simulating molecular excitations using quantum mechanics and digital computers

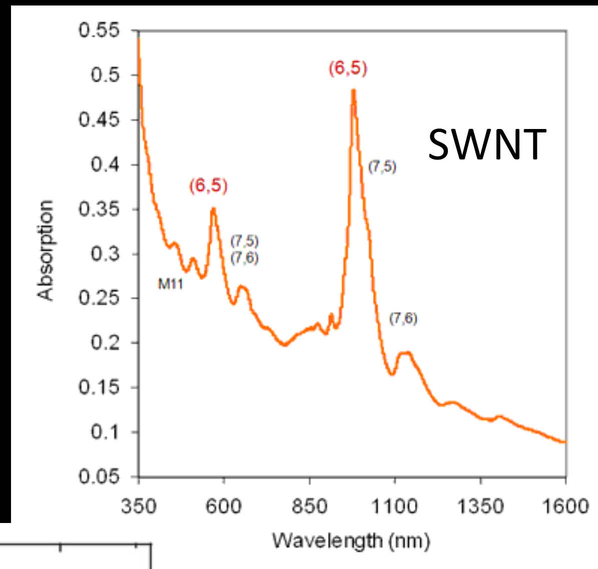
Stefano Baroni

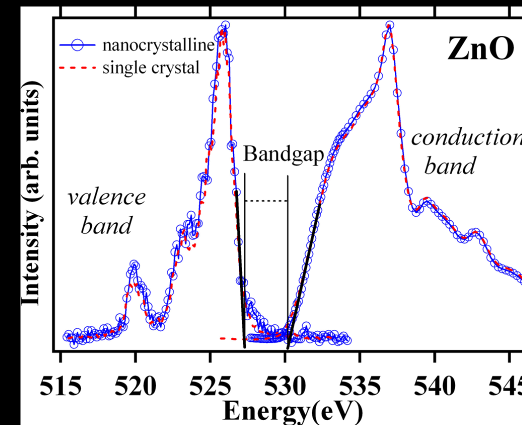
SISSA - Scuola Internazionale Superiore di Studi Avanzati

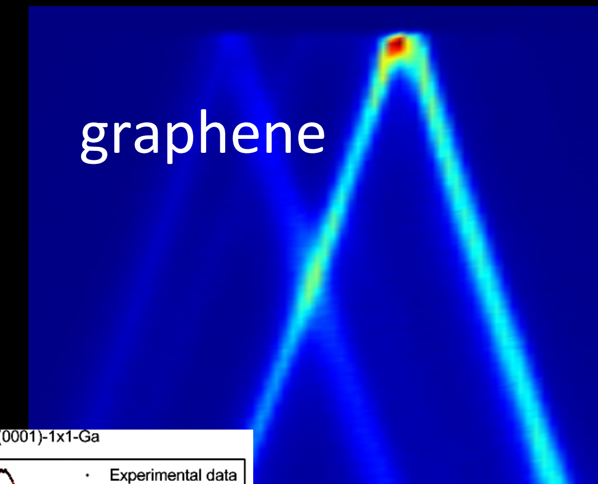
lecture given at the *Workshop on Density Functional Theory and Beyond: Computational Materials Science for Real Materials*, August 6-15, 2013, the *Abdus Salam International Centre for Theoretical Physics*, Trieste

absorption

lattice and molecular vibrations

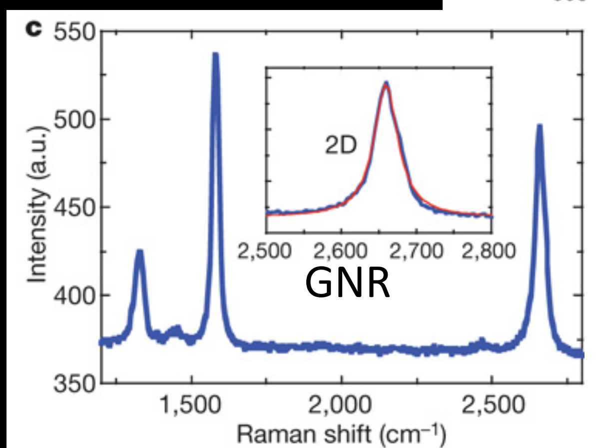






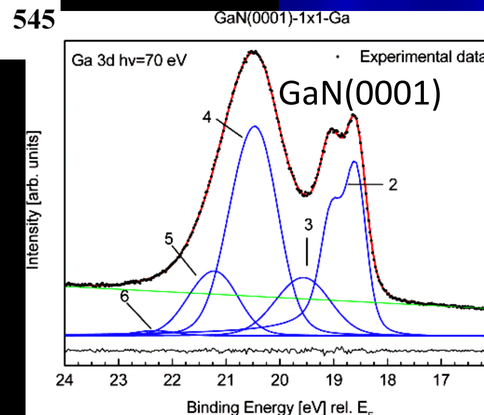
XAS/XES

ARPES



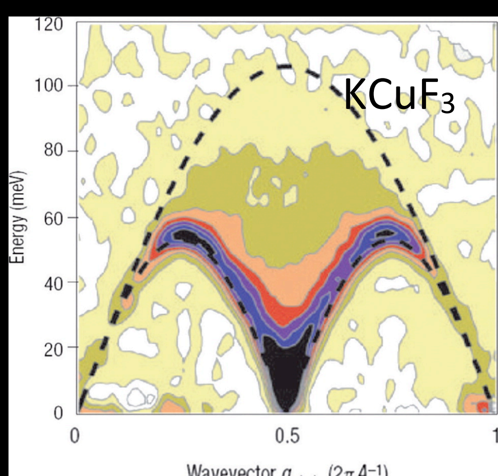
Raman

electronic transitions

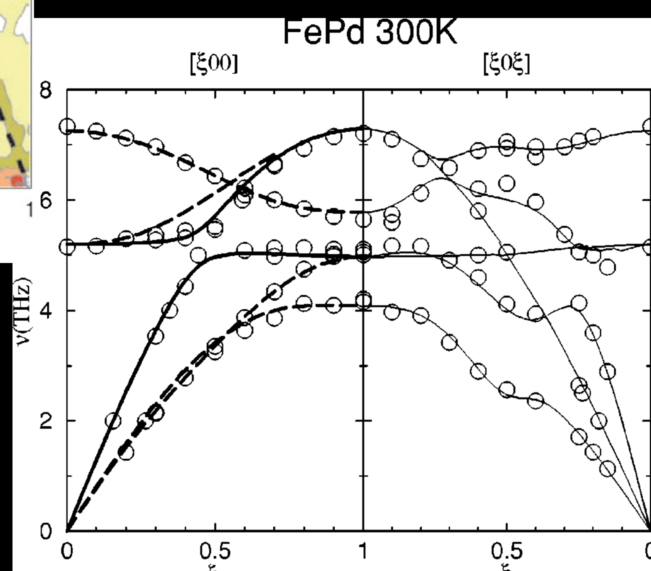


XPS

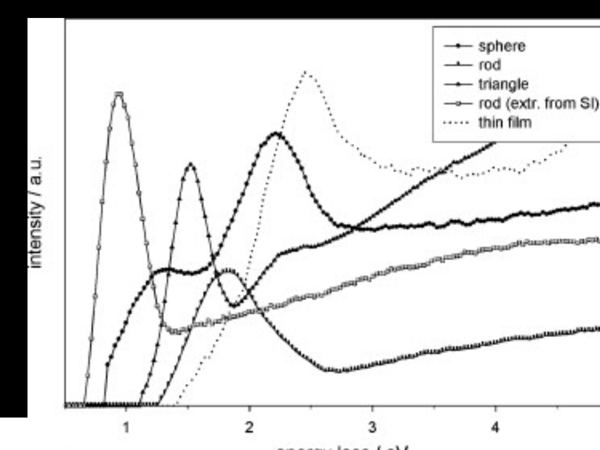
spectroscopies

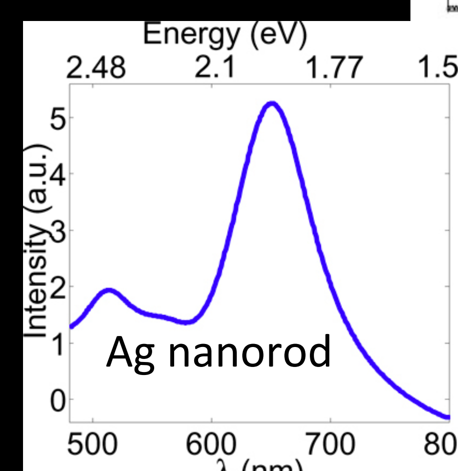


spin fluctuations



eels





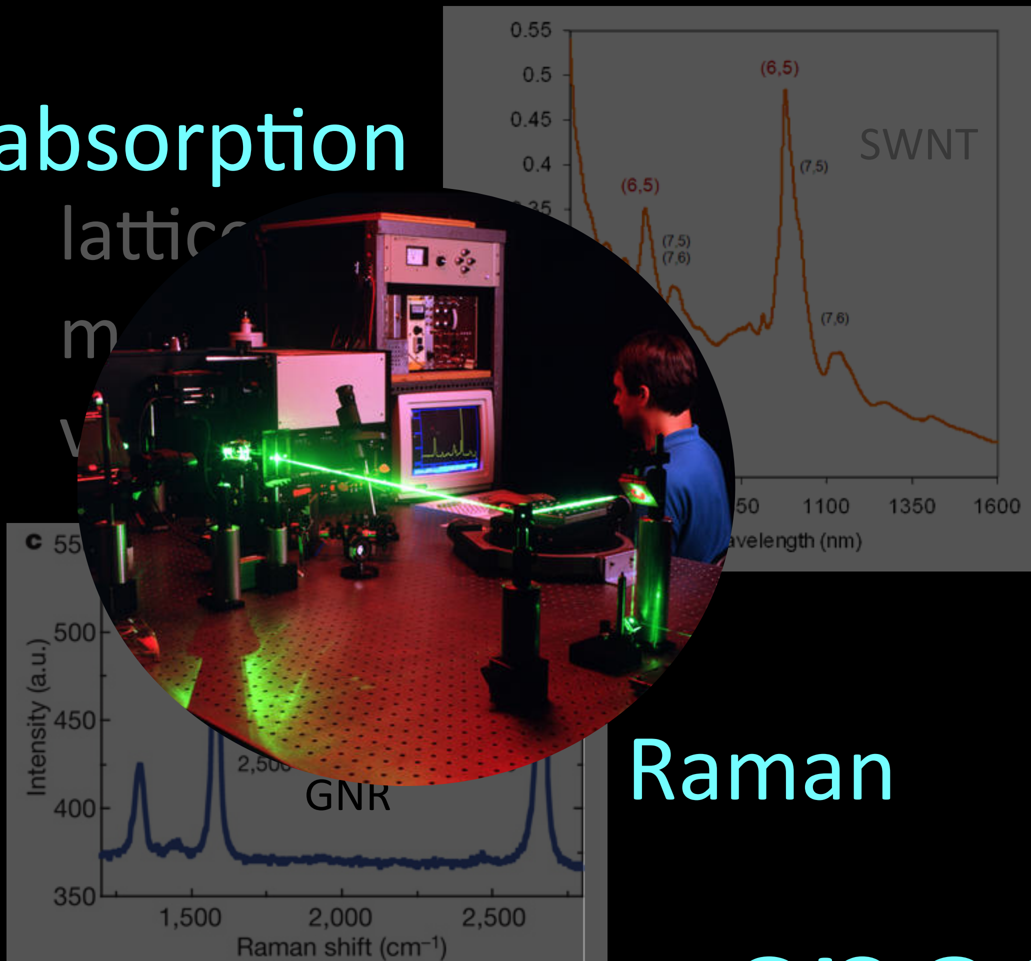
charge fluctuations

inelastic neutron scattering

lattice vibrations

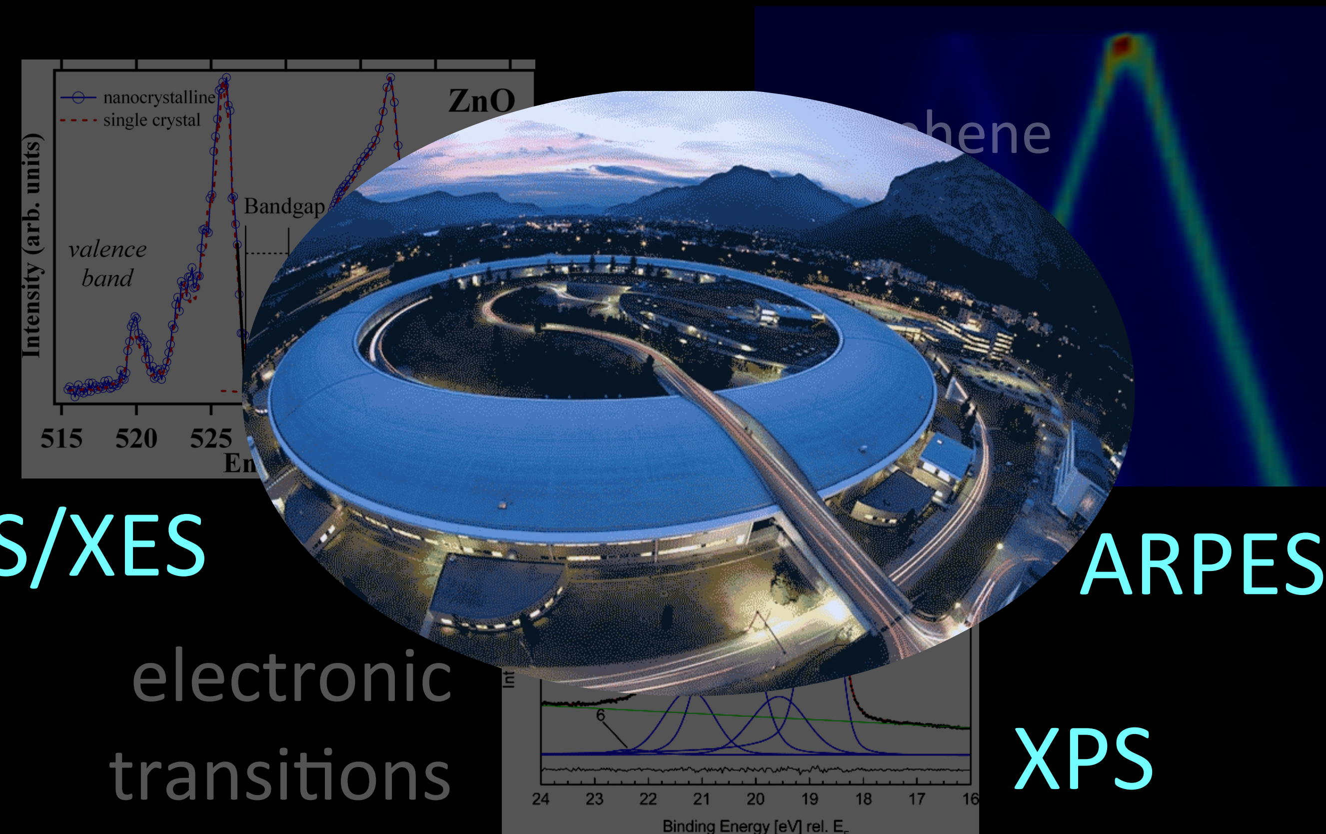
. . .

absorption



Raman

XAS/XES



ARPES

electronic
transitions

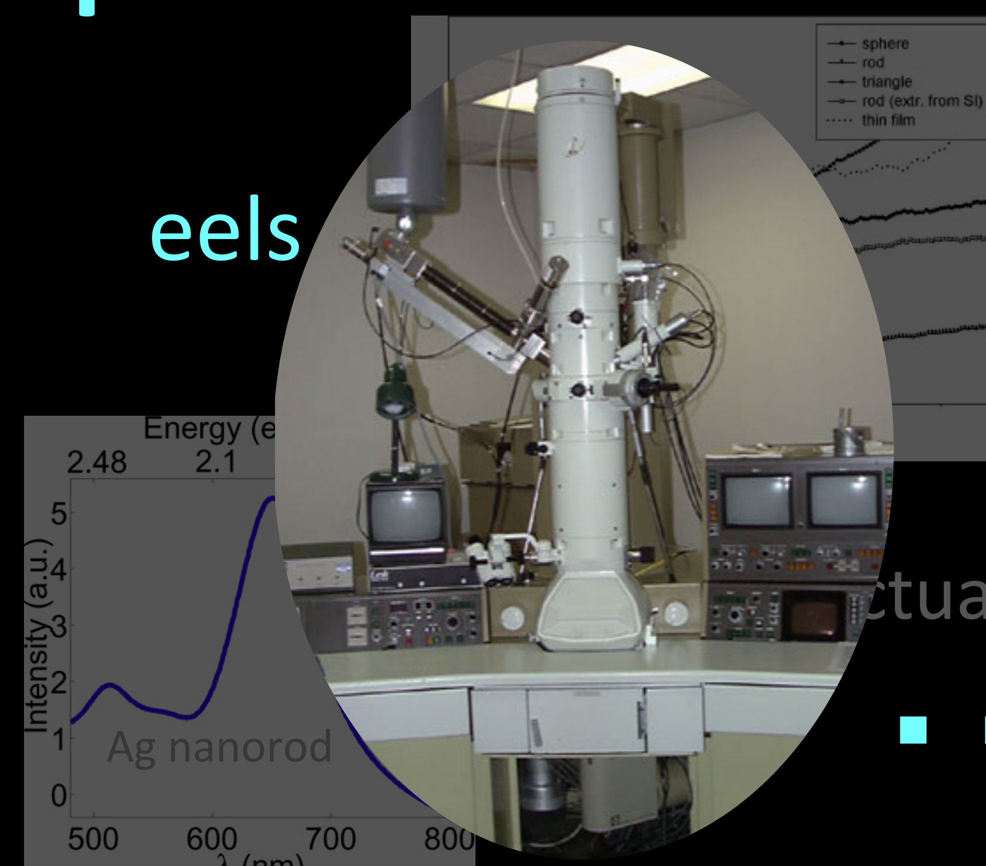
XPS

spectroscopies

inelastic
neutron
scattering

lattice vibrations

eels



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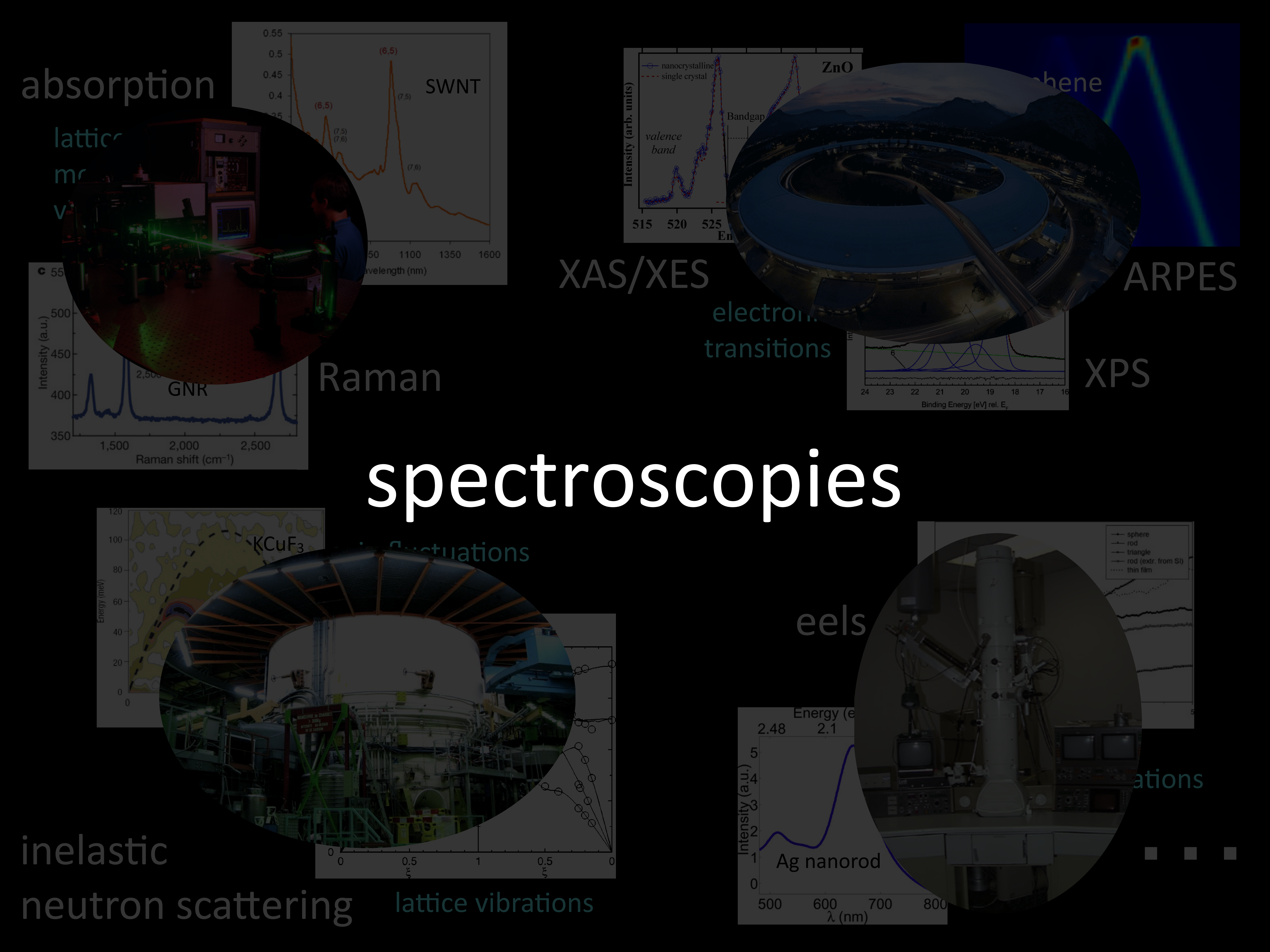
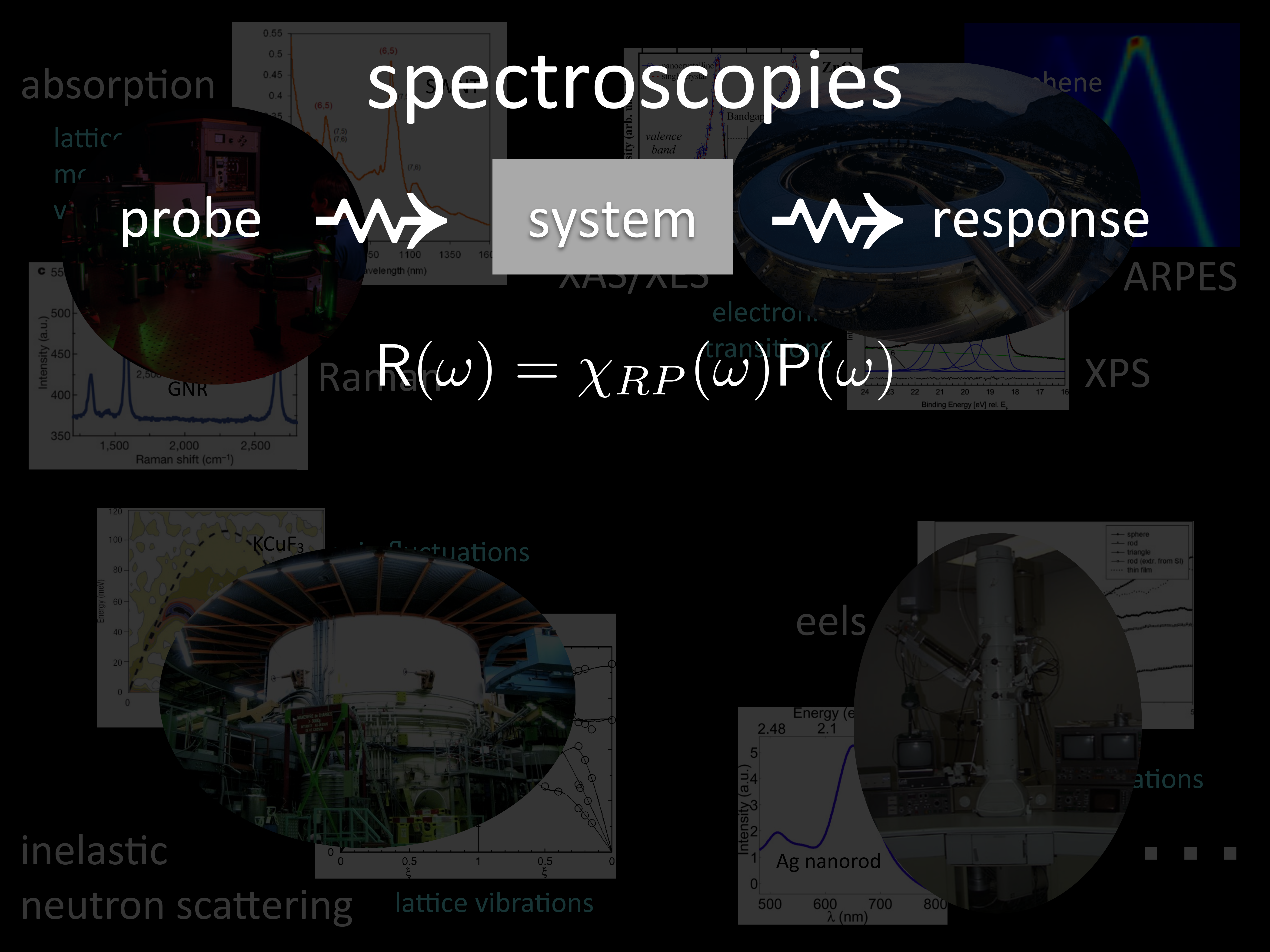

spectroscopies
absorption
SWNT
(6,5)
Raman
GNR
Raman shift (cm⁻¹)
XAS/XES
ZnO
nanocrystalline
single crystal
valence band
Bandgap
Intensity (arb. units)
electron
transitions
ARPES
XPS
Binding Energy [eV] rel. E_F
KCuF3
fluctuations
Energy (meV)
inelastic
neutron scattering
lattice vibrations
eels
Ag nanorod
λ (nm)
Intensity (a.u.)
sphere
rod
triangle
rod (extr. from SI)
thin film
...



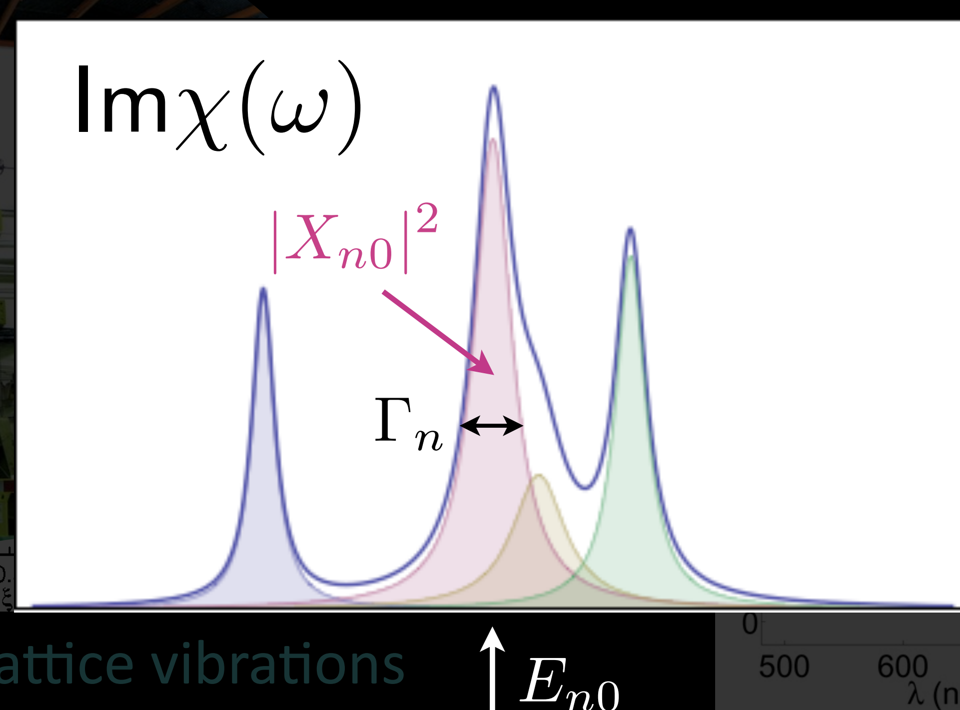
spectroscopies
probe
system
response
$$R(\omega) = \chi_{RP}(\omega)P(\omega)$$
absorption
Raman
XAS/XES
ARPES
XPS
eels
inelastic
neutron scattering
lattice vibrations
Ag nanorod
GNR
KCuF3
...

spectroscopies

probe → system → response

$$R(\omega) = \chi_{RP}(\omega) P(\omega)$$

$$\chi_{RP}(\omega) = \sum_{n \neq 0} \left[\frac{R_{0n} P_{n0}}{\omega - E_{n0} + i\delta} - \frac{P_{0n} R_{n0}}{\omega + E_{n0} + i\delta} \right]$$



probing the filckers of matter

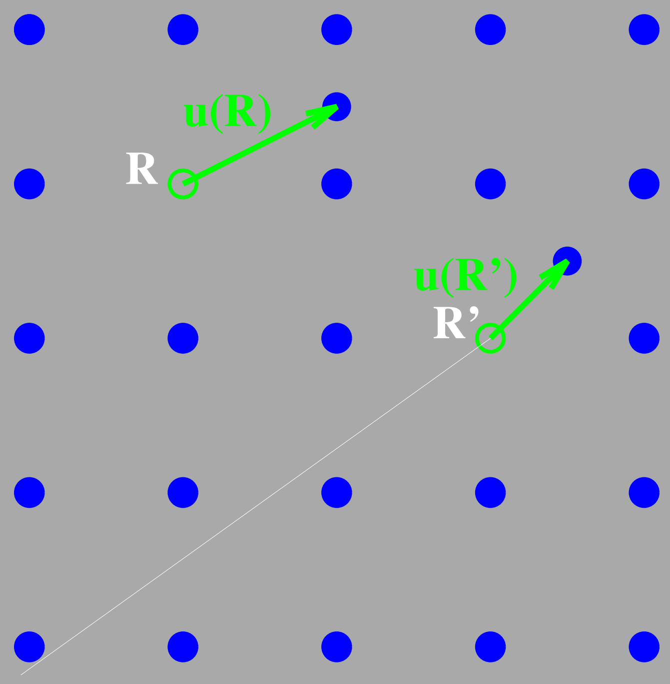
flicker	probe
molecular vibration	IR, Raman, INS, HREELS, ⋯
spin fluctuation	INS, EPR, MCD, ⋯
charge fluctuation	optical and PE spectra, EELS, ⋯
⋯	⋯

probing the filckers of matter

flicker	probe	theory
molecular vibration	IR, Raman, INS, HREELS, ⋯	DFT
spin fluctuation	INS, EPR, MCD, ⋯	constrained DFT
charge fluctuation	optical and PE spectra, EELS, ⋯	TDDFT, MBPT, ⋯
⋯	⋯	⋯

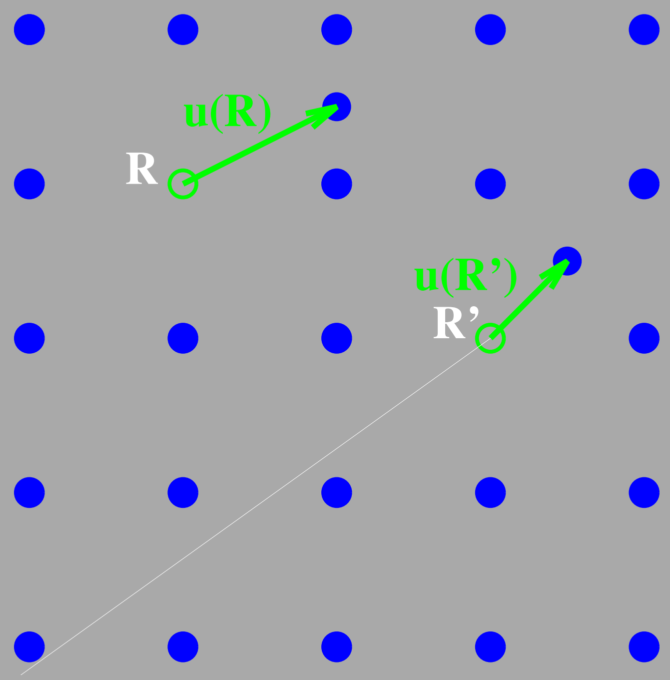
simulating atomic vibrations ...

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

lattice dynamics

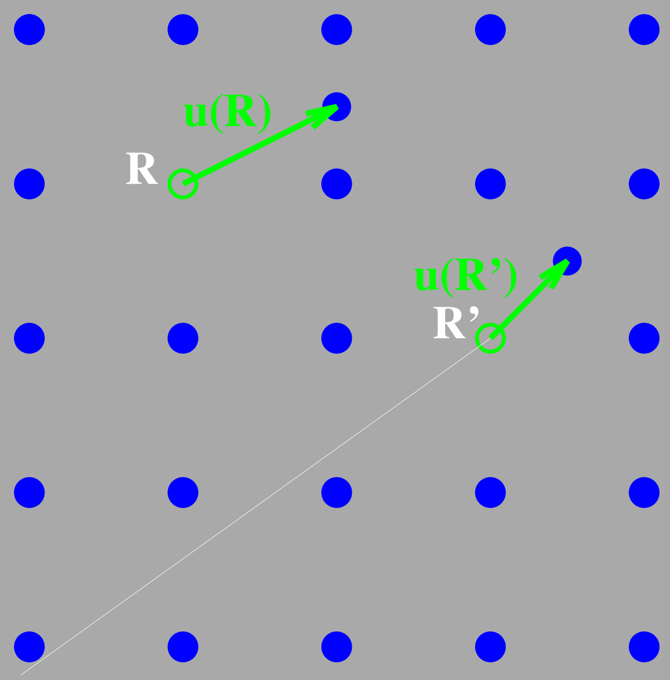


$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

lattice dynamics



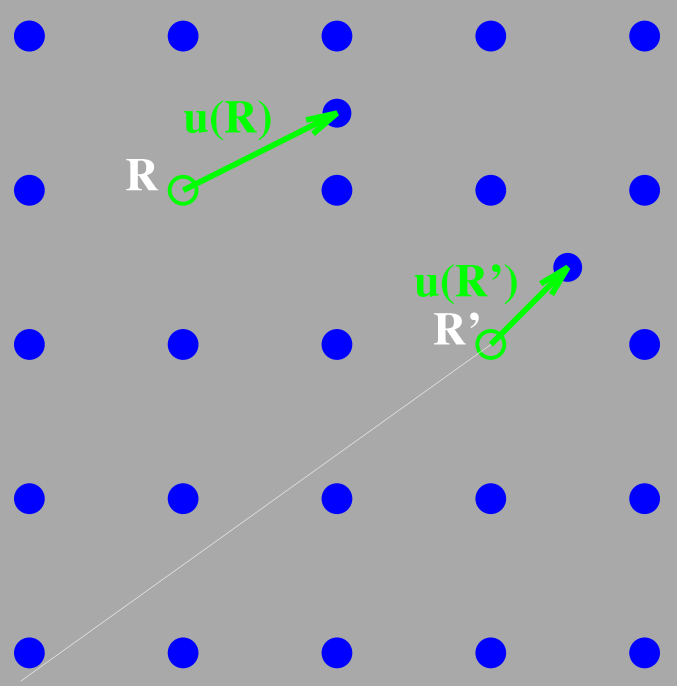
$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

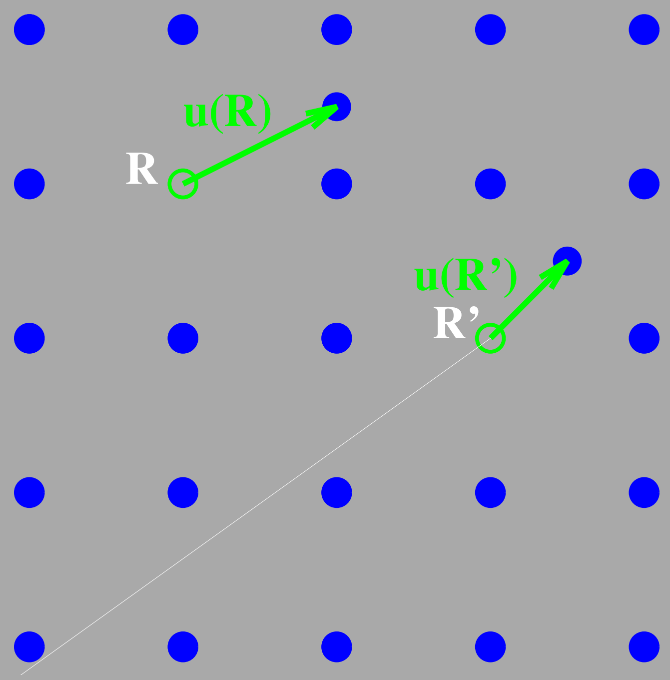
$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

$$\det \left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R}) \delta_{\mathbf{R},\mathbf{R}'} \right] = 0$$

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

DFT

DPFT

$$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$$

$$E = E_0 + \frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R})\partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')$$

$$+ \cdots$$

$$\det\left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R})\partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R})\delta_{\mathbf{R},\mathbf{R}'}\right] = 0$$

density-functional perturbation theory

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i u_i V_i'(\mathbf{r})$$

density-functional perturbation theory

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i u_i V_i'(\mathbf{r})$$

$$\frac{\partial E(\mathbf{u})}{\partial u_i} = \int n_{\mathbf{u}}(\mathbf{r}) V_i'(\mathbf{r}) d\mathbf{r}$$

Hellmann-Feynman

density-functional perturbation theory

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i u_i V_i'(\mathbf{r})$$

$$\frac{\partial E(\mathbf{u})}{\partial u_i} = \int n_{\mathbf{u}}(\mathbf{r}) V_i'(\mathbf{r}) d\mathbf{r}$$

Hellmann-Feynman

$$\frac{\partial^2 E(\mathbf{u})}{\partial u_i \partial u_j} = \int \frac{\partial n_{\mathbf{u}}(\mathbf{r})}{\partial u_j} V_i'(\mathbf{r}) d\mathbf{r}$$

DFPT

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi'_v(\mathbf{r})$$

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re} \sum_v \phi_v^{\circ *}(\mathbf{r}) \phi'_v(\mathbf{r})$$

$$= 2\mathrm{Re} \sum_{cv} \rho'_{vc} \phi_v^{\circ *}(\mathbf{r}) \phi_c^{\circ}(\mathbf{r})$$

$$\phi'_v = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi_v'(\mathbf{r})$$

$$= 2\mathrm{Re}\sum_{cv} \rho_{vc}'\phi_v^{\circ *}(\mathbf{r})\phi_c^{\circ}(\mathbf{r})$$

$$\phi_v' = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ}|V'|\phi_v^{\circ}\rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

$$(H^{\circ} - \epsilon_v^{\circ})\phi_v' = -P_c V' \phi_v^{\circ}$$

calculating the response

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi_v'(\mathbf{r})$$

$$(H^\circ - \epsilon_v^\circ)\phi_v' = -P_c V' \phi_v^\circ$$

DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$\big(-\Delta + V_{SCF}(\mathbf{r})\big)\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$(-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$

DFPT

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$

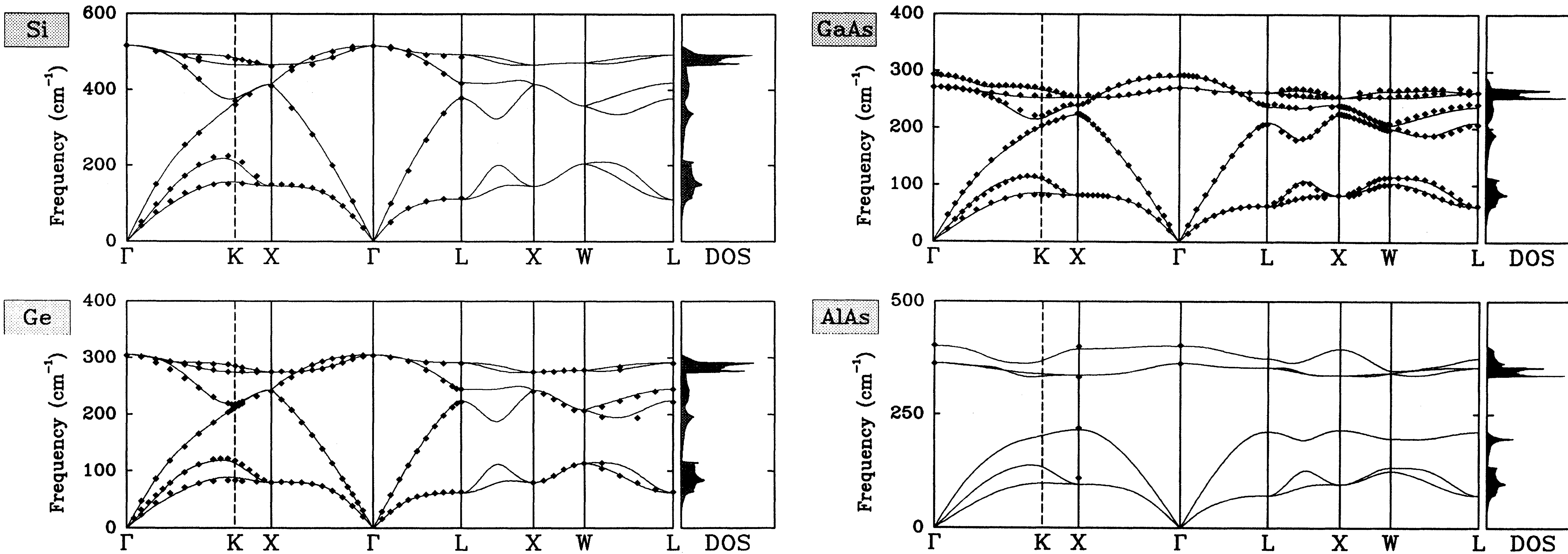
$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

$$n'(\mathbf{r}) = 2 \ \mathrm{Re} \sum_{\epsilon_v < E_F} \phi^*_v(\mathbf{r})\phi'_v(\mathbf{r})$$

$$(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r})\phi_v(\mathbf{r})$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

phonons from DFPT



P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)

applications done so far

- Dielectric properties
- Piezoelectric properties
- Elastic properties
- Phonon in crystals and alloys
- Phonon at surfaces, interfaces, super-lattices, and nano-structures
- Raman and infrared activities
- Anharmonic couplings and vibrational line widths
- Mode softening and structural transitions
- Electron-phonon interaction and superconductivity
- Thermal expansion
- Isotopic effects on structural and dynamical properties
- Thermo-elasticity and other thermal properties of minerals
- …

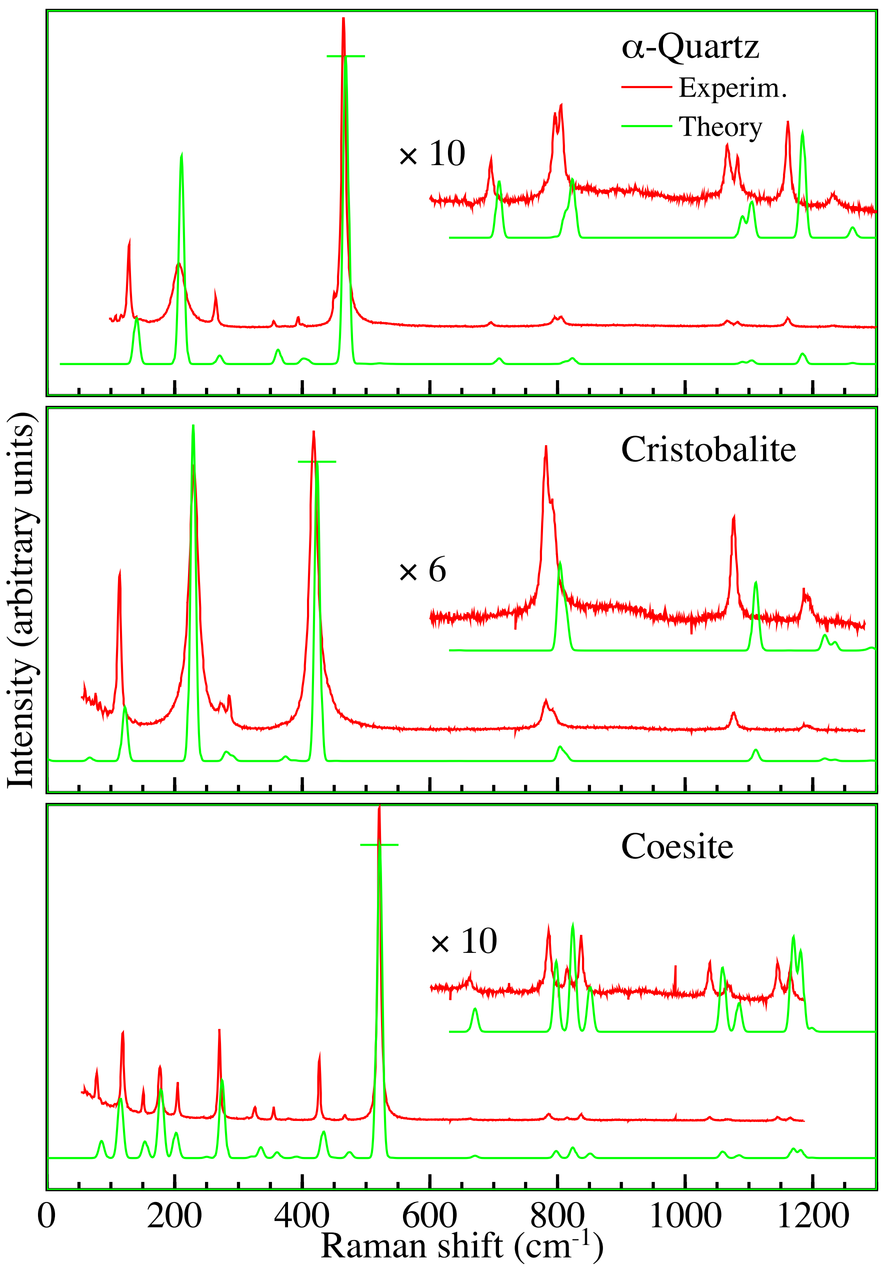
SB, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, *Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001)

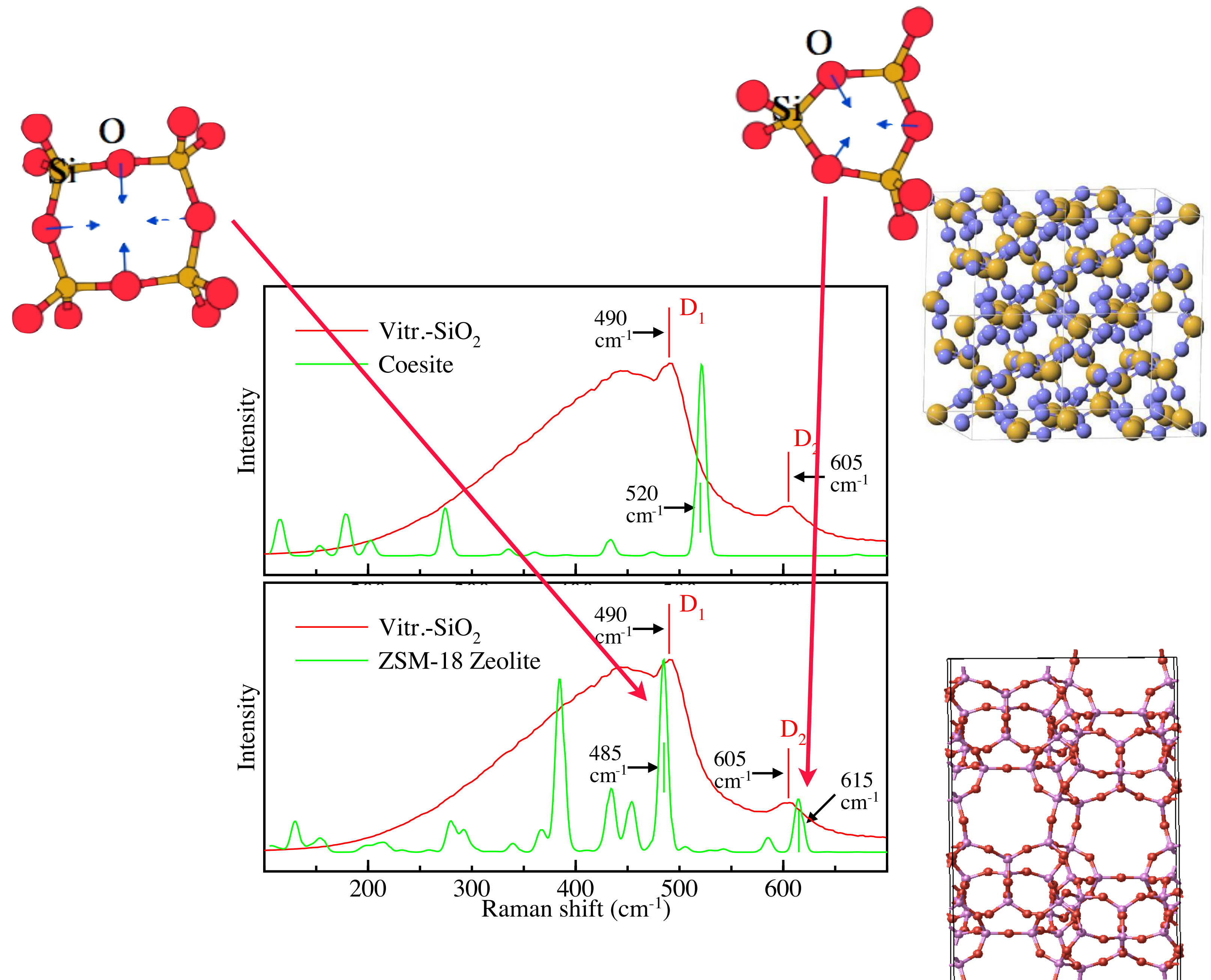
a sampler of recent applications

VOLUME 90, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 24 JANUARY 2003

First-Principles Calculation of Vibrational Raman Spectra in Large Systems: Signature of Small Rings in Crystalline SiO_2

Michele Lazzeri and Francesco Mauri





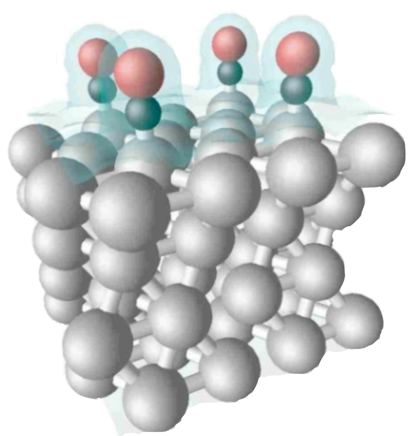
a sampler of recent applications

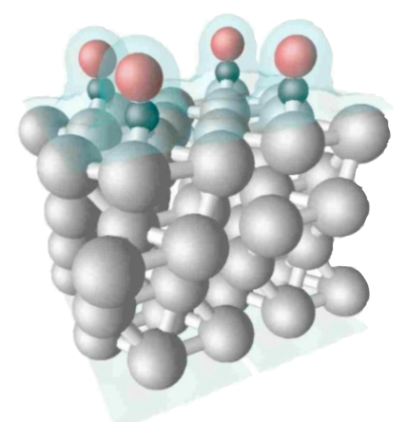
J|A|C|S
ARTICLES
Published on Web 08/17/2007

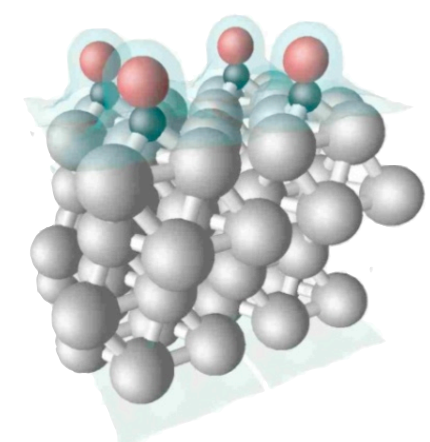
Vibrational Recognition of Adsorption Sites for CO on Platinum and Platinum−Ruthenium Surfaces

Ismaila Dabo,*,† Andrzej Wieckowski,‡ and Nicola Marzari†

11046 J. AM. CHEM. SOC. ■ VOL. 129, NO. 36, 2007







atop ($CO@Pt_1$)
E_{DFT} = +0.10 eV
ν_{DFT} = 2050 cm^{-1}
ν_{exp} = 2070 cm^{-1}

bridge ($CO@Pt_2$)
E_{DFT} = +0.03 eV
ν_{DFT} = 1845 cm^{-1}
ν_{exp} = 1830 cm^{-1}

fcc ($CO@Pt_3$)
E_{DFT} = 0 eV
ν_{DFT} = 1743 cm^{-1}
ν_{exp} = 1780 cm^{-1}

expt

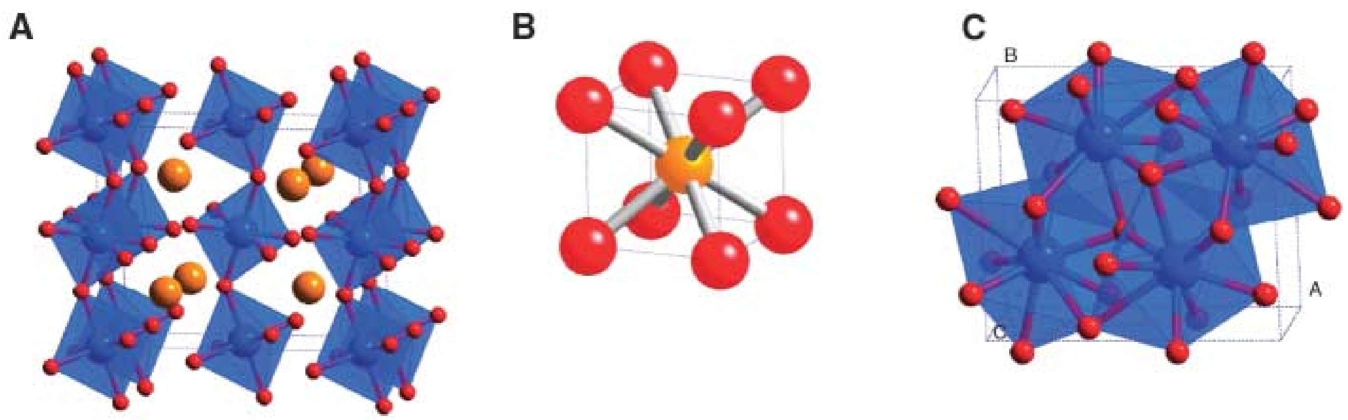
DFT

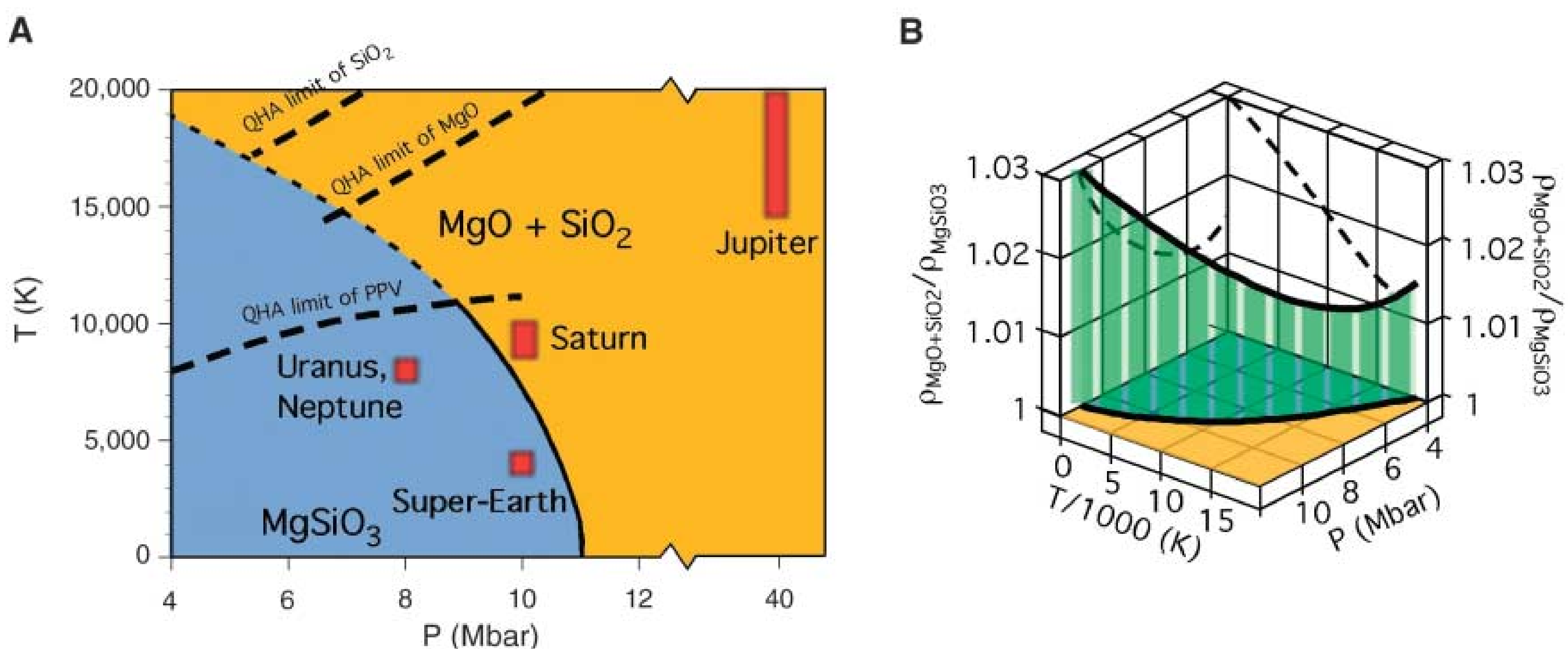
a sampler of recent applications

Dissociation of $MgSiO_3$ in the Cores of Gas Giants and Terrestrial Exoplanets

Koichiro Umemoto,[1] Renata M. Wentzcovitch,[1]* Philip B. Allen[2]

www.sciencemag.org SCIENCE VOL 311 17 FEBRUARY 2006 983





a sampler of recent applications

PRL **100,** 257001 (2008) PHYSICAL REVIEW LETTERS week ending 27 JUNE 2008

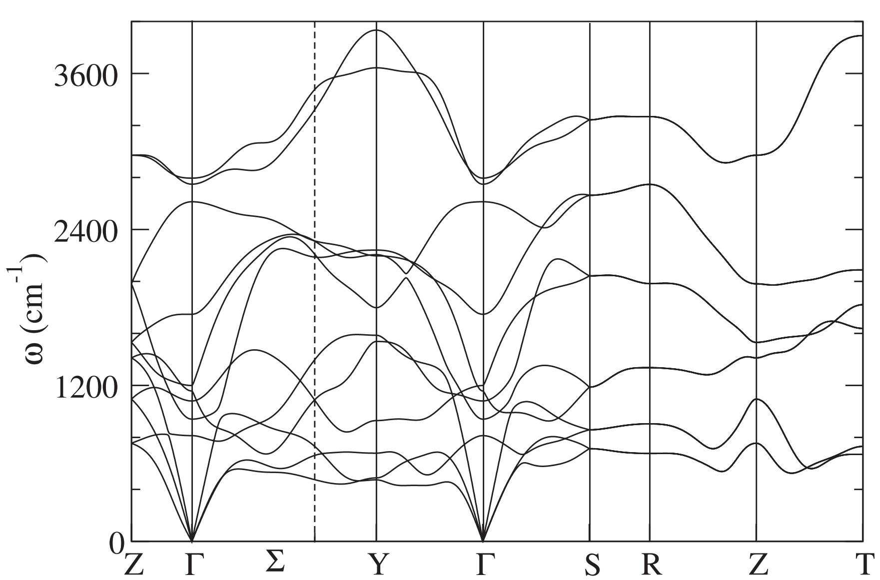
Ab Initio Description of High-Temperature Superconductivity in Dense Molecular Hydrogen

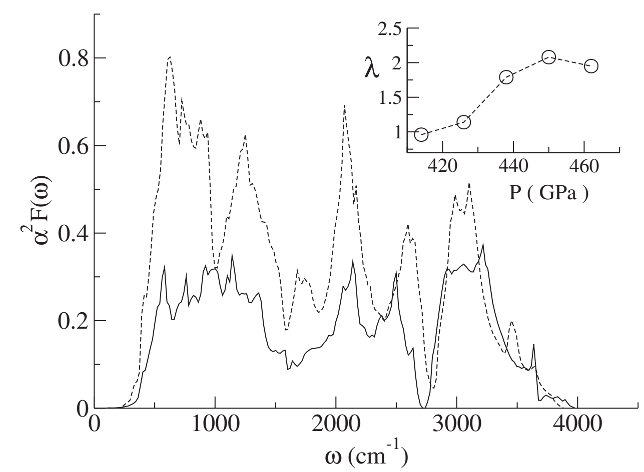
P. Cudazzo,[1] G. Profeta,[1] A. Sanna,[2,3] A. Floris,[3] A. Continenza,[1] S. Massidda,[2] and E. K. U. Gross[3]

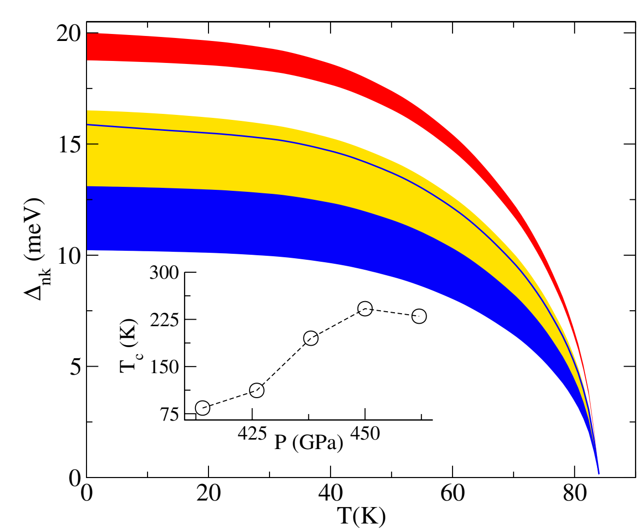
[1]*CNISM - Dipartimento di Fisica, Università degli Studi dell'Aquila, Via Vetoio 10, I-67010 Coppito (L'Aquila) Italy*
[2]*SLACS-INFM/CNR—Dipartimento di Fisica, Università degli Studi di Cagliari, I-09124 Monserrato (CA), Italy*
[3]*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

(Received 7 December 2007; published 23 June 2008; corrected 27 June 2008)

414 GPa







a sampler of recent applications

PRL **100,** 257001 (2008) PHYSICAL REVIEW LETTERS week ending 27 JUNE 2008

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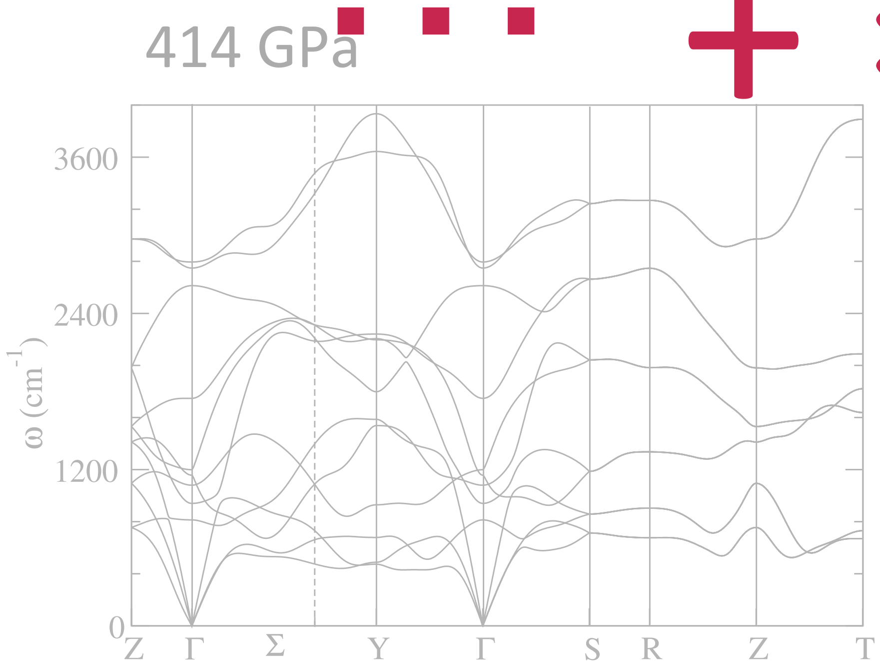
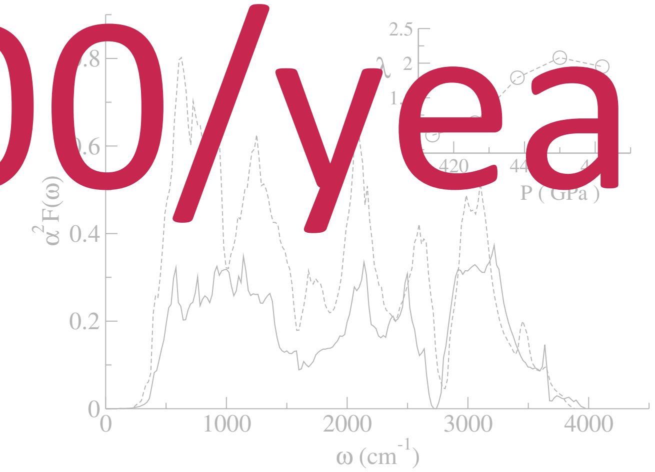
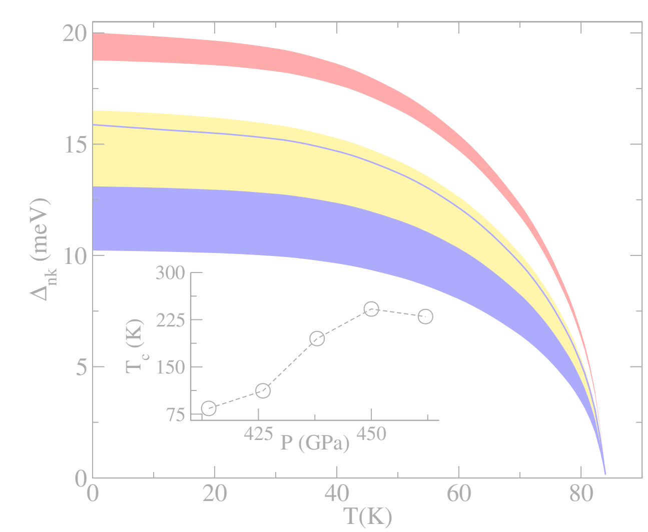
··· + ≈200/year







simulating electronic
charge fluctuations ...

optical spectra from TDDF (perturbation) T

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

$$v_{KS}(\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_v |\phi_v(\mathbf{r},t)|^2$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

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E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

$$v(\mathbf{r},t) \rightarrow n(\mathbf{r},t)$$

$$v_0(\mathbf{r}) - e\mathbf{r}\cdot\mathbf{E}(t) \rightarrow n_0(\mathbf{r}) + n'(\mathbf{r},t)$$

optical spectra from TDDF (perturbation) T

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

$$v_{KS}(\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_v |\phi_v(\mathbf{r},t)|^2$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

$$v(\mathbf{r},t) \to n(\mathbf{r},t)$$

$$v_0(\mathbf{r}) - e\mathbf{r}\cdot\mathbf{E}(t) \to n_0(\mathbf{r}) + n'(\mathbf{r},t)$$

$$\mathbf{d}(t) = -e\int \mathbf{r}n'(\mathbf{r},t)d\mathbf{r}$$

$$\alpha(\omega) = \frac{\tilde{\mathbf{d}}(\omega)}{\tilde{\mathbf{E}}(\omega)}$$

optical spectra from TDDF (perturbation) T

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

$$v_{KS}(\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_v |\phi_v(\mathbf{r},t)|^2$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

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

$$\langle A(t)\rangle = \mathsf{Tr}\big(\rho(t)A\big)$$

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

optical spectra from TDDF (perturbation) T

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

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

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

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

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

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

optical spectra from TDDF (perturbation) T

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

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

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

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

optical spectra from TDDF (perturbation) T

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

optical spectra from TDDF (perturbation) T

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

free oscillations

$$\mathcal{L}\ \tilde{\rho}' = \omega\tilde{\rho}'$$

excitation energies
and oscillator strengths

optical spectra from TDDF (perturbation) T

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

- ☺ ideally suited to chase after individual excitation energies / oscillator strengths

- ☹ inefficient for large systems and/or in the continuum of even small ones

free oscillations

$$\mathcal{L}\ \tilde{\rho}' = \omega \tilde{\rho}'$$

Casida's equation

excitation energies
and oscillator strengths

optical spectra from TDDF (perturbation) T

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

optical spectra from TDDF (perturbation) T

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

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

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

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

the Lanczos connection

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

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

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

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

the Lanczos connection

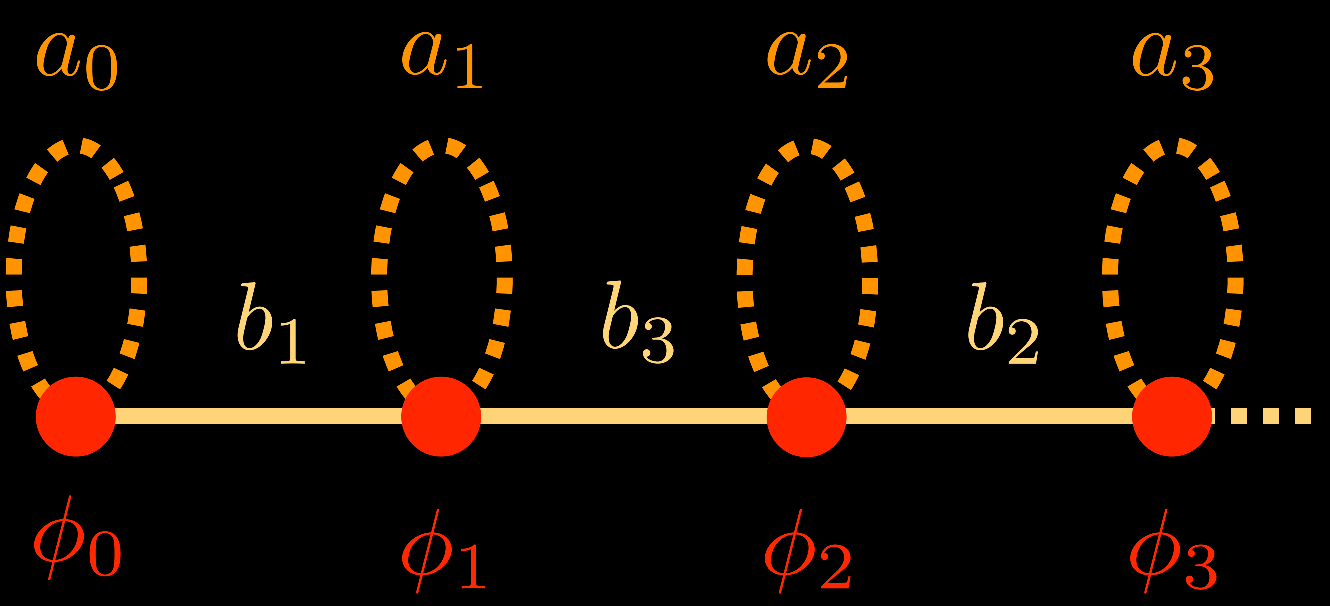
$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

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

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

the Lanczos connection

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

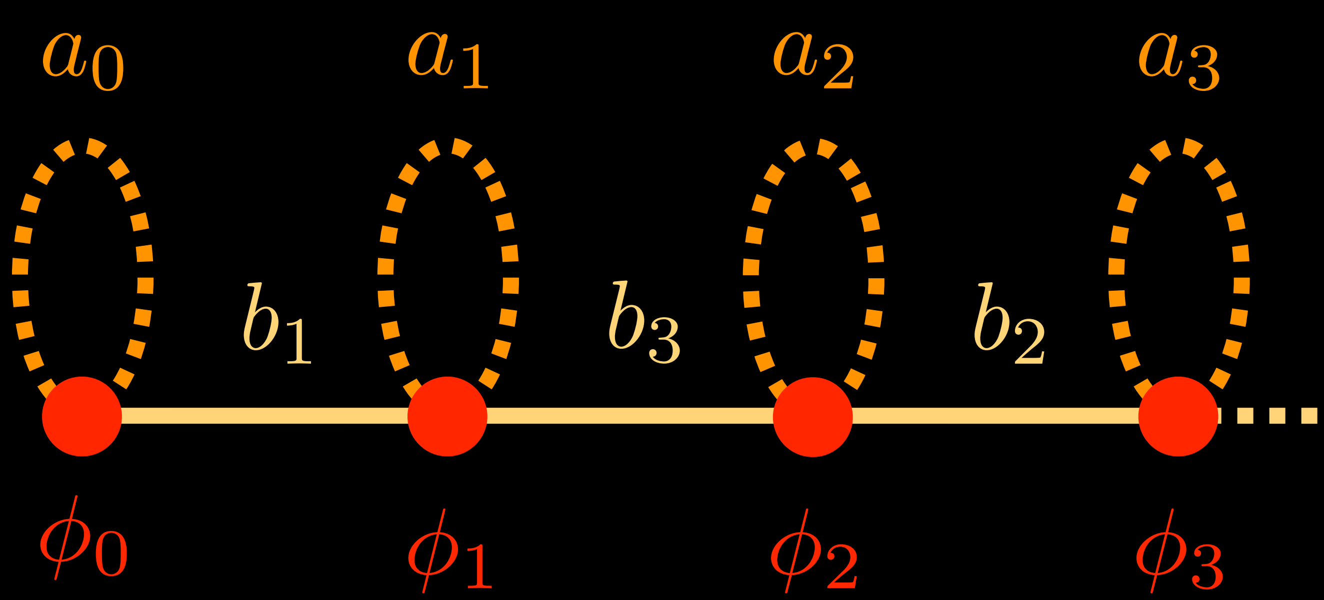


$$\mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

the Lanczos connection

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

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



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

the DFPT representation

$$\tilde{\rho}'(\omega) = \begin{pmatrix} 0 & Y^\dagger \\ X & 0 \end{pmatrix}\begin{matrix} \text{v} \\ \text{c} \end{matrix}$$

$$\begin{matrix} \text{v} & \quad \text{c} \end{matrix}$$

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

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

$$= \sum_{v}\Big(|\varphi'_v(\omega)\rangle\langle\varphi^\circ_v| + |\varphi^\circ_v\rangle\langle\varphi'_v(-\omega)| \Big)$$

the DFPT representation

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

$$= \sum_{v} \Big(|\varphi_v'(\omega)\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle\varphi_v'(-\omega)| \Big)$$

↓

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

$$P_v x_v = P_v y_v = 0$$

the DFPT representation

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

$$= \sum_{v}\Big(|\varphi_v'(\omega)\rangle\langle\varphi_v^\circ| + |\varphi_v^\circ\rangle\langle\varphi_v'(-\omega)| \Big)$$

$$\downarrow$$

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

$$P_v x_v = P_v y_v = 0$$

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

the DFPT representation

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

↓

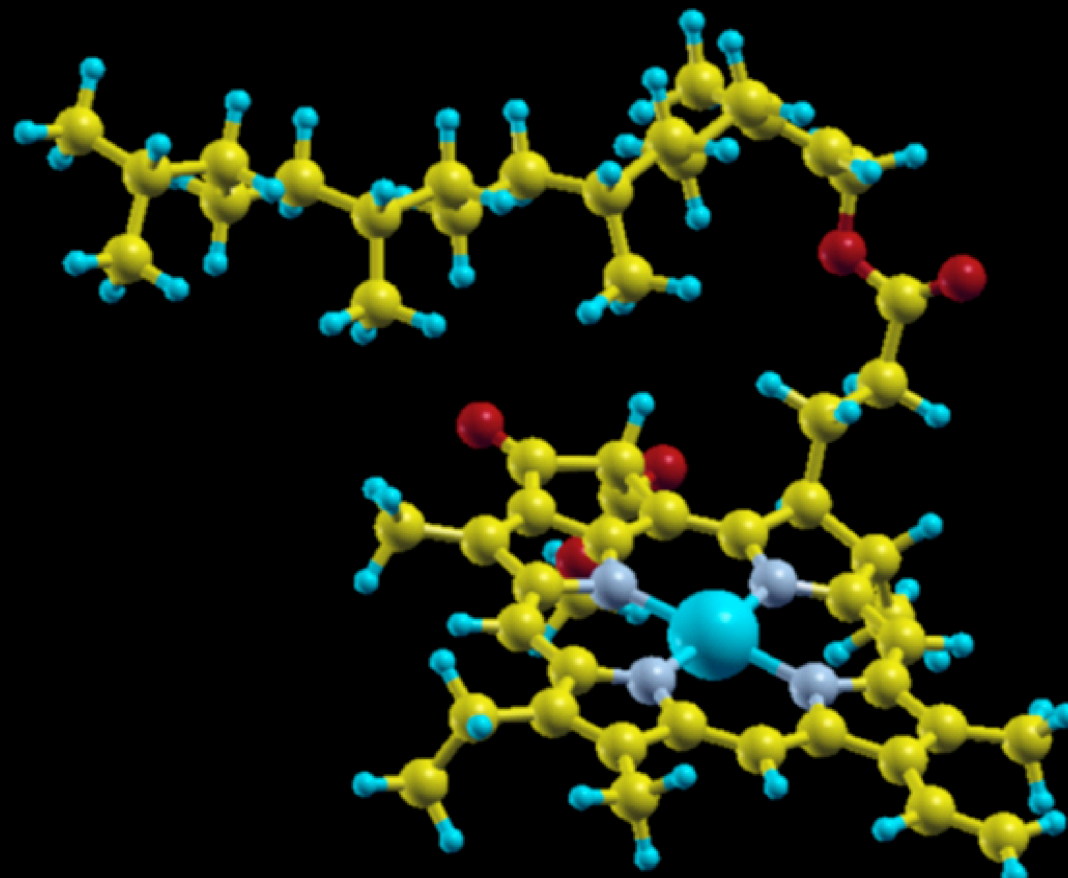
$$|\{x_v(\mathbf{r})\},\{y_v(\mathbf{r})\}\rangle$$

$$P_v x_v = P_v y_v = 0$$

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

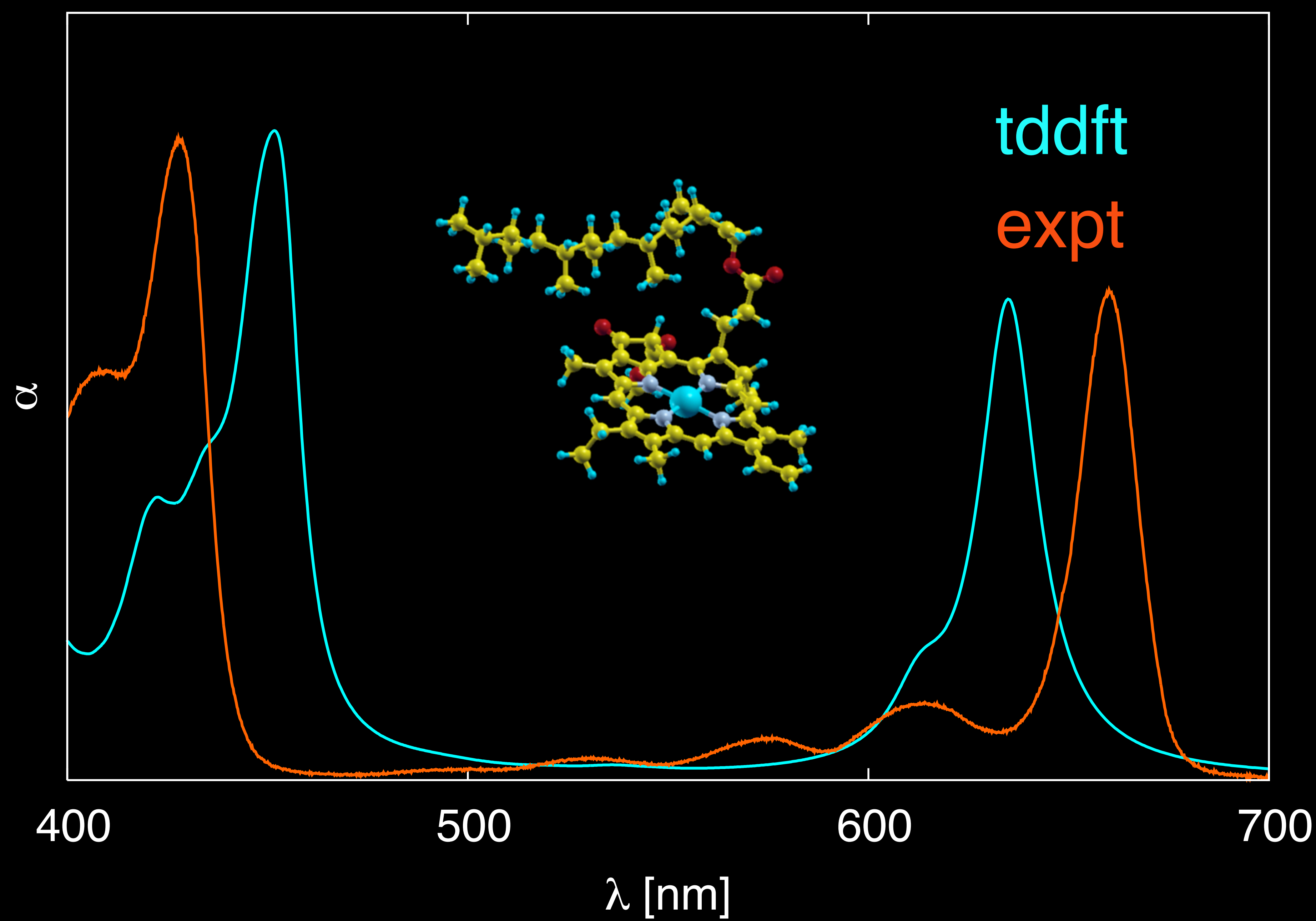
$$n'(\mathbf{r}) = \frac{1}{2}\sum_v \big(x_v(\mathbf{r}) + y_v(\mathbf{r})\big)\varphi^\circ_v(\mathbf{r})$$

chlorofyll a

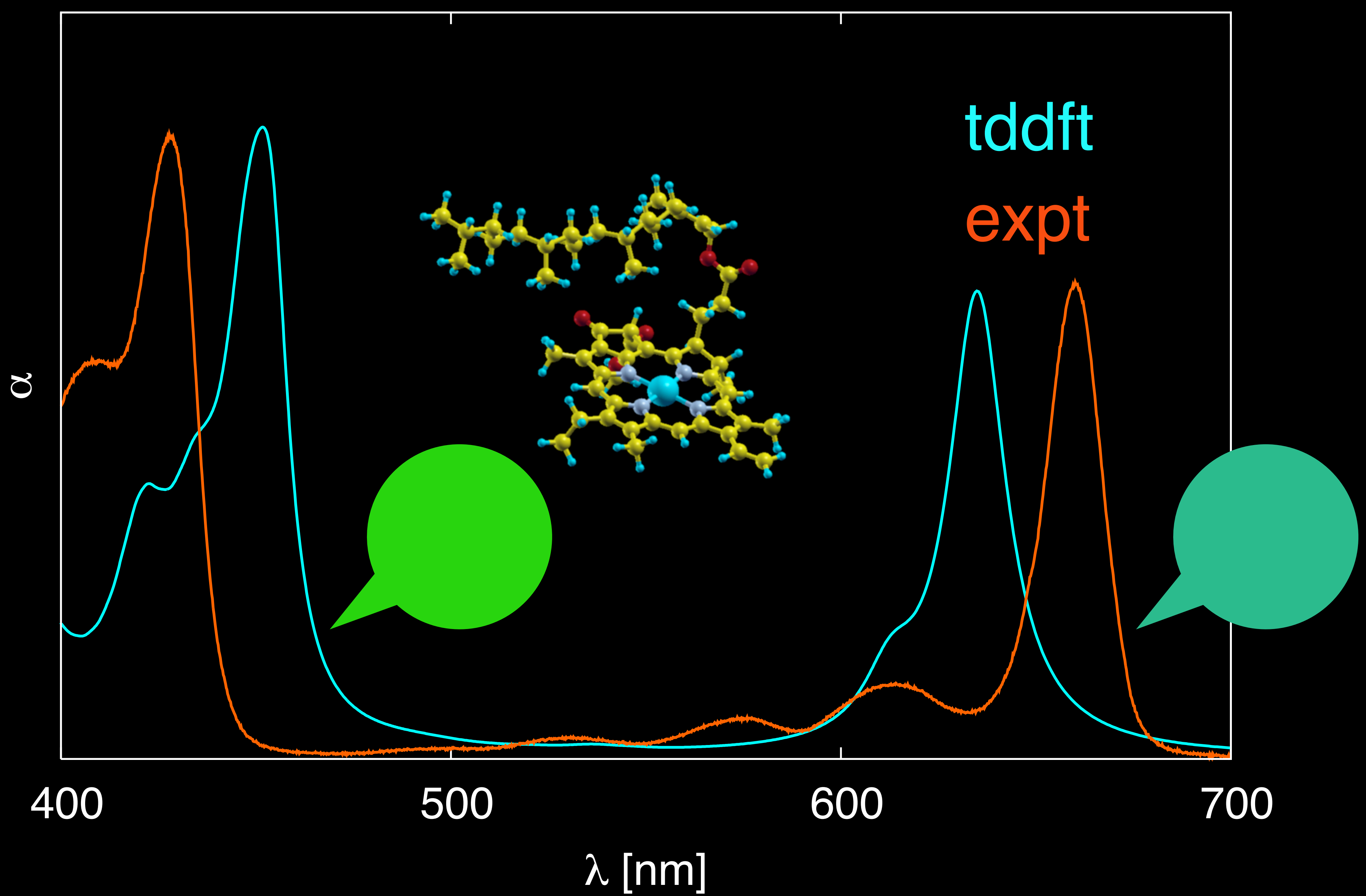


$C_{55}H_{72}MgN_4O$

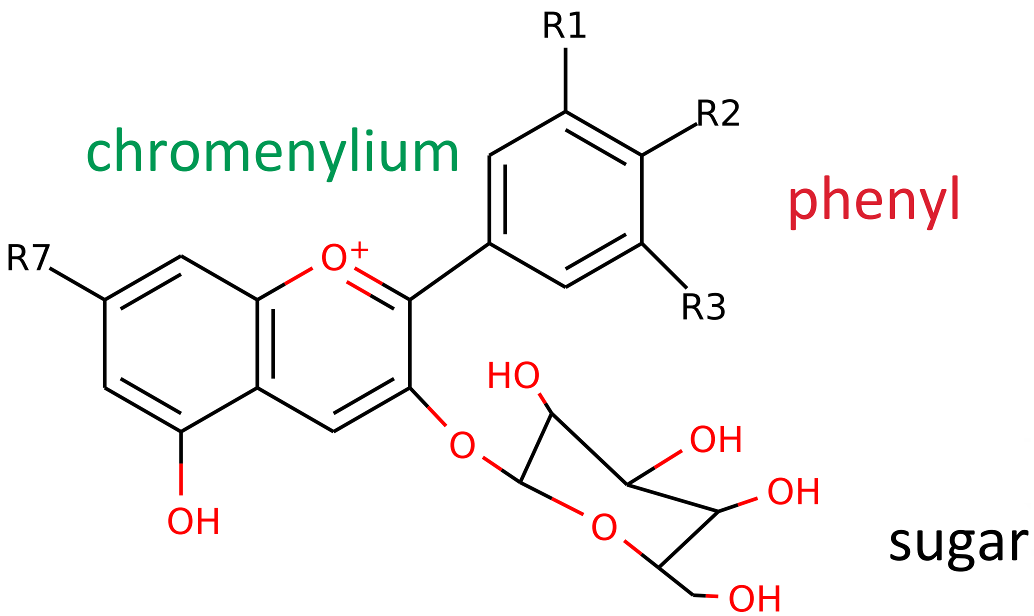
chlorofyll a

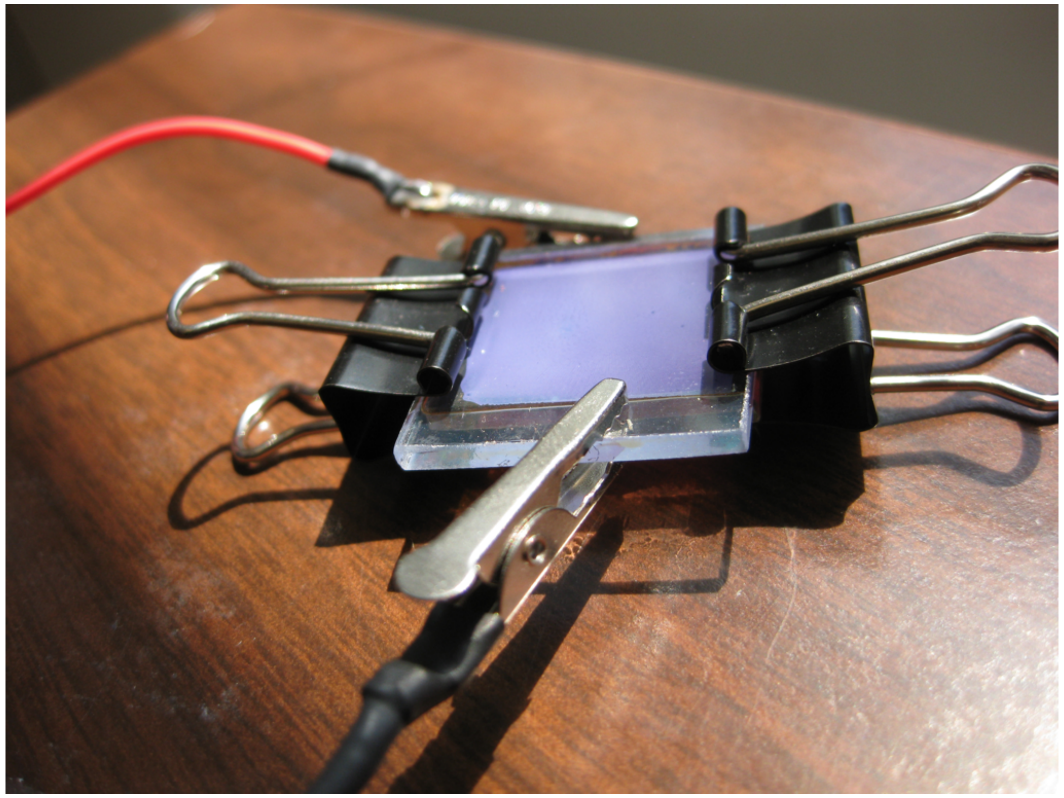


chlorofyll a



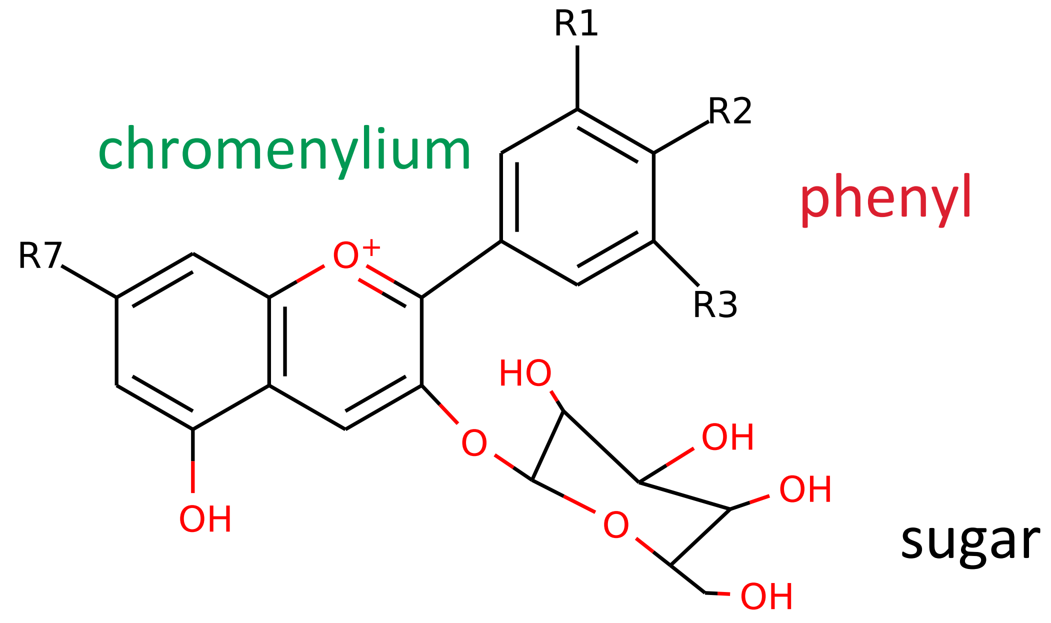
anthocyanins



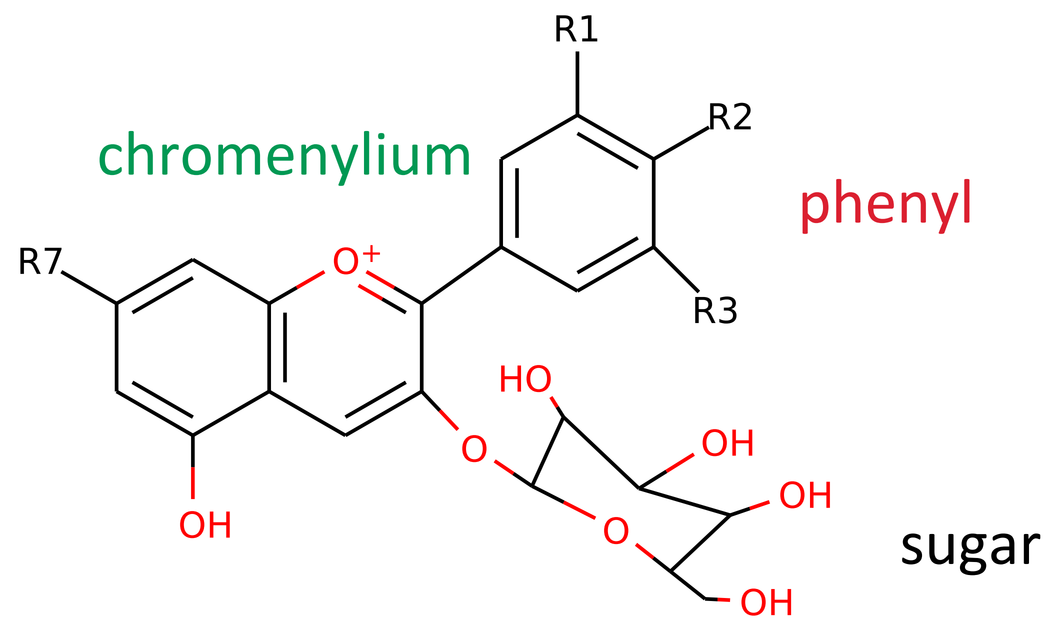


N.J. Cherepy, G.P Smestad, M. Grätzel, and J.Z Zhang, J. Phys. Chem. B **101**, 9342 (1997)

anthocyanins

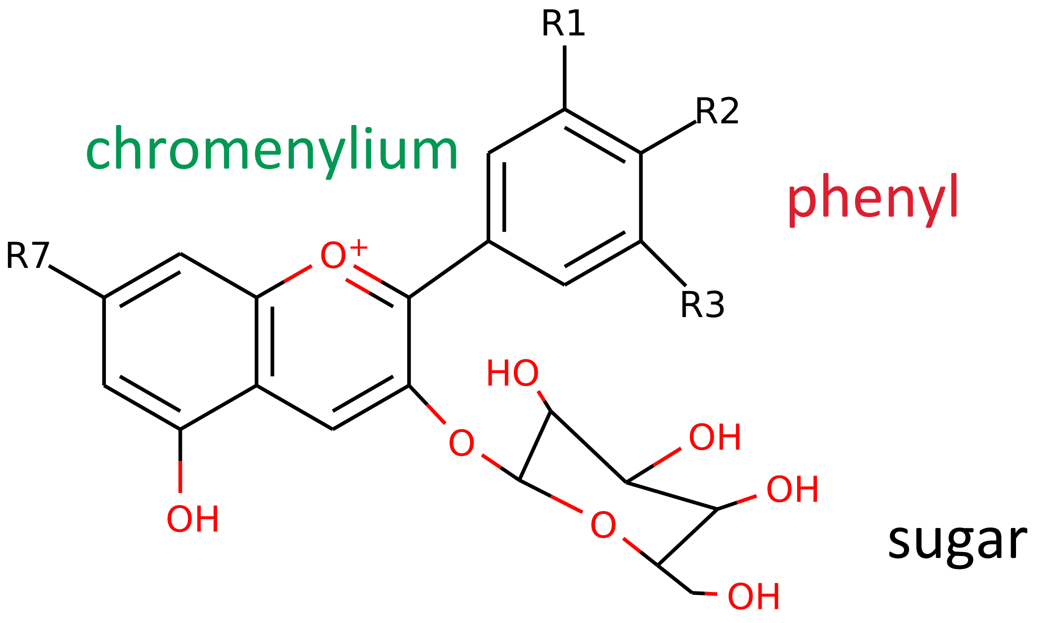


anthocyanins



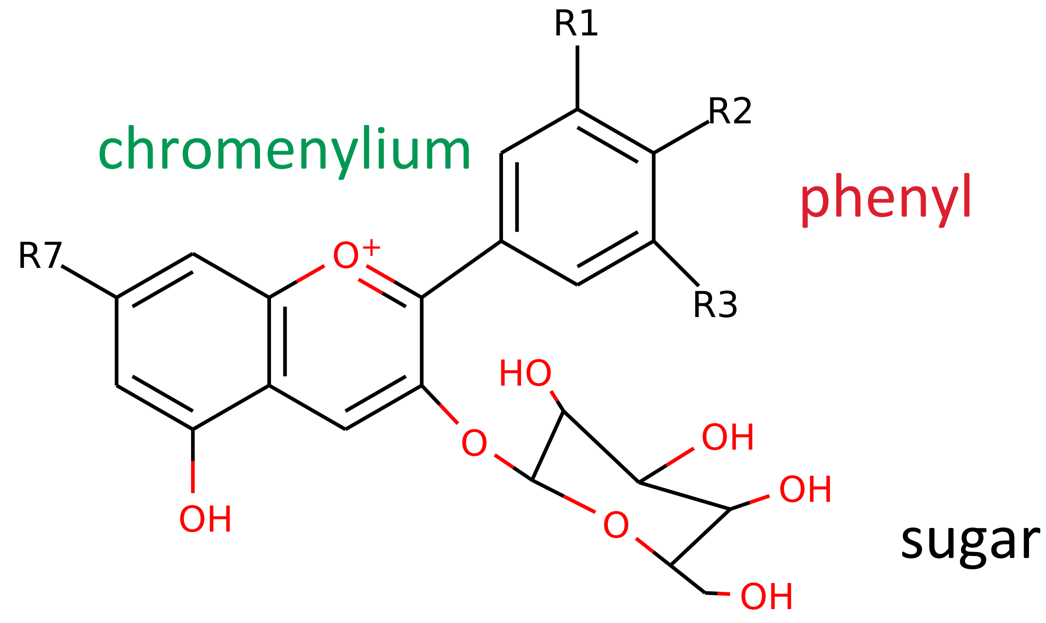
anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH

anthocyanins



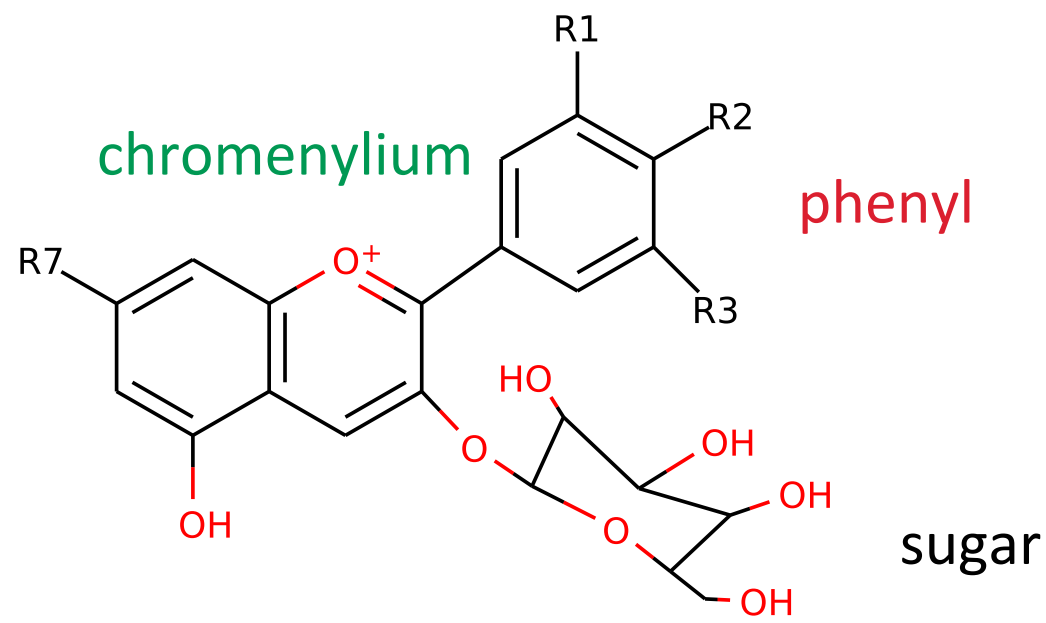
anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH
peonin	$-OCH_3$	−OH	−H	−OH

anthocyanins



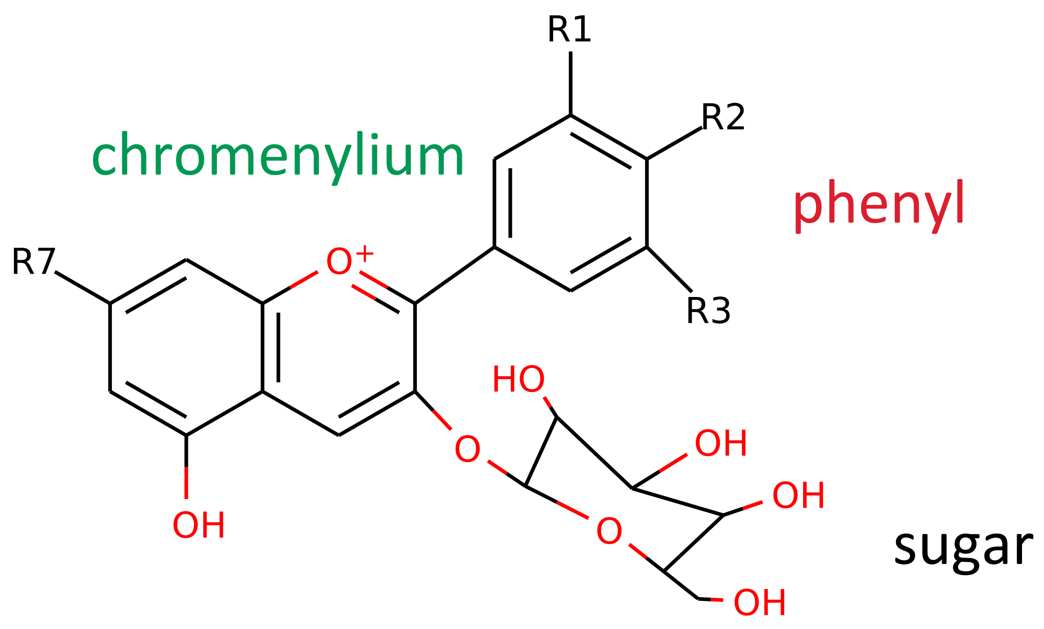
anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH
peonin	$-OCH_3$	−OH	−H	−OH
rosinin	−OH	−OH	−H	$-OCH_3$

anthocyanins



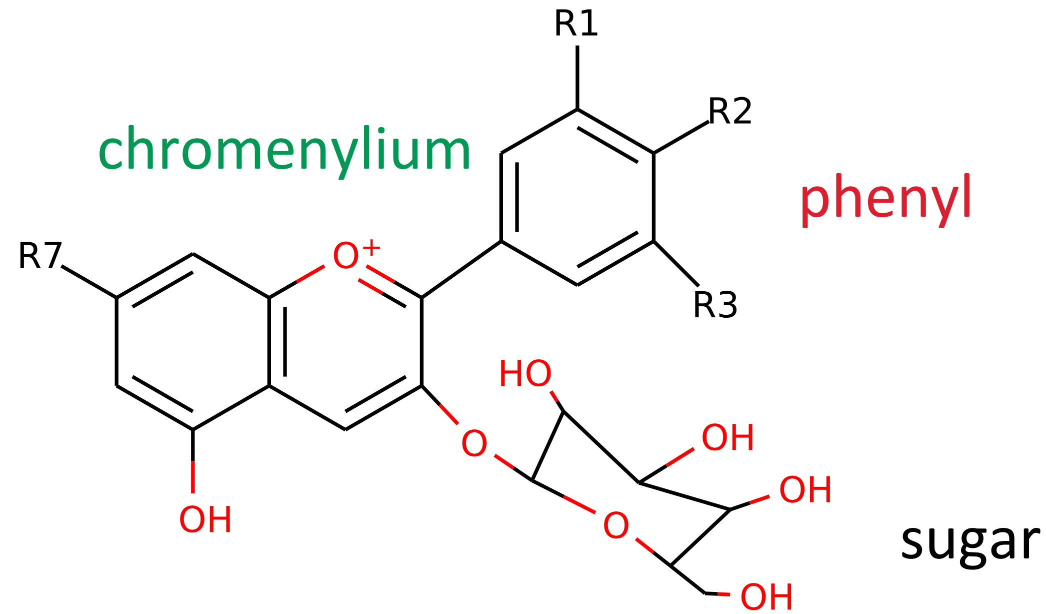
anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH
peonin	$-OCH_3$	−OH	−H	−OH
rosinin	−OH	−OH	−H	$-OCH_3$
malvin	$-OCH_3$	−OH	$-OCH_3$	−OH

anthocyanins



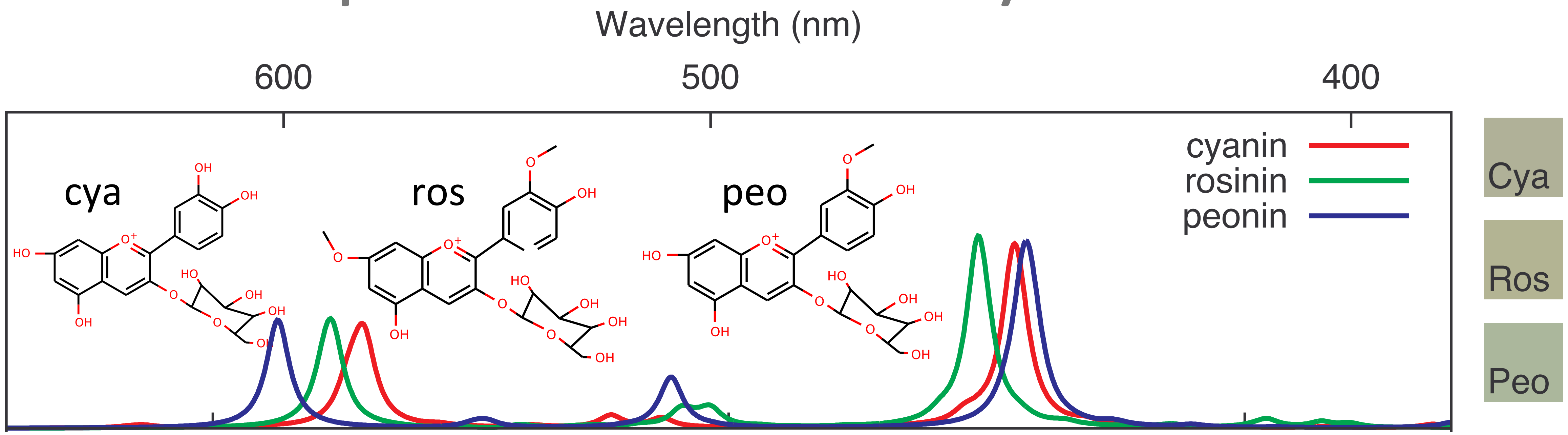
anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH
peonin	$-OCH_3$	−OH	−H	−OH
rosinin	−OH	−OH	−H	$-OCH_3$
malvin	$-OCH_3$	−OH	$-OCH_3$	−OH
delphinin	−OH	−OH	$-OCH_3$	−OH

anthocyanins

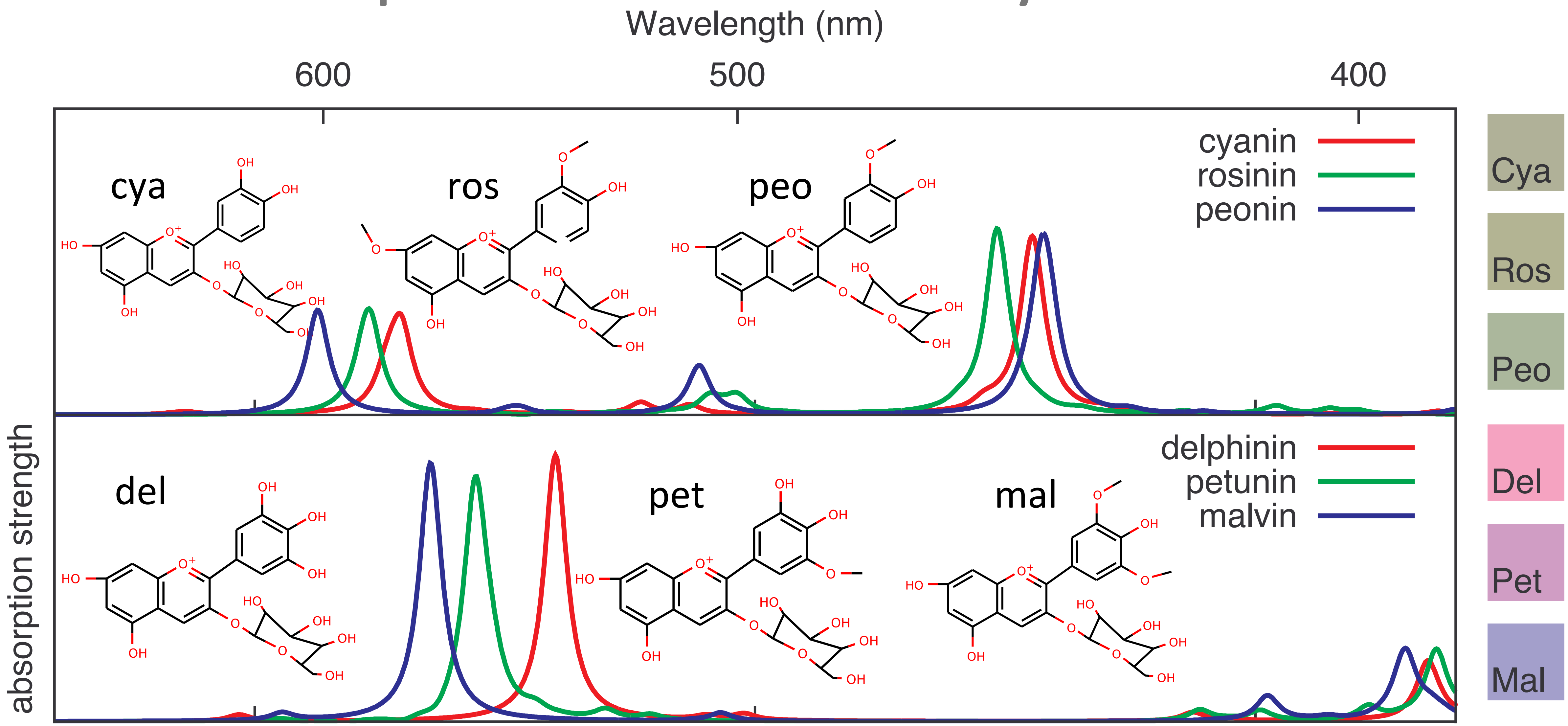


anthocyanin	R1	R2	R3	R7
cyanin	−OH	−OH	−H	−OH
peonin	$-OCH_3$	−OH	−H	−OH
rosinin	−OH	−OH	−H	$-OCH_3$
malvin	$-OCH_3$	−OH	$-OCH_3$	−OH
delphinin	−OH	−OH	$-OCH_3$	−OH
pelargonin	−H	−OH	−OH	−OH

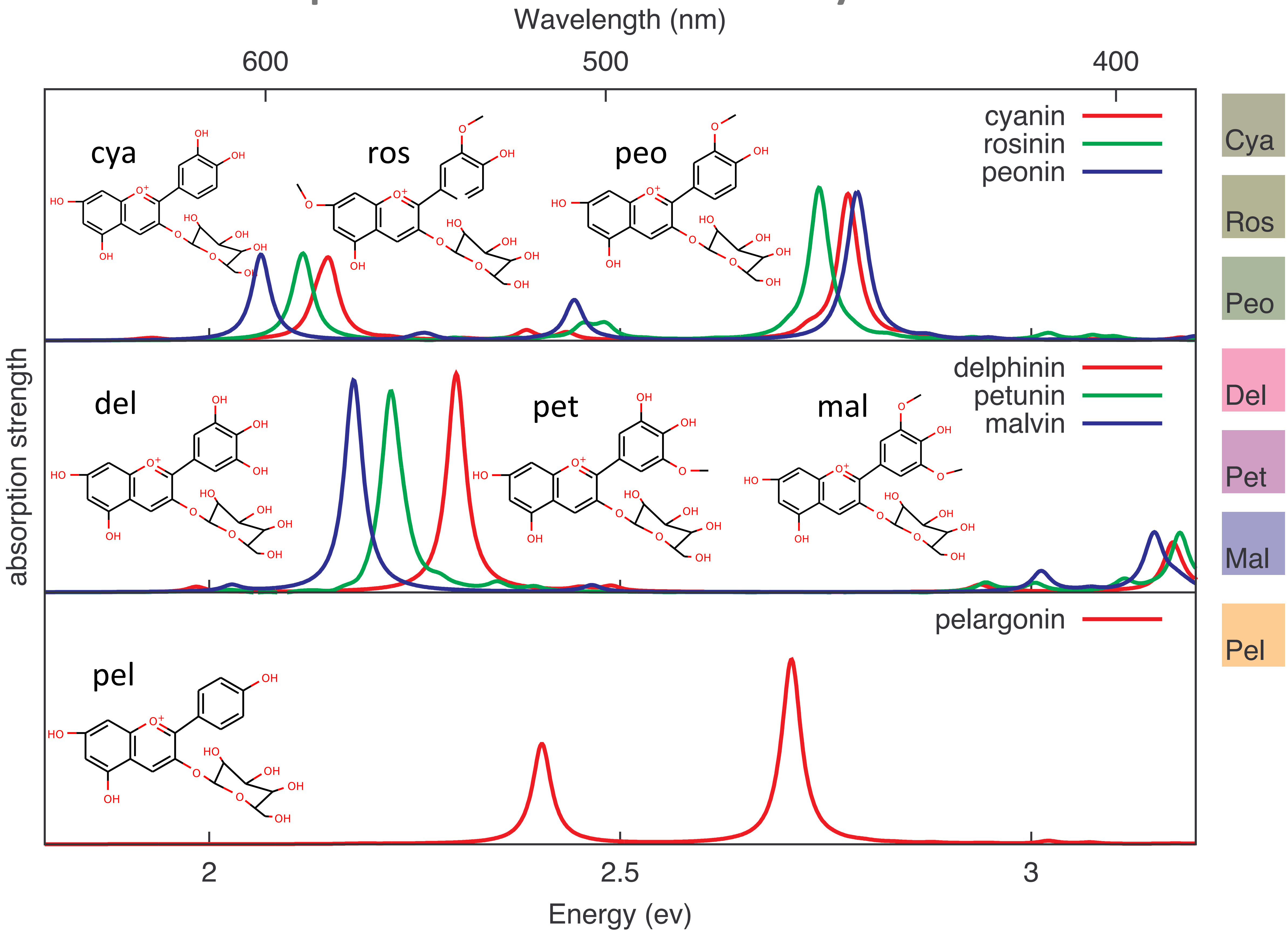
spectrum of anthocyanins



spectrum of anthocyanins



spectrum of anthocyanins



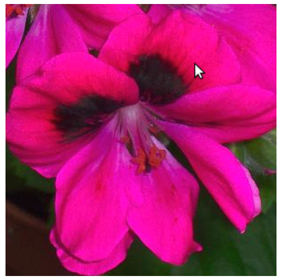
X. Ge, S. Binnie, A. Calzolari, and SB, in preparation

spectrum of anthocyanins

delphinin

delphinium

pelargonin

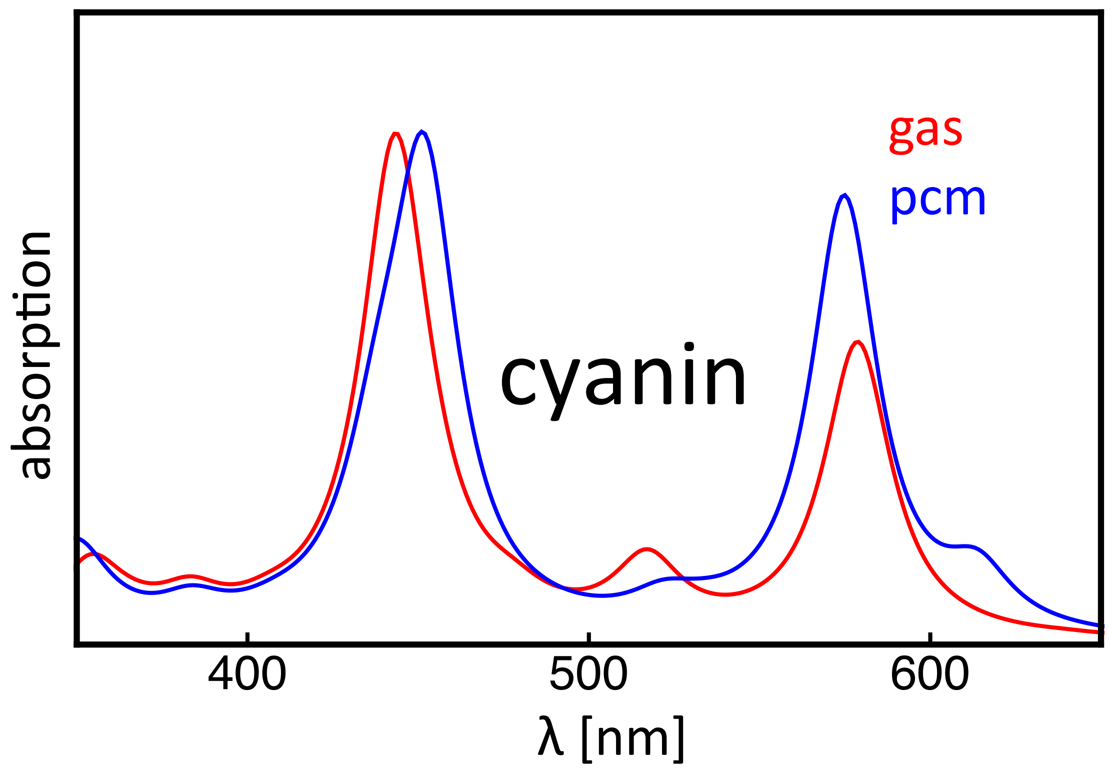


pelargonium

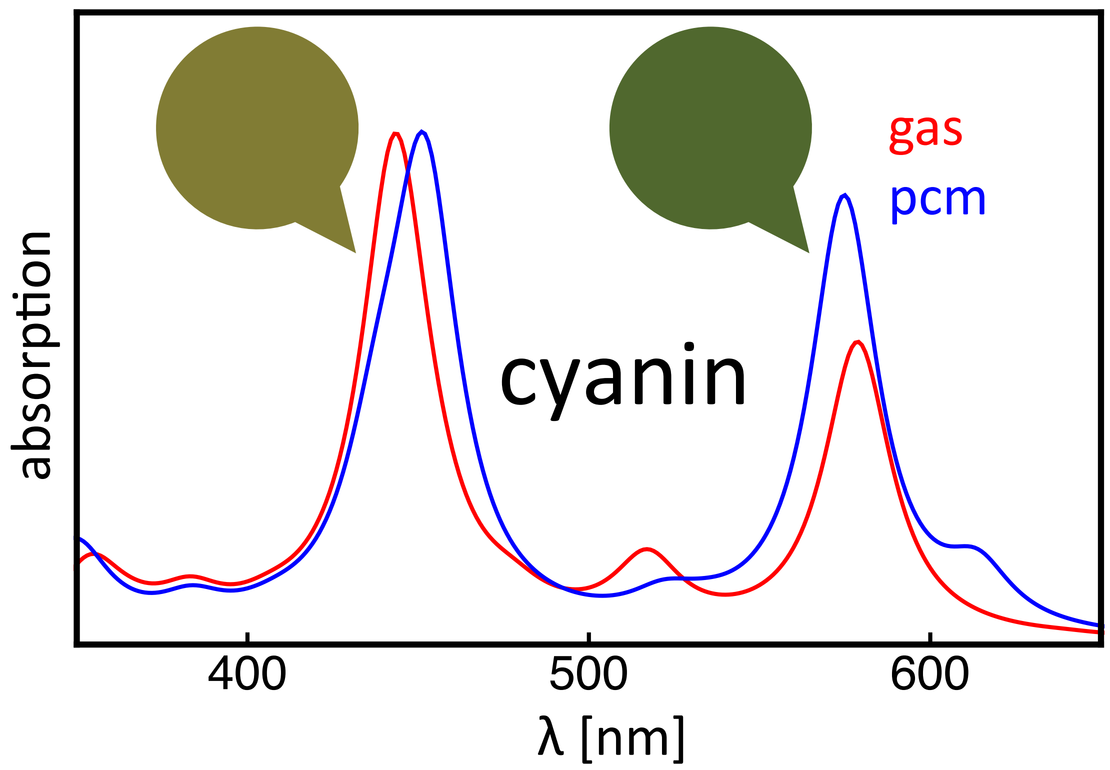
cyanin

blueberry

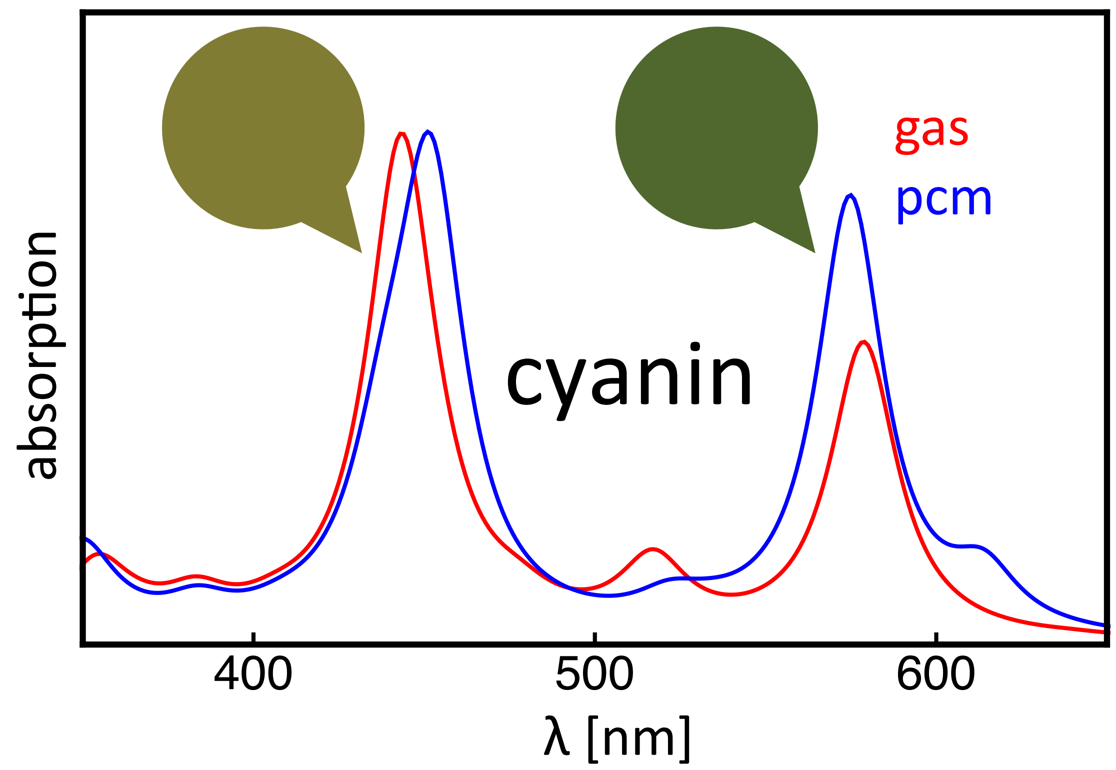
optical effect of the solvent

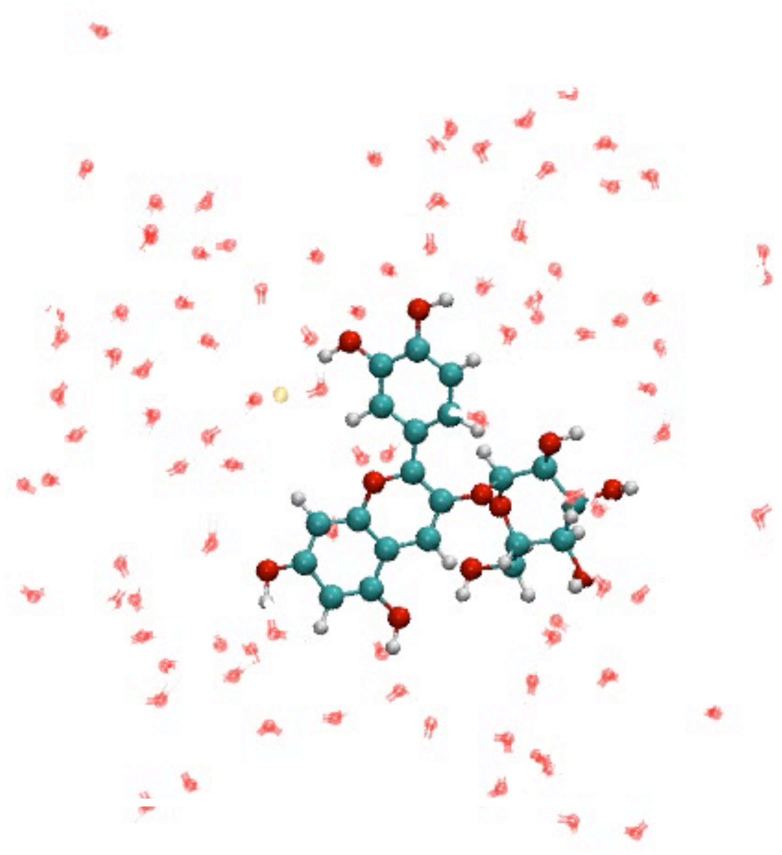


optical effect of the solvent



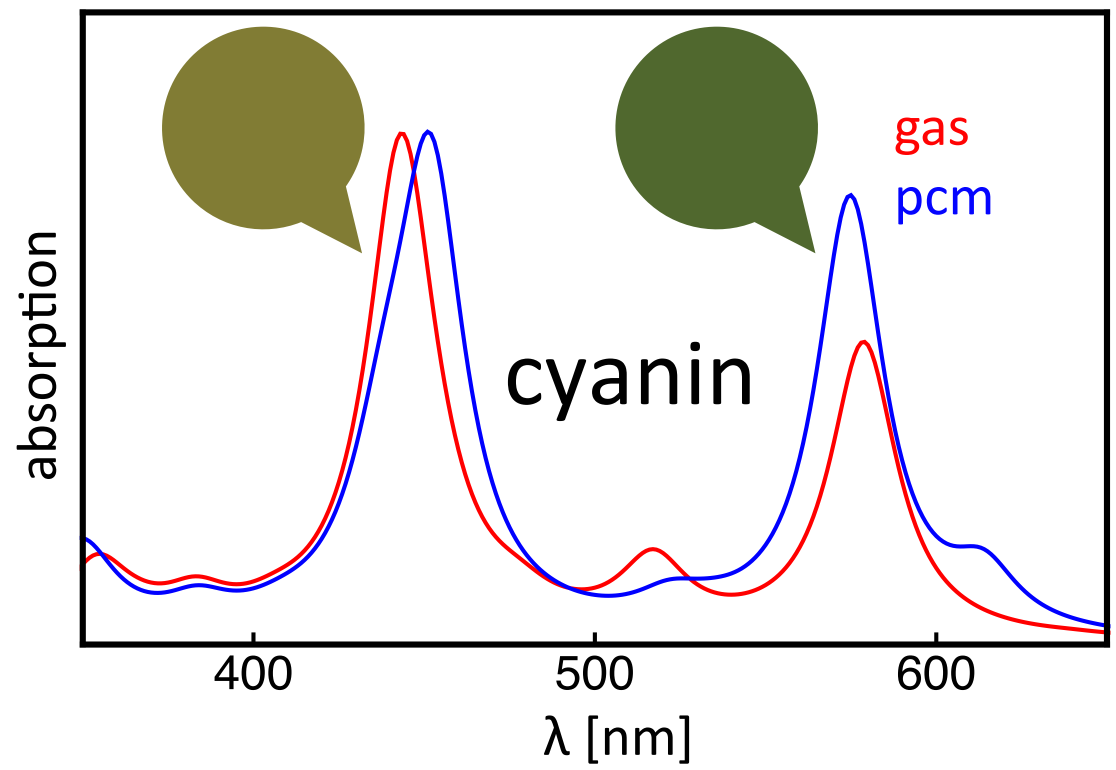
optical effect of the solvent

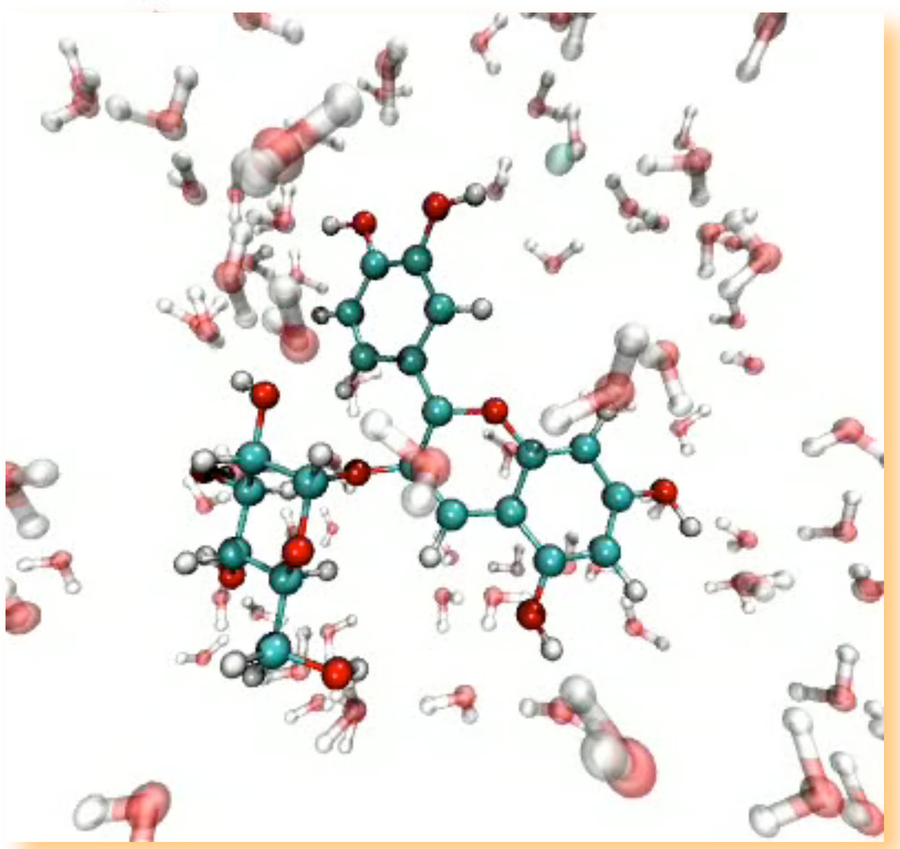


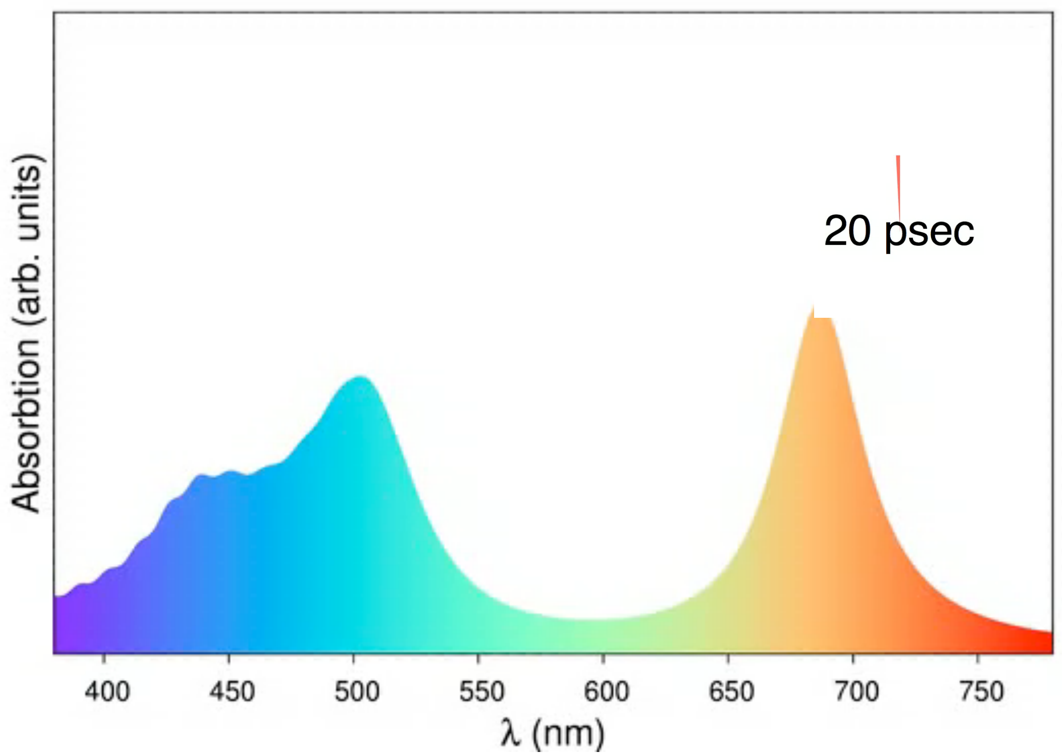


$C_{21}H_{21}O_{11}Cl@(H_2O)_{95}$
339 atoms
938 electrons

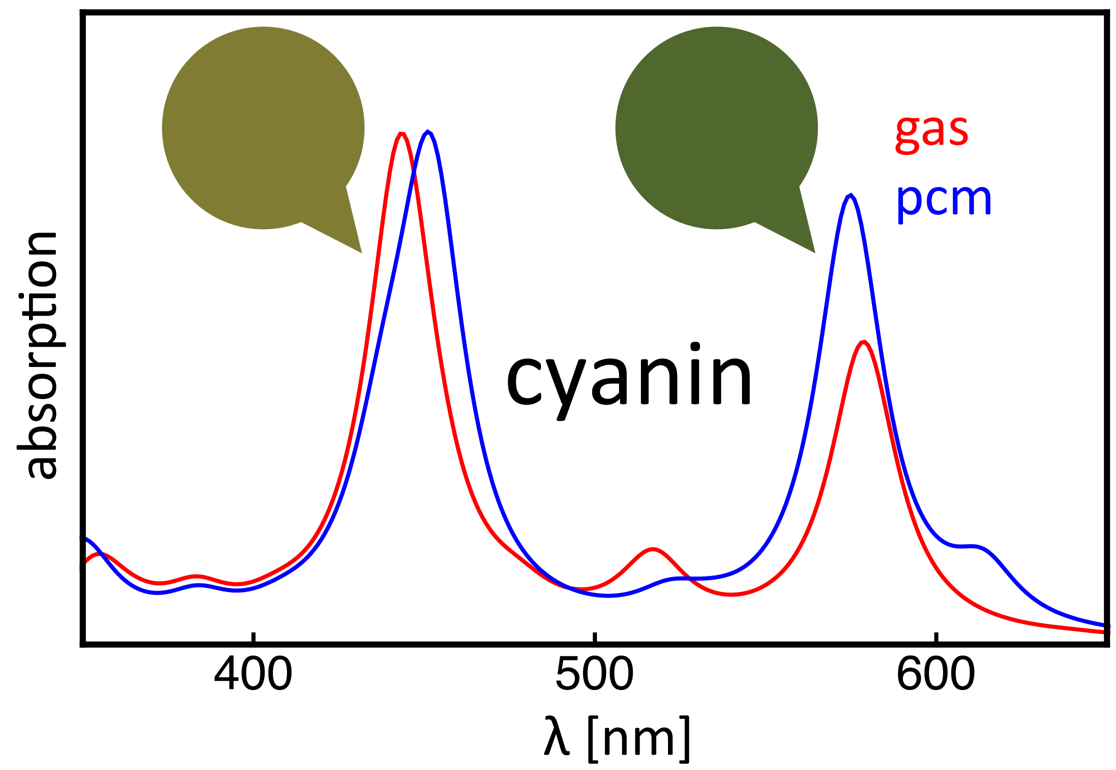
optical effect of the solvent

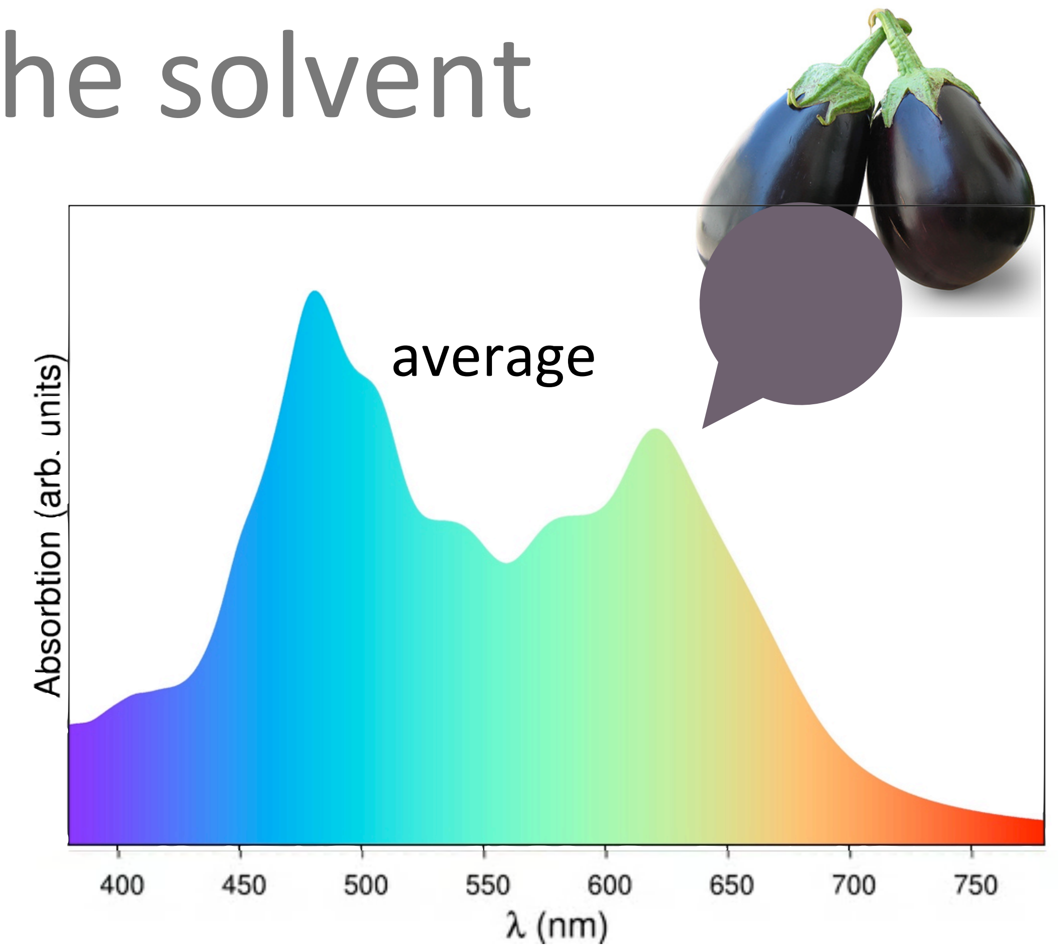


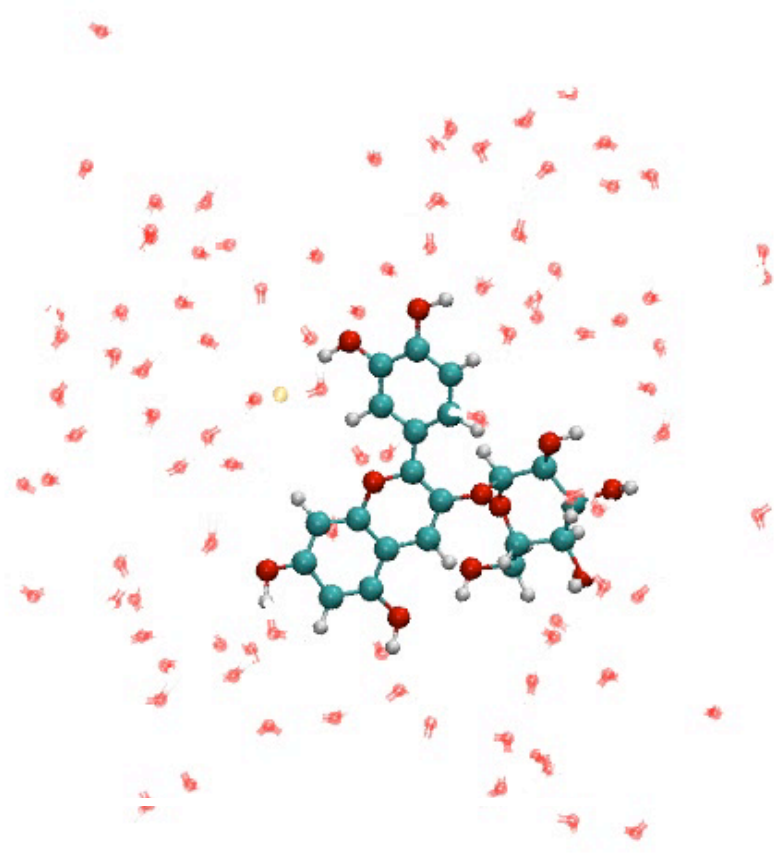


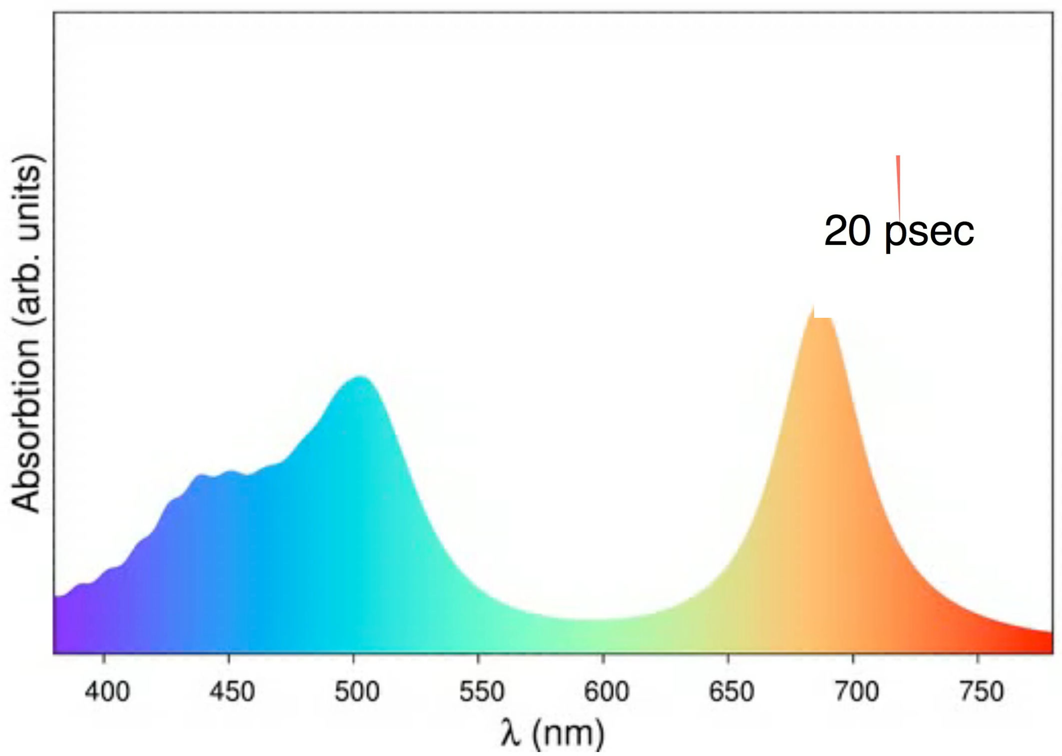


optical effect of the solvent

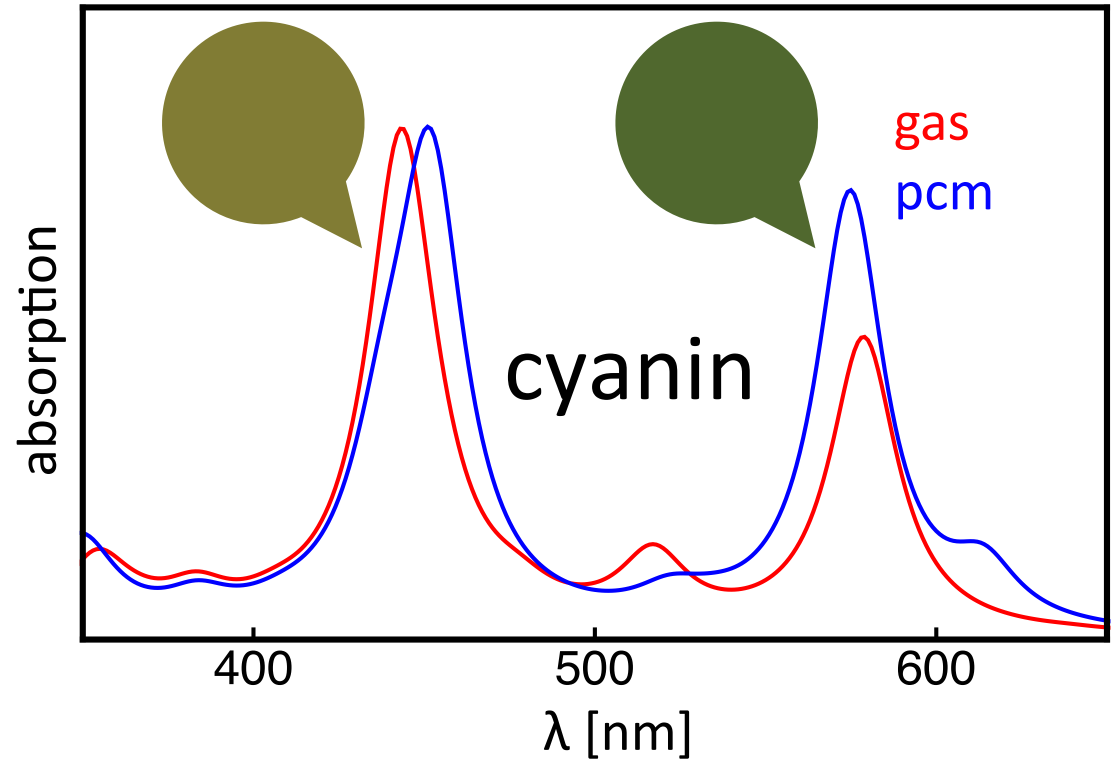


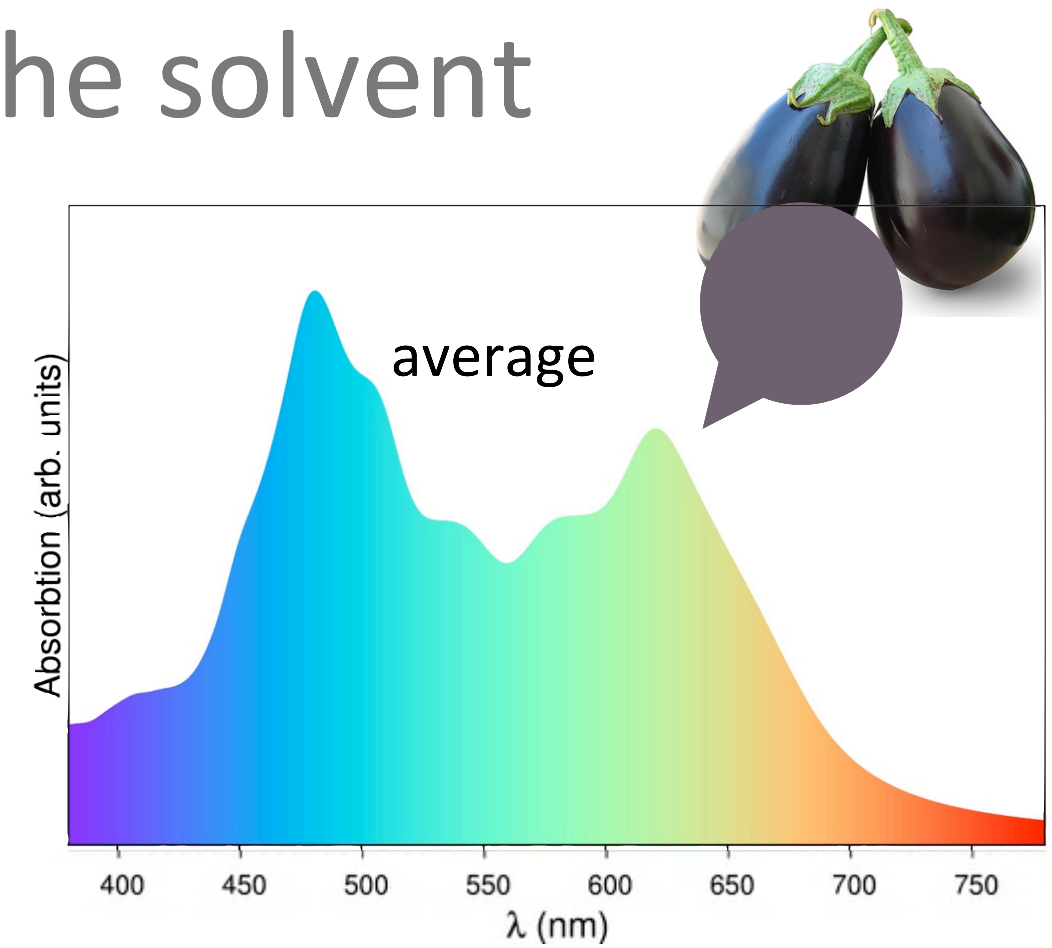


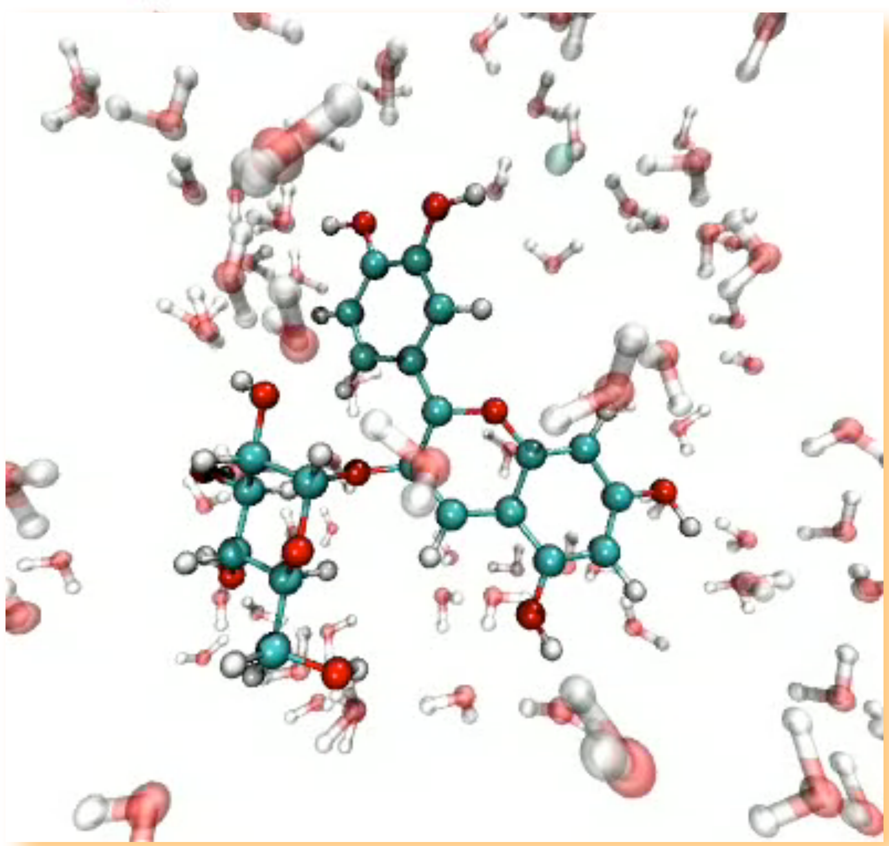


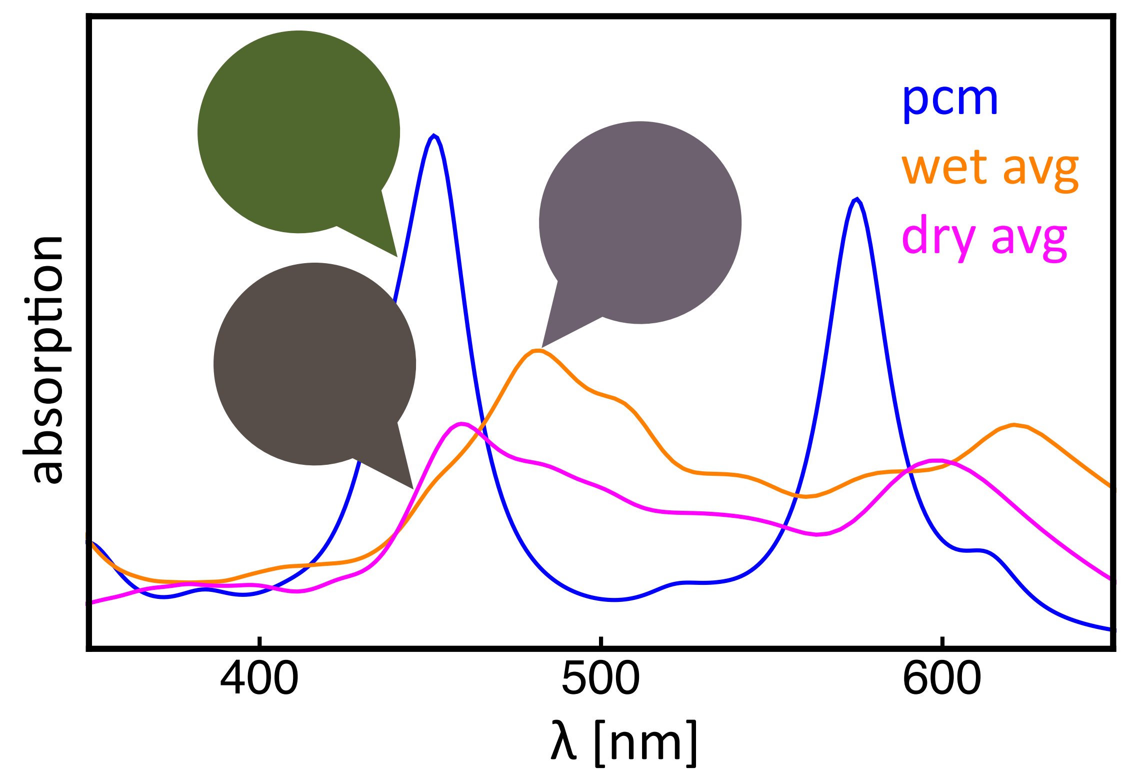


optical effect of the solvent









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

optical effect of the solvent

delphinin

pelargonin

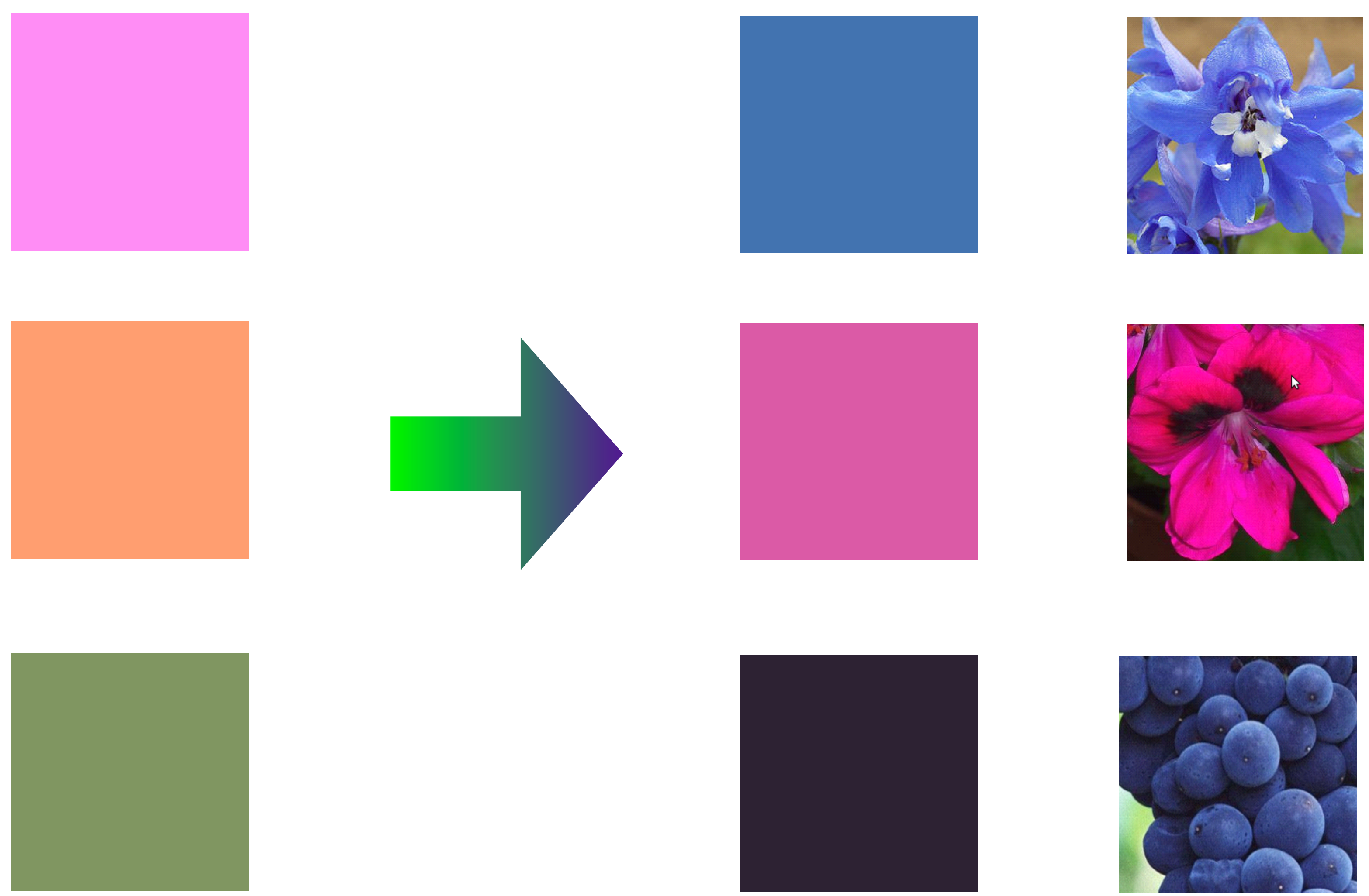
cyanin

optical effect of the solvent

delphinin

pelargonin

cyanin



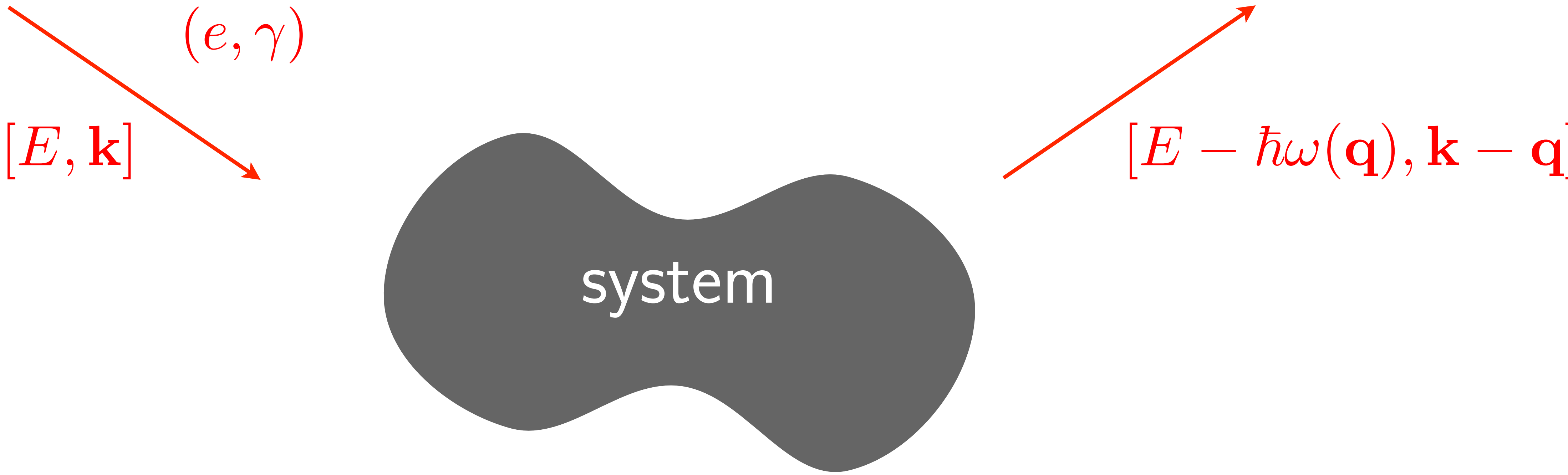
delphinium

pelargonium

blueberry

X. Ge, S. Binnie, A. Calzolari, and SB, in preparation

electron energy loss & inelastic X-ray scattering spectroscopies



$$\frac{d^2\sigma}{d\Omega_{\mathbf{q}}d\omega} \propto -\frac{4\pi e^2}{|\mathbf{q}|^2}\mathsf{Im}\chi(\mathbf{q},\mathbf{q};\omega)$$

traditional dielectric-matrix approach

$$\chi = \chi_0 + \chi_0 \cdot \kappa \cdot \chi$$

traditional dielectric-matrix approach

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}\delta(t-t') + \frac{\delta\mu_{xc}(\mathbf{r},t)}{\delta n(\mathbf{r}',t')}$$

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traditional dielectric-matrix approach

$$\begin{aligned} \chi &= \chi_0 + \chi_0 \cdot \kappa \cdot \chi \\ &= (1 - \chi_0 \kappa)^{-1} \cdot \chi_0 \end{aligned}$$

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$$
\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{cv} \Big[\frac{\phi_c^*(\mathbf{r})\phi_v(\mathbf{r})\phi_v^*(\mathbf{r}')\phi_c(\mathbf{r}')}{\omega - \epsilon_c + \epsilon_v + i\delta} - \frac{\phi_c^*(\mathbf{r}')\phi_v(\mathbf{r}')\phi_v^*(\mathbf{r})\phi_c(\mathbf{r})}{\omega + \epsilon_c - \epsilon_v + i\delta} \Big]
$$

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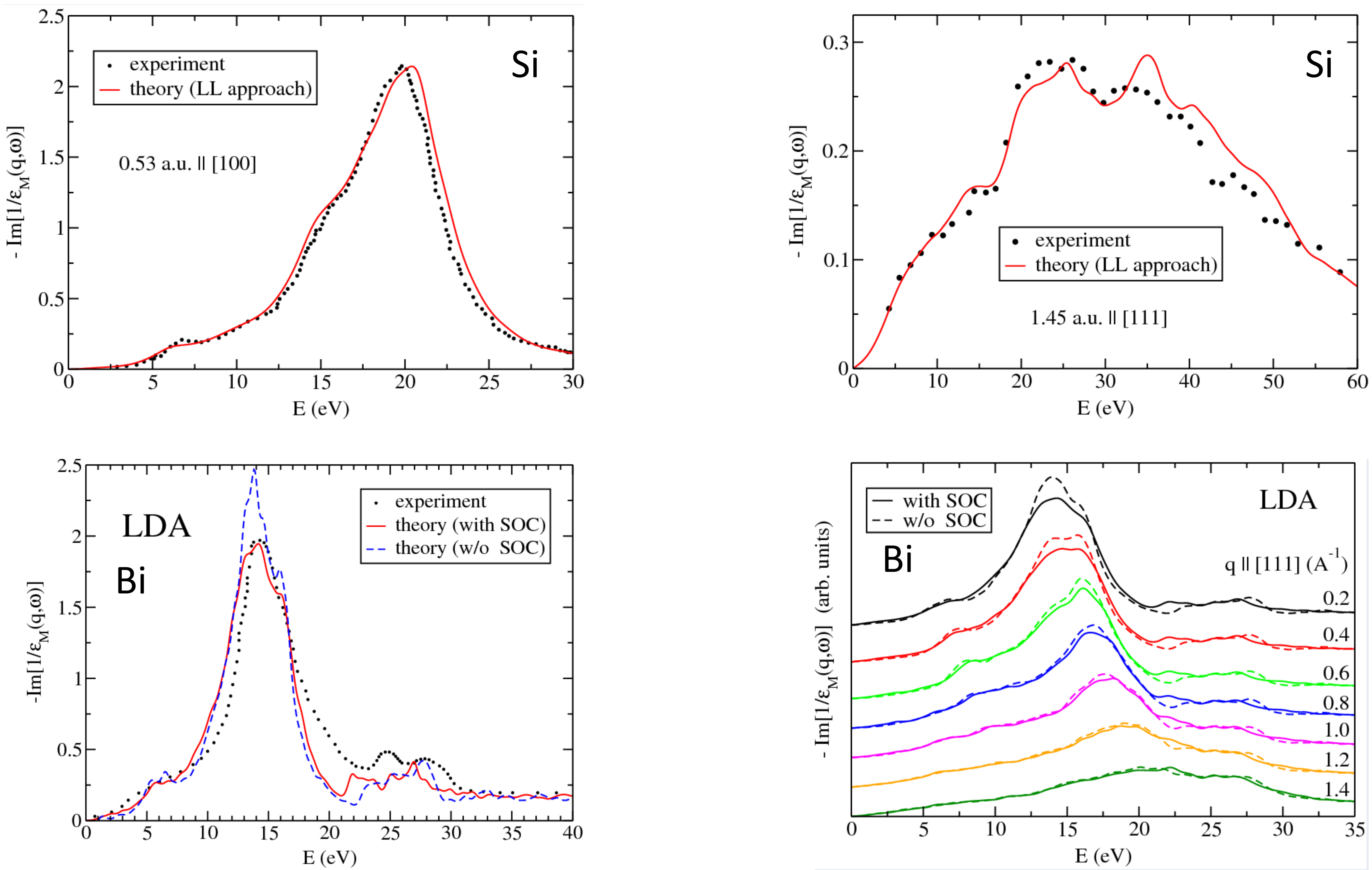
- ☹ Huge matrices need to be calculated [$O(N^2) \times O(N^2)$]
- ☹ Time consuming matrix operations [products, inversions: $O(N^3)$] need to be repeated for many different frequencies
- ☹ Worst of all, most of the information thus computed is wasted

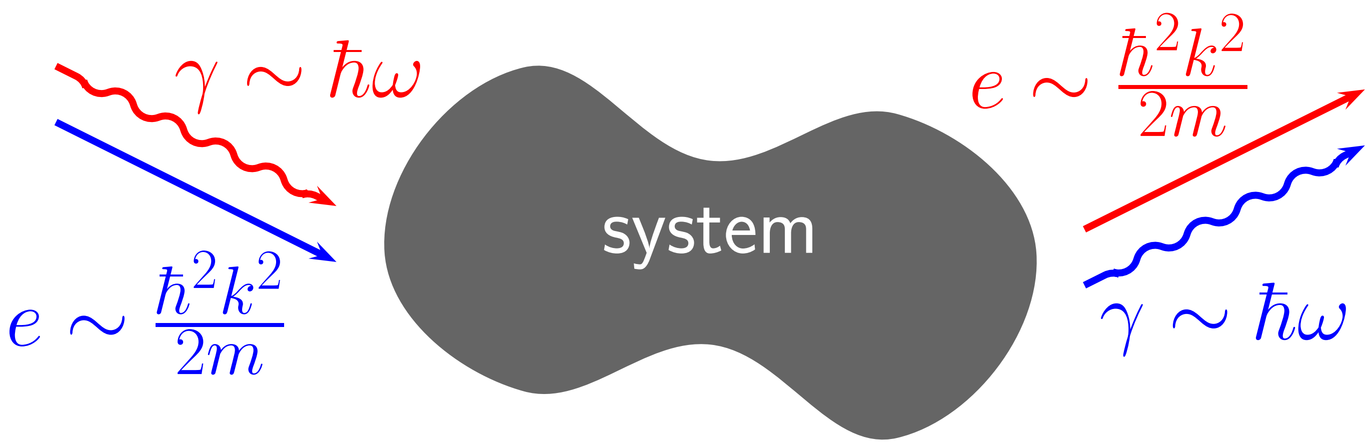
do Lanczos!

EELS & IXS spectra from Liouville-Lanczos TDDF(P)T



I. Timrov, N. Vast, R. Gebauer, & SB, PRB **88**, 64301 (2013) photoemission spectroscopy …

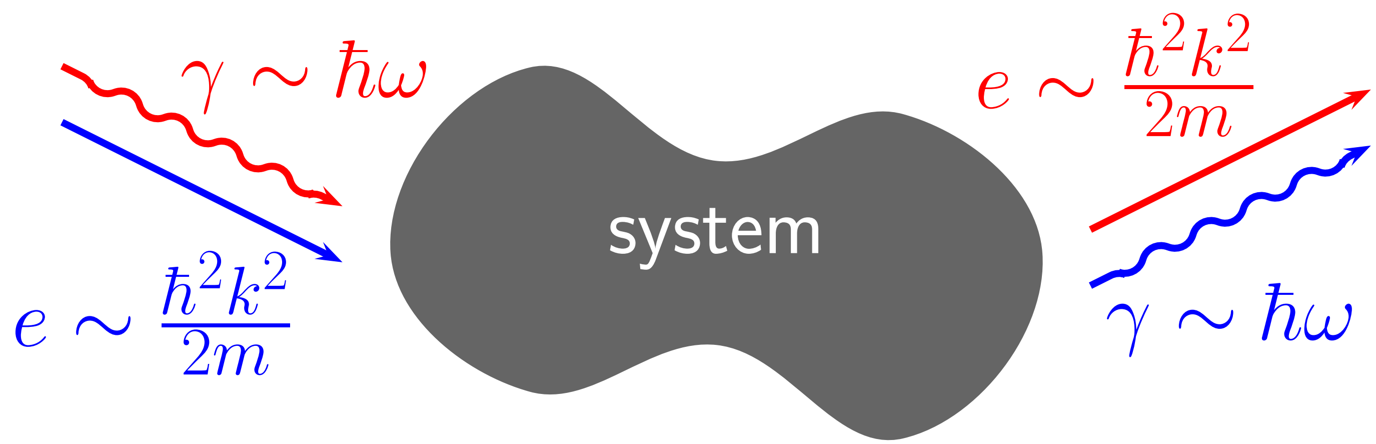
photoemission spectroscopy



$$E_N + \hbar\omega = E^\star_{N-1} + \frac{\hbar^2 k^2}{2m}$$ photoemission

$$E_N + \frac{\hbar^2 k^2}{2m} = E^\star_{N+1} + \hbar\omega$$ inverse photoemission

photoemission spectroscopy



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$$\left(-\frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_n(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_n)\psi_n(\mathbf{r}')d\mathbf{r}' = \epsilon_n \psi_n(\mathbf{r})$$

$$\epsilon_n = \begin{cases} E_N - E^\star_{N-1} & \text{if } \epsilon_n < \mu \\ E^\star_{N+1} - E_N & \text{if } \epsilon_n > \mu \end{cases}$$

the GW approximation

$$\Sigma(\mathbf{r},\mathbf{r}';t-t') \approx iG(\mathbf{r},\mathbf{r}';t-t')W(\mathbf{r},\mathbf{r}';t-t')$$

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$$iG(x,x') = \begin{cases} \langle\Psi_N|\hat{\psi}(x)\hat{\psi}^\dagger(x')|\Psi_N\rangle \approx \sum_c \psi_c(\mathbf{r})\psi_c^*(\mathbf{r}')\mathrm{e}^{-i\epsilon_c(t-t')} & t \geq t' \\ -\langle\Psi_N|\hat{\psi}^\dagger(x')\hat{\psi}(x)|\Psi_N\rangle \approx -\sum_v \psi_v(\mathbf{r})\psi_v^*(\mathbf{r}')\mathrm{e}^{-i\epsilon_v(t-t')} & t < t' \end{cases}$$

$$W = \frac{1}{|\mathbf{r}-\mathbf{r}'|}\delta(t-t') + \int \frac{1}{|\mathbf{r}-\mathbf{r}''|}\Pi(\mathbf{r}'',\mathbf{r}''';t-t')\frac{1}{|\mathbf{r}'''-\mathbf{r}'|}d\mathbf{r}''d\mathbf{r}'''$$

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$\Sigma_X \mapsto$ Hartree-Fock

$\Sigma_C \mapsto$ GW

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how is that?

- ☹ the calculation of the screened interaction requires the manipulation of huge matrices
- ☹ the calculation of the electronic polarizability and electron self-energy requires extensive sums over virtual states

choosing a (reduced) basis for the polarizability

$$\Pi(\mathbf{r},\mathbf{r}',t-t') = \frac{\delta n(\mathbf{r},t)}{\delta V_{ext}(\mathbf{r}',t')}$$

$$\tilde{\Pi}(\mathbf{r},\mathbf{r}',\omega) = \tilde{P}\cdot(1-v\cdot\tilde{P})^{-1}$$

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- most important eigenvectors of $P(t = 0)$ (Umari, 2010)
- a decent model would also do ...

avoiding the sum over virtual states

$$\begin{aligned} P(\mathbf{r},\mathbf{r}';i\omega) &= 2\text{Re}\sum_{cv}\psi_c(\mathbf{r})\psi_v(\mathbf{r})\psi_c(\mathbf{r}')\psi_v(\mathbf{r}')\frac{1}{i\omega-\epsilon_c+\epsilon_v} \\ &\doteq \sum_{\alpha\beta}\Phi_\alpha(\mathbf{r})\Phi_\beta(\mathbf{r}')P_{\alpha\beta}(i\omega) \end{aligned}$$

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do Lanczos!

(a similar trick can be used to calculate matrix elements of Σ_c)

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&= 2\mathrm{Re}\sum_{v,lm}T_{v\alpha,l}T_{v\beta,m}\langle t_l|(i\omega+\epsilon_v-H)^{-1}|t_m\rangle
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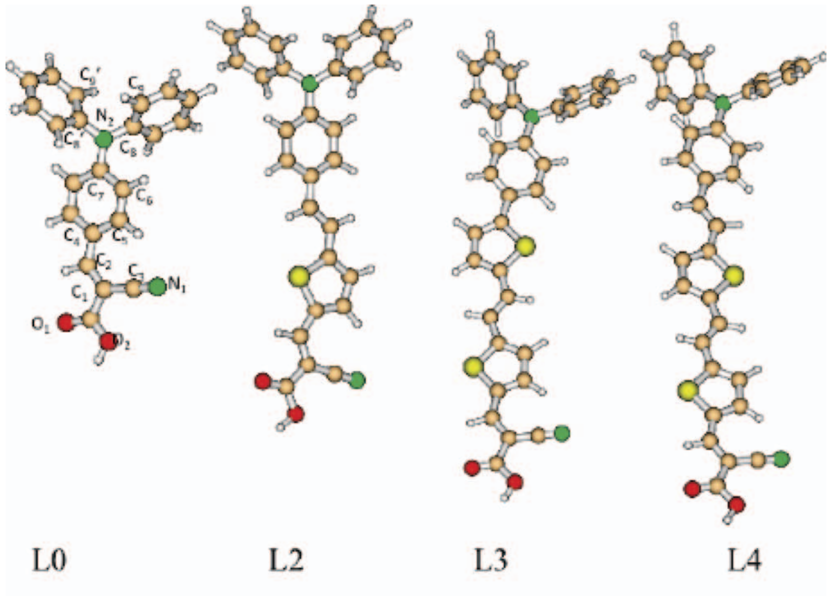
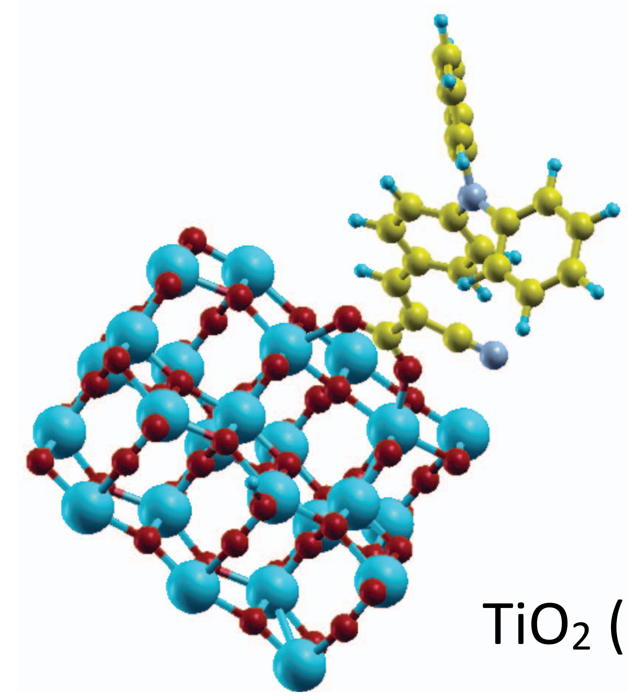
P. Umari, G. Stenuit, and S. Baroni, Phys. Rev. B **81**, 115104 (2010)

energy levels in all-organic DSSCs



triphenylamine (TPA)- based sensitizers



TiO_2 (010)

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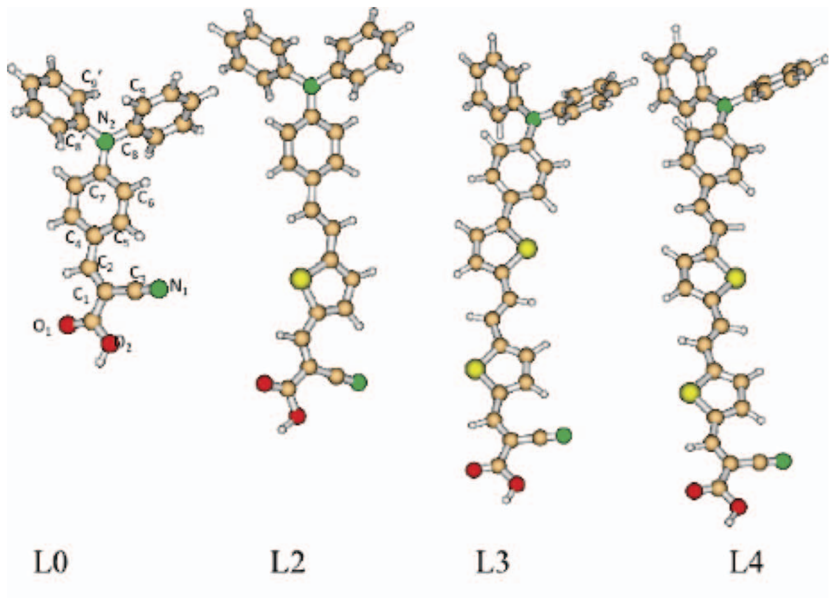

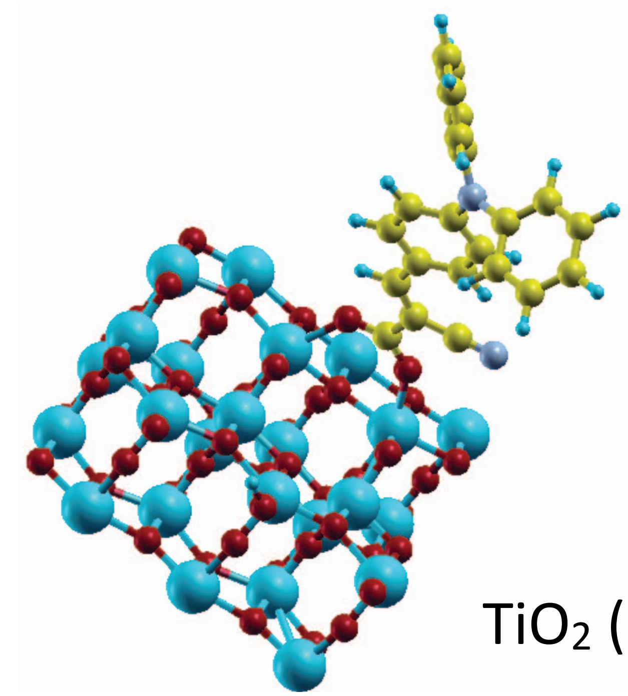

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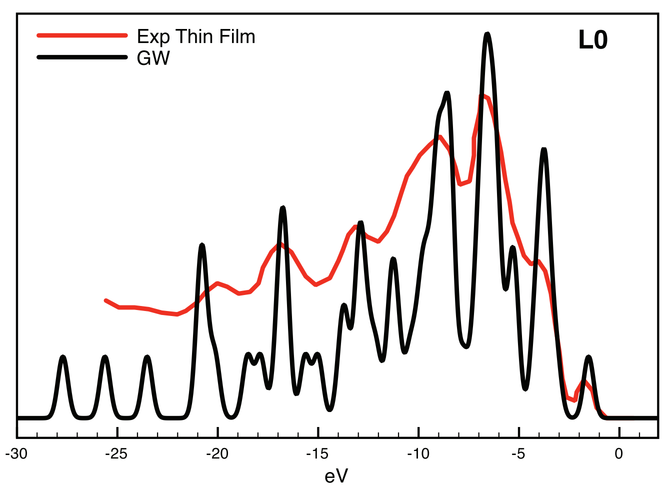

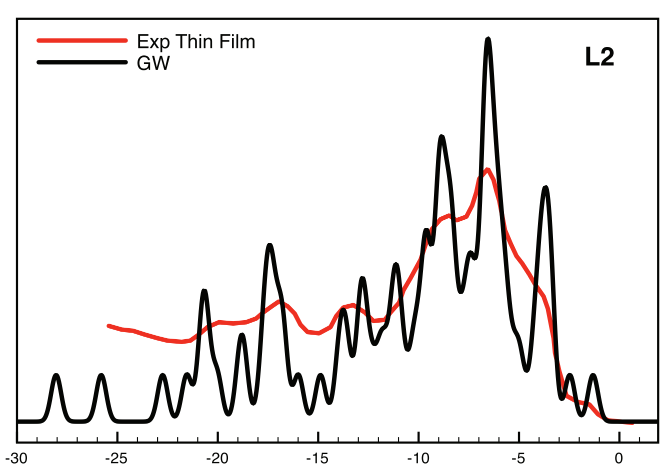

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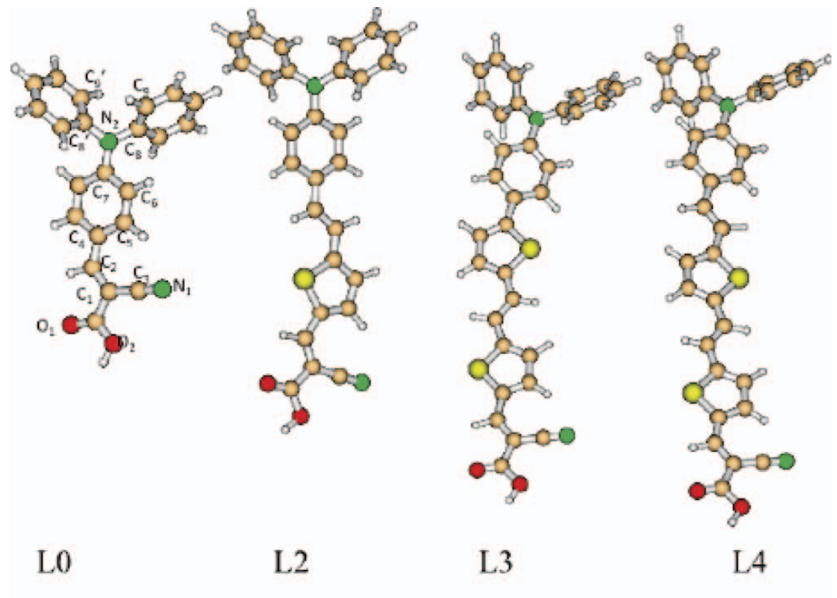

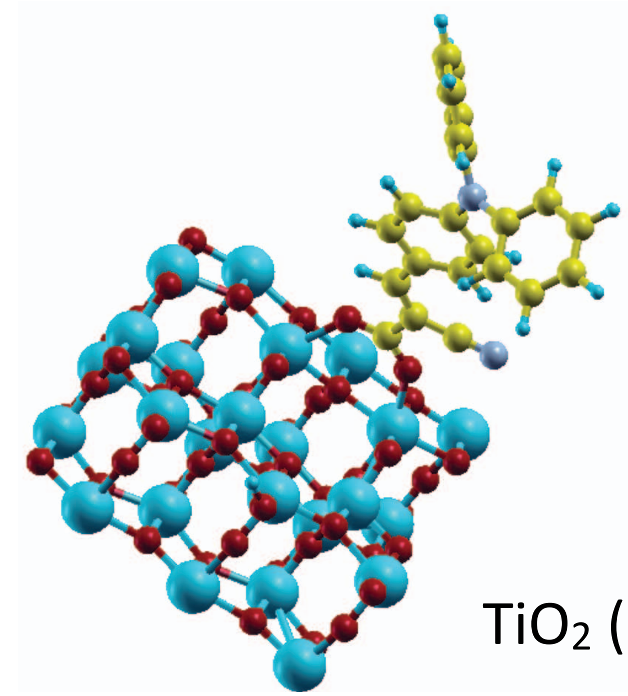

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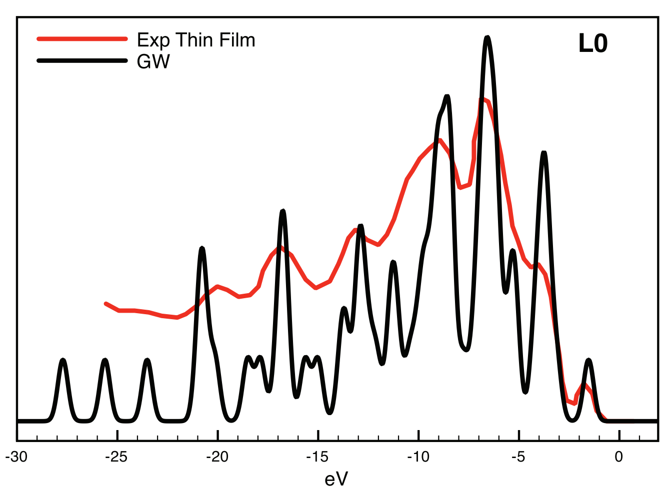

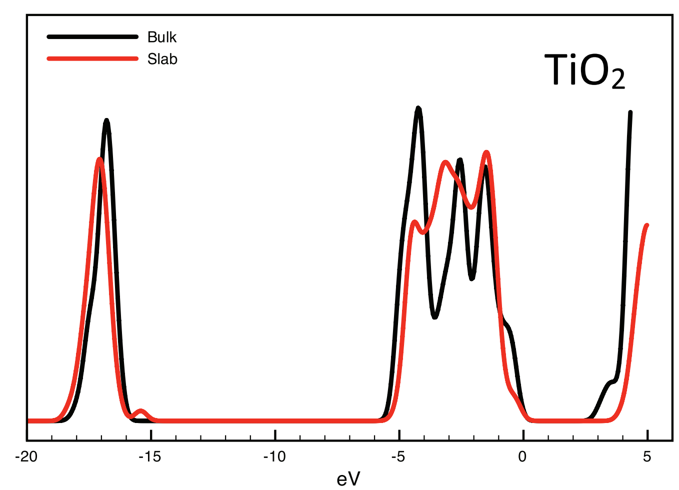

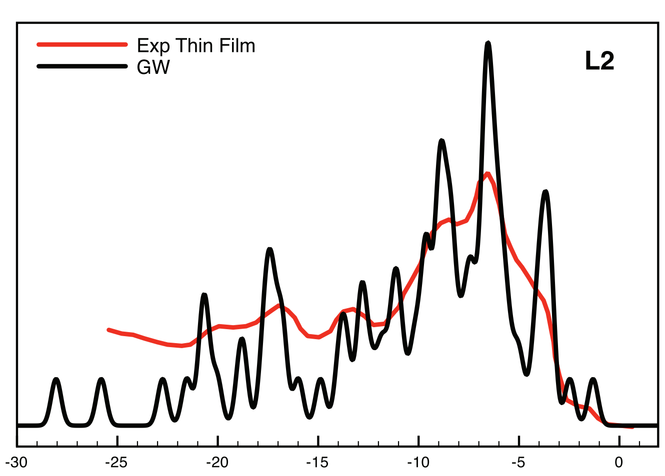

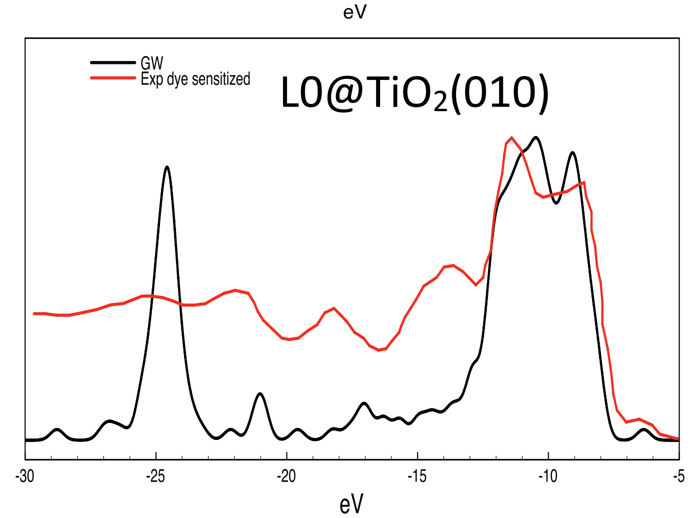

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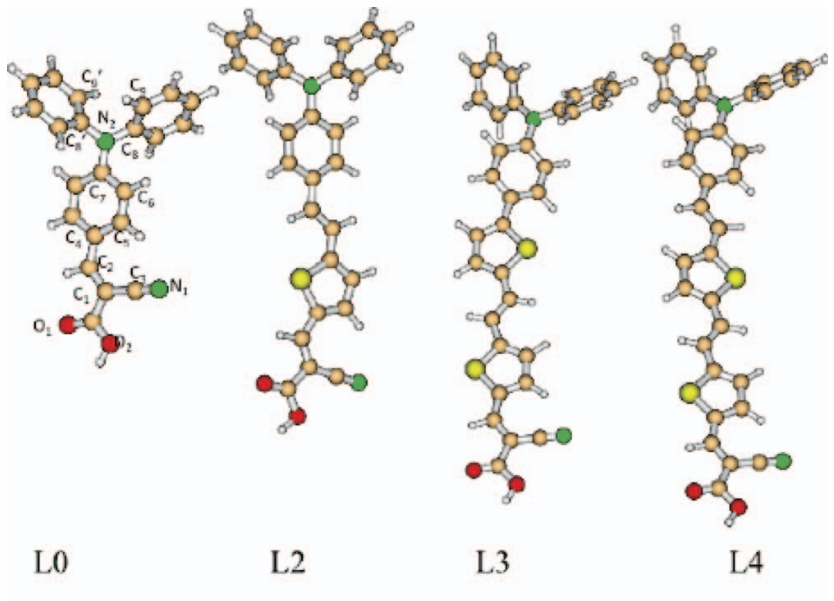

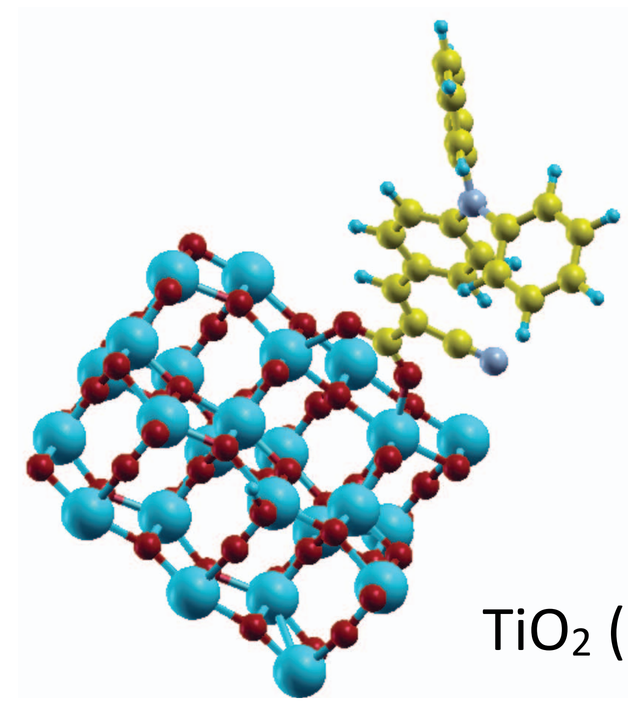

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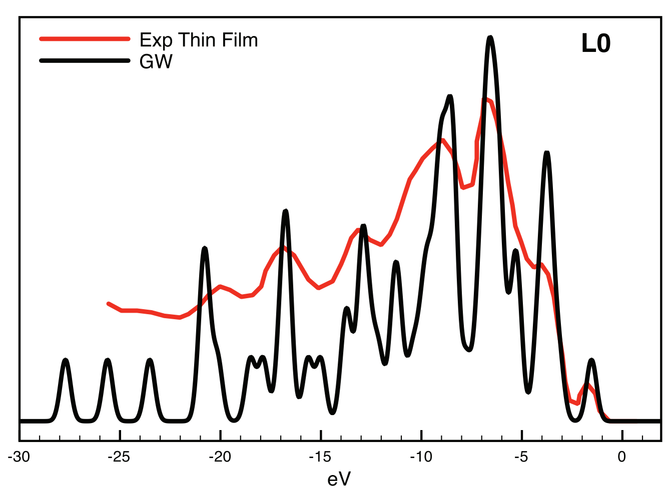

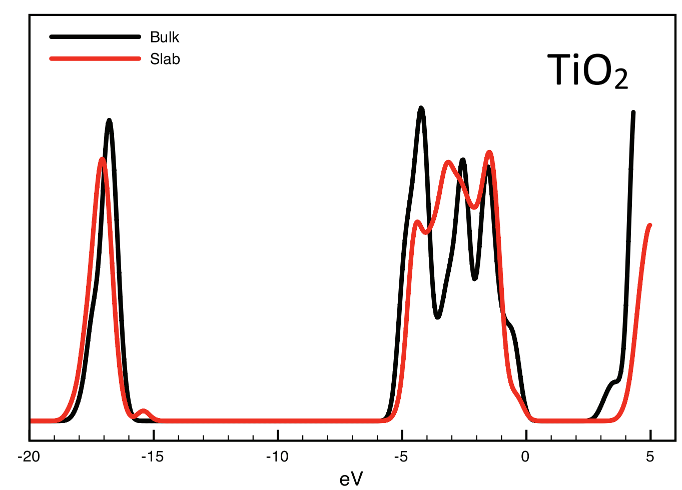

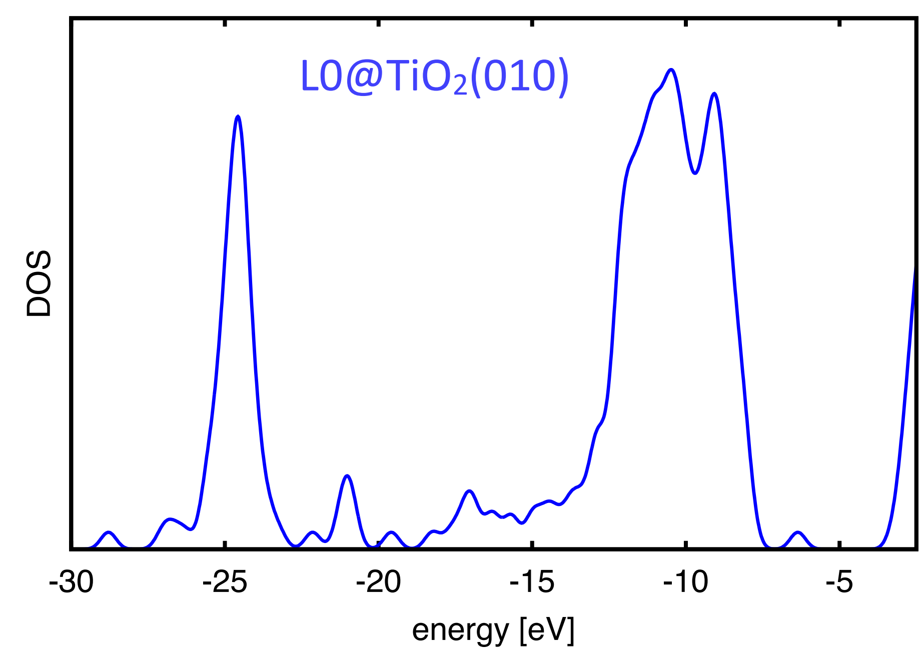

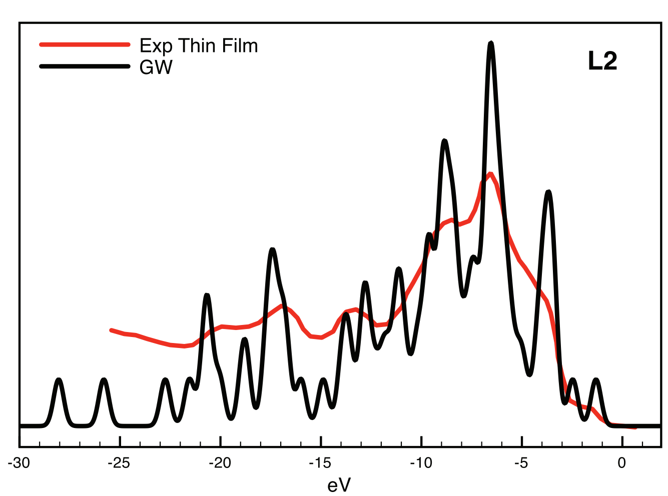

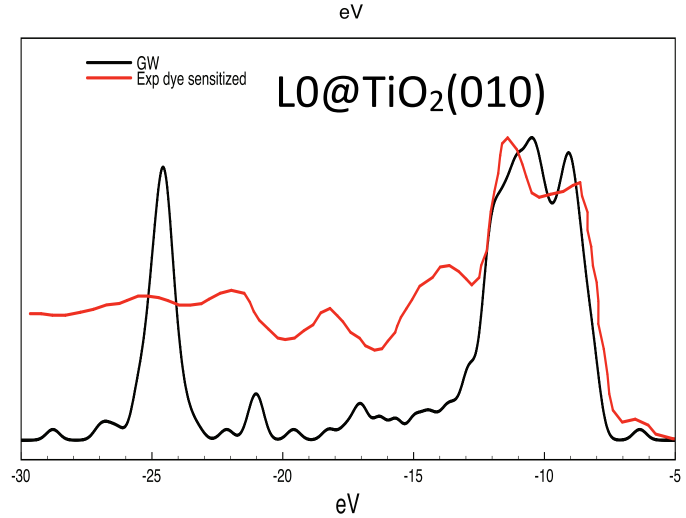

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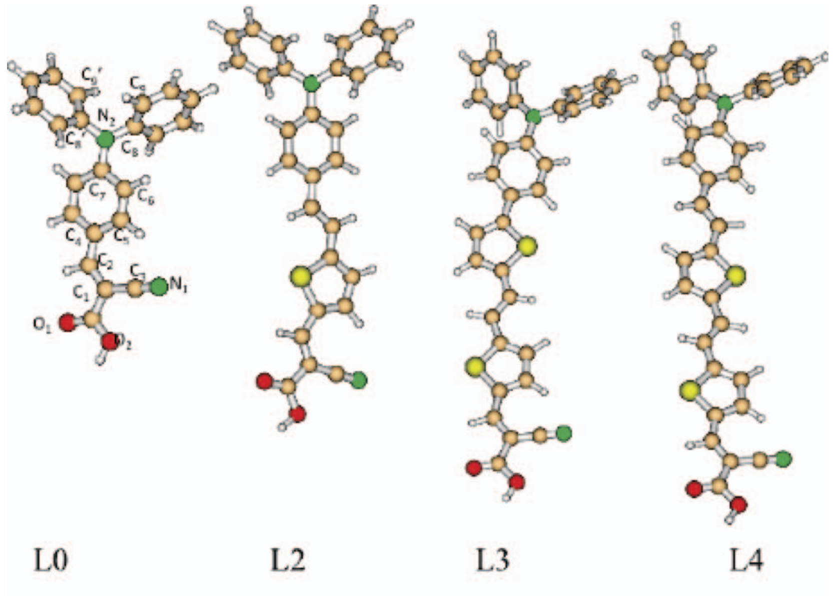
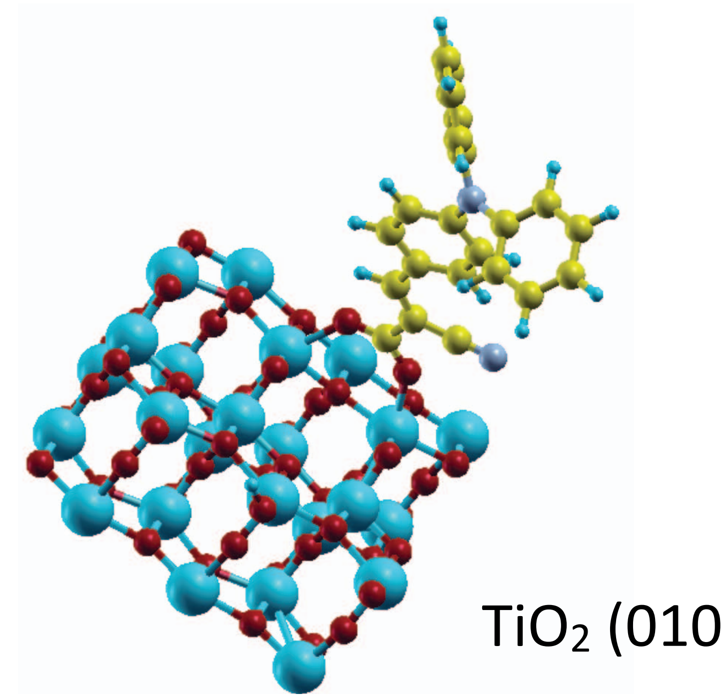
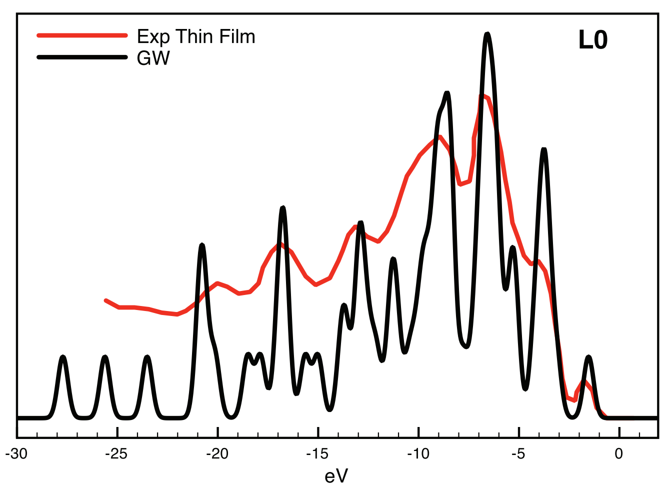
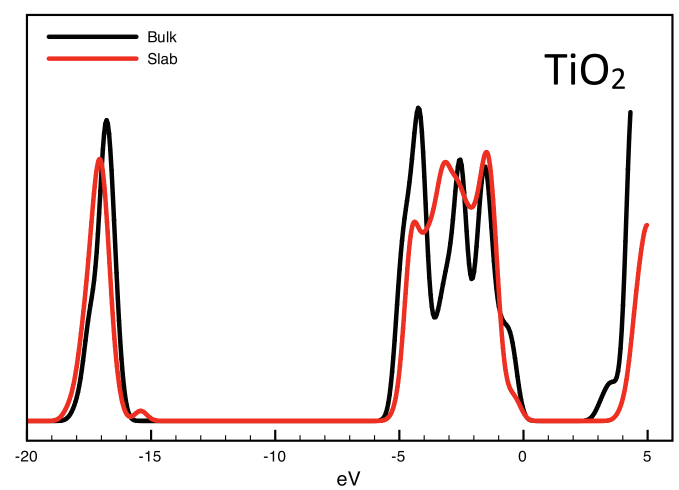
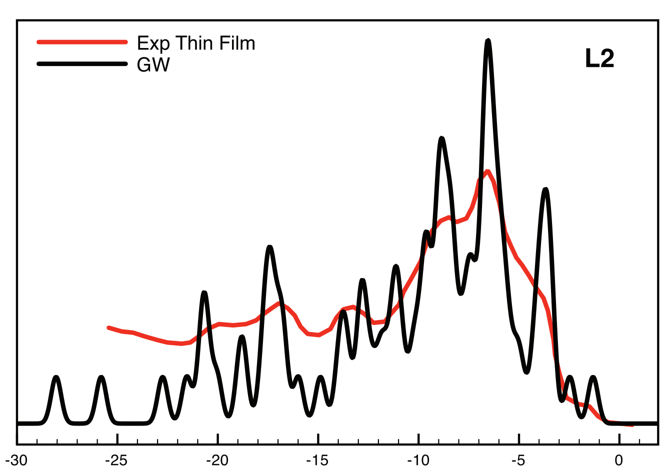


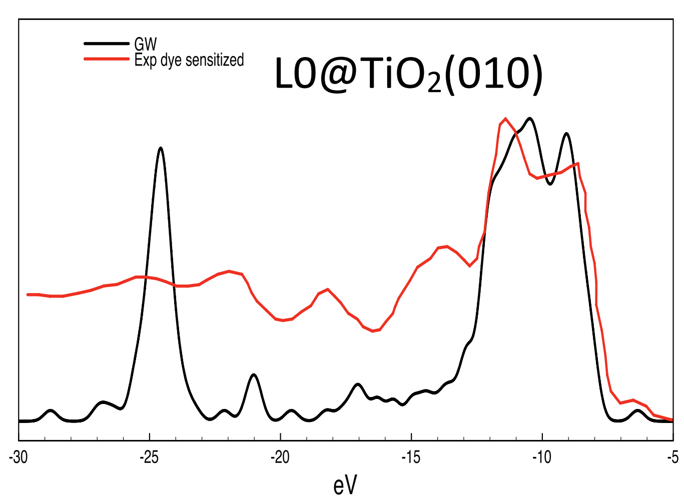


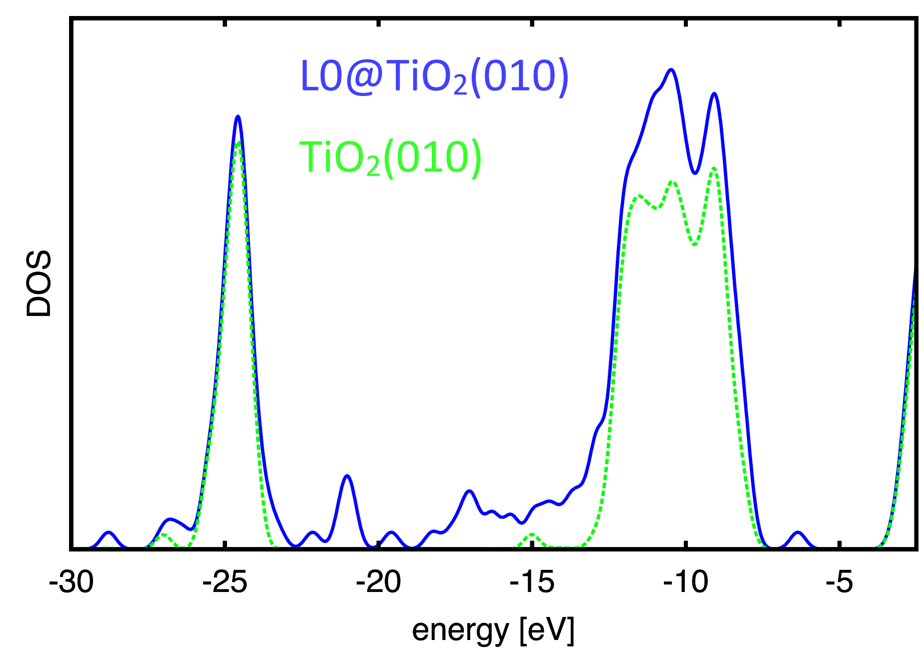
triphenylamine (TPA)- based sensitizers



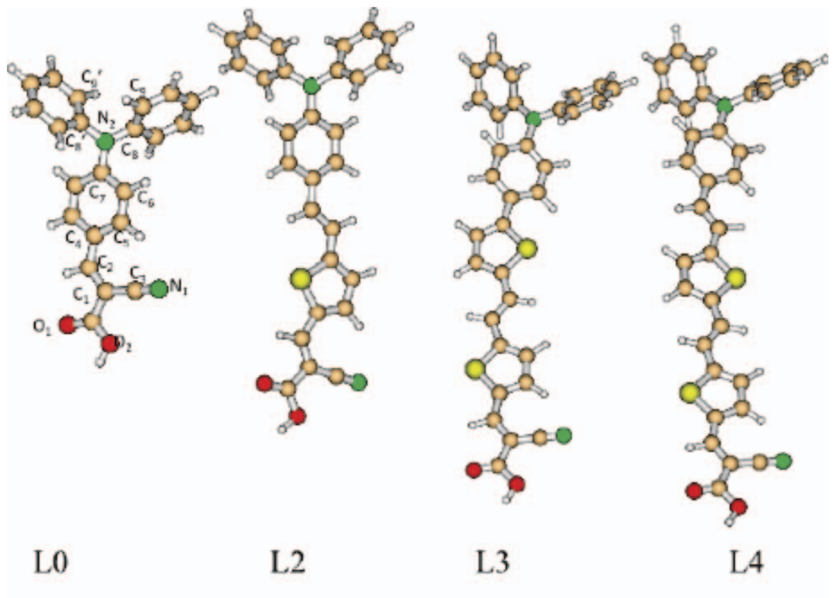


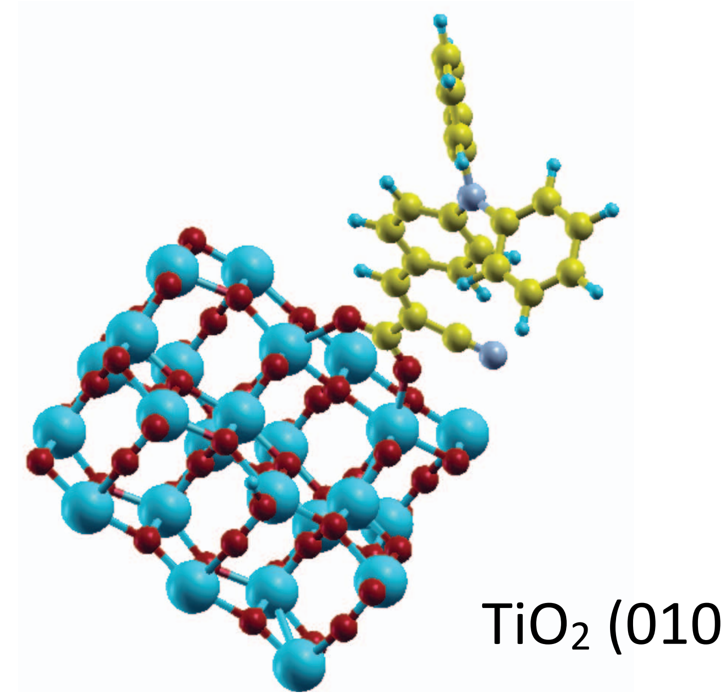




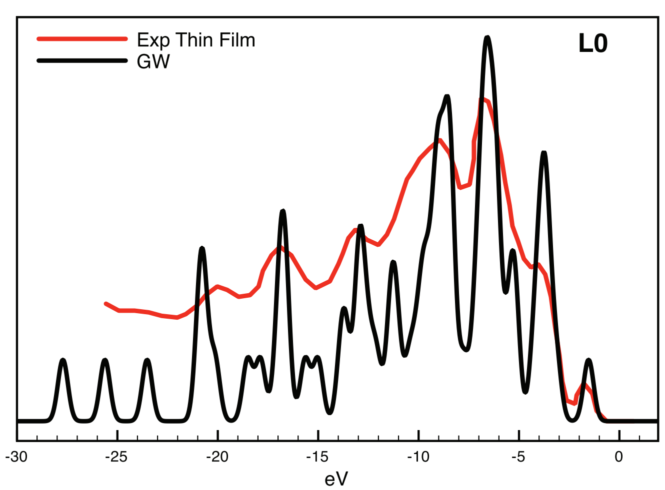


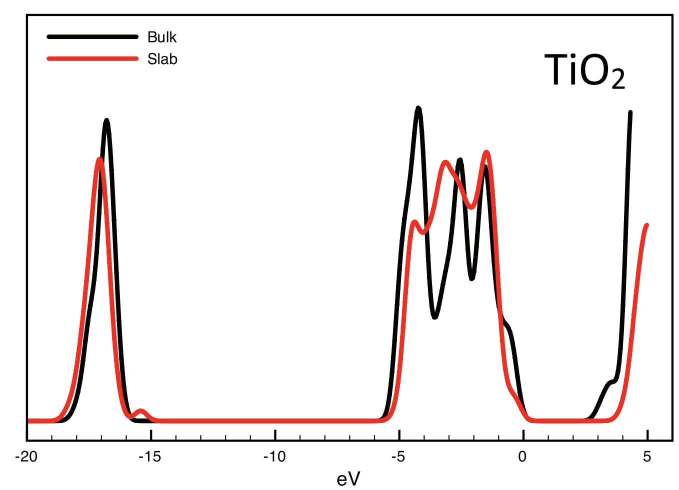
energy levels in all-organic DSSCs

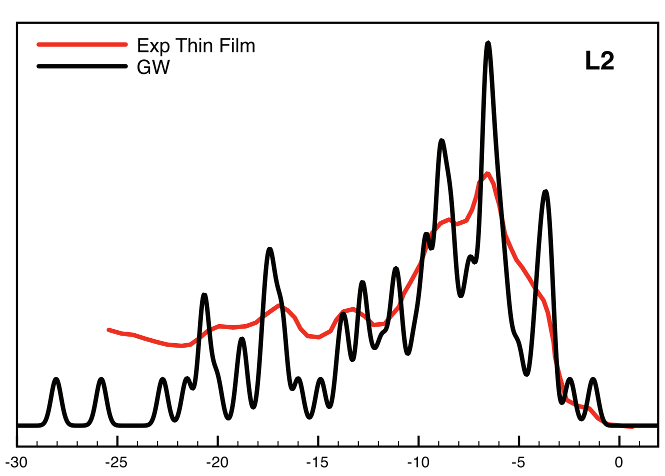


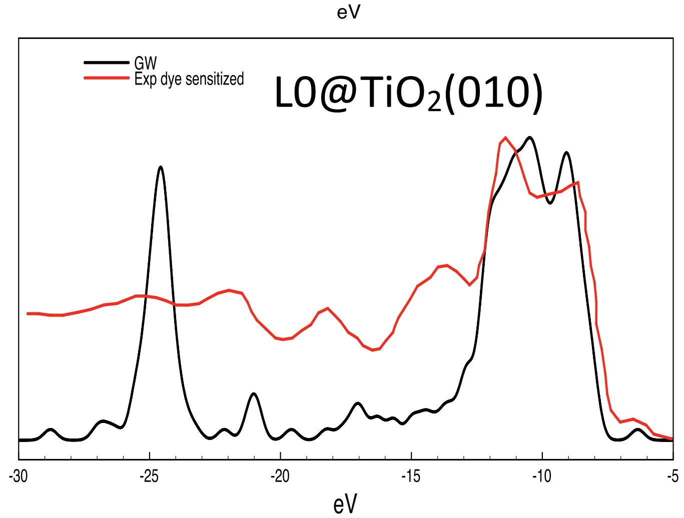


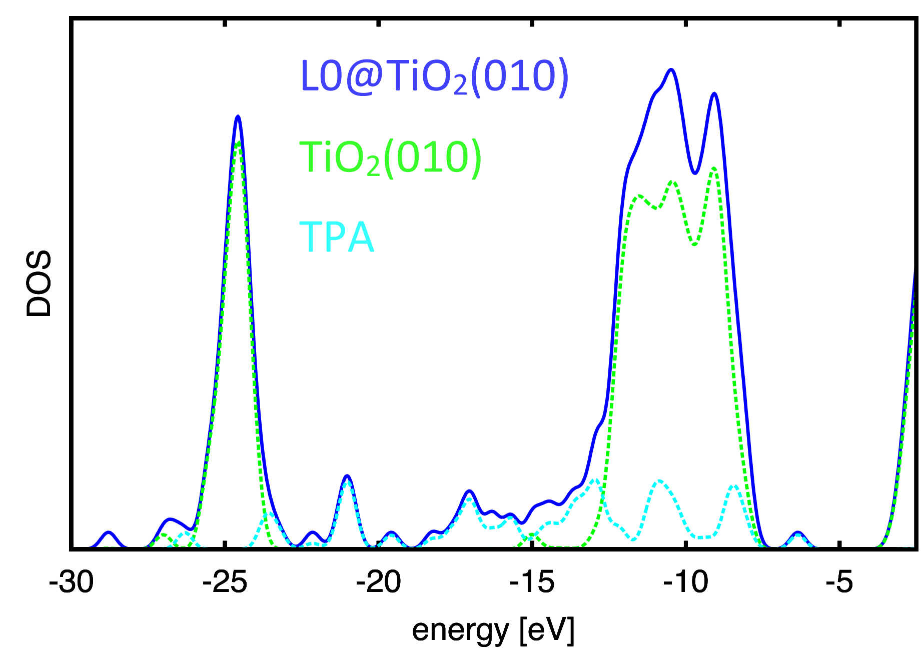
triphenylamine (TPA)- based sensitizers



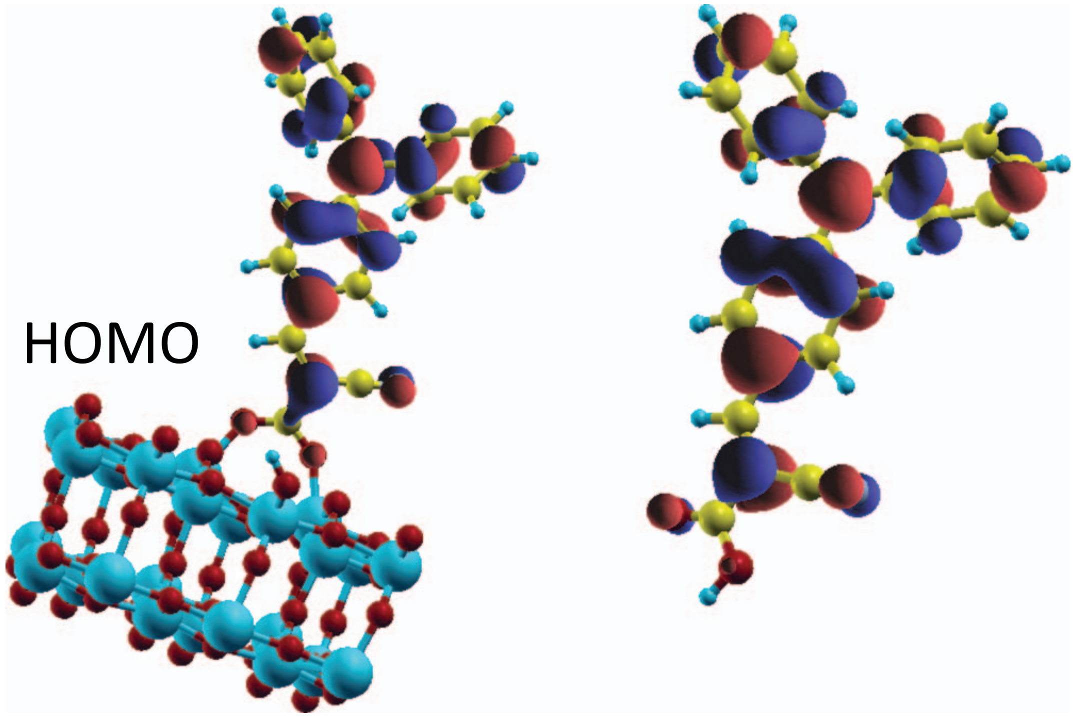








energy levels in all-organic DSSCs



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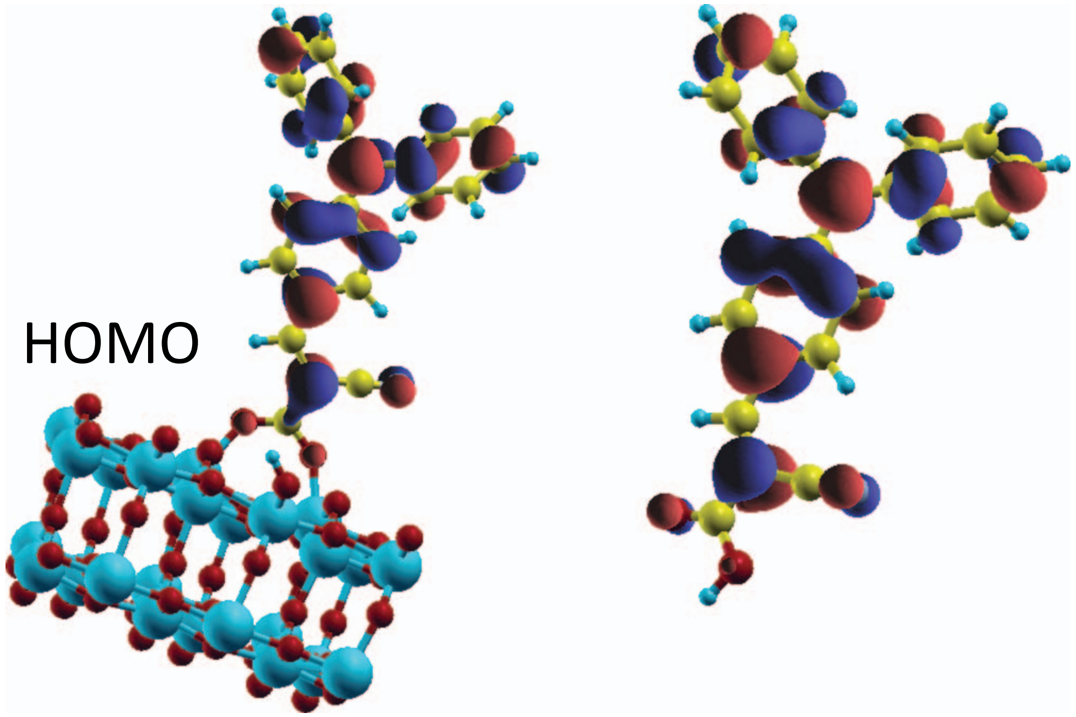
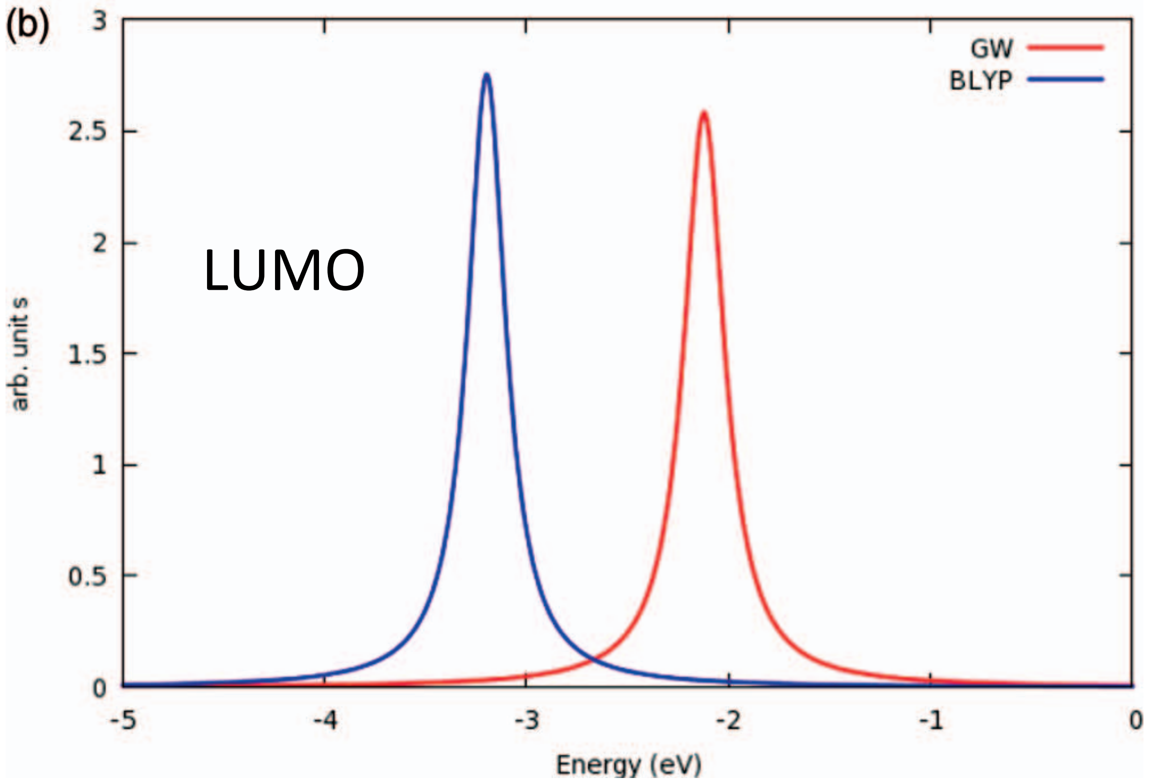
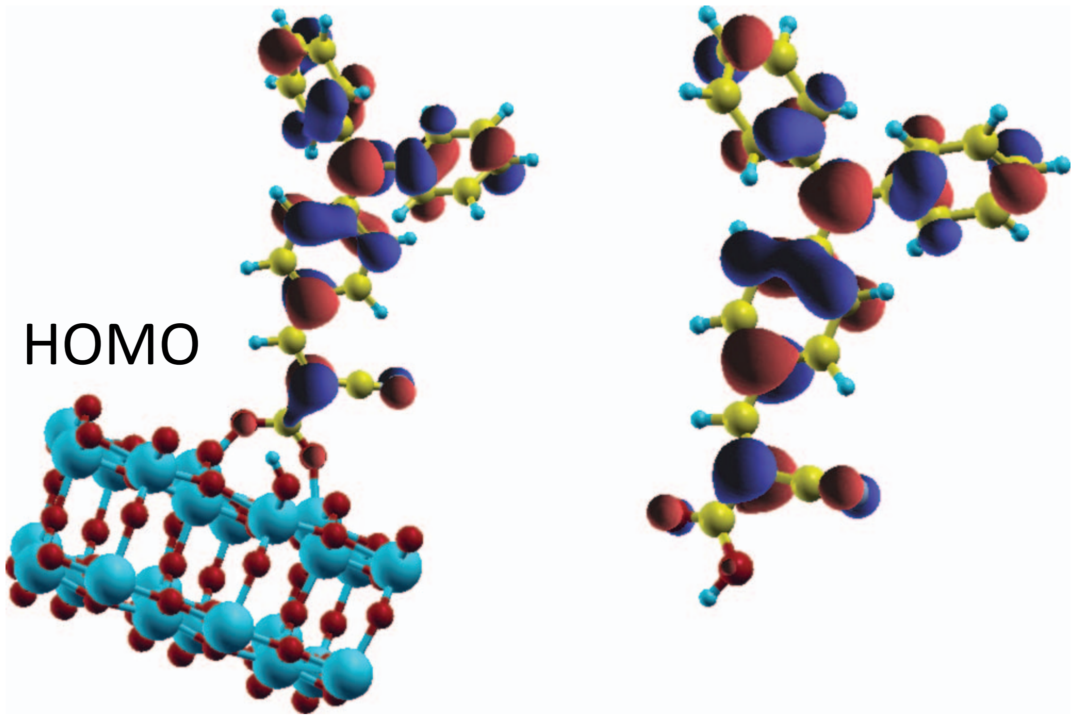
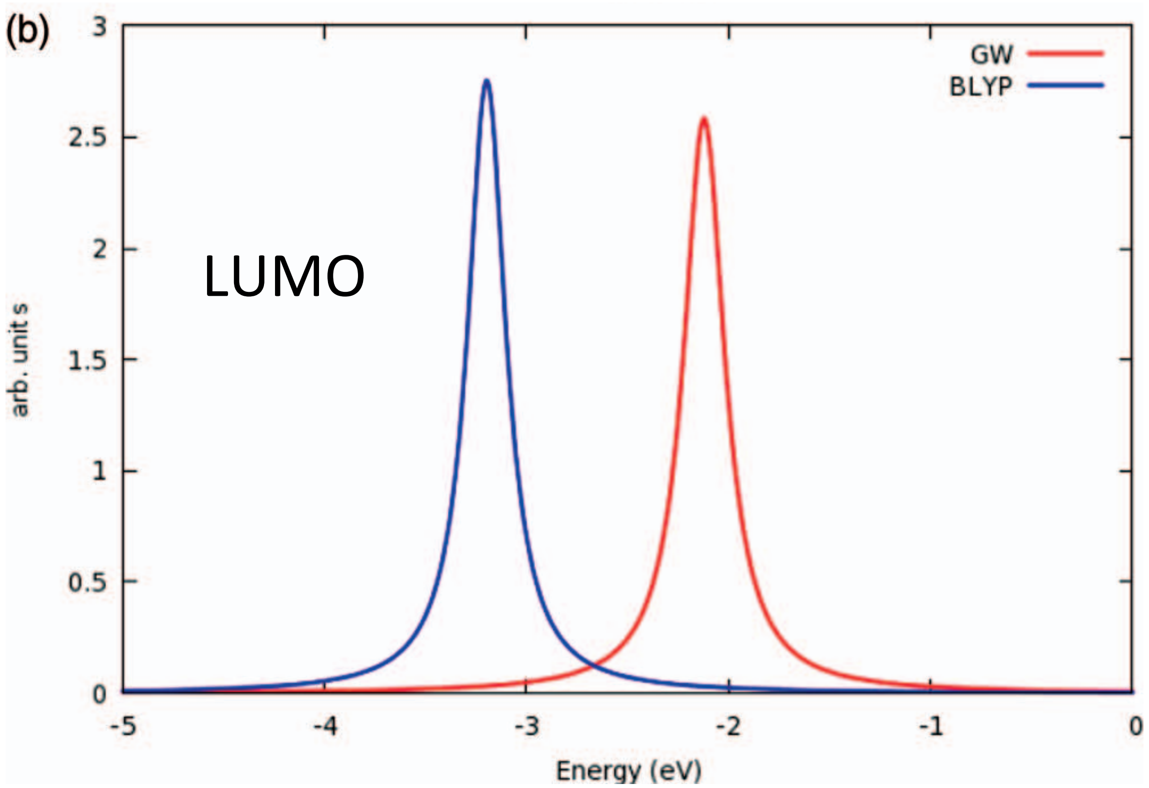




$$g_{LUMO}(\epsilon) = \sum_n |\langle\psi_n|\phi_{LUMO}\rangle|^2 \delta(\epsilon - \epsilon_n)$$

energy levels in all-organic DSSCs

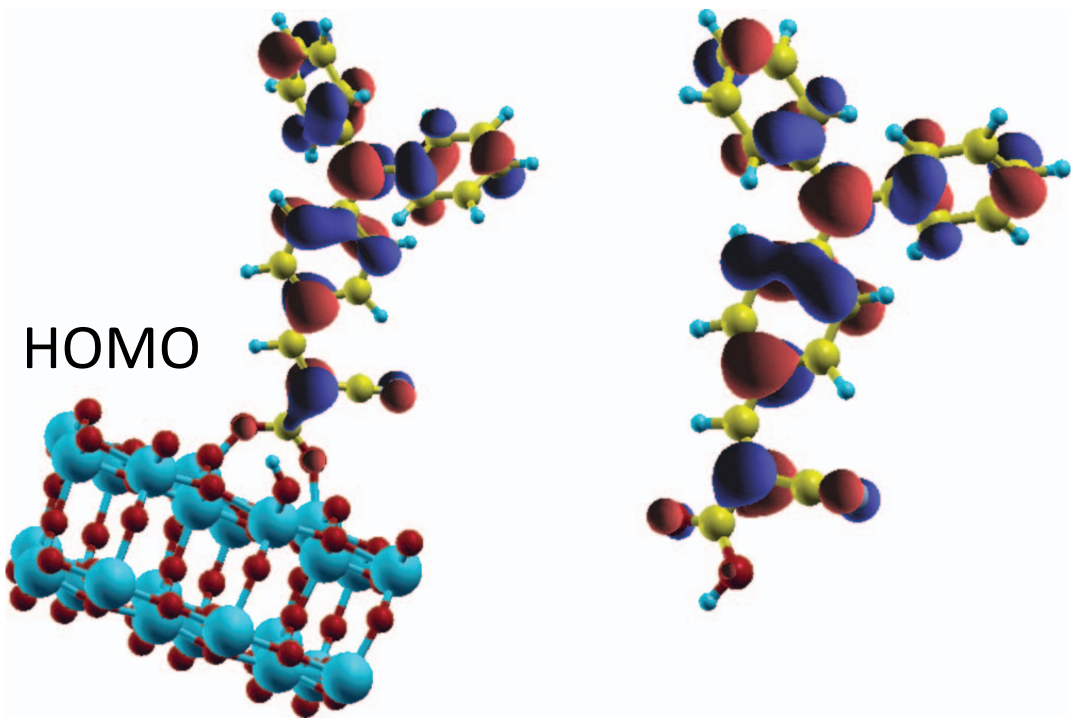


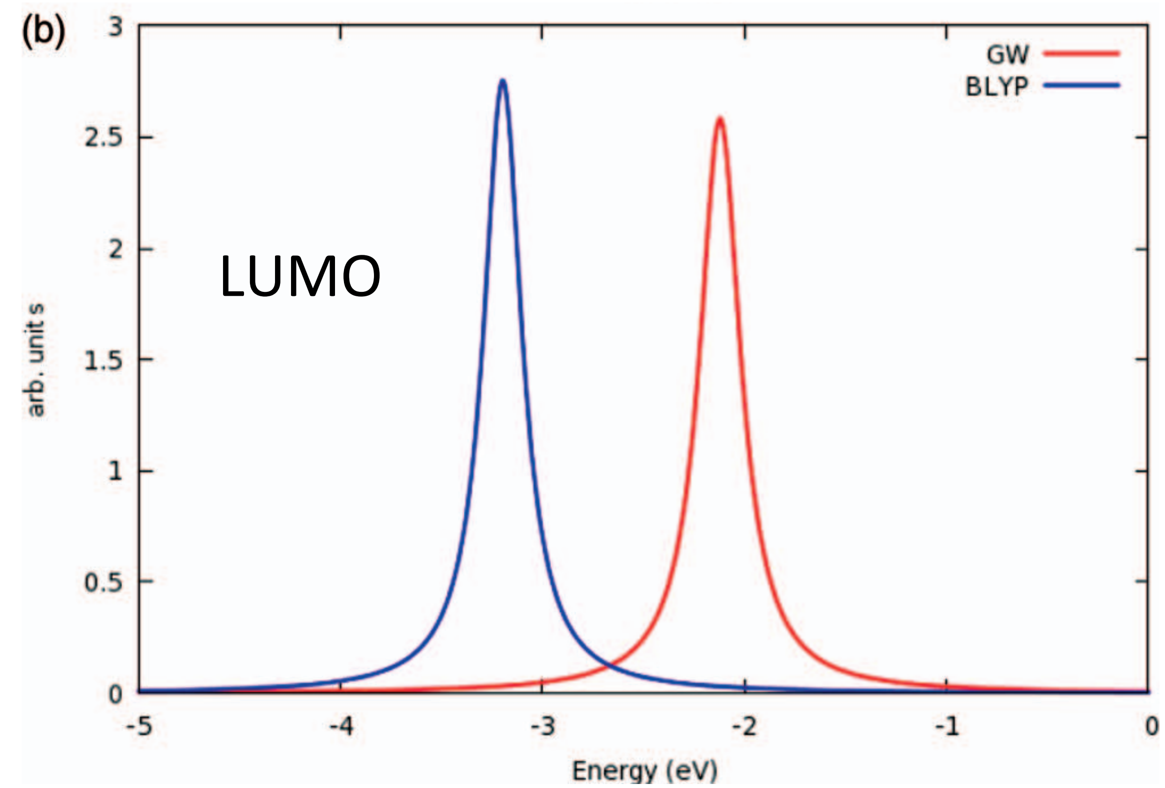


$$g_{LUMO}(\epsilon) = \sum_n |\langle \psi_n | \phi_{LUMO} \rangle|^2 \delta(\epsilon - \epsilon_n)$$

$$\tau \ [\mathrm{fs}] = \frac{658}{\Gamma \ [\mathrm{meV}]}$$
$$\approx 2.7 \div 2.8 \ [\mathrm{fs}]$$

energy levels in all-organic DSSCs





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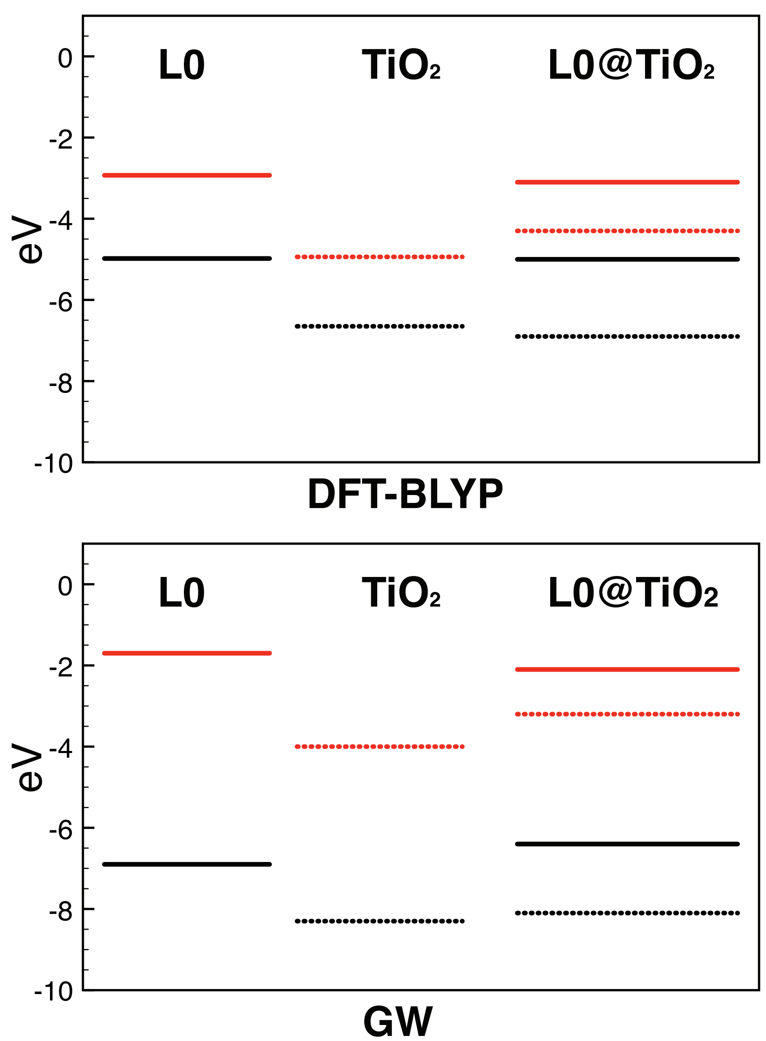

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P. Umari et al. JCP **139**, 014709 (2013)

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31.10.12

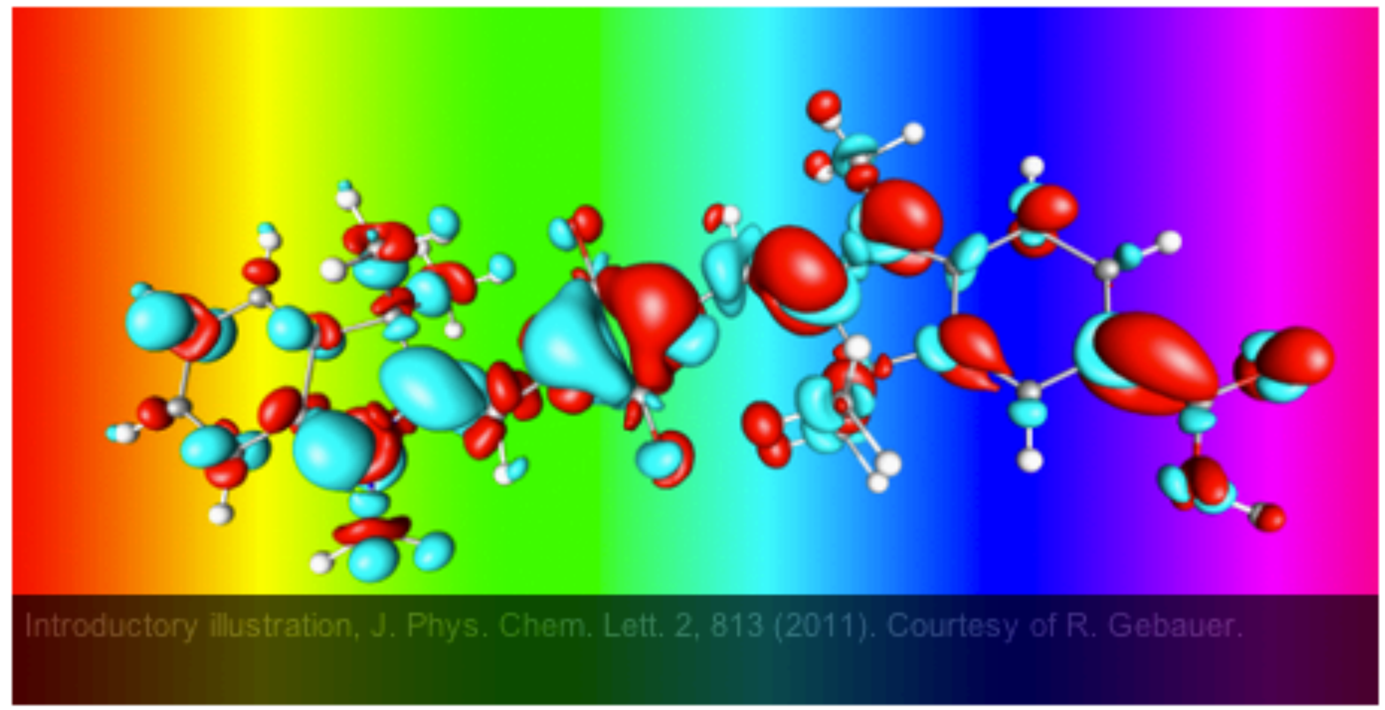
SCHOOL FOR QUANTUM ESPRESSO DEVELOPERS

We would like to draw your attention to the *Workshop on Computer Programming and Advanced Tools for Scientific Research Work & Quantum ESPRESSO Developer Training*, 11-28 March 2013 in Trieste. Everybody interested in learning how to develop code within Quantum ESPRESSO is welcome to participate. Registration for the Quantum ESPRESSO part only, 25 to 28 March, is possible. Deadline: 6 January.

02.10.12

QE OPEN INVITATION TO CONTRIBUTE

All users and developers are warmly encouraged to share their own developments



Introductory illustration, J. Phys. Chem. Lett. 2, 813 (2011). Courtesy of R. Gebauer.

QUANTUM ESPRESSO

is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

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in electronic-structure theory and simulation

Thanks to

Alessandro Biancardi
Simon Binnie
Arrigo Calzolari
Xiaochuan Ge
Ralph Gebauer
Baris Malcıoğlu
Dario Rocca
Iurii Timrov
Paolo Umari
Brent Walker

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Paolo Umari
Brent Walker

and to the QUANTUM ESPRESSO development & maintenance team

Dario Alfè, Francesco Antoniella, Gerardo Ballabio, Stefano Baroni, Simon Binnie, Mauro Boero, Claudia Bungaro, Giovanni Bussi, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Paolo Cazzato, Davide Ceresoli, Gabriele Cipriani, Matteo Cococcioni, Andrea Dal Corso, Alberto Debernardi, Gernot Deinzer, Oswaldo Dieguez, Stefano Fabris, Guido Fratesi, Xiaochuan Ge, Ralph Gebauer, Paolo Giannozzi, Stefano de Gironcoli, Martin Hilgeman, Yosuke Kanai, Anton Kokalj, Axel Kohlmeyer, Konstantin Kudin, Michele Lazzeri, Baris Malcioglu, Francesco Mauri, Kurt Mäder, O. Barış Malcıoğlu, Layla Martin Samos Colomer, Nicola Marzari, Nicolas Mounet, Adriano Mosca Conte, Alfredo Pasquarello, Lorenzo Paulatto, Pasquale Pavone, Mickael Profeta, Dario Rocca, Guido Roma, Riccardo Sabatini, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauzero, Manu Sharma, Alexander Smogunov, Kurt Stokbro, Pascal Thibaudeau, Antonio Tilocca, Andrea Trave, Paolo Umari, Brent Walker, Renata Wentzcovitch, Yudong Wu, Xiaofei Wang ...

... and let me apologize to anybody I may have forgotten.

these slides at
http://talks.baroni.me