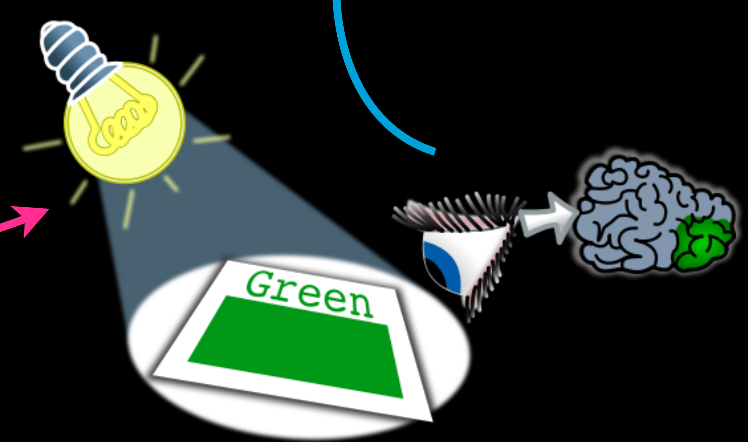


what makes things glitter the way they do

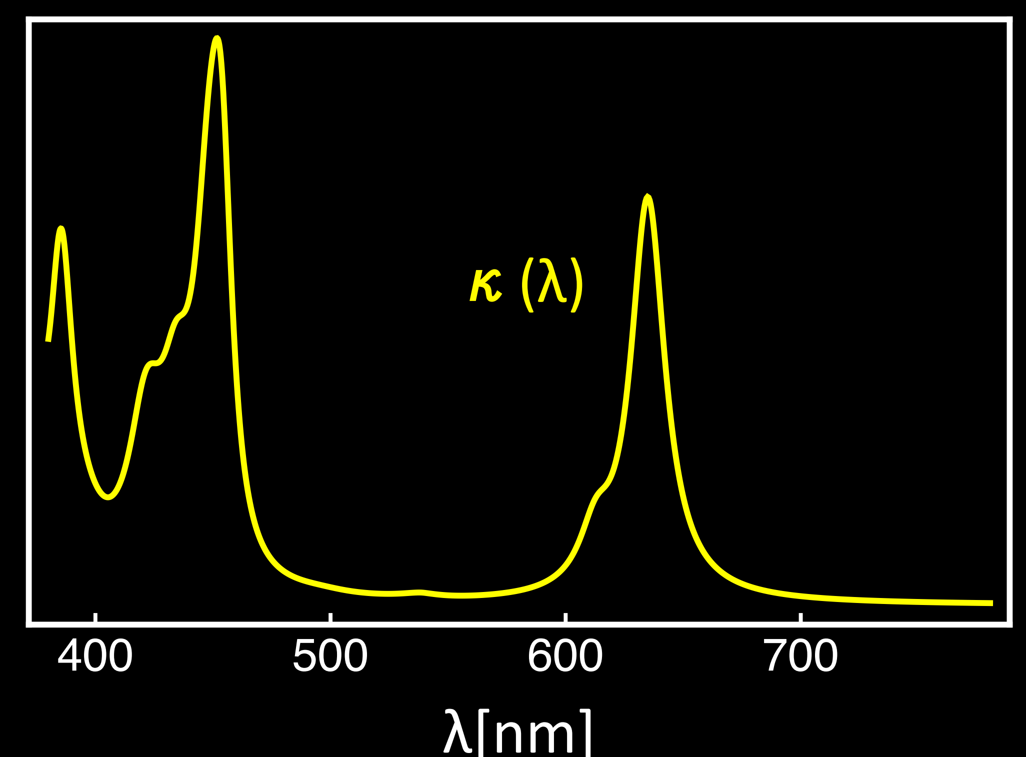




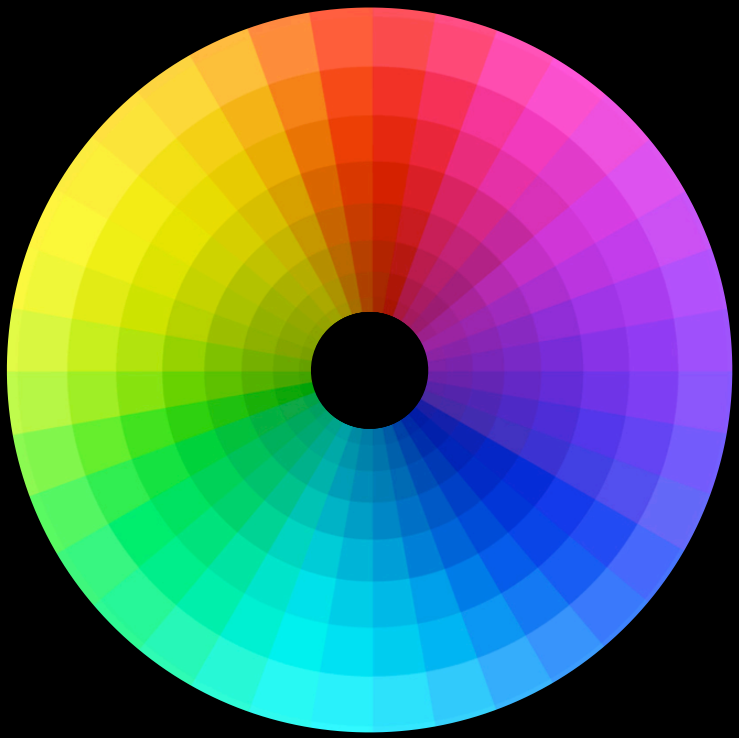




$$\mathrm{RGB}(x) = \int \mathrm{S}(\lambda)\mathrm{e}^{-\kappa(\lambda)x}\,\mathrm{rgb}(\lambda)\,d\lambda$$

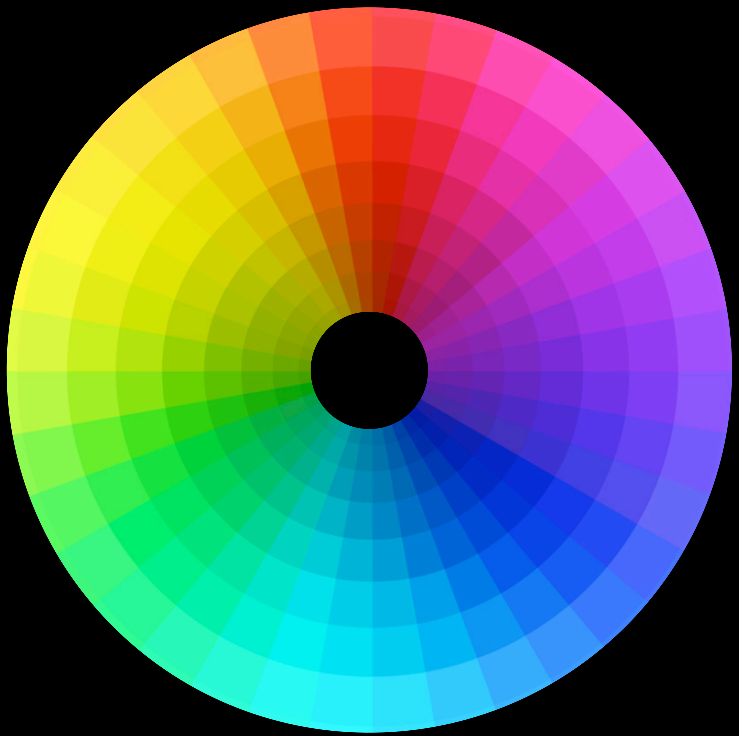


a puzzle for you



a puzzle for you

hint: the solution is contained in one of the previous slides



spectroscopy

$$\kappa(\omega) \propto \omega\, \mathrm{Im}\alpha(\omega)$$

$$\mathsf{d}(\omega) = \alpha(\omega)\mathsf{E}(\omega)$$

spectroscopy

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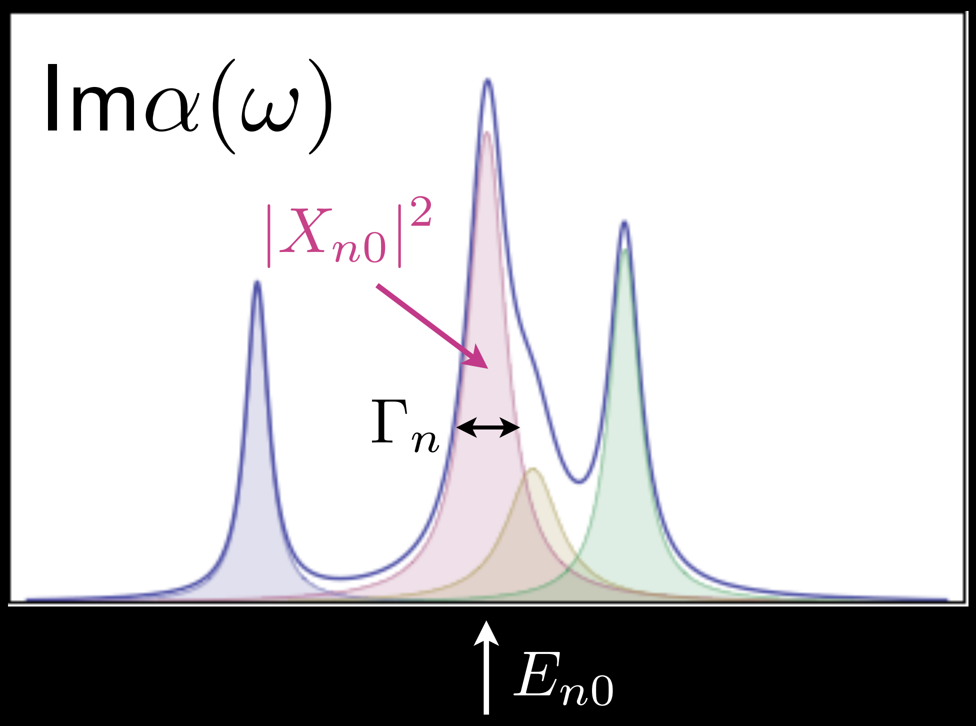
$$\mathsf{d}(\omega) = \alpha(\omega)\mathsf{E}(\omega)$$

$$\alpha(\omega) = \sum_{n\neq 0}\left[\frac{\mathsf{X}_{0n}\mathsf{X}_{n0}}{\omega - E_{n0} + i\delta} - \frac{\mathsf{X}_{0n}\mathsf{X}_{n0}}{\omega + E_{n0} + i\delta}\right]$$



spectroscopy

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probe $\rightsquigarrow$ system $\rightsquigarrow$ response

optical spectra from TDDF (perturbation) T

$$\mathbf{d}(t) = \mathsf{Tr}\big(\mathbf{d}\rho(t)\big)$$

optical spectra from TDDF (perturbation) T

$$\mathbf{d}(t) = \mathsf{Tr}\big(\mathbf{d}\rho(t)\big)$$

$$\rho(t) = \sum_v |\phi_v(t)\rangle\langle\phi_v(t)|$$

optical spectra from TDDF (perturbation) T

$$\mathbf{d}(t) = \mathsf{Tr}\big(\mathbf{d}\rho(t)\big)$$

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$$i\frac{\partial\phi_v(\mathbf{r},t)}{\partial t} = \big(-\Delta + v_{KS}(\mathbf{r},t)\big)\phi_v(\mathbf{r},t)$$

optical spectra from TDDF (perturbation) T

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$$i\dot{\rho}(t) = \big[H_{KS}(t), \rho(t)\big]$$

optical spectra from TDDF (perturbation) T

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optical spectra from TDDF (perturbation) T

$$i\dot{\rho}(t) = \left[H_{KS}(t), \rho(t)\right]$$

$$\rho(t) = \rho^\circ + \rho'(t)$$
$$H_{KS}(t) = H^\circ + V'_{ext}(t) + V'_{HXC}(t)$$

$$i\ \dot{\rho}' = [H^\circ, \rho'] + [V'_{HXC}, \rho^\circ] + [V'_{ext}, \rho^\circ] + \mathcal{O}\left(V'^2\right)$$

optical spectra from TDDF (perturbation) T

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$$i\ \dot{\rho}' = \mathcal{L}\ \rho' + [V'_{ext}, \rho^\circ]$$

optical spectra from TDDF (perturbation) T

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$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

optical spectra from TDDF (perturbation) T

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optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

$$\boldsymbol{\alpha}(\omega) \quad = \quad \mathsf{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big)$$

optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

$$\begin{aligned} \boldsymbol{\alpha}(\omega) &= \mathsf{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big) \\ &= \big(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^\circ]\big) \end{aligned}$$

optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]$$

$$\begin{aligned} \boldsymbol{\alpha}(\omega) &= \mathrm{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big) \\ &= \big(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^\circ]\big) \\ &\equiv \big(u, (\omega - \mathcal{L})^{-1} \cdot v\big) \end{aligned}$$

the Lanczos connection

$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

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J. Phys. C: Solid State Phys., Vol. 5, 1972. Printed in Great Britain. © 1972

Electronic structure based on the local atomic environment for tight-binding bands

R HAYDOCK, VOLKER HEINE and M J KELLY
Cavendish Laboratory, Cambridge, UK

the Lanczos connection

$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

$$\begin{aligned}
\phi_{-1} &= 0 \\
b_{n+1}\phi_{n+1} &= (\mathcal{H} - a_n)\phi_n - b_n\phi_{n-1} \\
\langle \phi_{n+1} | \phi_{n+1} \rangle &= 1 \\
a_n &= \langle \phi_n | \mathcal{H} | \phi_n \rangle
\end{aligned}$$

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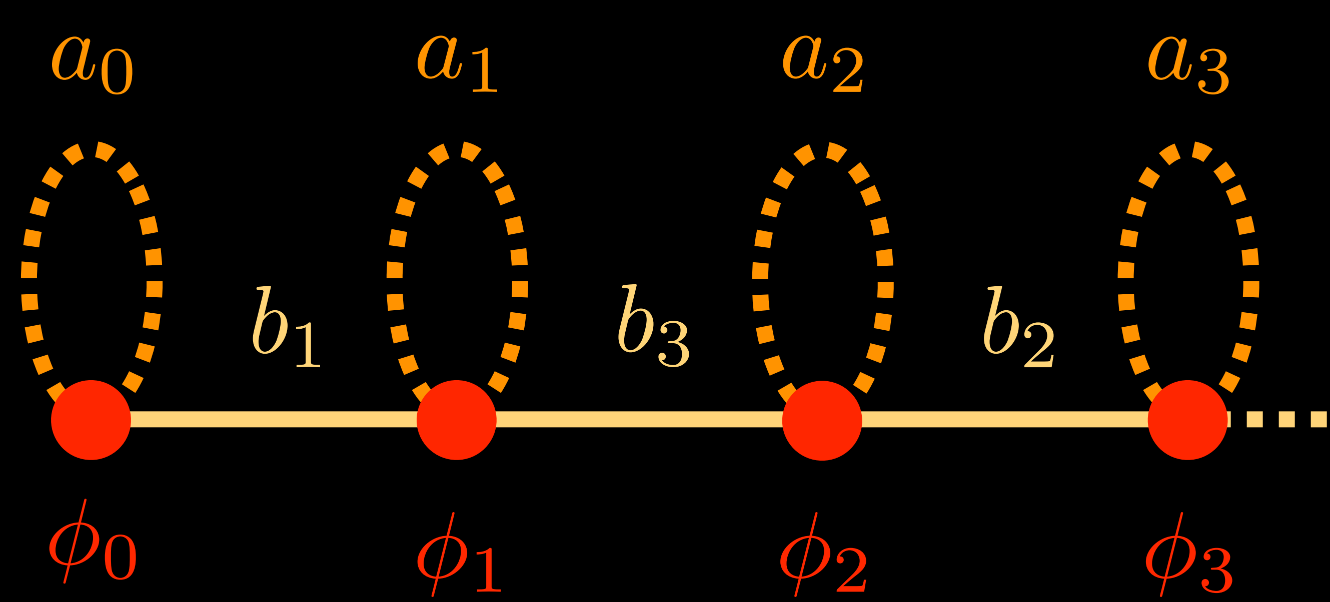
\langle \phi_{n+1} | \phi_{n+1} \rangle &= 1 \\
a_n &= \langle \phi_n | \mathcal{H} | \phi_n \rangle
\end{aligned}$$

$$\mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

the Lanczos connection

$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$



$$\mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

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$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

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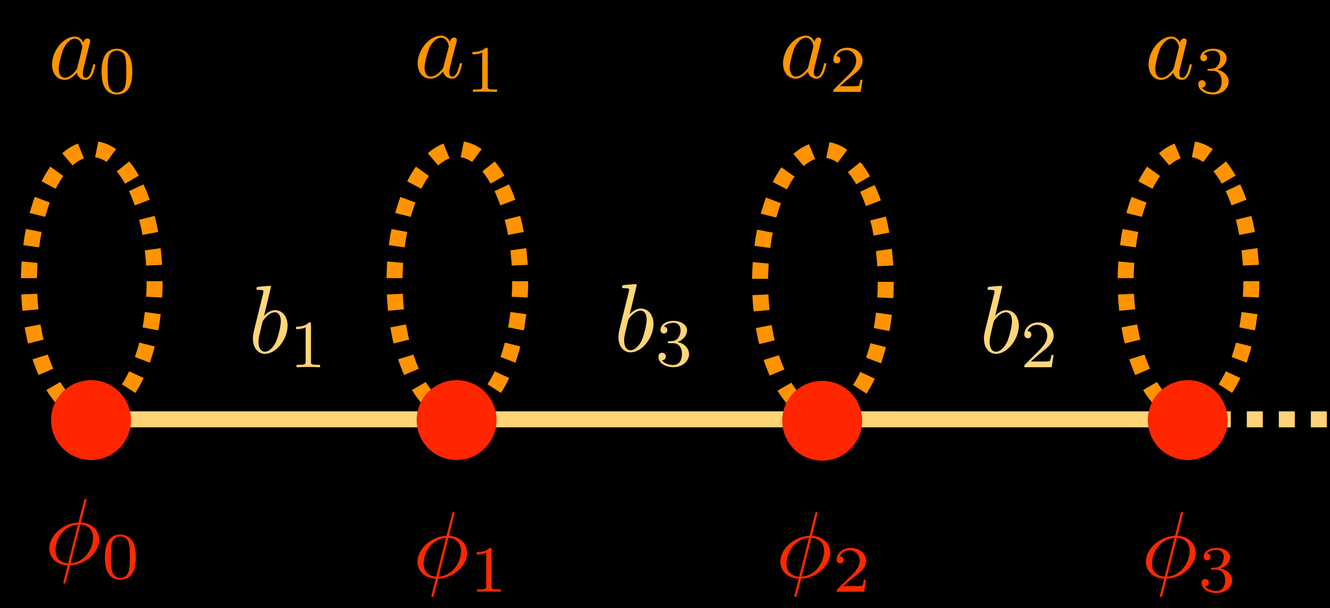

$$g(\omega) = \cfrac{1}{\omega - a_0 + \cfrac{b_1^2}{\omega - a_1 + \cfrac{b_2^2}{\omega - a_2 + \cdots}}}$$

the DFPT representation

$$\tilde{\rho}'(\omega) = \begin{array}{cc} \left(\begin{array}{cc} 0 & Y^\dagger \\ X & 0 \end{array}\right) & \begin{array}{c} \mathrm{v} \\ \mathrm{c} \end{array} \\ \begin{array}{cc} \mathrm{v} & \quad\mathrm{c} \end{array} & \end{array}$$

the DFPT representation

$$\tilde{\rho}'(\omega) \quad = \quad \sum_{cv} \Big(X_{cv}(\omega) |\varphi_c^\circ\rangle\langle\varphi_v^\circ| + Y_{cv}(\omega) |\varphi_v^\circ\rangle\langle\varphi_c^\circ| \Big)$$

the DFPT representation

$$
\begin{aligned}
\tilde{\rho}'(\omega) &= \sum_{cv}\Big(X_{cv}(\omega)|\varphi_c^\circ\rangle\langle\varphi_v^\circ| + Y_{cv}(\omega)|\varphi_v^\circ\rangle\langle\varphi_c^\circ| \Big) \\
&= \sum_{v}\Big(|\varphi_v'(\omega)\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle\varphi_v'(-\omega)| \Big)
\end{aligned}
$$

the DFPT representation

$$\tilde{\rho}'(\omega) = \sum_{cv}\Big(X_{cv}(\omega)|\varphi_c^\circ\rangle\langle\varphi_v^\circ| + Y_{cv}(\omega)|\varphi_v^\circ\rangle\langle\varphi_c^\circ| \Big)$$
$$= \sum_{v}\Big(|\varphi_v'(\omega)\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle\varphi_v'(-\omega)| \Big)$$

$$\downarrow$$

$$|\{x_v(\mathbf{r})\}, \{y_v(\mathbf{r})\}\rangle$$

$$P_v x_v = P_v y_v = 0$$

the DFPT representation

$$\tilde{\rho}'(\omega) = \sum_{cv} \Big(X_{cv}(\omega) |\varphi_c^\circ\rangle\langle\varphi_v^\circ| + Y_{cv}(\omega) |\varphi_v^\circ\rangle\langle\varphi_c^\circ| \Big)$$

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$$\downarrow$$

$$|\{x_v(\mathbf{r})\}, \{y_v(\mathbf{r})\}\rangle$$

$$P_v x_v = P_v y_v = 0$$

$$\begin{matrix} \mathcal{L}\ \tilde{\rho}' \\ \mathcal{L}^\top \tilde{\rho}' \end{matrix} \quad \Rightarrow \quad \begin{matrix} \{H^\circ x_v(\mathbf{r})\} \\ \{H^\circ y_v(\mathbf{r})\} \end{matrix} \quad \& \quad \{V'_{ee}(\mathbf{r})\varphi_v^\circ(\mathbf{r})\}$$

the DFPT representation

$$\tilde{\rho}'(\omega) = \sum_{cv}\Big(X_{cv}(\omega)|\varphi^\circ_c\rangle\langle\varphi^\circ_v| + Y_{cv}(\omega)|\varphi^\circ_v\rangle\langle\varphi^\circ_c| \Big)$$
$$= \sum_{v}\Big(|\varphi'_v(\omega)\rangle\langle\varphi^\circ_v| + |\varphi^\circ_v\rangle\langle\varphi'_v(-\omega)| \Big)$$

$$\downarrow$$

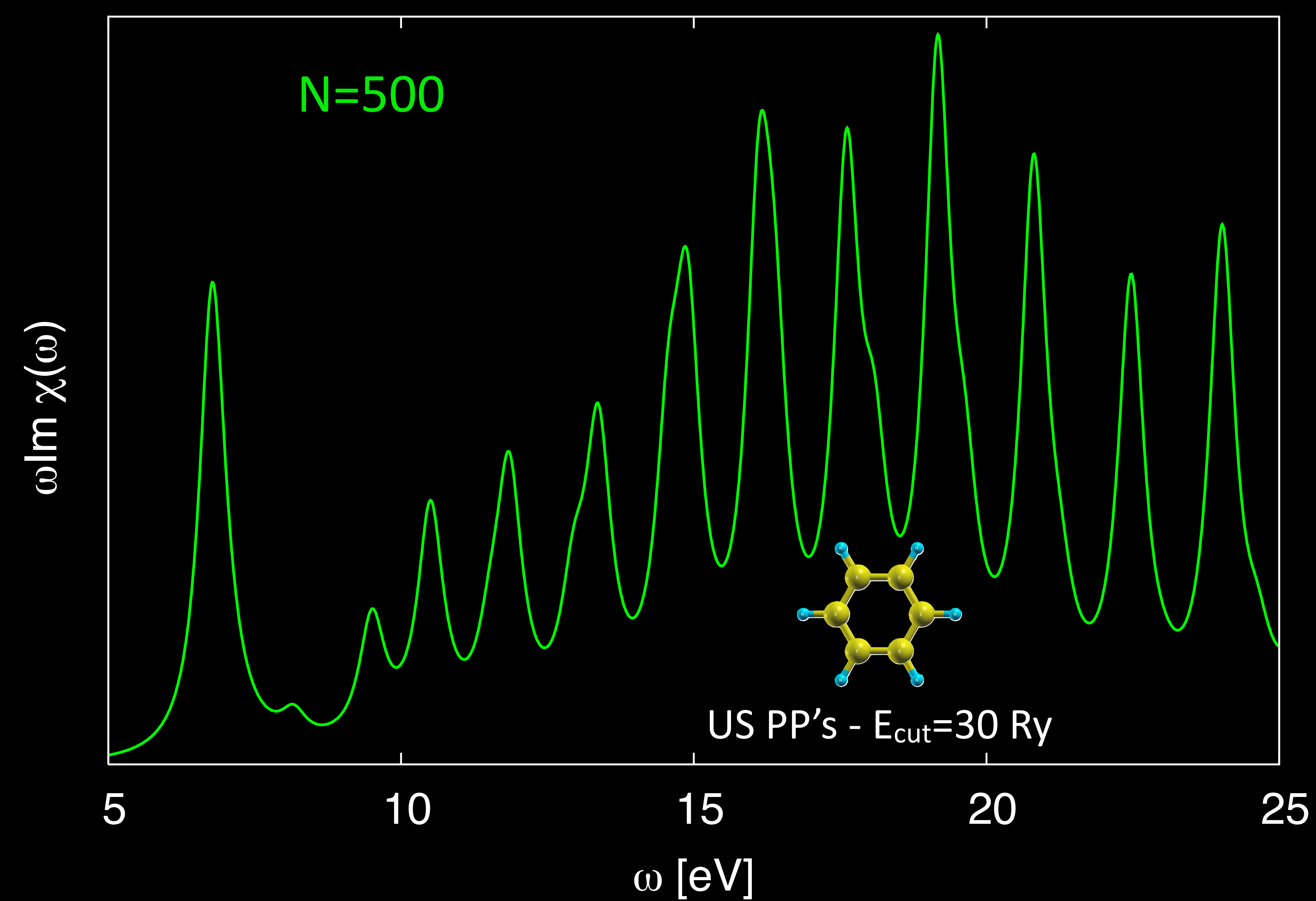
$$|\{x_v(\mathbf{r})\},\{y_v(\mathbf{r})\}\rangle$$

$$P_v x_v = P_v y_v = 0$$

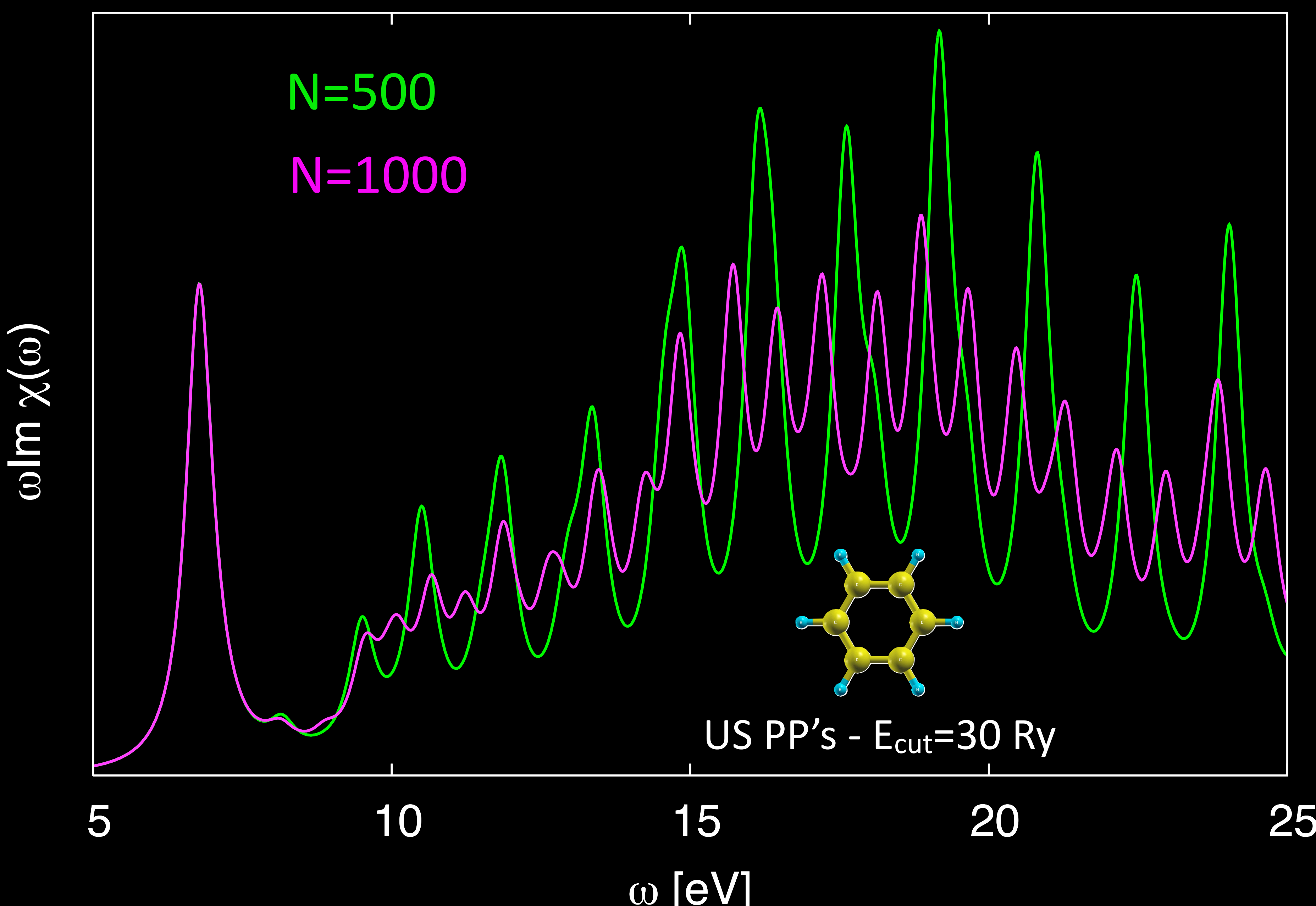
$$\begin{matrix} \mathcal{L}\ \ \tilde{\rho}' \\ \mathcal{L}^\top \tilde{\rho}' \end{matrix} \Rightarrow \begin{matrix} \{H^\circ x_v(\mathbf{r})\} \\ \{H^\circ y_v(\mathbf{r})\} \end{matrix} \quad \& \quad \{V'_{ee}(\mathbf{r})\varphi^\circ_v(\mathbf{r})\}$$

$$n'(\mathbf{r}) = \frac{1}{2}\sum_v \big(x_v(\mathbf{r}) + y_v(\mathbf{r})\big)\varphi^\circ_v(\mathbf{r})$$

benzene, a benchmark



benzene, a benchmark



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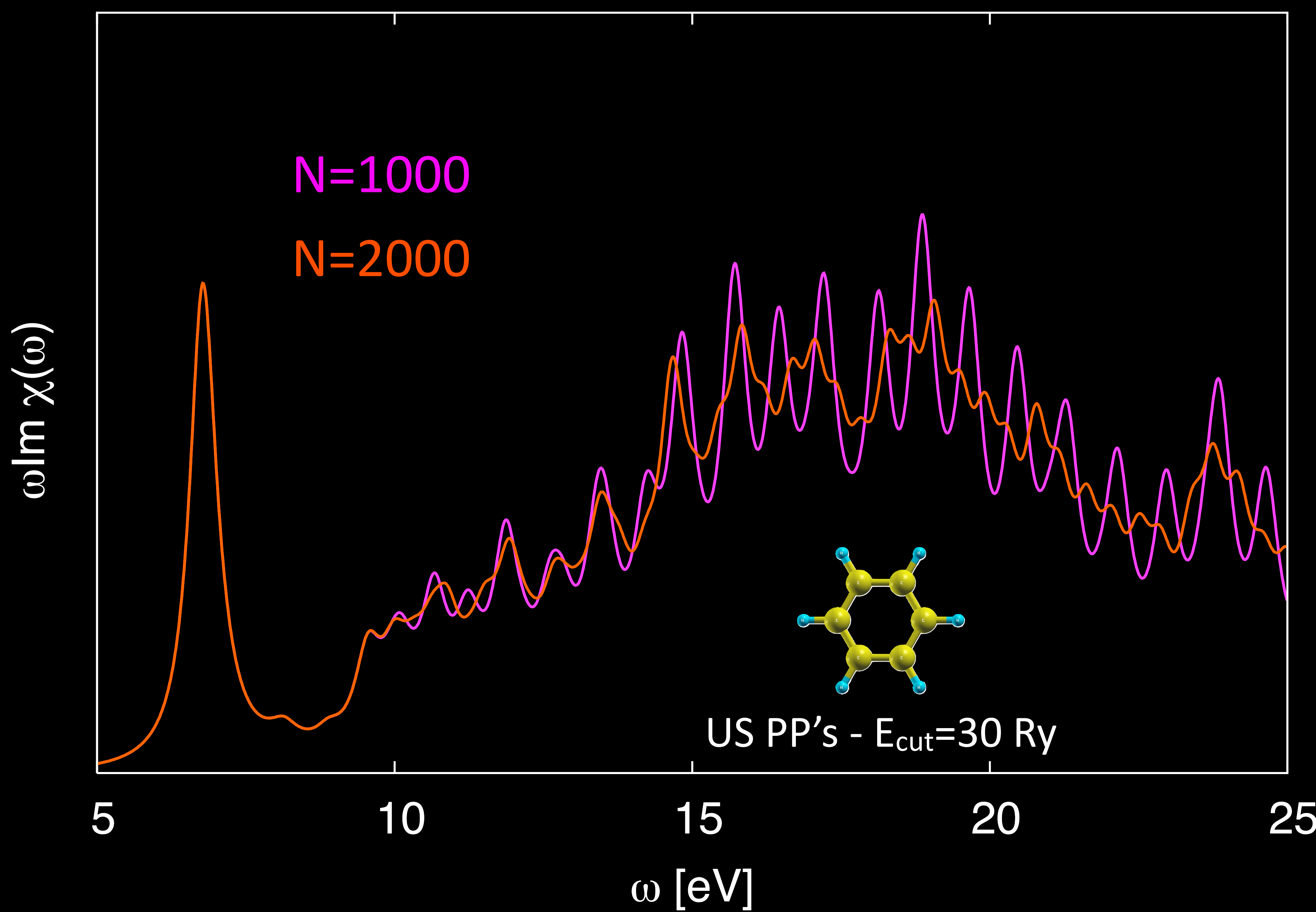

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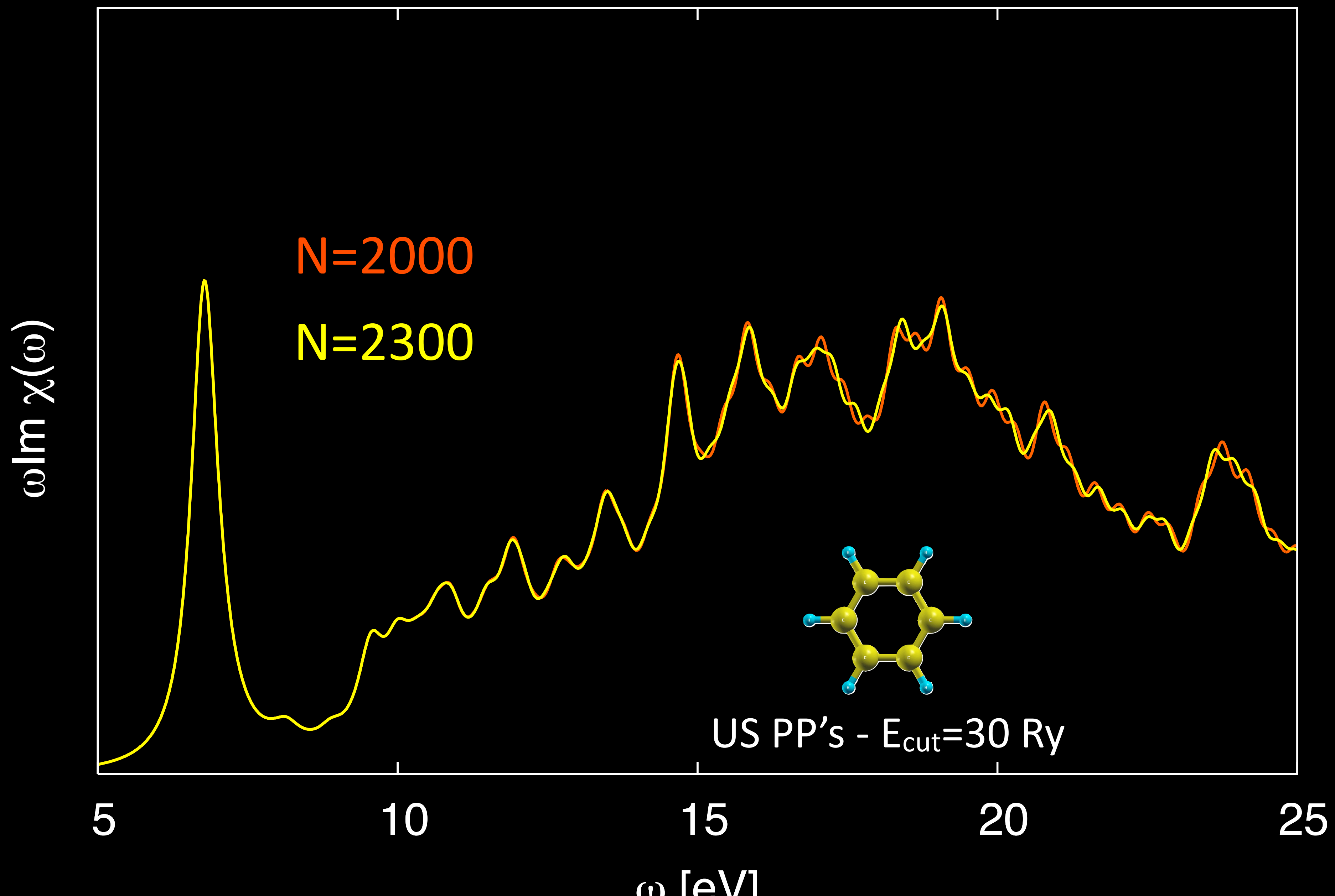
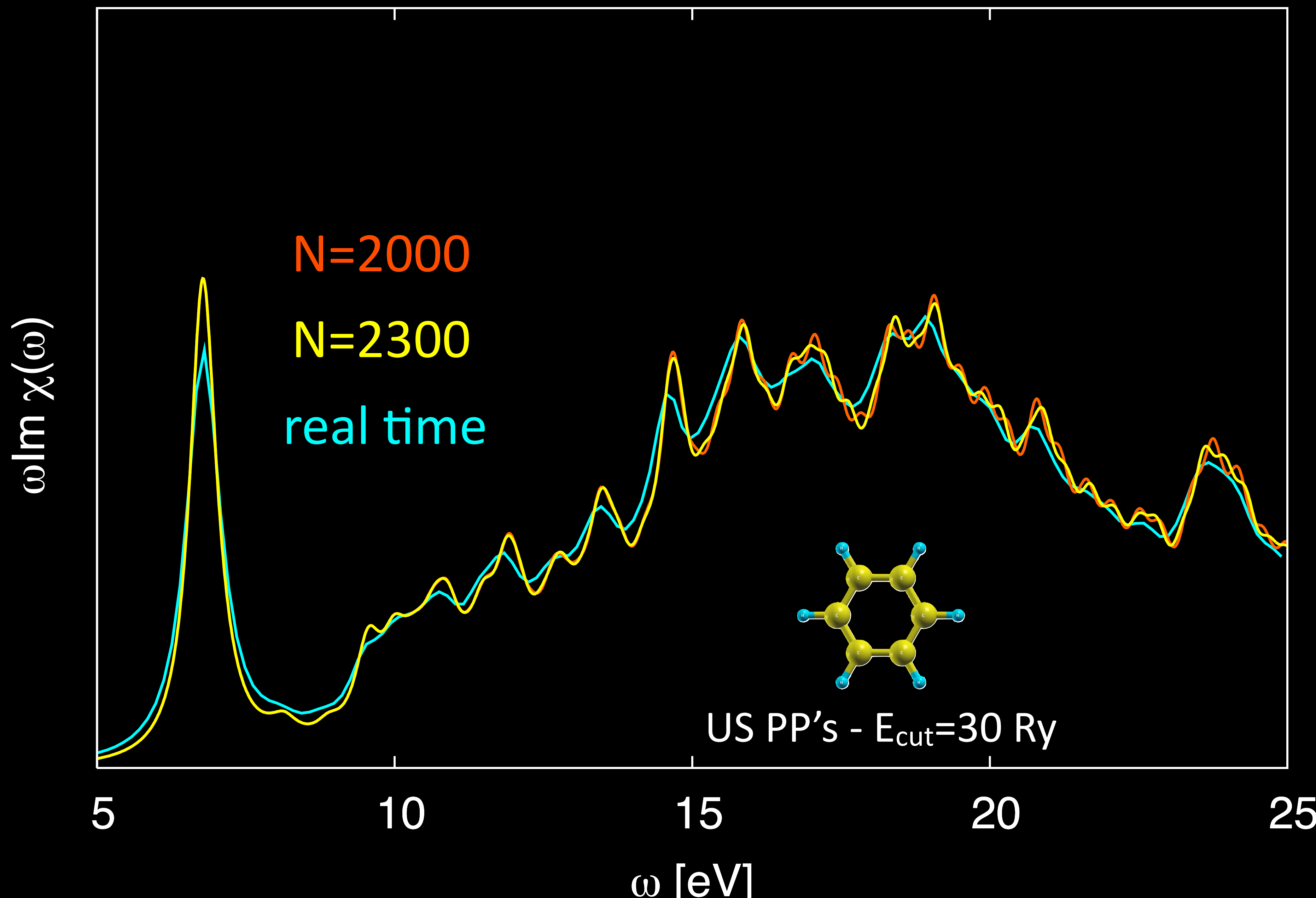


benzene, a benchmark



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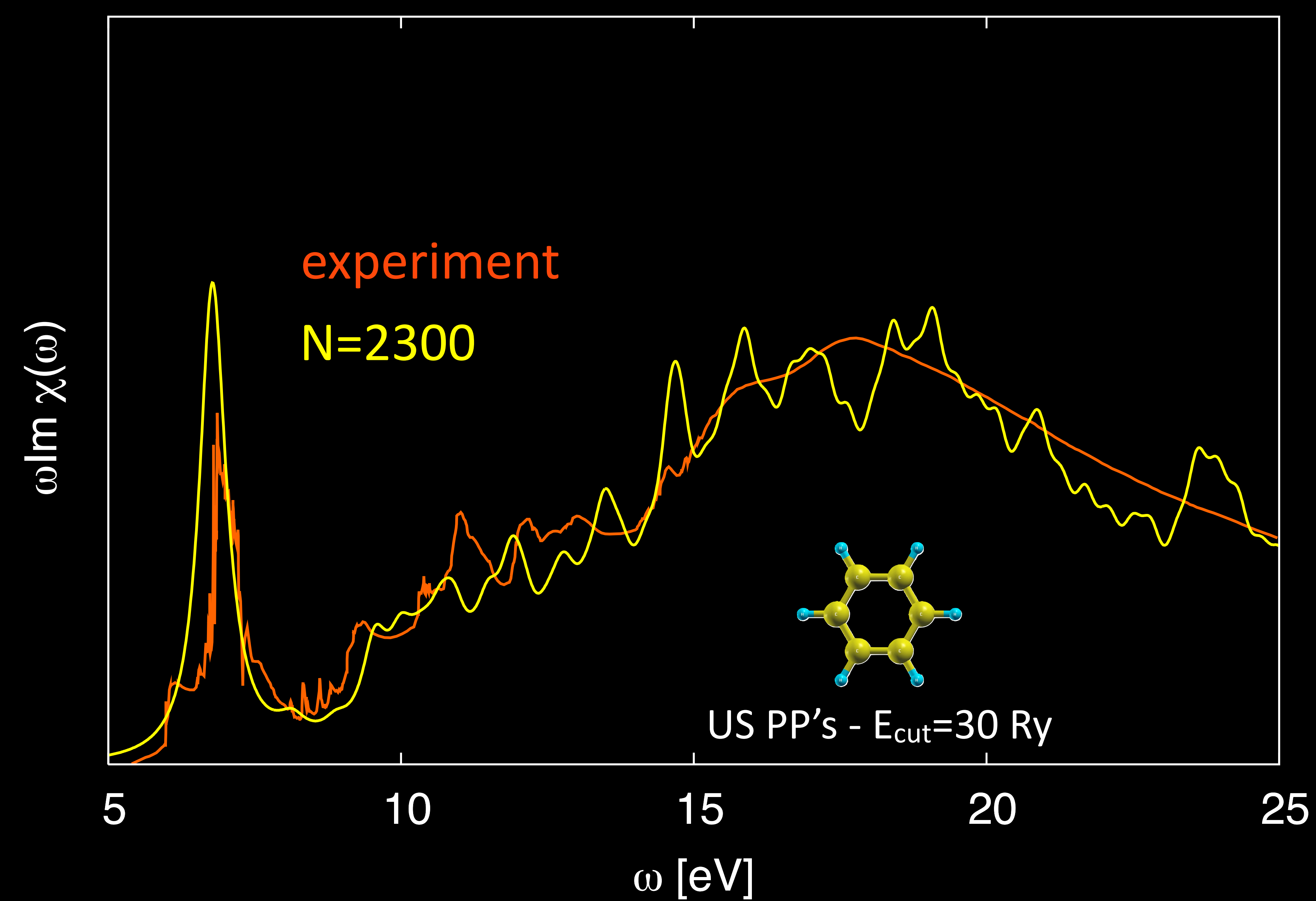
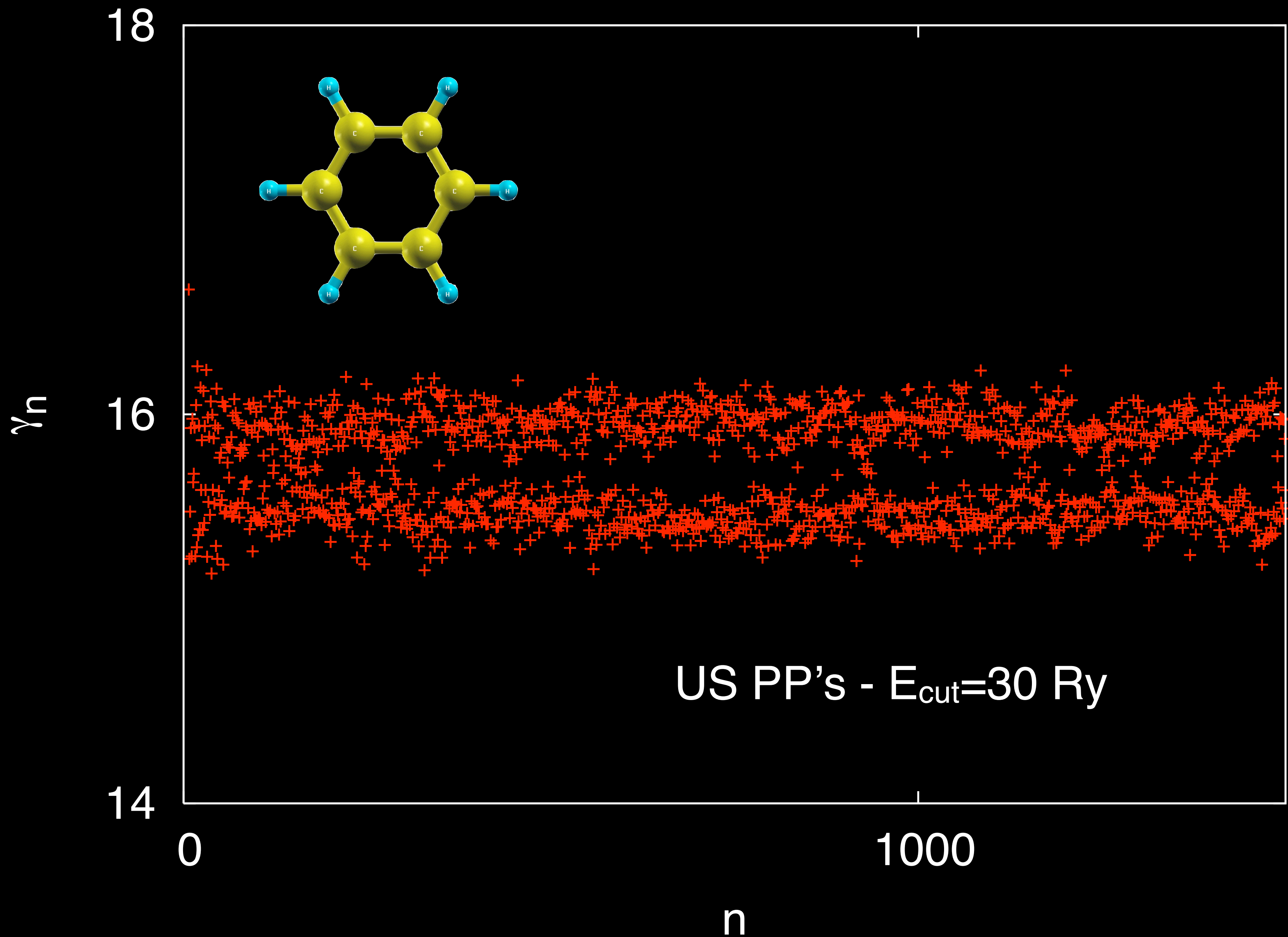


speeding up the convergence



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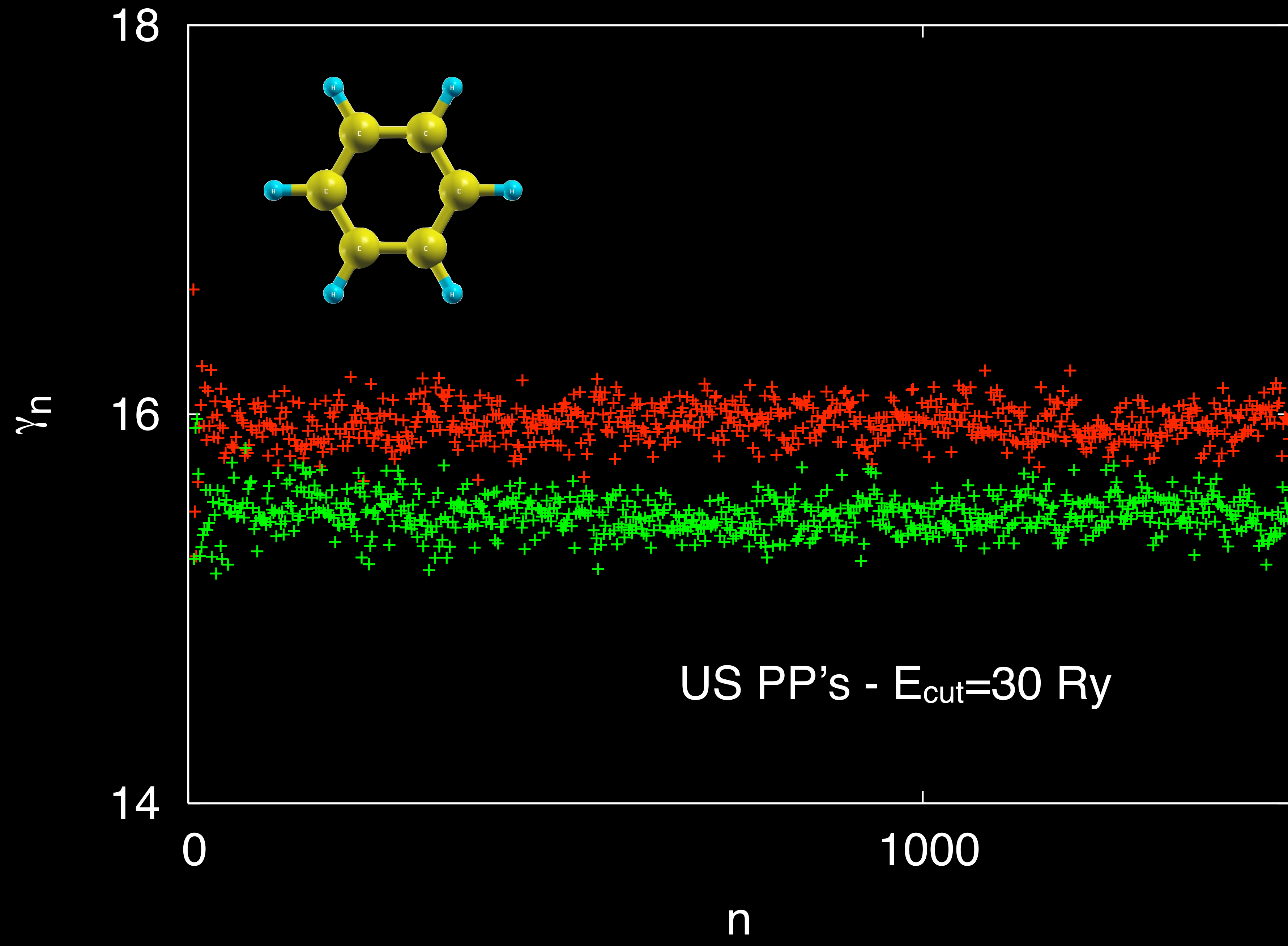

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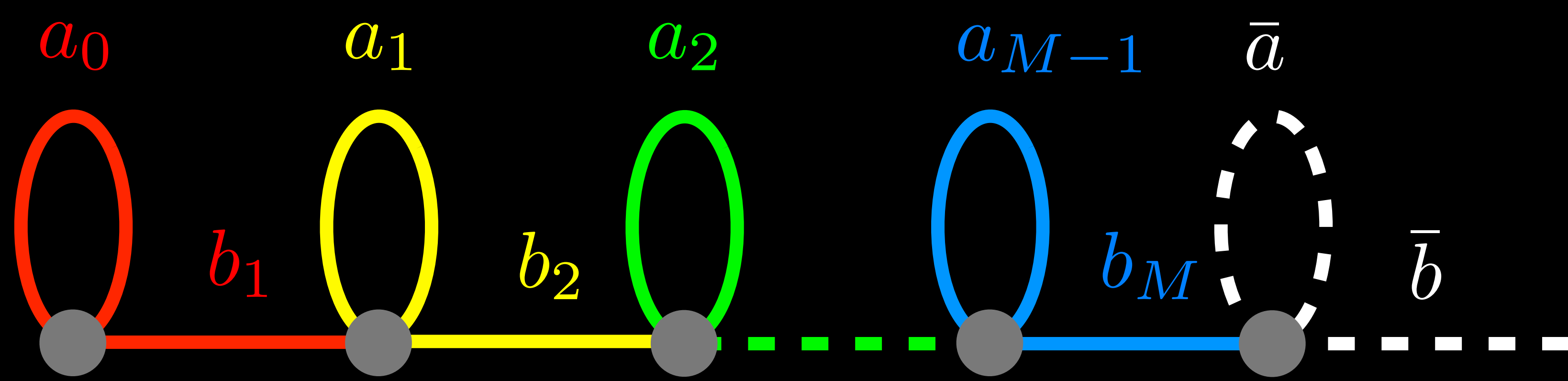
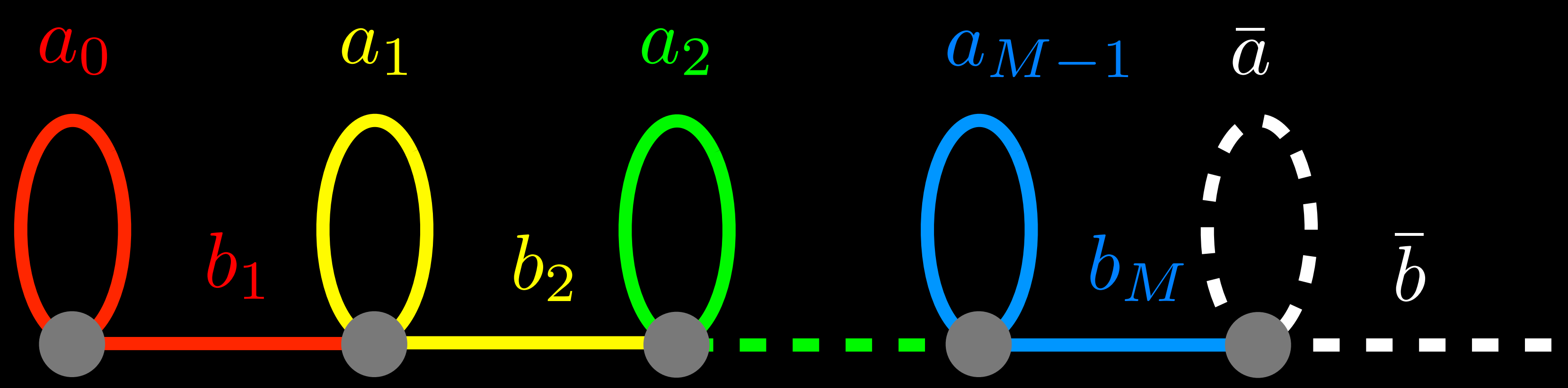
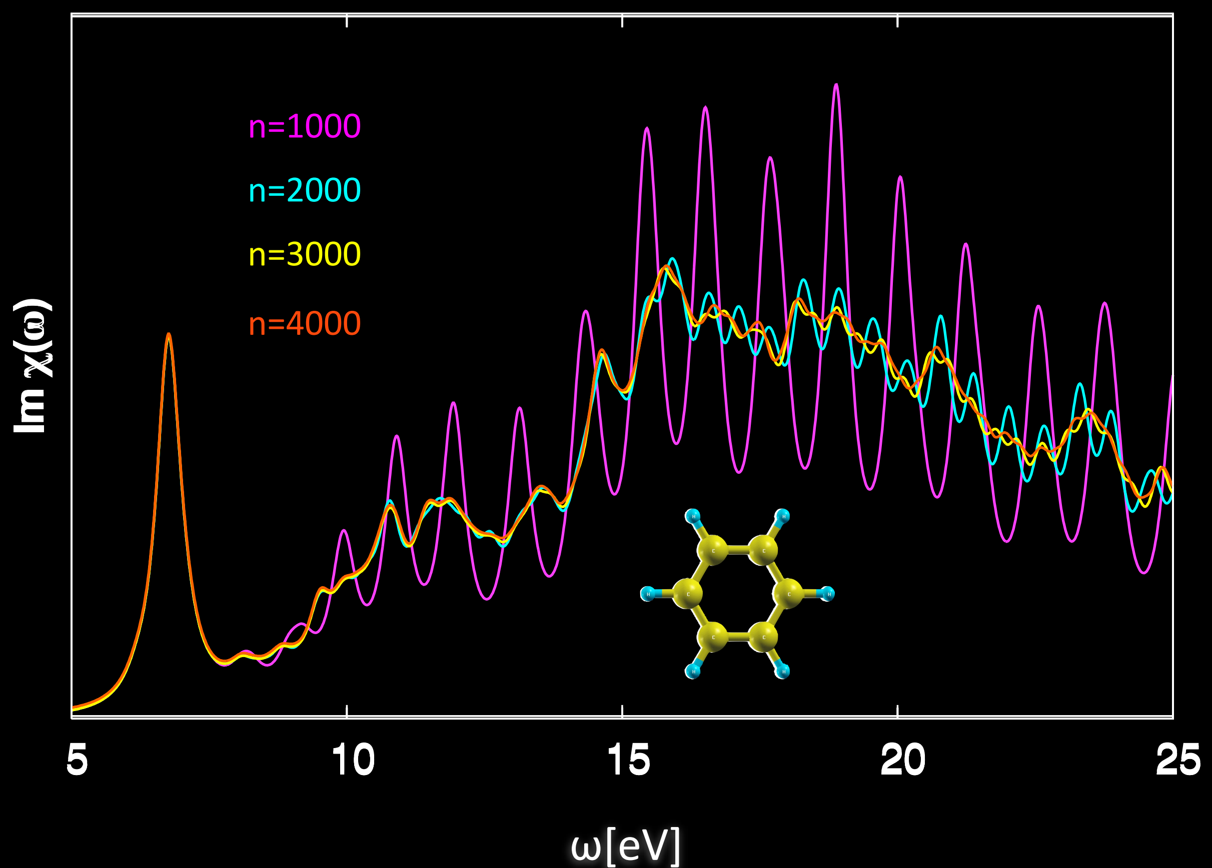


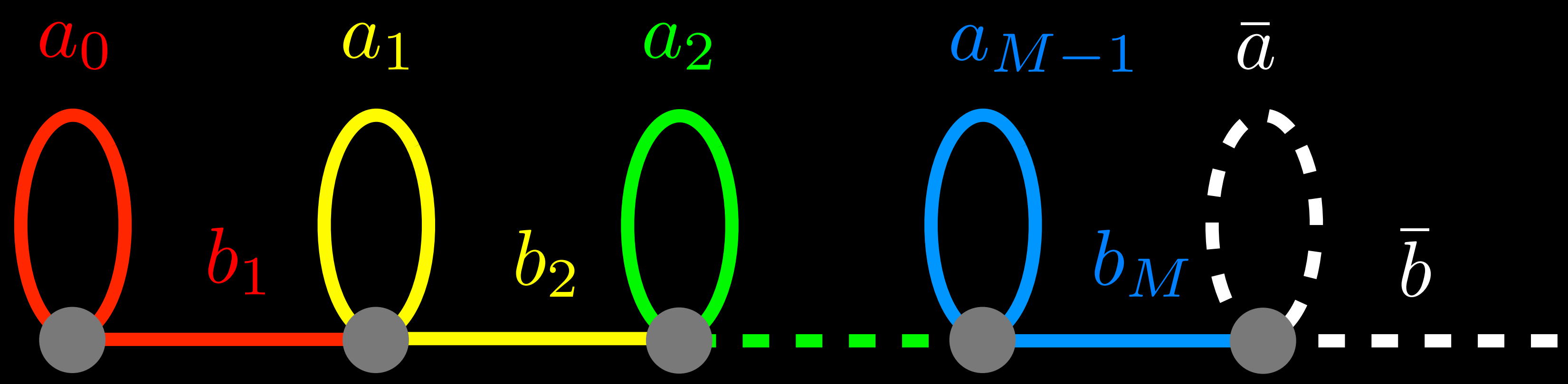
speeding up the convergence

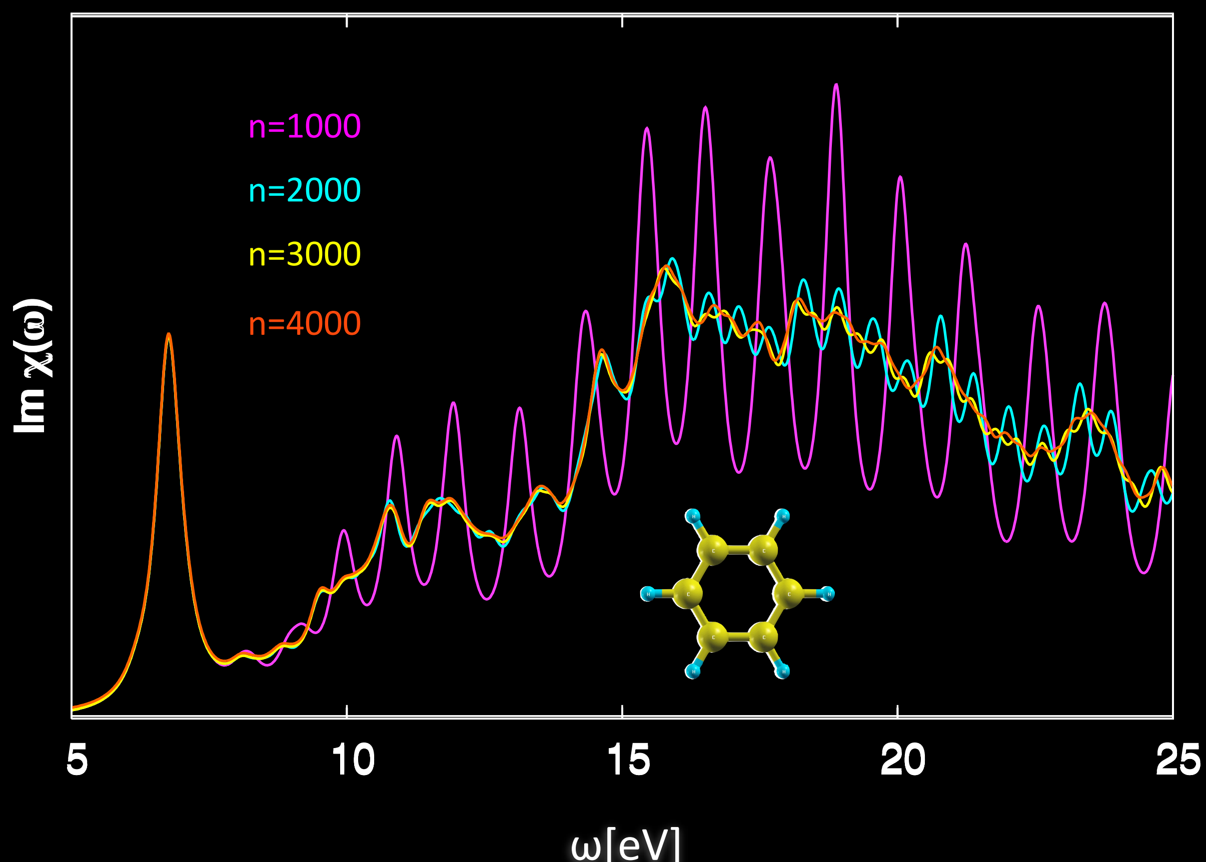




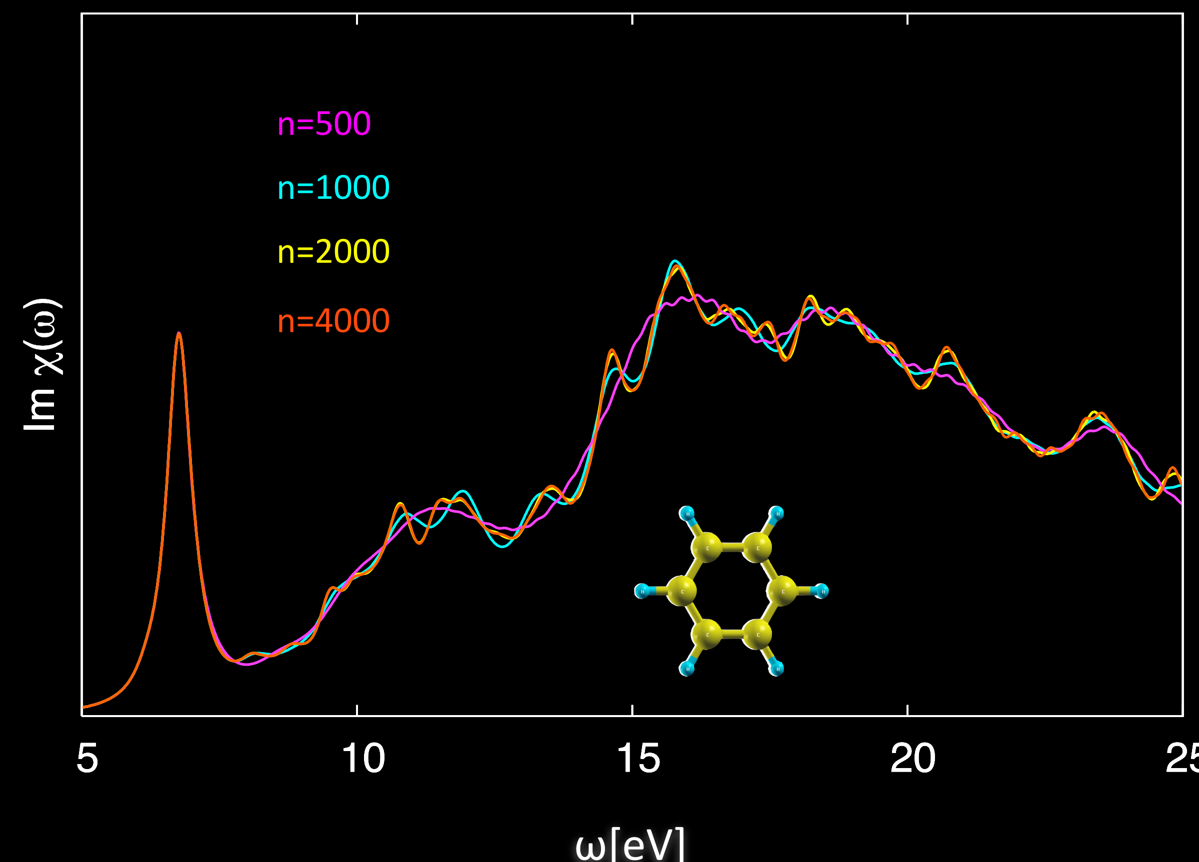
no extrapolation

speeding up the convergence



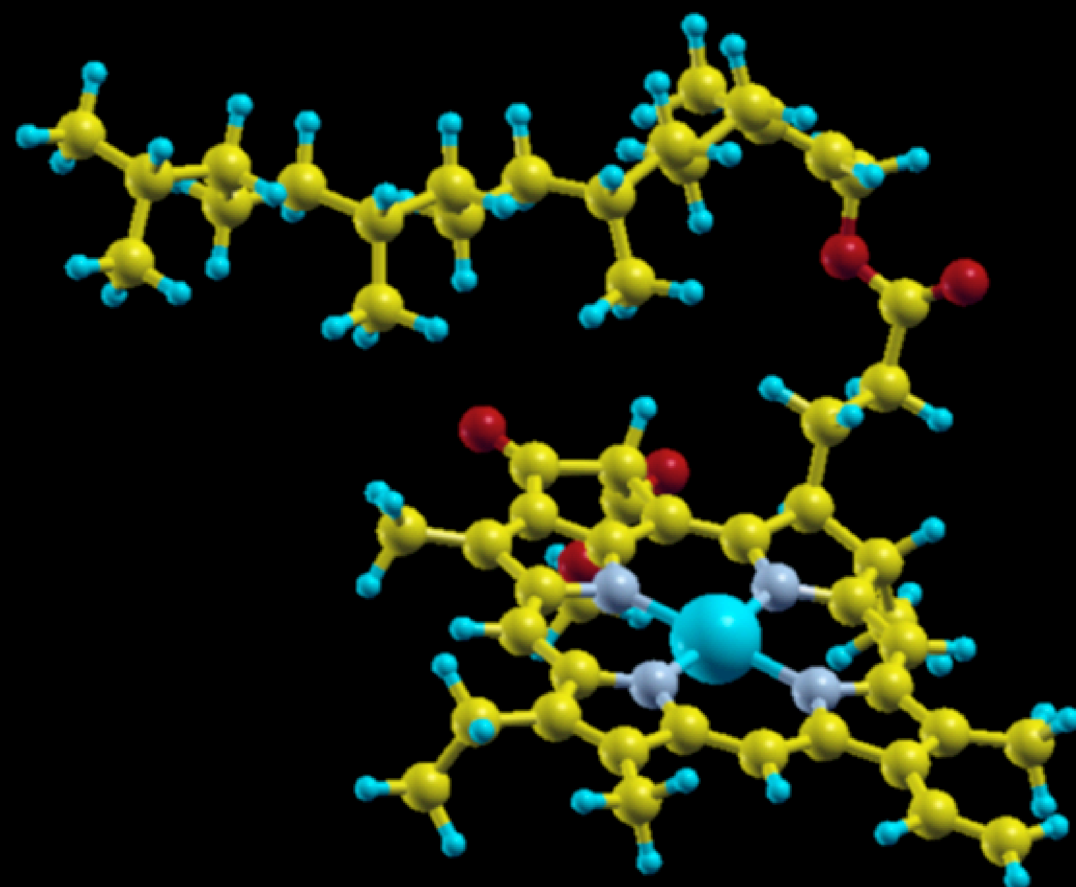


no extrapolation



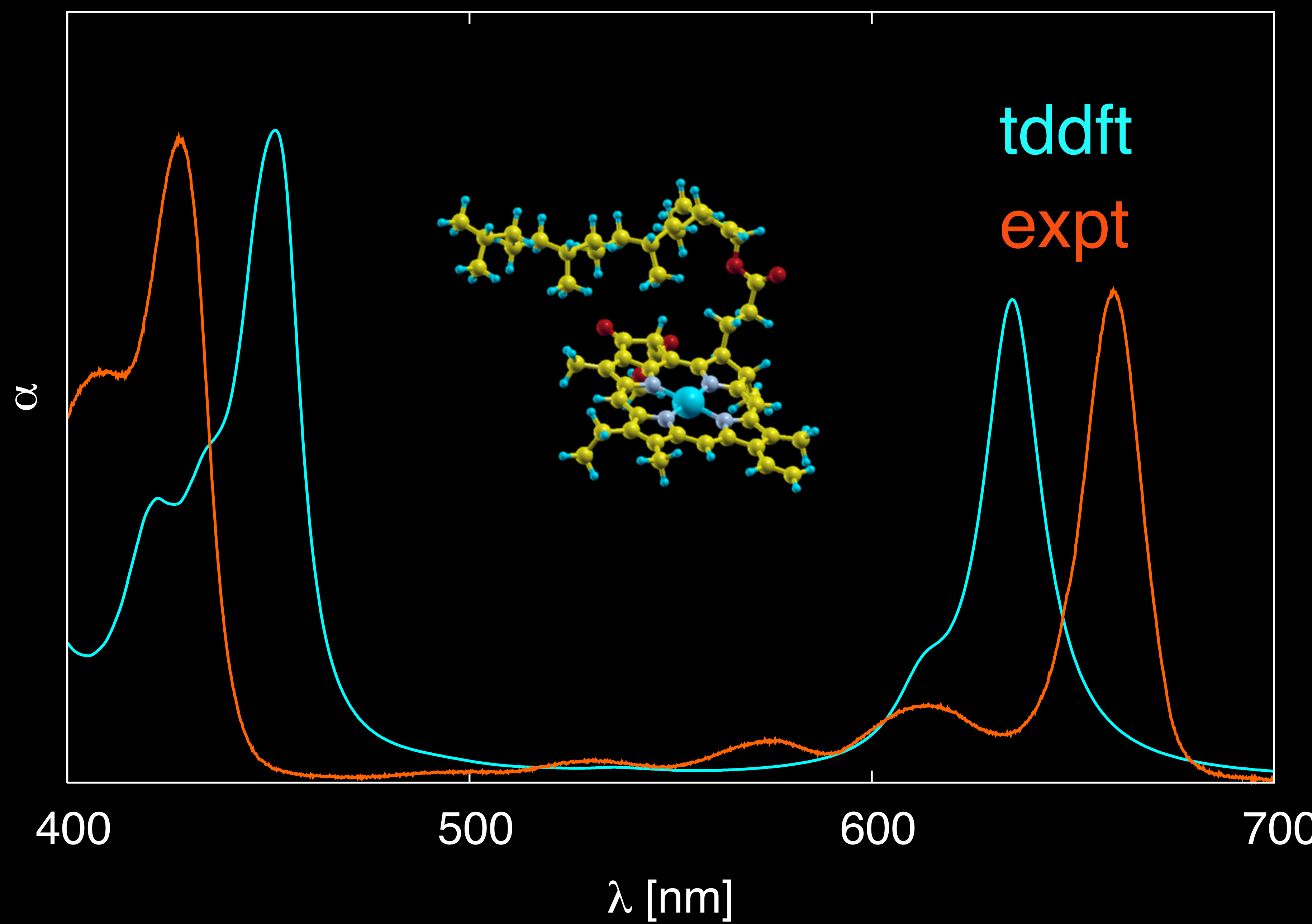
extrapolation

chlorofyll a



$C_{55}H_{72}MgN_4O$

chlorofyll a



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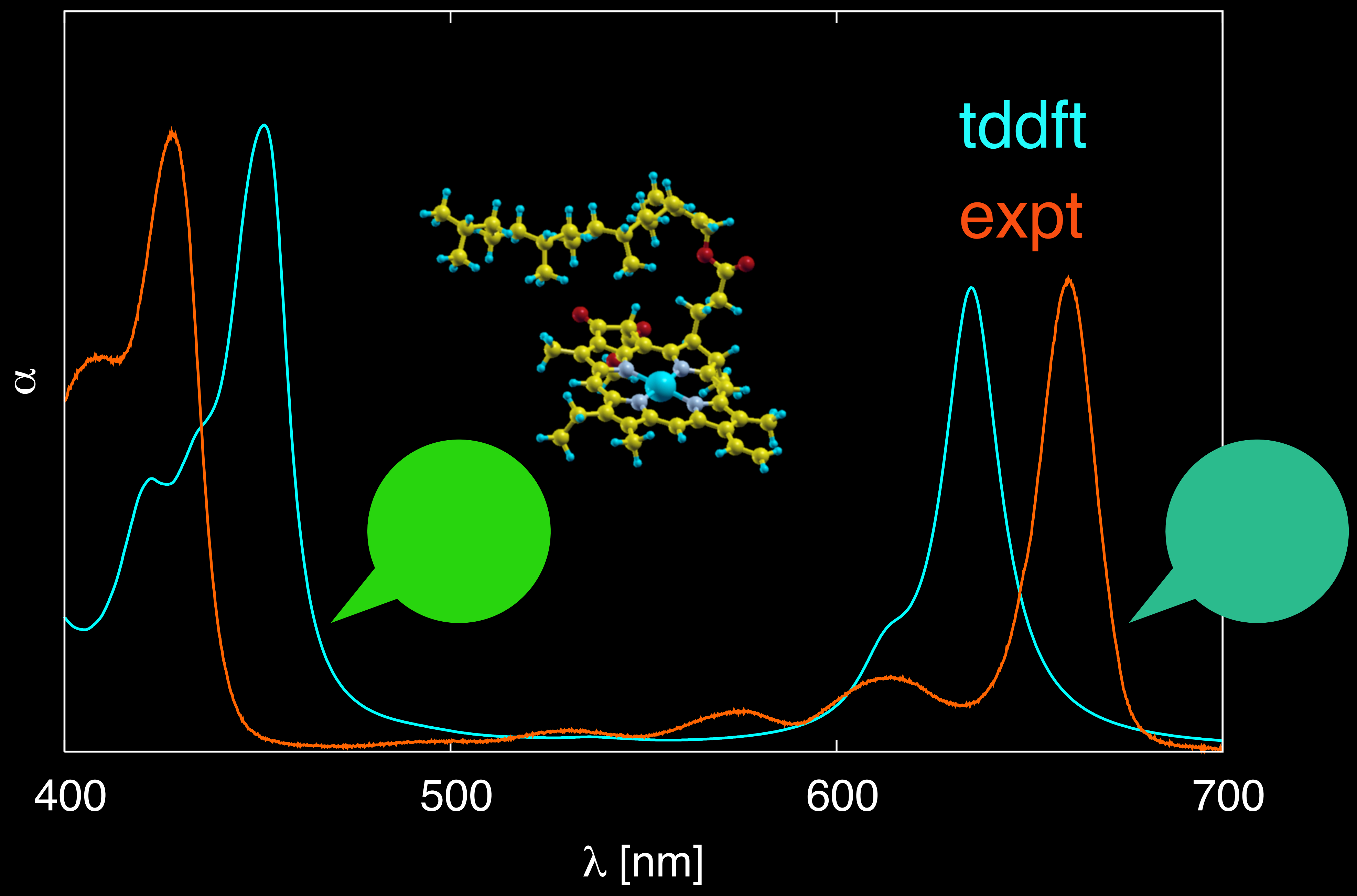
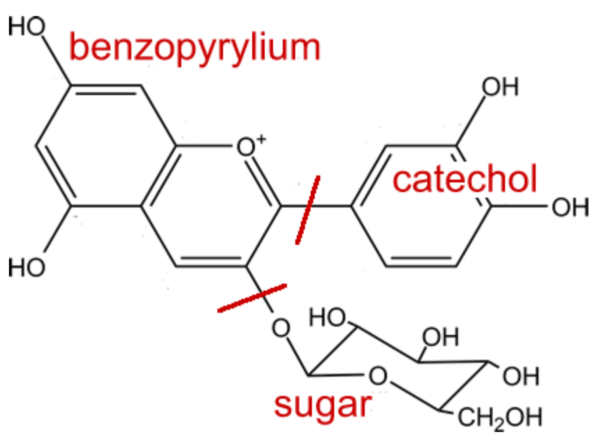
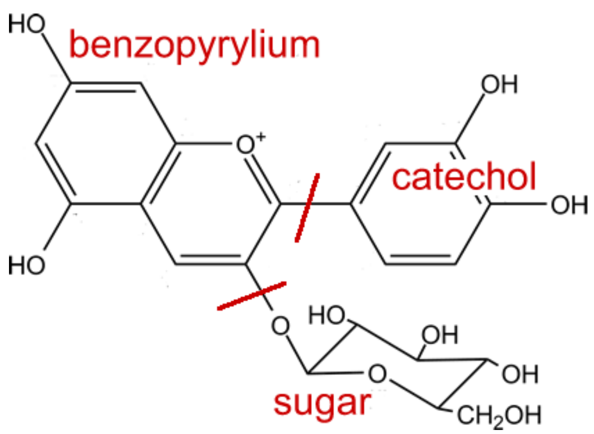


color and function of anthocyanins

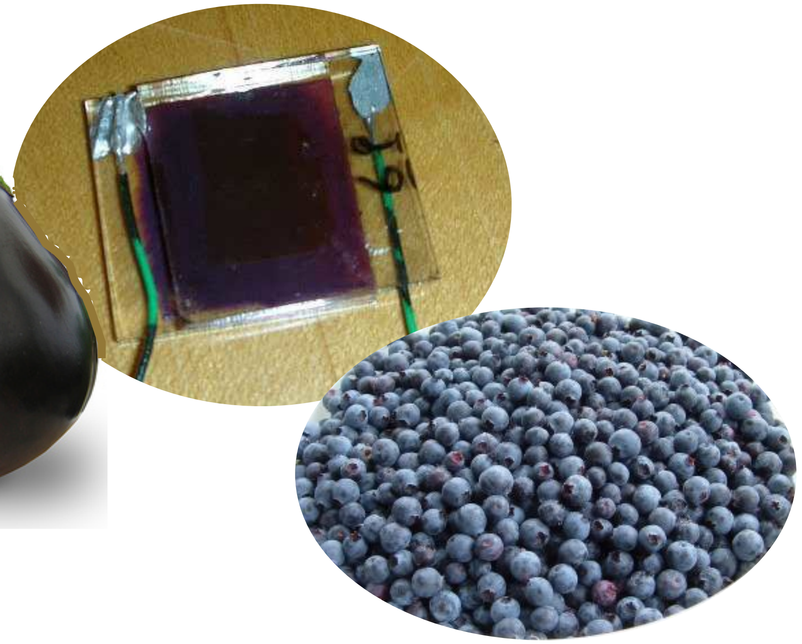


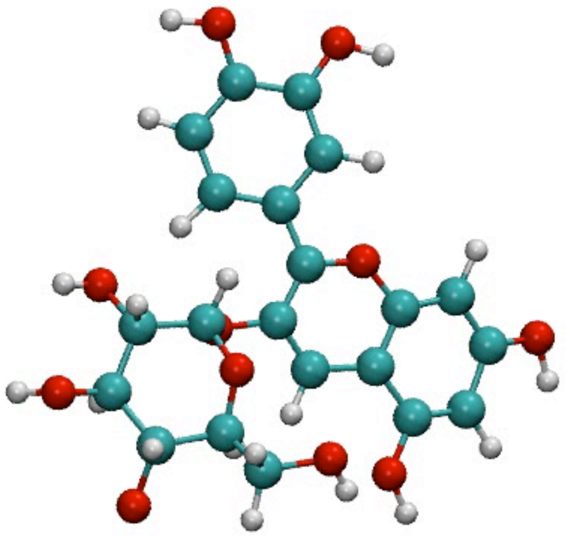
cyanidin-3-glucoside

color and function of anthocyanins



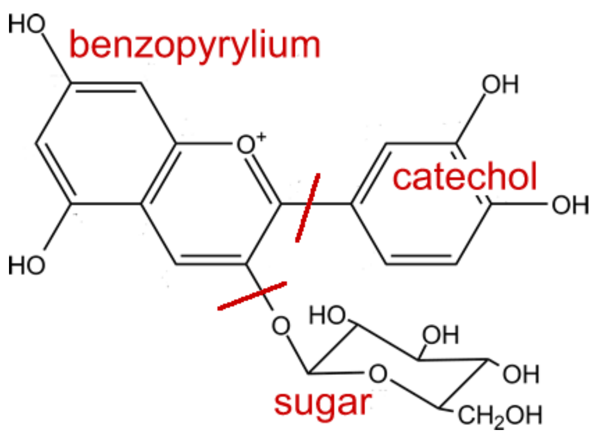
cyanidin-3-glucoside



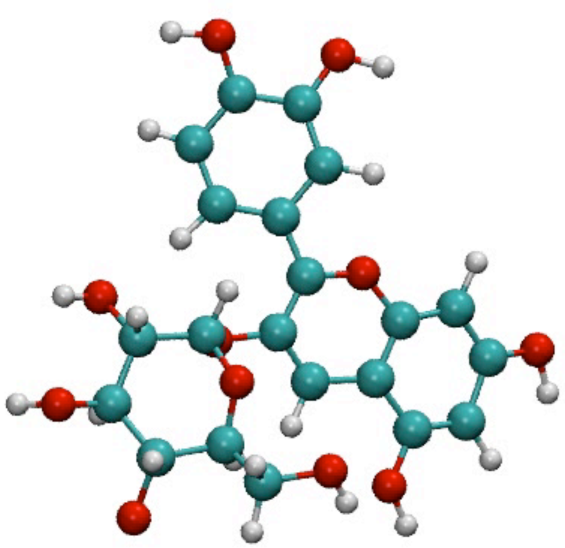


TDDFT ?

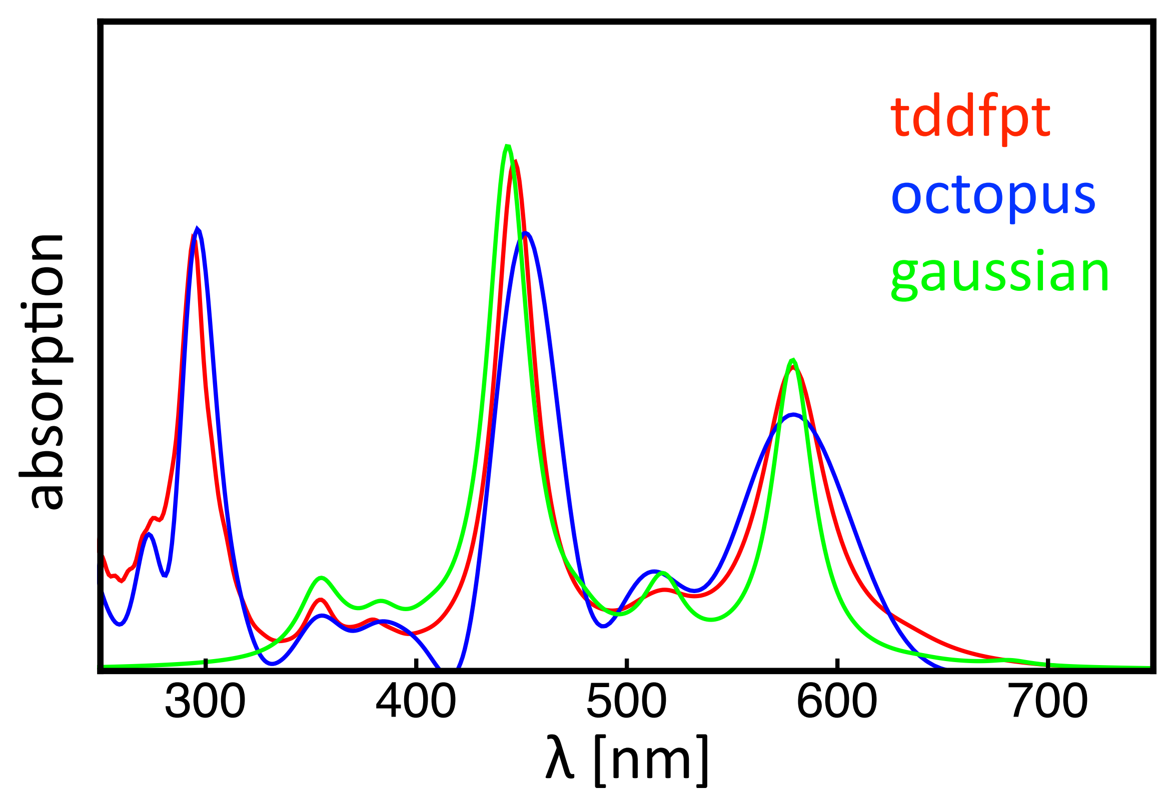
color and function of anthocyanins



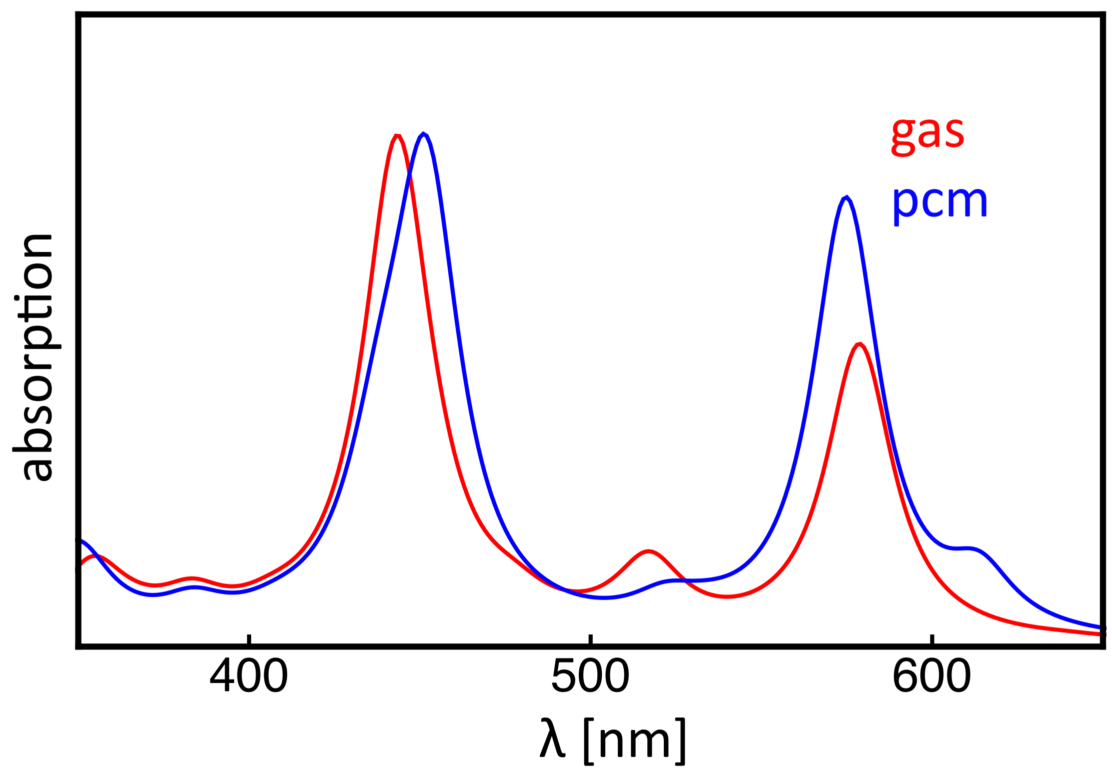
cyanidin-3-glucoside



TDDFT :-(



optical effect of the solvent



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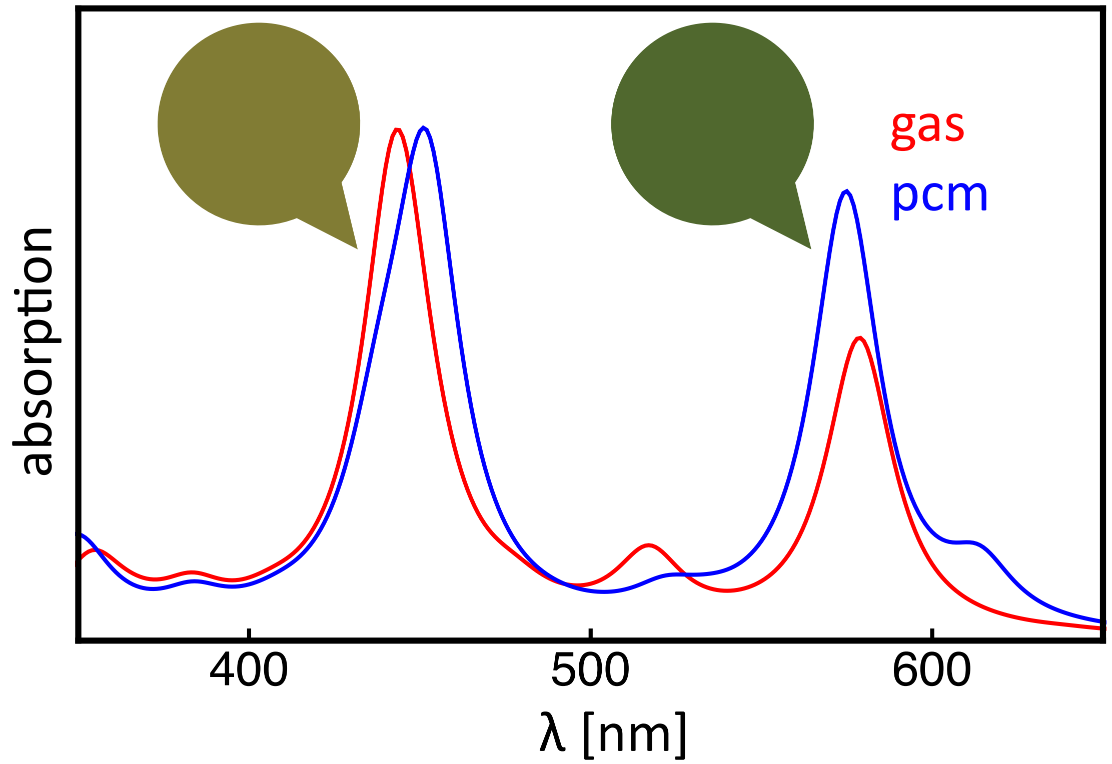

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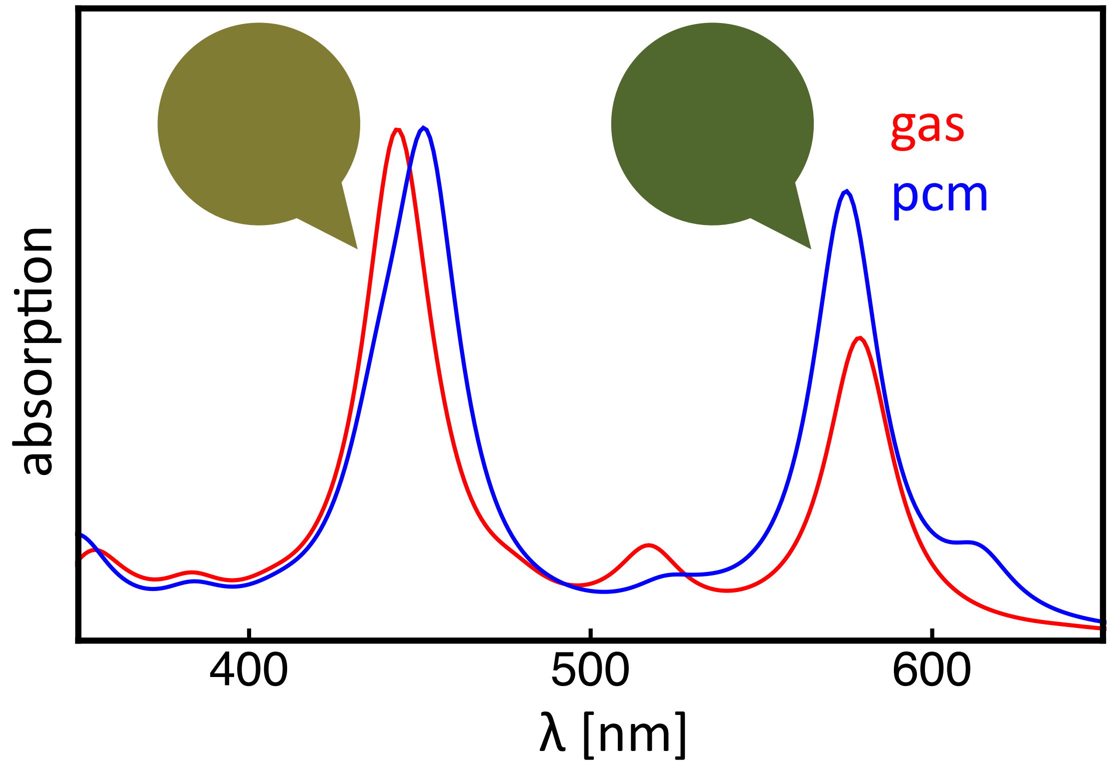
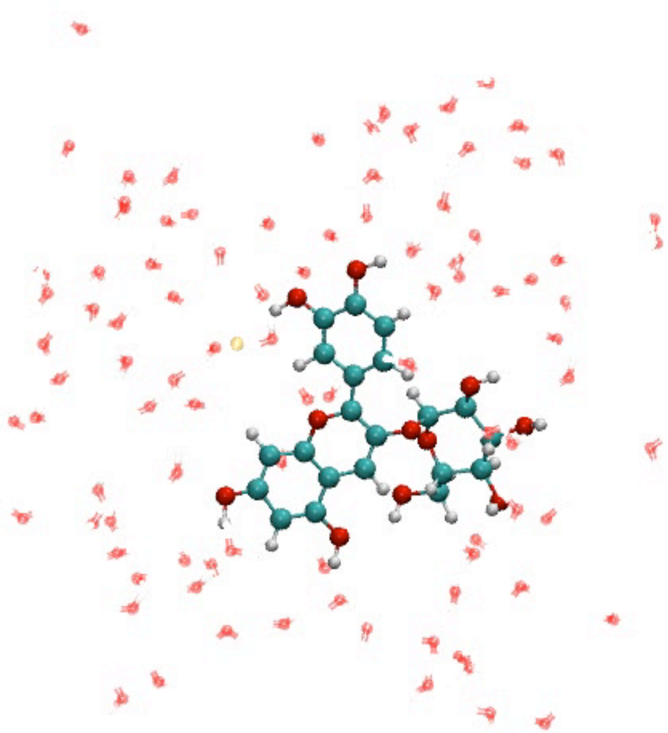
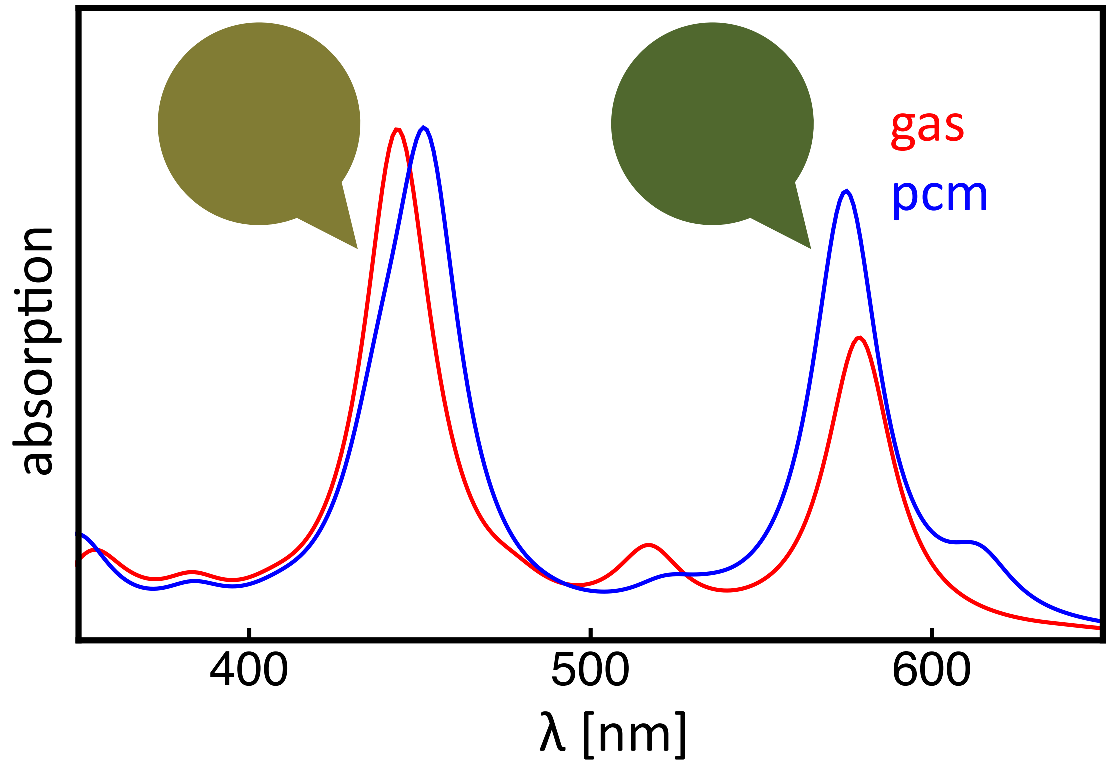
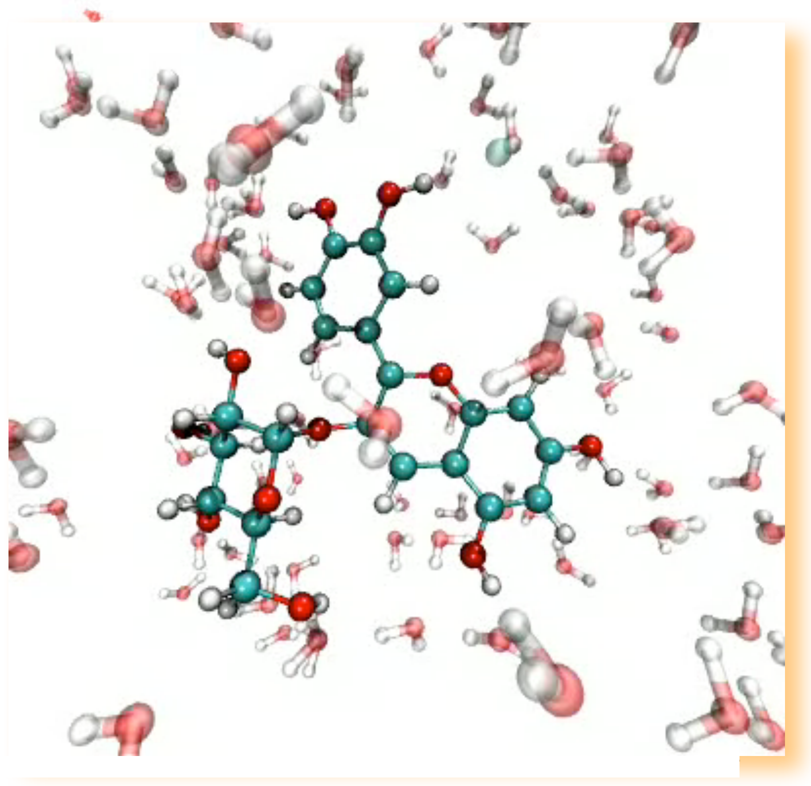


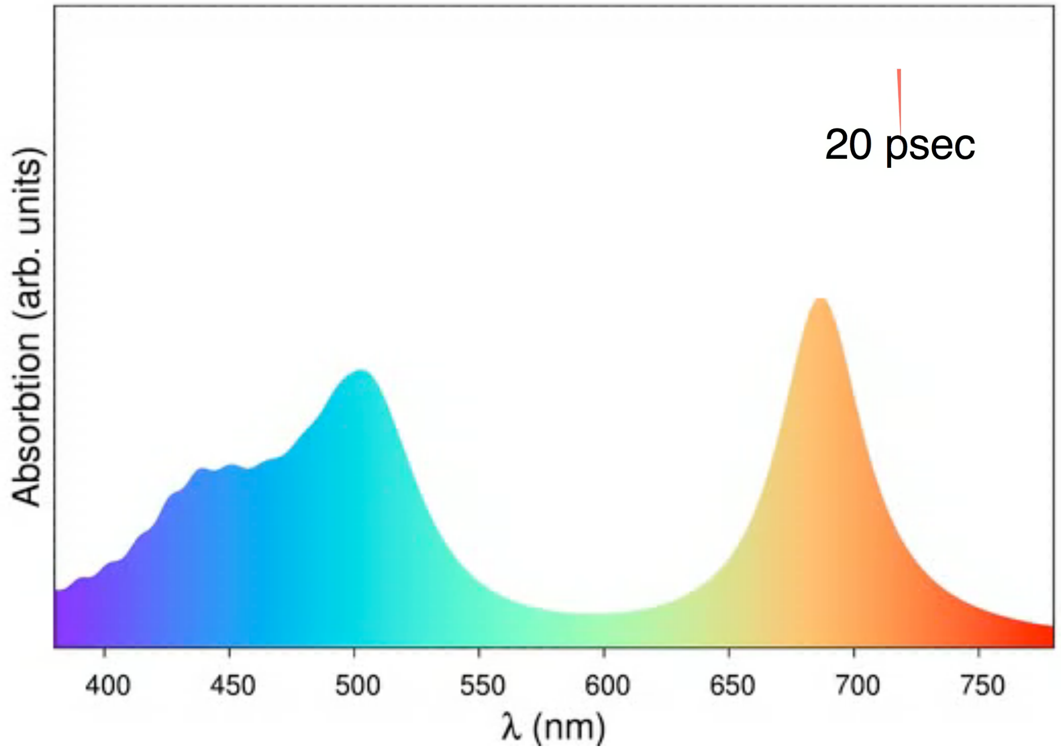


$C_{21}H_{21}O_{11}Cl@(H_2O)_{95}$
339 atoms
938 electrons

optical effect of the solvent







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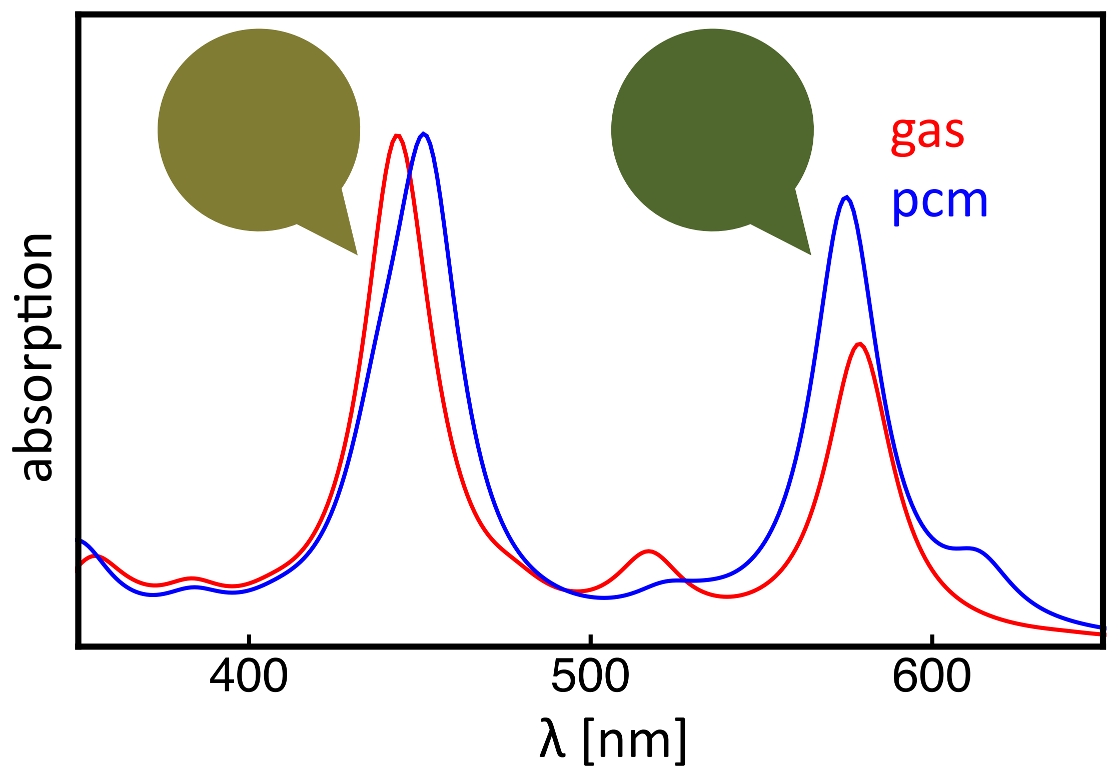

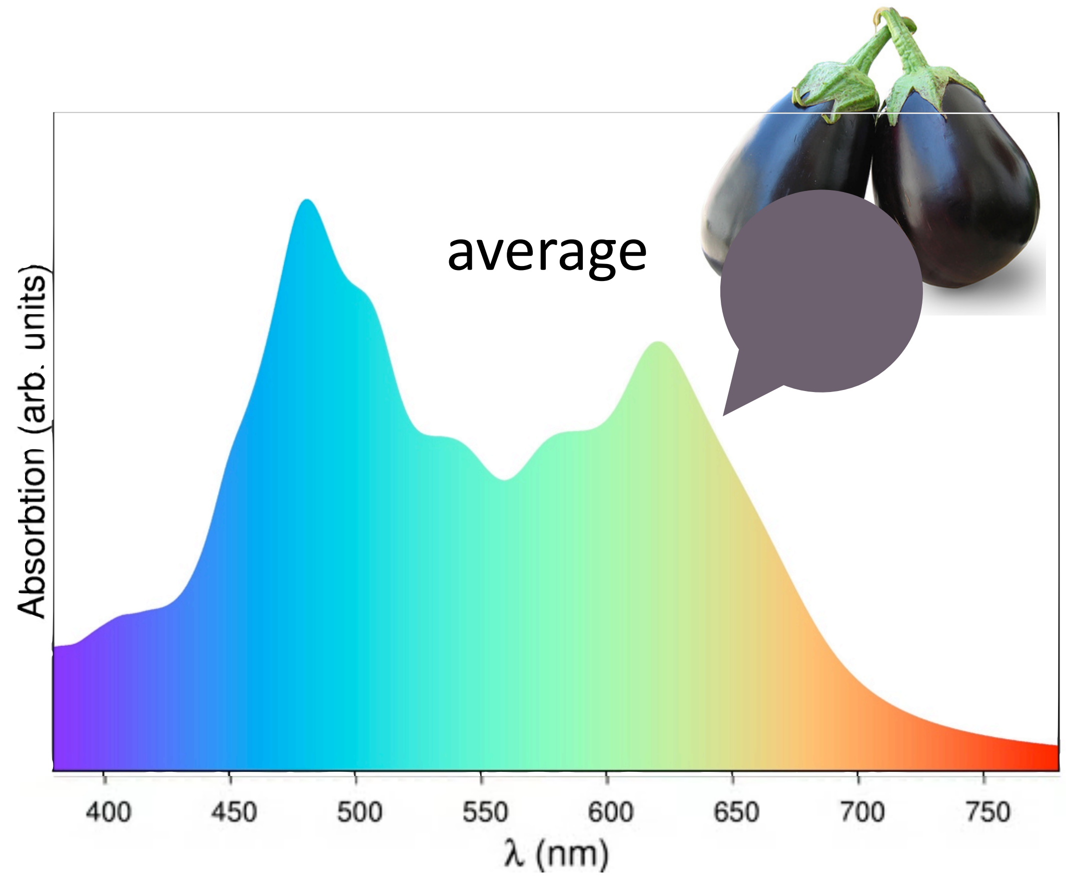

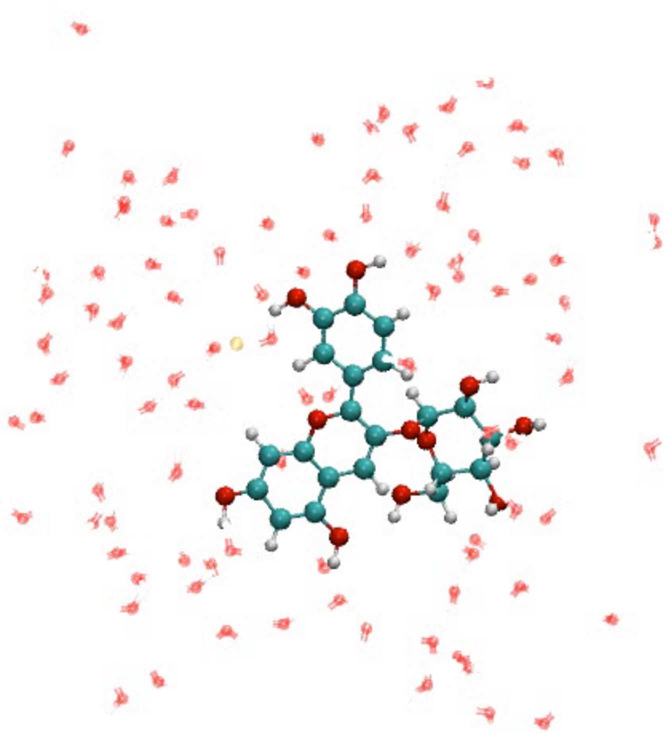

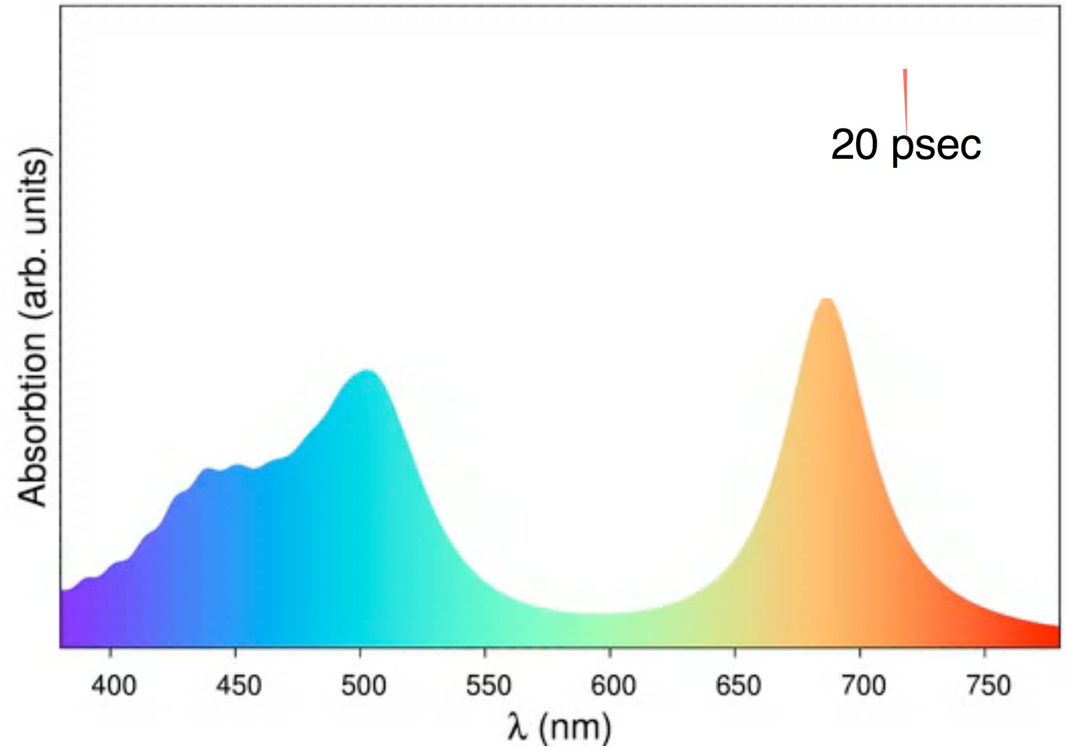

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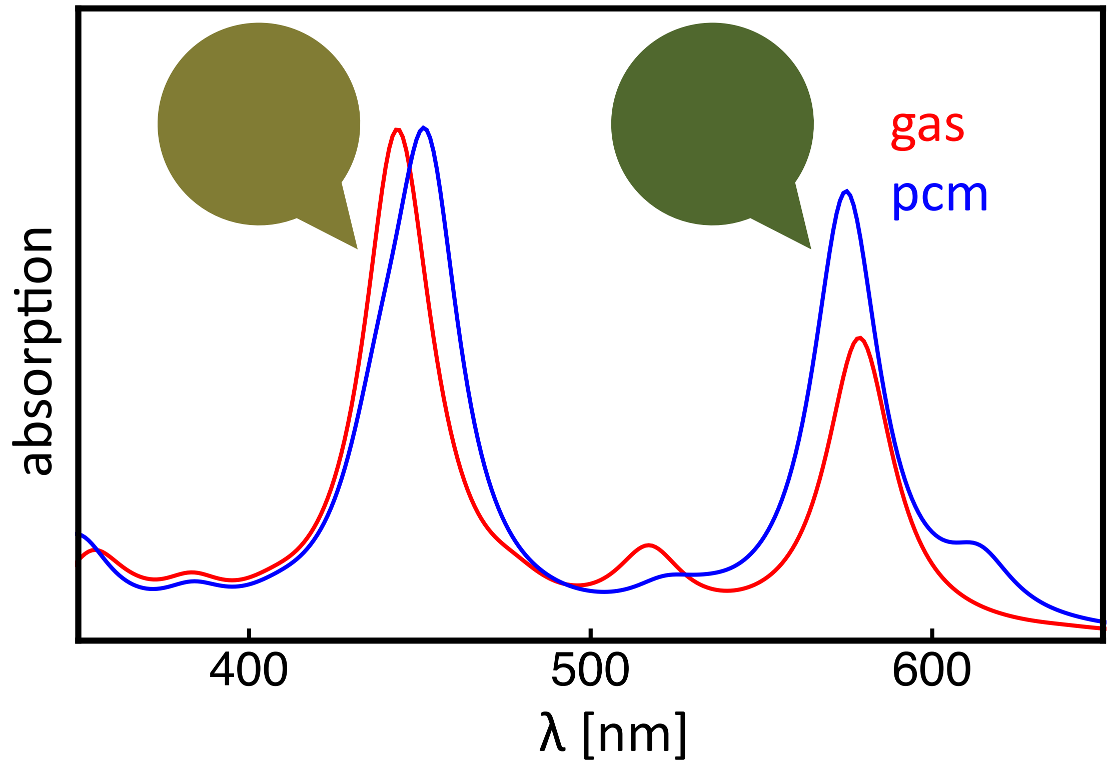
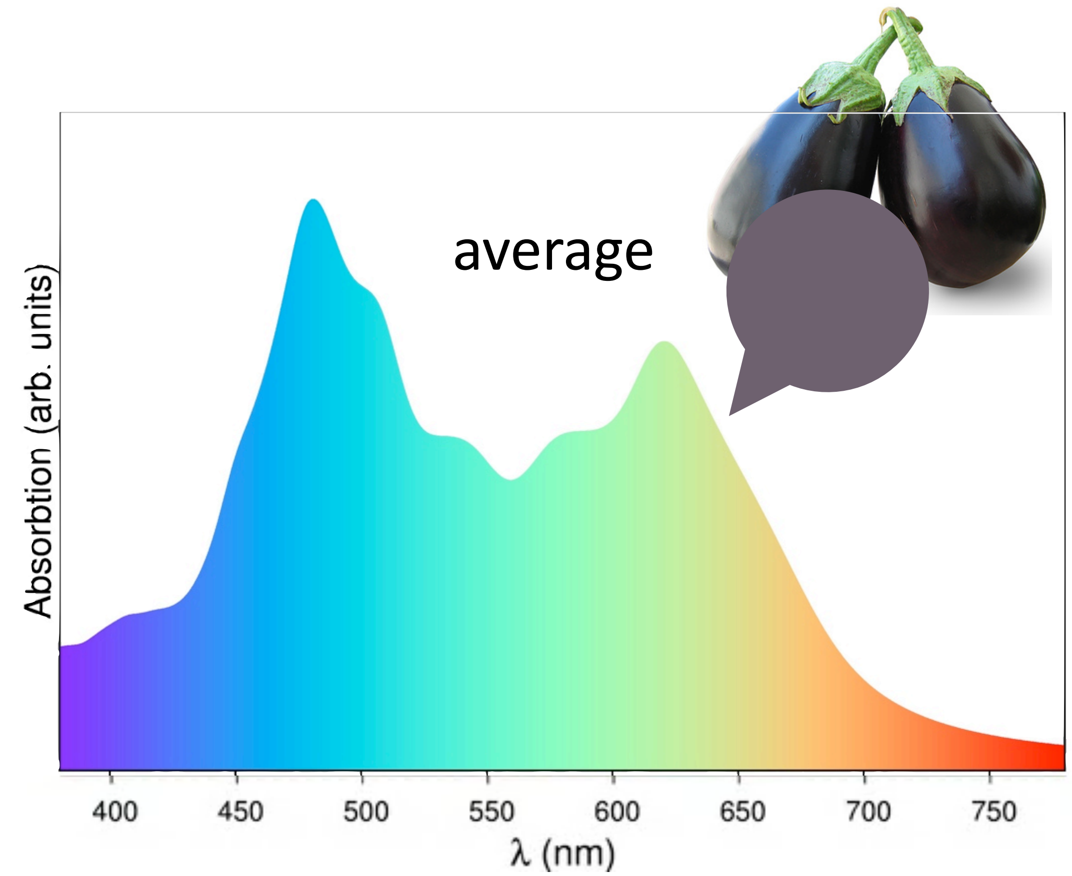
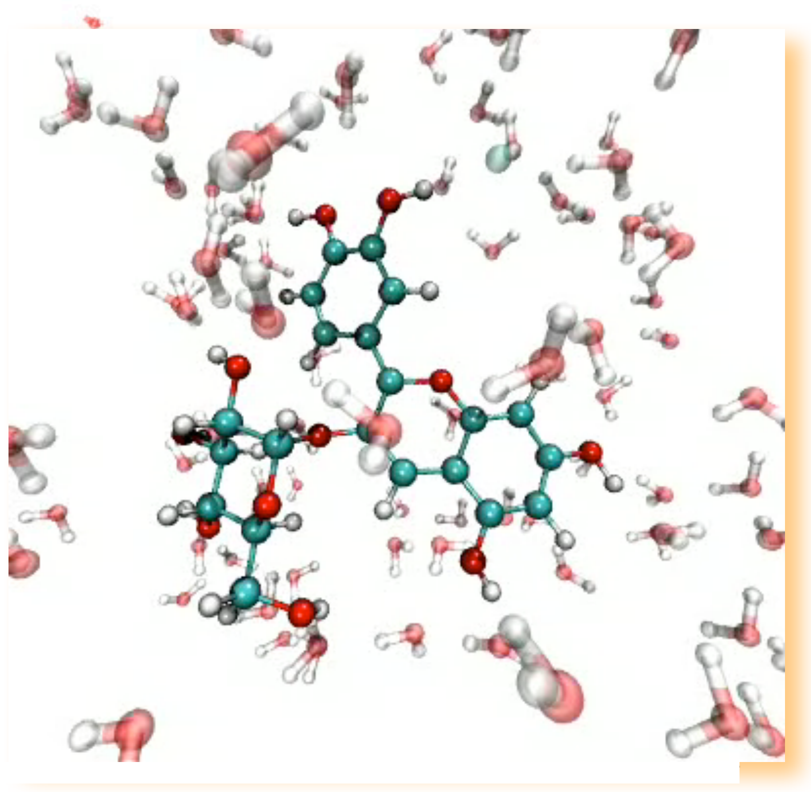
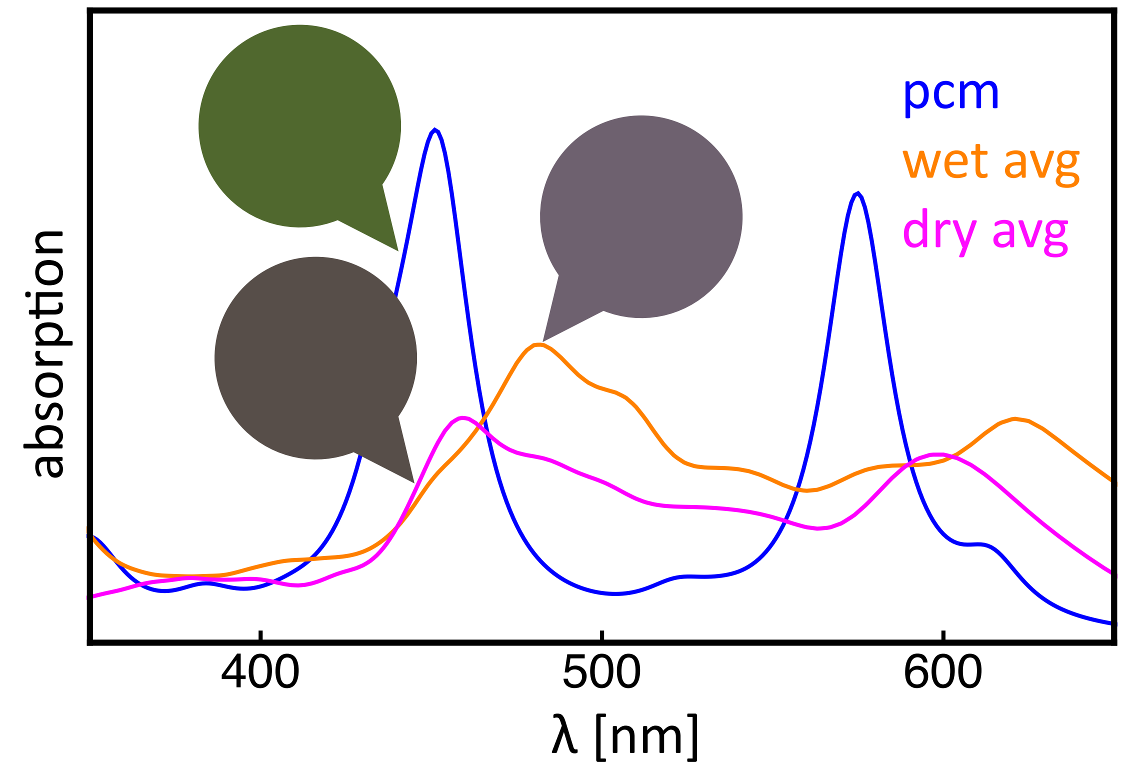
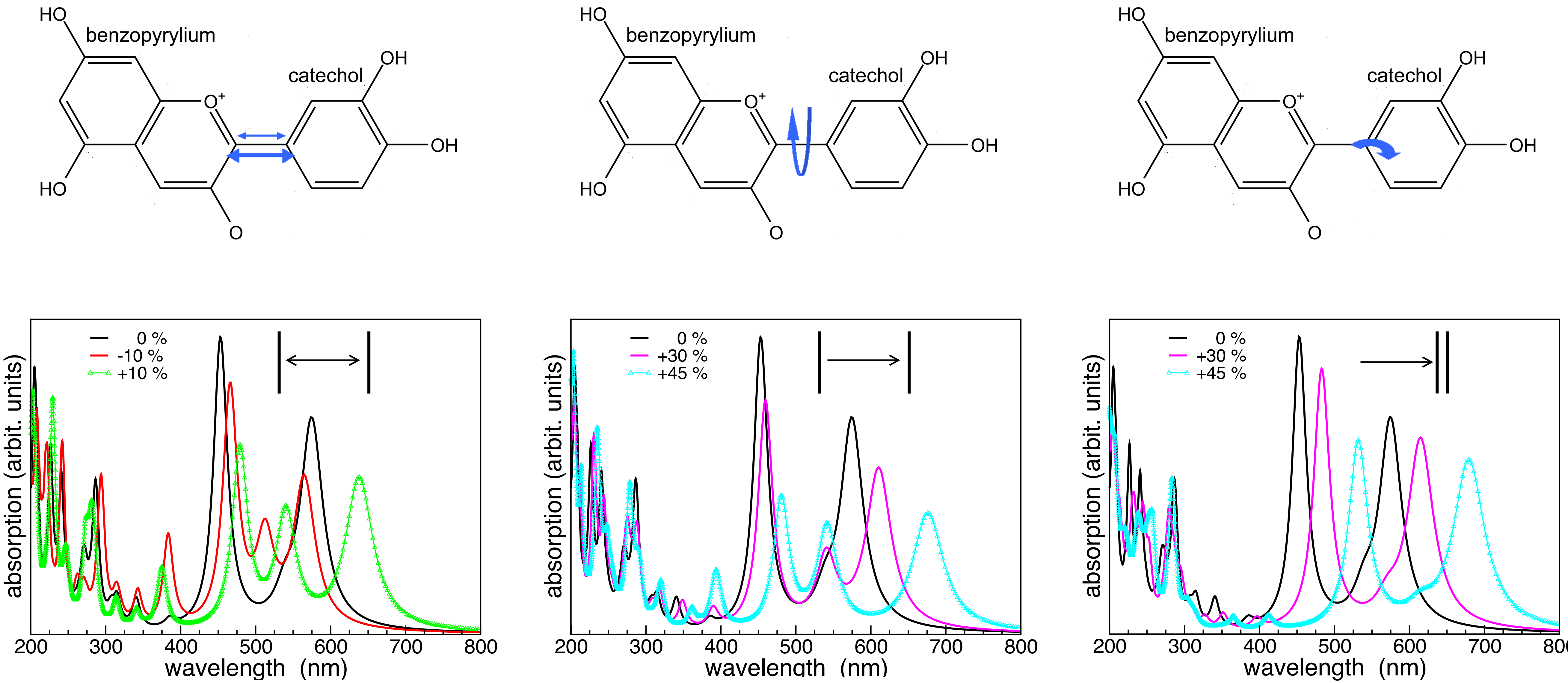








optical effects of intramolecular motion



O.B. Malcioğlu, A. Calzolari, R. Gebauer, D. Varsano, and S.B., JACS **133**, 15425 (2011)

O.B. Malcıoğlu, R. Gebauer, D. Rocca, and S.B., CPC **182**, 1744 (2011)

everything’s fine?

everything's fine? nay ...

no Coulombic tail in the eh interaction

- no Rydberg states in molecules
- no excitons in extended systems
- wrong charge-transfer excitations

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the fix

- exotic frequency-dependent functionals
- non-local (Fock) exchange
  - hybrid functionals
  - BSE equation

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THE JOURNAL OF CHEMICAL PHYSICS **133**, 164109 (2010)

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Dario Rocca,[1,a)] Deyu Lu,[1,b)] and Giulia Galli[1,2]
[1]*Department of Chemistry, University of California, Davis, Davis, California 95616, USA*
[2]*Department of Physics, University of California, Davis, Davis, California 95616, USA*

(Received 28 May 2010; accepted 8 September 2010; published online 27 October 2010)

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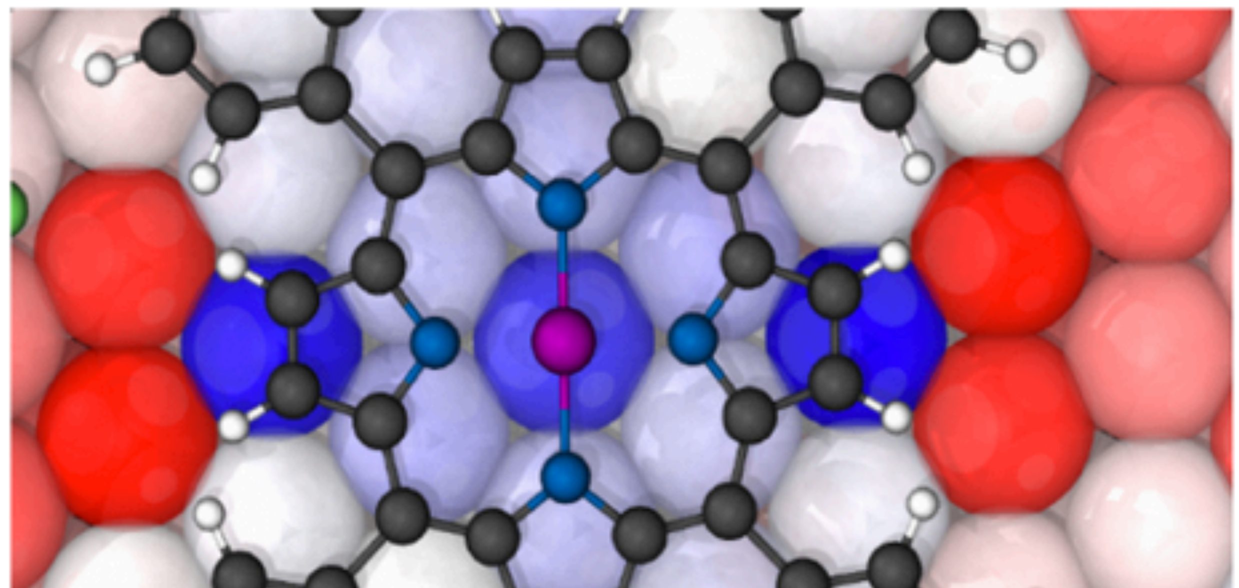
Quantum ESPRESSO Workshop, Pennsylvania State University, Jun 25 – Jun 29

Joint ICTP-TWAS Caribbean School on Electronic Structure Fundamentals and Methodologies (an Ab-initio Perspective) Cartagena, Colombia, August 27 – September 21



Spatially Extended Kondo State in Magnetic Molecules Induced by Interfacial Charge Transfer. Phys. Rev. Lett. 105 106601 (2010). Courtesy of H. Kulik.

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QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

Paolo Giannozzi[1,2], Stefano Baroni[1,3], Nicola Bonini[4], Matteo Calandra[5], Roberto Car[6], Carlo Cavazzoni[7,8], Davide Ceresoli[4], Guido L Chiarotti[9], Matteo Cococcioni[10], Ismaila Dabo[11], Andrea Dal Corso[1,3], Stefano de Gironcoli[1,3], Stefano Fabris[1,3], Guido Fratesi[12], Ralph Gebauer[1,13], Uwe Gerstmann[14], Christos Gougoussis[5], Anton Kokalj[1,15], Michele Lazzeri[5], Layla Martin-Samos[1], Nicola Marzari[4], Francesco Mauri[5], Riccardo Mazzarello[16], Stefano Paolini[3,9], Alfredo Pasquarello[17,18], Lorenzo Paulatto[1,3], Carlo Sbraccia[1,†], Sandro Scandolo[1,13], Gabriele Sclauzero[1,3], Ari P Seitsonen[5], Alexander Smogunov[13], Paolo Umari[1] and Renata M Wentzcovitch[10,19]

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Quantum ESPRESSO: a global community

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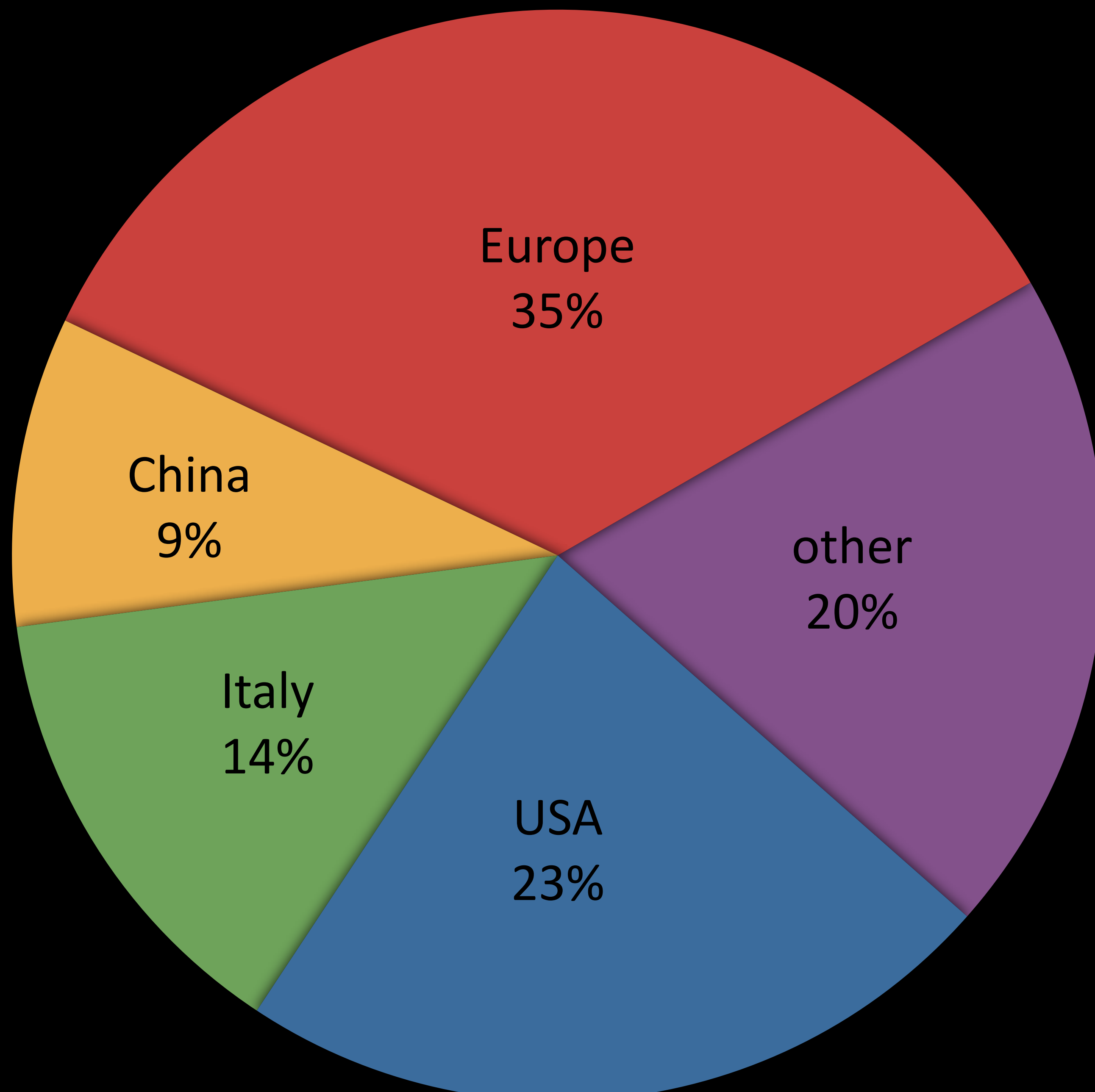

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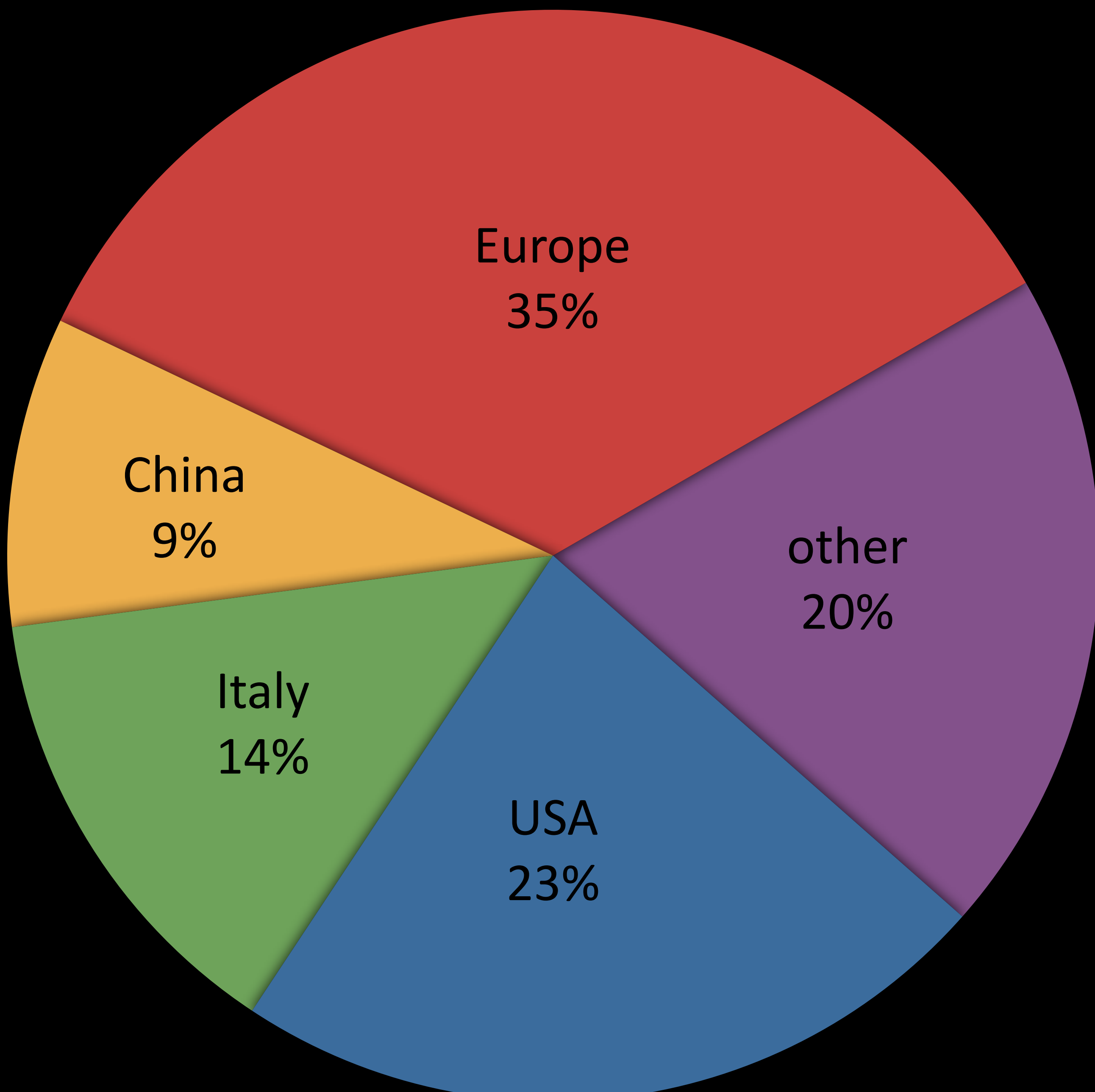

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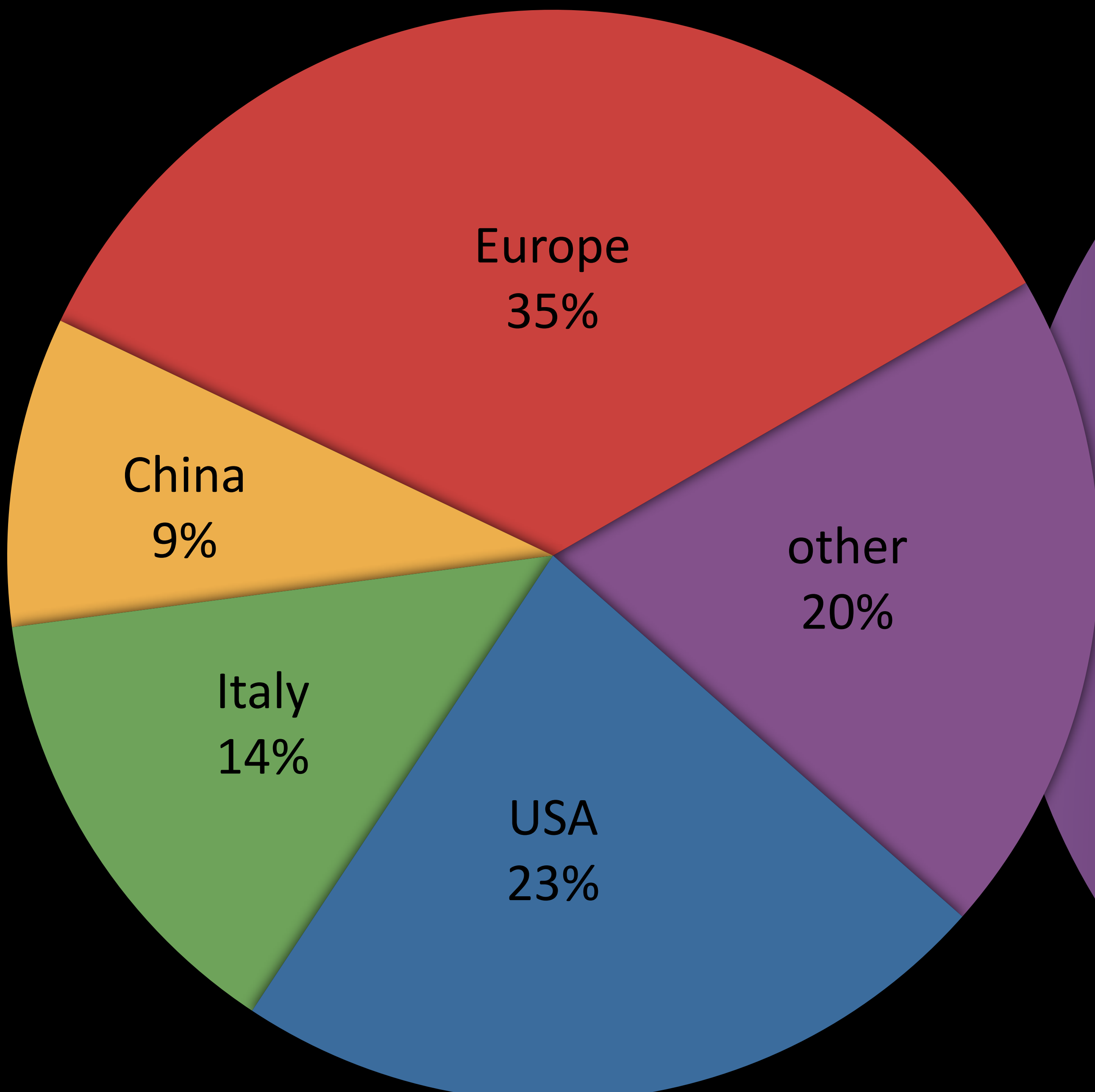

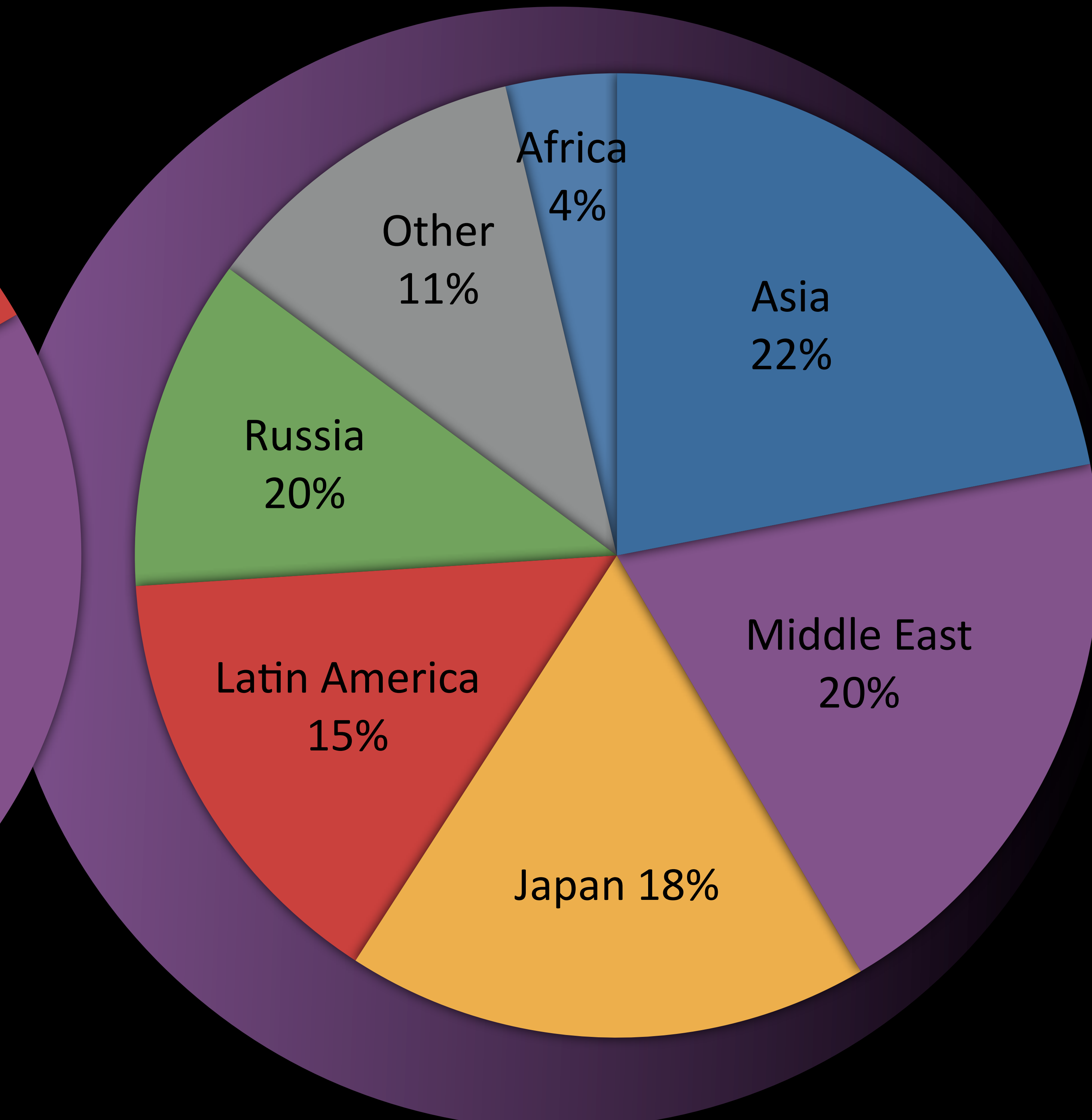

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