Absorption Spectra Calculations of Organic Molecules with QE+Environ

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Quantum-Multiscale School on Quantum Espresso

Denton, TX

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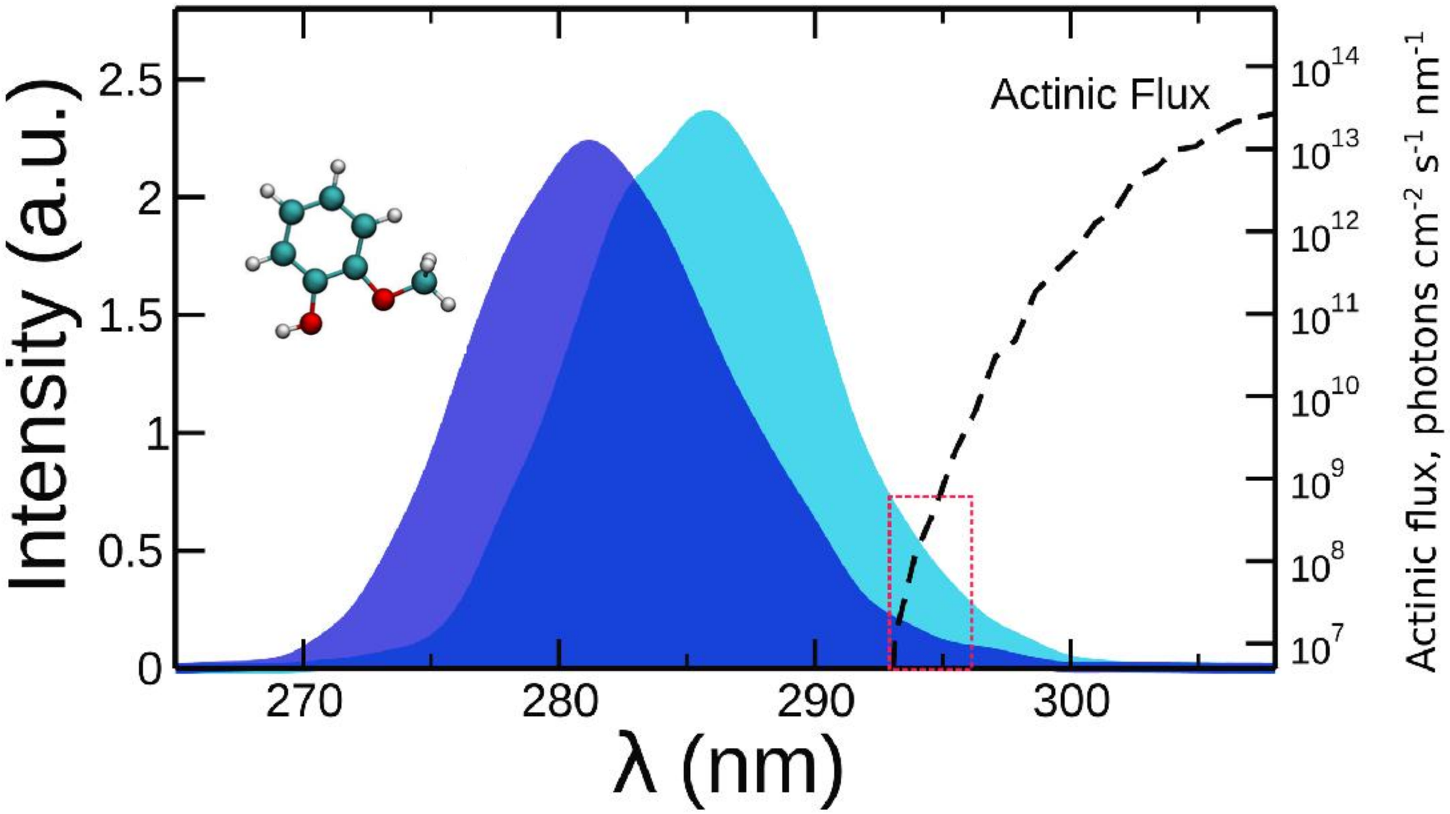
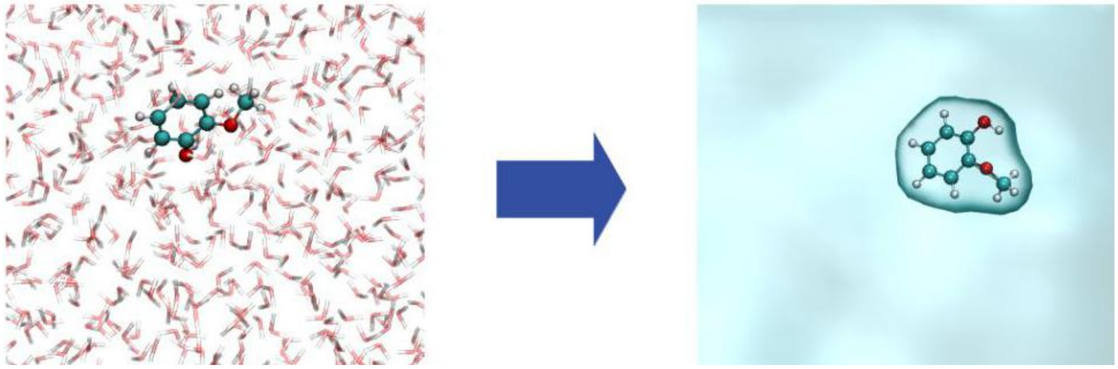
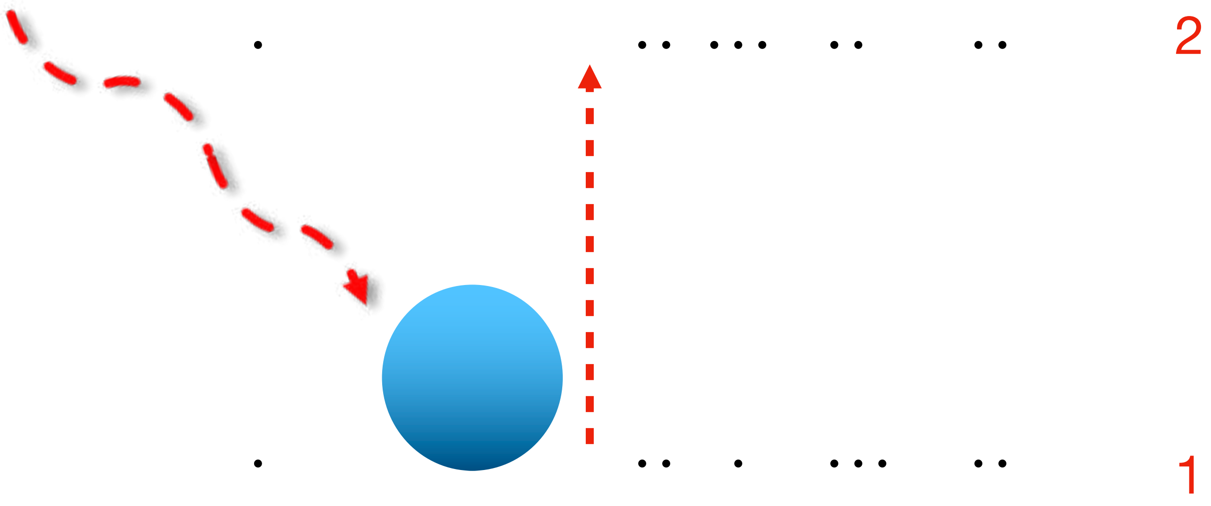




From ground-state to excited state



$$i\hbar\frac{\partial}{\partial t}\Psi_{el}(\{r_1\},t) = \hat{H}(\{r_1\},t)\Psi_{el}(\{r_1\},t)$$

Solution for the many-electron system is even more complex than the solution of the static Schrödinger equation

Similar to the static case, instead of considering the electronic wavefunction of 3N+1 variables we can consider the electronic charge density, a **function of only 4 variables (coordinates and time)**

Trying to follow the same steps of the static case is not possible in the time-dependent domain, because here the **total energy changes with time**

From ground-state to excited state

Runge-Gross Theorem

For a system with interacting electrons at an initial state ($t = 0$), the external potential $v(r, t)$ acting on it is determined only by the time evolution of the one-electron density, $\rho(r, t)$ for $t > 0$.

** We need to know the initial state

Observables: functionals of the time-dependent charge density

$$\boxed{i\hbar\frac{\partial}{\partial t}\phi_i(r,t) = \left[-\frac{\hbar}{2}\nabla^2 + v_{KS}(r,t)\right]\phi_i(r,t)}$$

$$v_{KS}(r,t) = v_H(r,t) + v_{xc}(r,t) + v_{ext}(r,t) \longrightarrow n(r,t) = \sum_i^N |\phi_i(r,t)|^2$$

** In the time-dependent case, the xc potential depends on density at all past times - it is more difficult to find an expression for it

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

Linear Response TDDFT

- External potential (perturbation) is weak:

$$V_{ext}(r,t) = V^{o}_{ext}(r) + V'_{ext}(r,t)$$

Density can be expanded in Taylor series with respect to the perturbation

$$n(\mathbf{r},t) = n^{o}(\mathbf{r}) + n'(\mathbf{r},t) \xcancel{+ n''}(\mathbf{r},t) + \ldots$$

As we are talking about linear response TDDFT, we can express the first-order change in density due to an external perturbation v'_{ext} in the frequency domain as:

$$n'(r,\omega) = \underbrace{\int \chi(r,r',\omega)}_{\text{Susceptibility}} v'_{ext}(r',\omega)\,dr$$

→ TDDF**P**T - Perturbation Theory + TDDFT

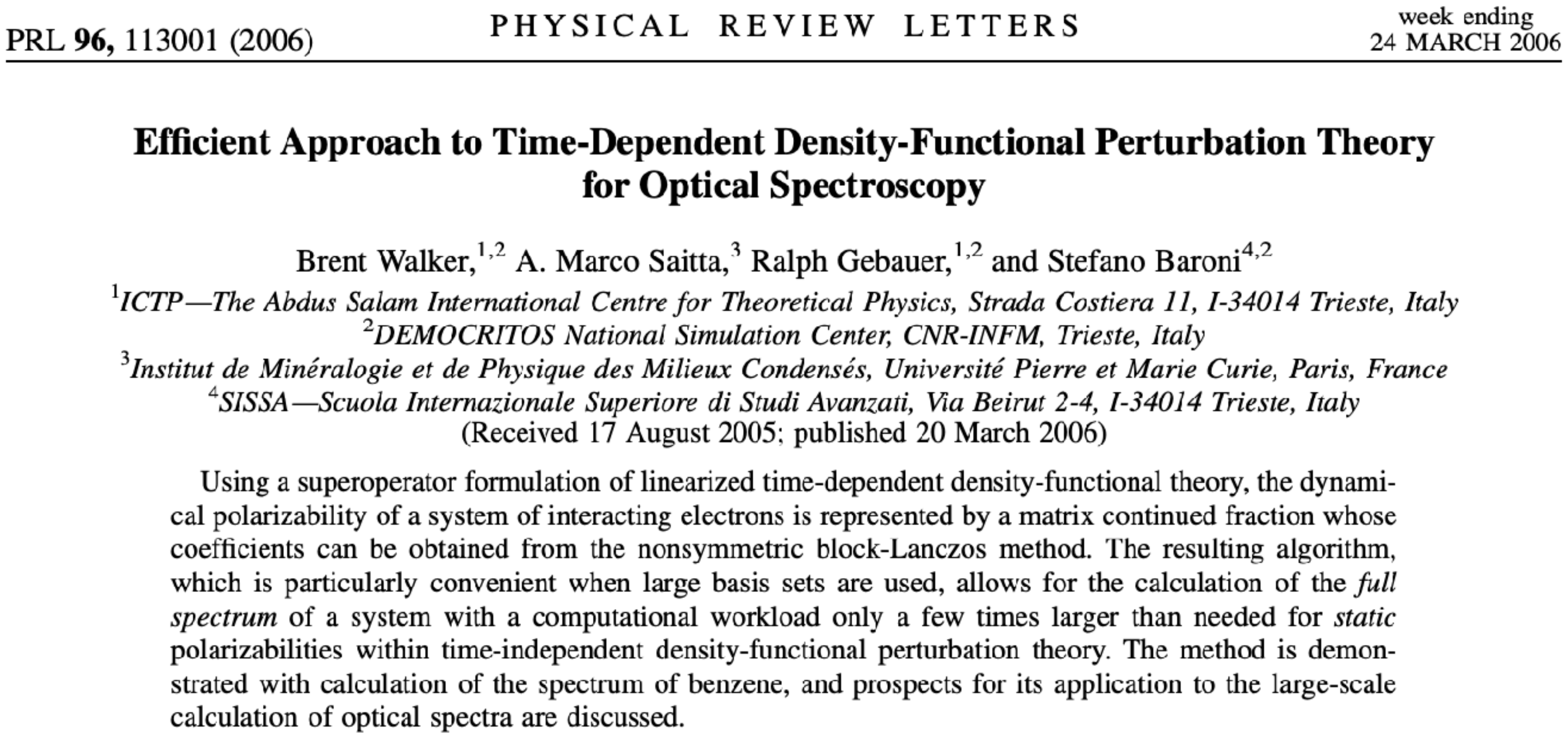
How to Compute Susceptibility?

-A variety of methods are available to compute susceptibility:

Ex: Casida-Davidson, Liouville-Lanczos

** For a more in depth lecture on some of those methods, check out the latest lecture on TDDFPT by Iurii Timrov at: http://indico.ictp.it/event/9616/session/47/contribution/80/material/video/

generalized susceptibility represented by a matrix element of the resolvent of the Liouvillian super-operator. This matrix element is then evaluated using a Lanczos recursion technique.



PRL **96,** 113001 (2006)   PHYSICAL REVIEW LETTERS   week ending 24 MARCH 2006

Efficient Approach to Time-Dependent Density-Functional Perturbation Theory for Optical Spectroscopy

Brent Walker,[1,2] A. Marco Saitta,[3] Ralph Gebauer,[1,2] and Stefano Baroni[4,2]

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[2]*DEMOCRITOS National Simulation Center, CNR-INFM, Trieste, Italy*
[3]*Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie, Paris, France*
[4]*SISSA—Scuola Internazionale Superiore di Studi Avanzati, Via Beirut 2-4, I-34014 Trieste, Italy*
(Received 17 August 2005; published 20 March 2006)

Using a superoperator formulation of linearized time-dependent density-functional theory, the dynamical polarizability of a system of interacting electrons is represented by a matrix continued fraction whose coefficients can be obtained from the nonsymmetric block-Lanczos method. The resulting algorithm, which is particularly convenient when large basis sets are used, allows for the calculation of the *full spectrum* of a system with a computational workload only a few times larger than needed for *static* polarizabilities within time-independent density-functional perturbation theory. The method is demonstrated with calculation of the spectrum of benzene, and prospects for its application to the large-scale calculation of optical spectra are discussed.

The TurboTDDFT code

- The dynamical polarizability of an interacting-electron system is represented as an off-diagonal matrix element of the resolvent of the Liouvillian super operator
- One-electron operators and density matrices are treated using a representation borrowed from time-independent DFPT - **avoid calculation of unoccupied Kohn-Sham orbitals**
- The resolvent of the Liouvillian is evaluated by an algorithm based on the non symmetric Lanczos method
- Allows for the bulk of the work to be done at once for all frequencies - **the full spectrum is obtained at once!**
- Extrapolation of Lanczos coefficients allows for reduction of number of Lanczos steps needed to obtain well converged spectra - **less expensive!**
- Particularly suitable for **larger molecular systems**

D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008)

Hands-on Tutorial

Absorption spectra calculations of organic molecules in vacuum, solution and ice surfaces

- Using the **turbo_lanczos.x** program - allows for calculation of absorption spectra using TDDFpT without computing empty states
- Overall absorption spectrum in a wide frequency range can be calculated once via an inexpensive post-processing step
- Extrapolation of Lanczos coefficients allows to speed up convergence

** The electronic transitions from occupied to empty states cannot be analyzed by this method - for this purpose, use **turbo_davidson.x**

Hands-on Tutorial

Absorption spectra calculations of organic molecules in vacuum, solution and ice surfaces

1. Absorption spectra calculation for benzene in vacuum
2. Absorption spectra convergence based on number of Lanczos steps
3. Absorption spectra calculation for benzene using Environ
4. Setting up calculations of absorption spectra for molecules on surfaces (ice)

Absorption Spectra Calculations

```
$ pw.x < input.scf.in > scf.out
```

Self-Consistent Field ground-state calculation

** Relax calculation can be performed before scf

```
$ turbo_lanczos.x < input-tddfpt.in > tddfpt.out
```

Lanczos recursions

```
$ turbo_spectrum.x < input-pp.in > spectrum.out
```

Post-processing to obtain the dynamical polarizability from the tridiagonal matrix

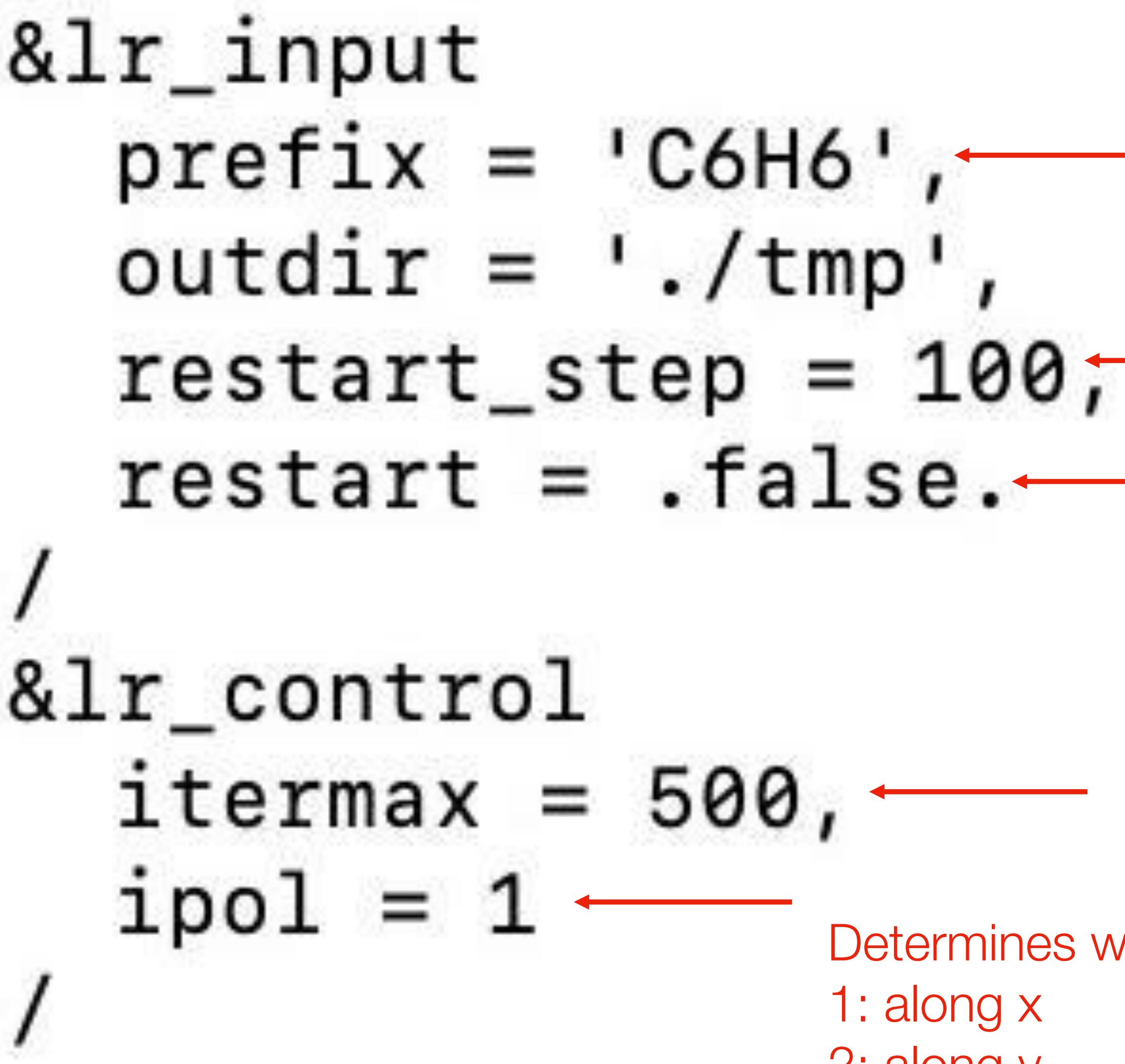
Produces file:

- spectrum.plot_chi.dat - **this is where we find the values for oscillator strength**

1. Absorption spectra calculations for benzene in vacuum

turbo_lanczos.x input

$ turbo_lanczos.x -np 4 < C6H6.tddfpt.in > tddfpt.out



```
&lr_input
  prefix = 'C6H6',
  outdir = './tmp',
  restart_step = 100,
  restart = .false.
/
&lr_control
  itermax = 500,
  ipol = 1
/
```

Same prefix as the scf calculation

Writes restart files every restart_step iterations

If .true., program will attempt to restart calculation if stopped

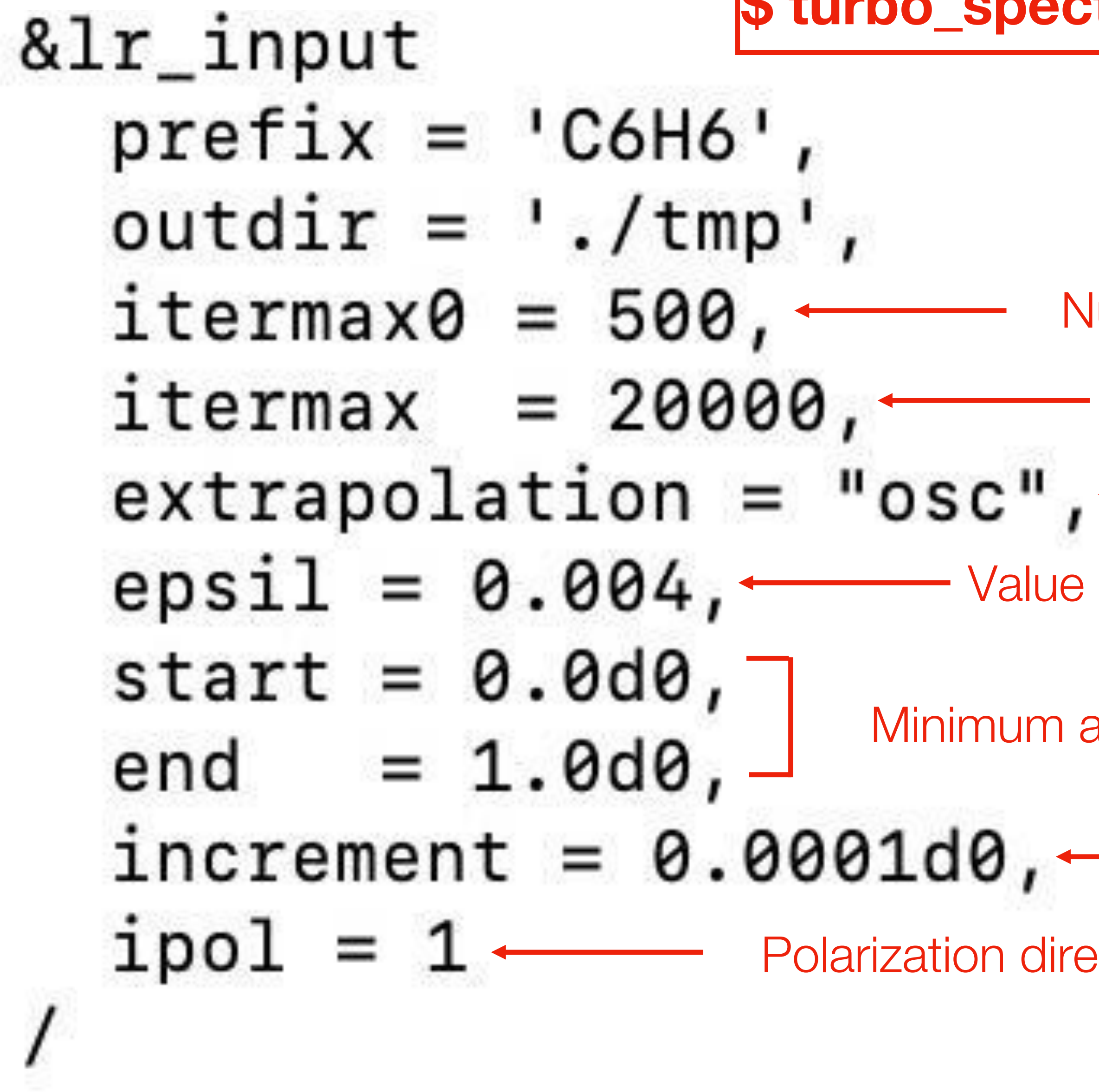
Number of lanczos iterations

Determines which element of the dynamical polarizability will be computed:
1: along x
2: along y
3: along z
4: 3 Lanczos chains are sequentially performed and the full polarizability tensor and absorption coefficient are computed.

Input Files

turbo_spectrum.x input

$ turbo_spectrum.x -np 4 < C6H6.tddfpt_pp.in > spectrum.out



```
&lr_input
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  itermax0 = 500,
  itermax  = 20000,
  extrapolation = "osc",
  epsil = 0.004,
  start = 0.0d0,
  end   = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

Number of calculated Lanczos coefficients

Number up to which coefficients will be extrapolated

Type of extrapolation (bi-constant)

Value of Lorentzian broadening in Ry

Minimum and maximum value of frequencies for a plot in Ry

Frequency step in Ry

Polarization direction (same as previous step)

Output

What we see:

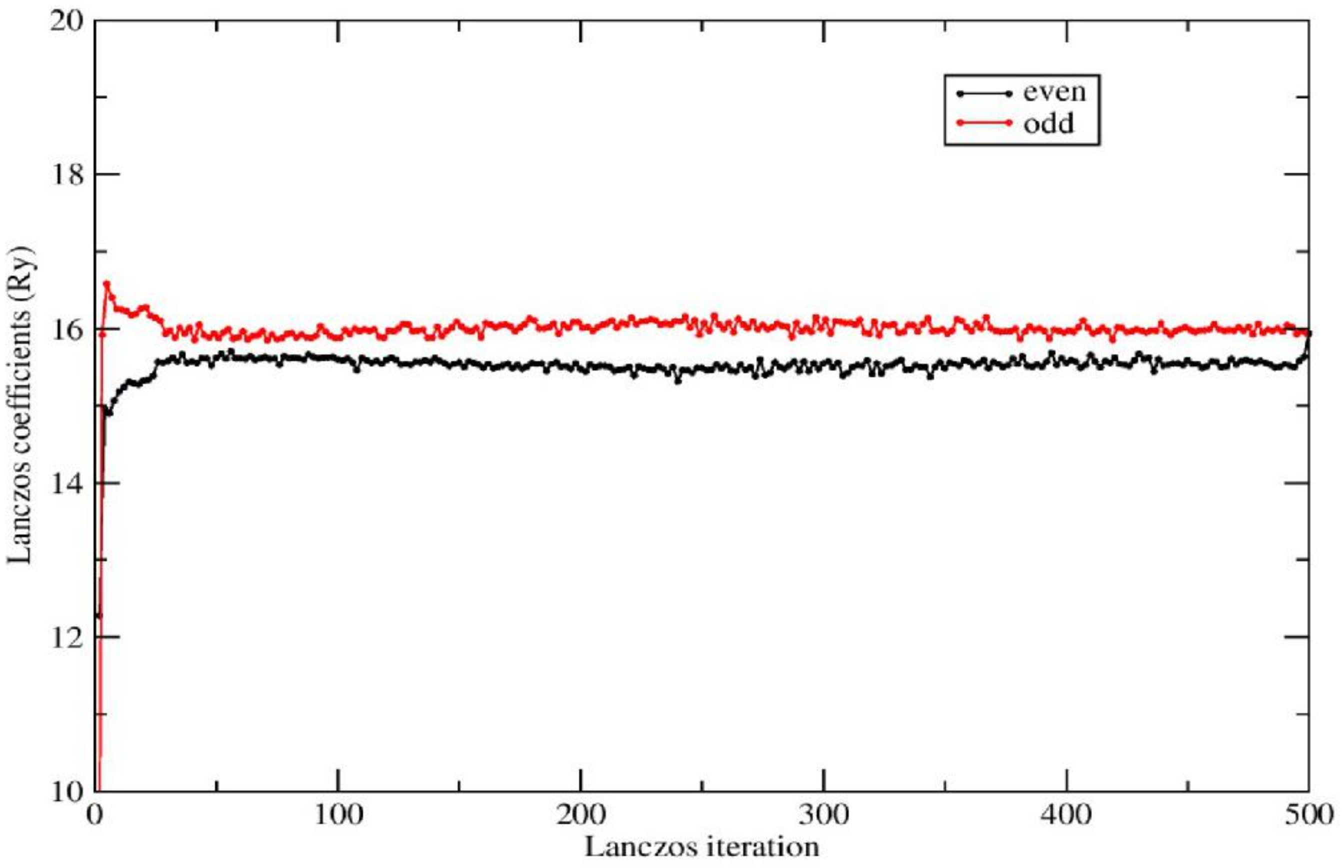
Tridiagonal matrix:

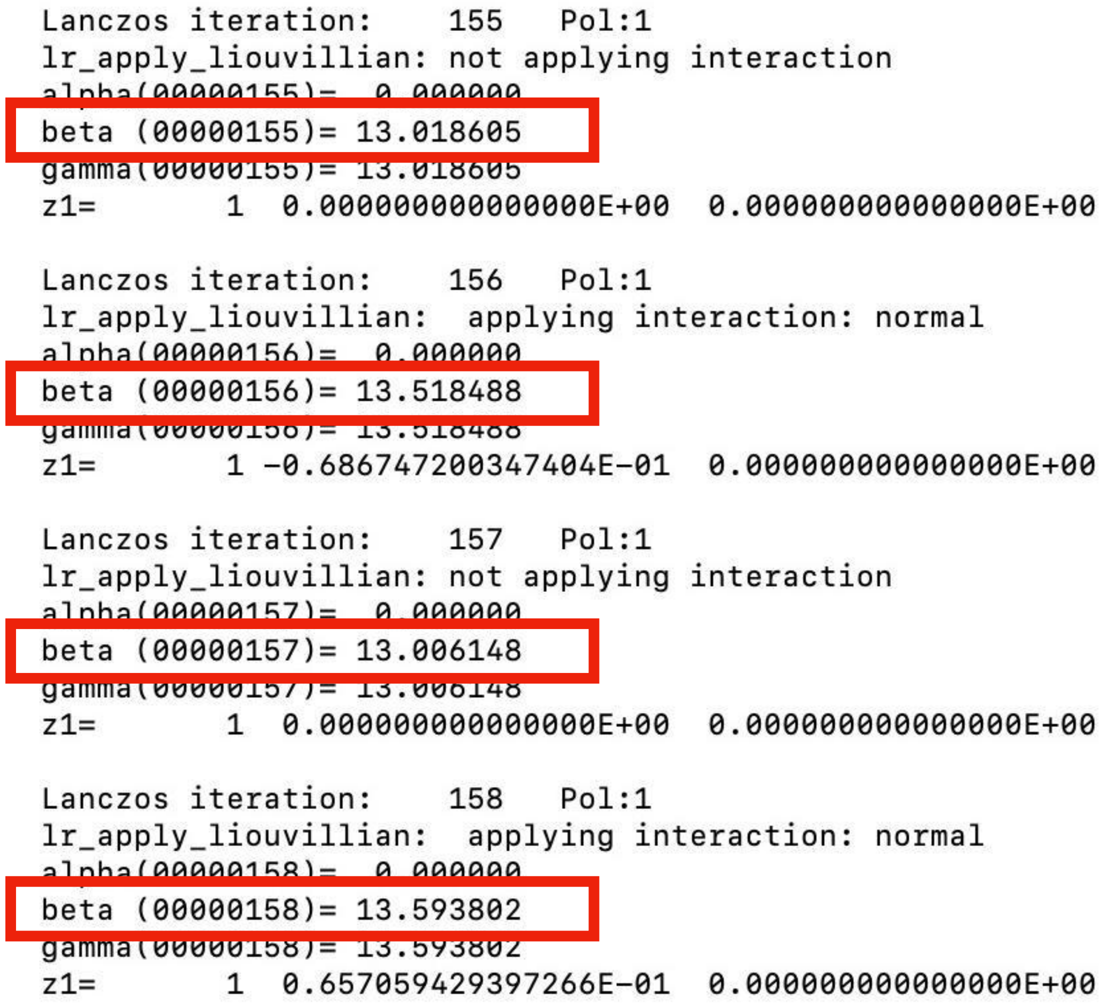
$$\hat{T}^N = \begin{pmatrix} 0 & \gamma_2 & 0 & \dots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \dots & 0 & \beta_N & 0 \end{pmatrix} \longrightarrow \chi_A(\omega) = \langle \zeta^N | \left(\hbar\omega \hat{I}^N - \hat{T}^N \right)^{-1} \cdot e_1^N \rangle$$

- tddfpt.out: output from lanczos recursion steps

- C6H6.plot_chi.dat: generated by post-processing step

Extrapolation





```
Lanczos iteration:    155   Pol:1
lr_apply_liouvillian: not applying interaction
alpha(00000155)=  0.000000
beta (00000155)= 13.018605
gamma(00000155)= 13.018605
z1=        1  0.000000000000000E+00  0.000000000000000E+00

Lanczos iteration:    156   Pol:1
lr_apply_liouvillian:  applying interaction: normal
alpha(00000156)=  0.000000
beta (00000156)= 13.518488
gamma(00000156)= 13.518488
z1=        1 -0.686747200347404E-01  0.000000000000000E+00

Lanczos iteration:    157   Pol:1
lr_apply_liouvillian: not applying interaction
alpha(00000157)=  0.000000
beta (00000157)= 13.006148
gamma(00000157)= 13.006148
z1=        1  0.000000000000000E+00  0.000000000000000E+00

Lanczos iteration:    158   Pol:1
lr_apply_liouvillian:  applying interaction: normal
alpha(00000158)=  0.000000
beta (00000158)= 13.593802
gamma(00000158)= 13.593802
z1=        1  0.657059429397266E-01  0.000000000000000E+00
```

Lanczos coefficients oscillate around half of the kinetic energy cutoff after a certain number of iterations - can be extrapolated

From http://indico.ictp.it/event/9616/session/47/contribution/81/material/slides/0.pdf

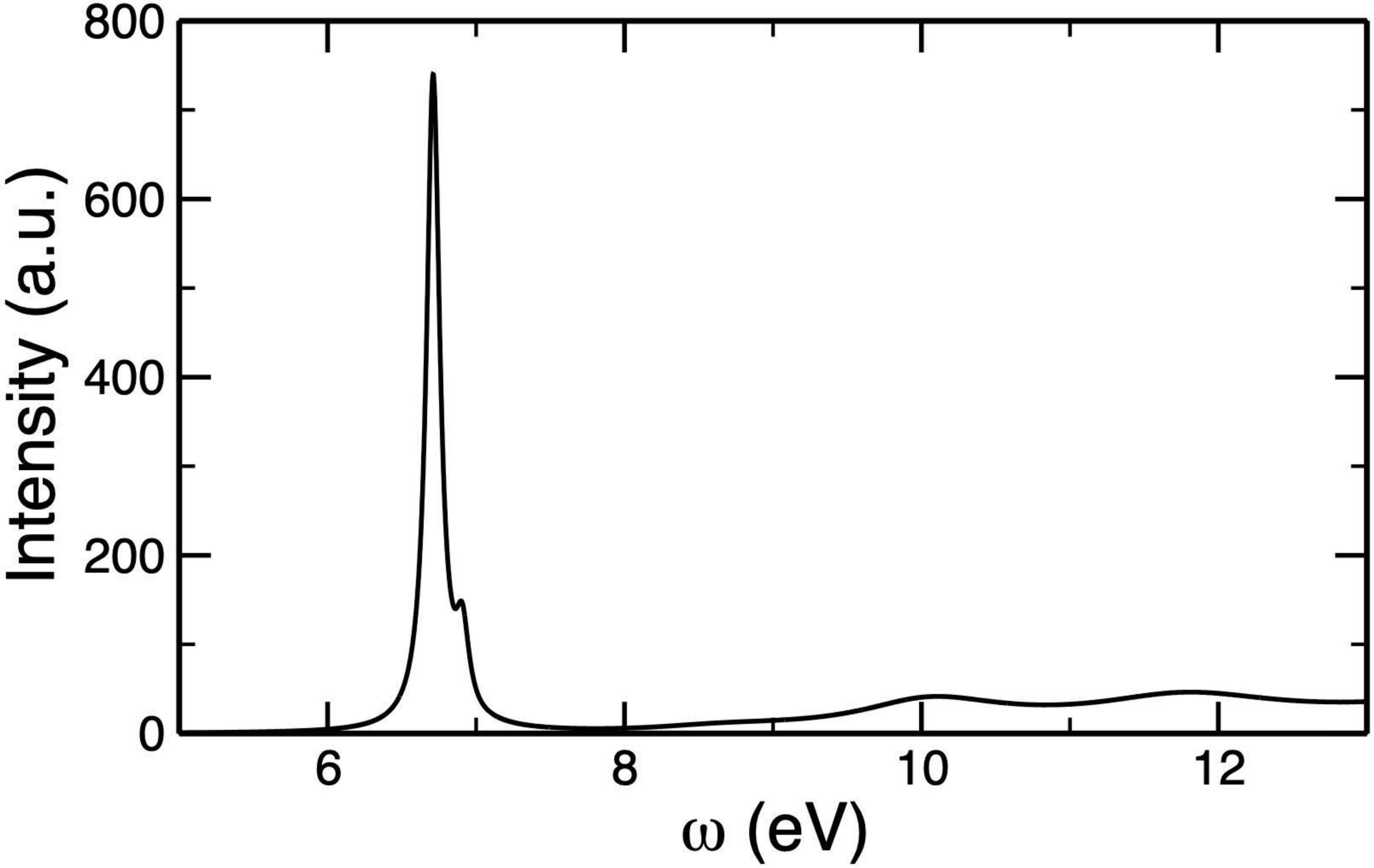
Extrapolation

$$\hat{T}_N = \begin{pmatrix} 0 & \gamma_2 & 0 & \cdots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \cdots & 0 & \beta_N & 0 \end{pmatrix} \longrightarrow \hat{T}_{N'} = \begin{pmatrix} 0 & \gamma_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \ddots & \ddots & \gamma_N & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_N & 0 & \langle\gamma\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \langle\beta\rangle & 0 & \langle\gamma\rangle & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \langle\beta\rangle & 0 & \langle\gamma\rangle \end{pmatrix}$$

$$\langle\beta\rangle = \frac{\beta_1 + \beta_2 + \ldots + \beta_N}{N} \qquad \langle\gamma\rangle = \frac{\gamma_1 + \gamma_2 + \ldots + \gamma_N}{N}$$

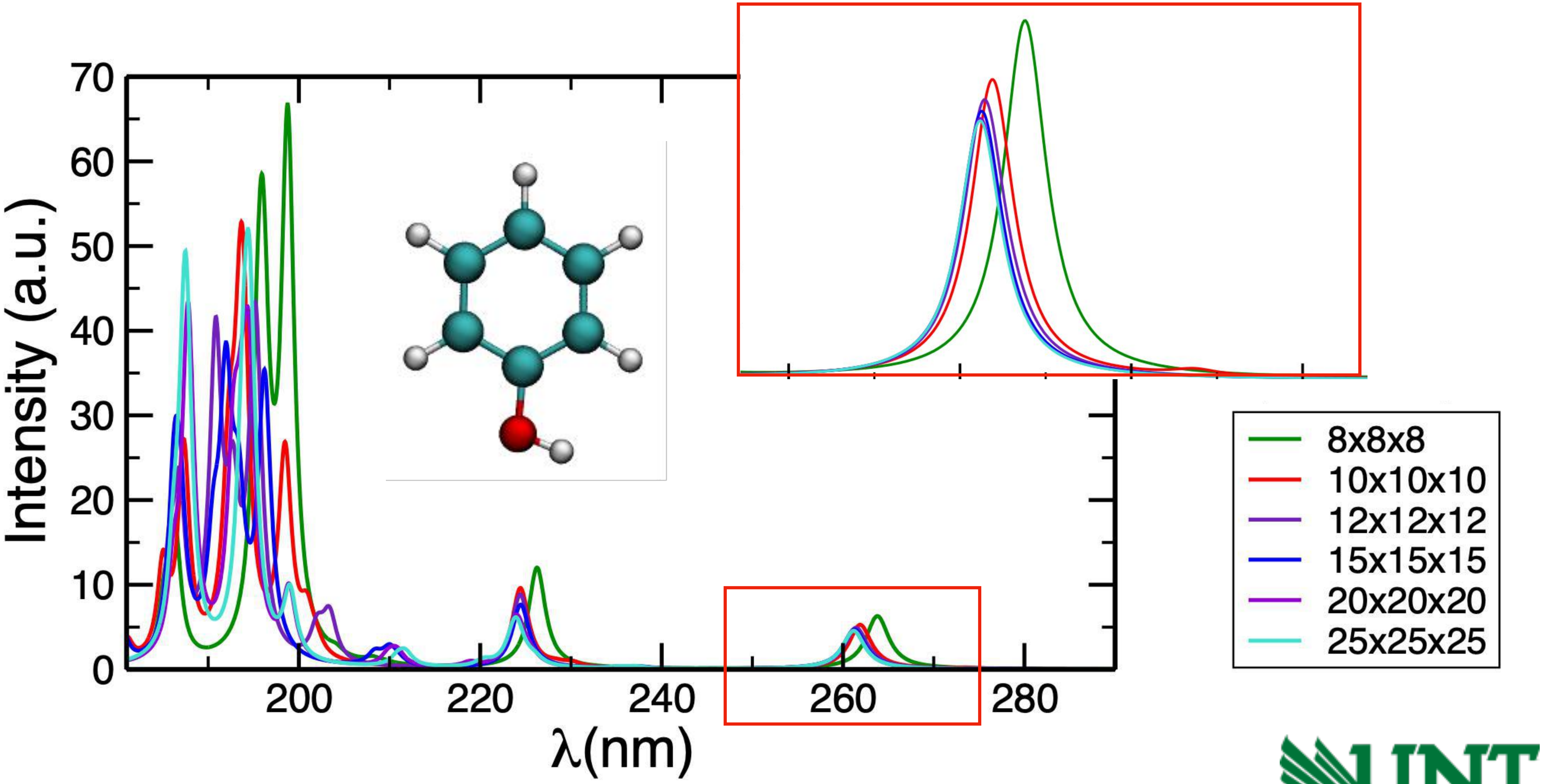
Where:
N = itermax0
N’ = intermix

Your first calculation



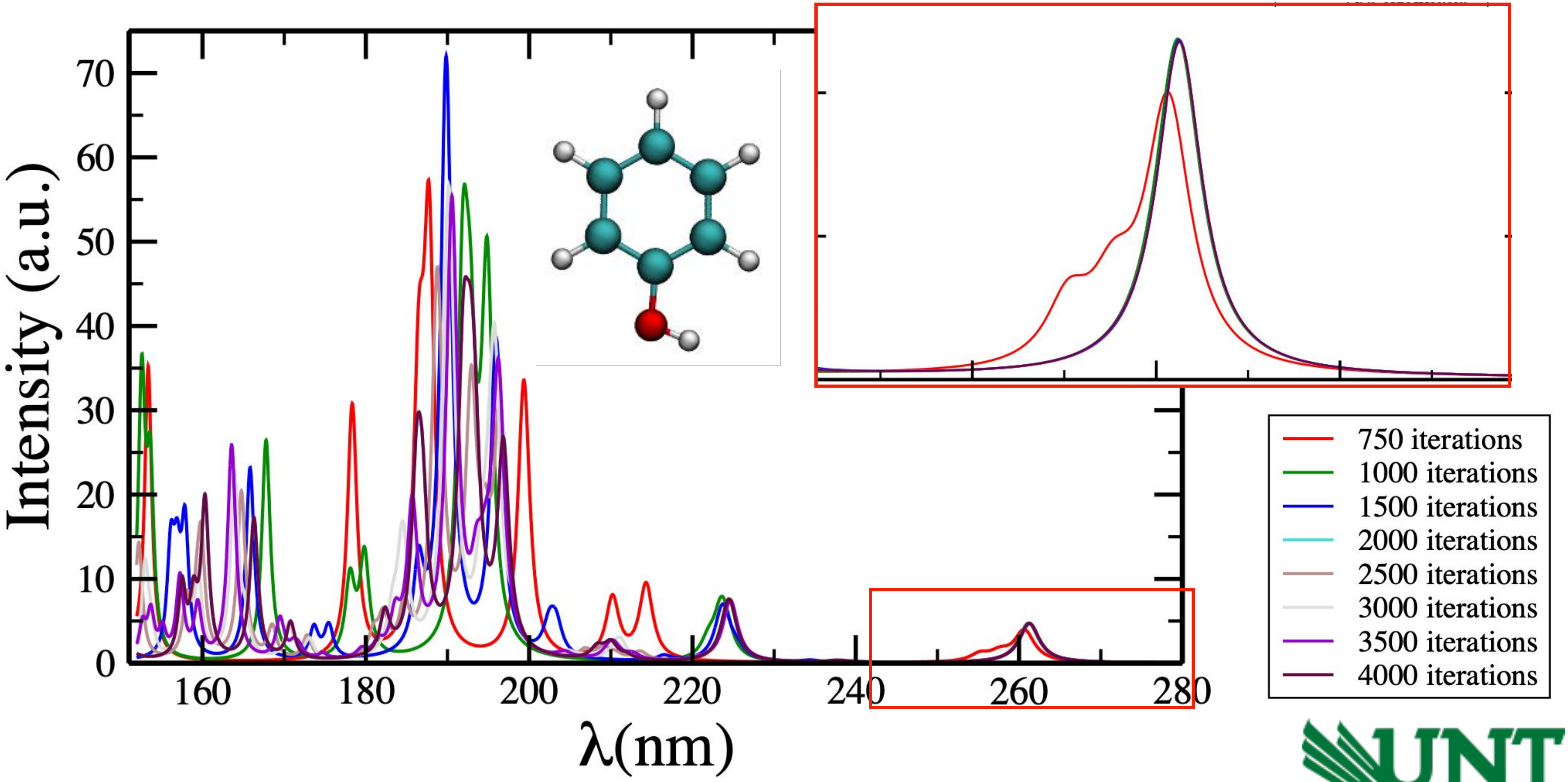
Convergence of spectrum calculations

Cell Size



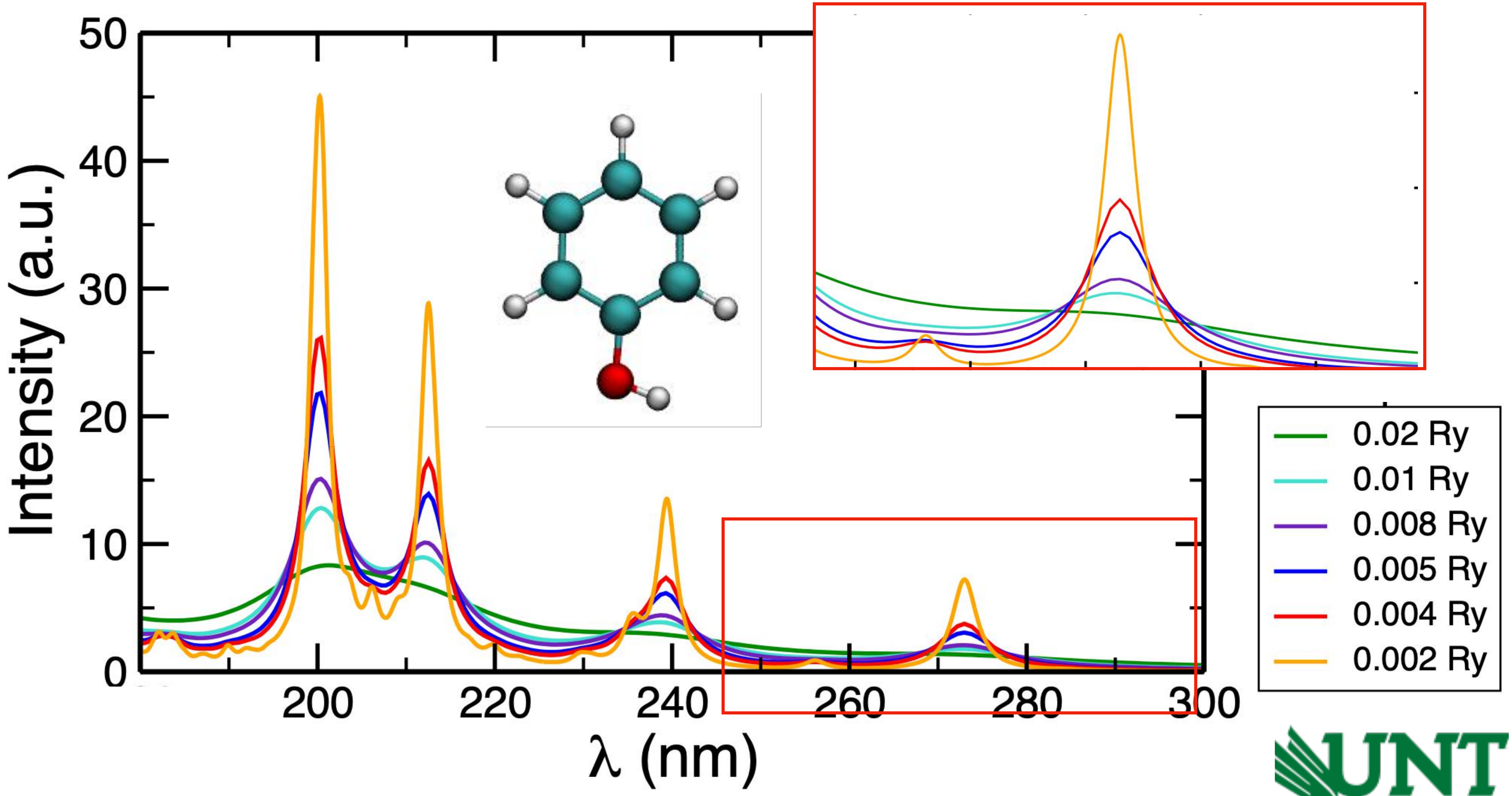
Convergence of spectrum calculations

Number of Lanczos Iterations



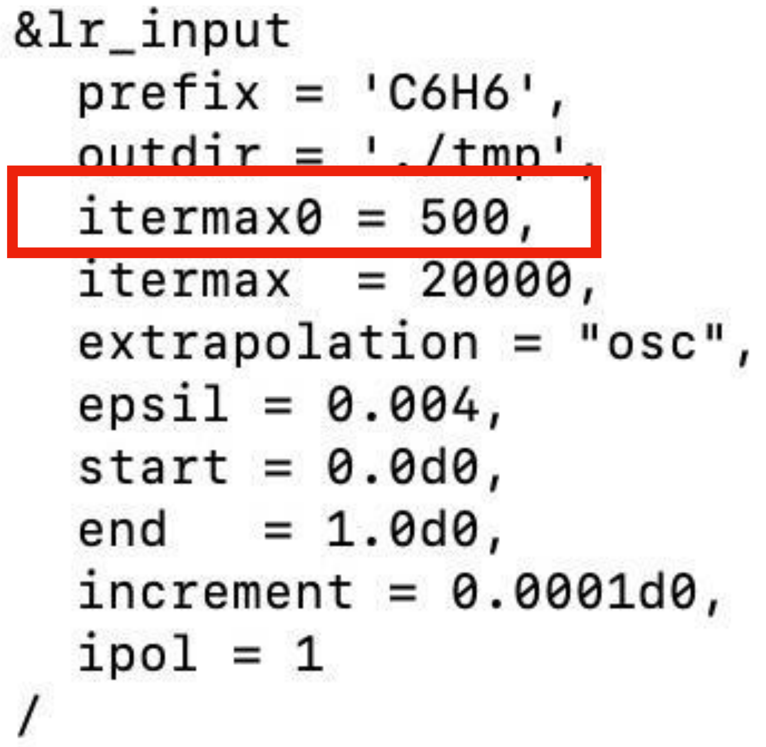
Convergence of spectrum calculations

Broadening



2. Absorption spectra convergence - Lanczos steps

- This exercise will help you determine the necessary number of lanczos steps to achieve convergence of the absorption spectra of benzene - the calculation you just performed
- The necessary output files have been generated for you (TDDFPT/benzene/conv_test)
- You will modify your post-processing file (C6H6.tddfpt_pp.in) to generate new C6H6.plot_chi.dat files where increasing number of lanczos steps are used to compute the spectra (ex: 500, 1000, 1500, 2000, …)
- This calculation was performed using 4000 lanczos steps

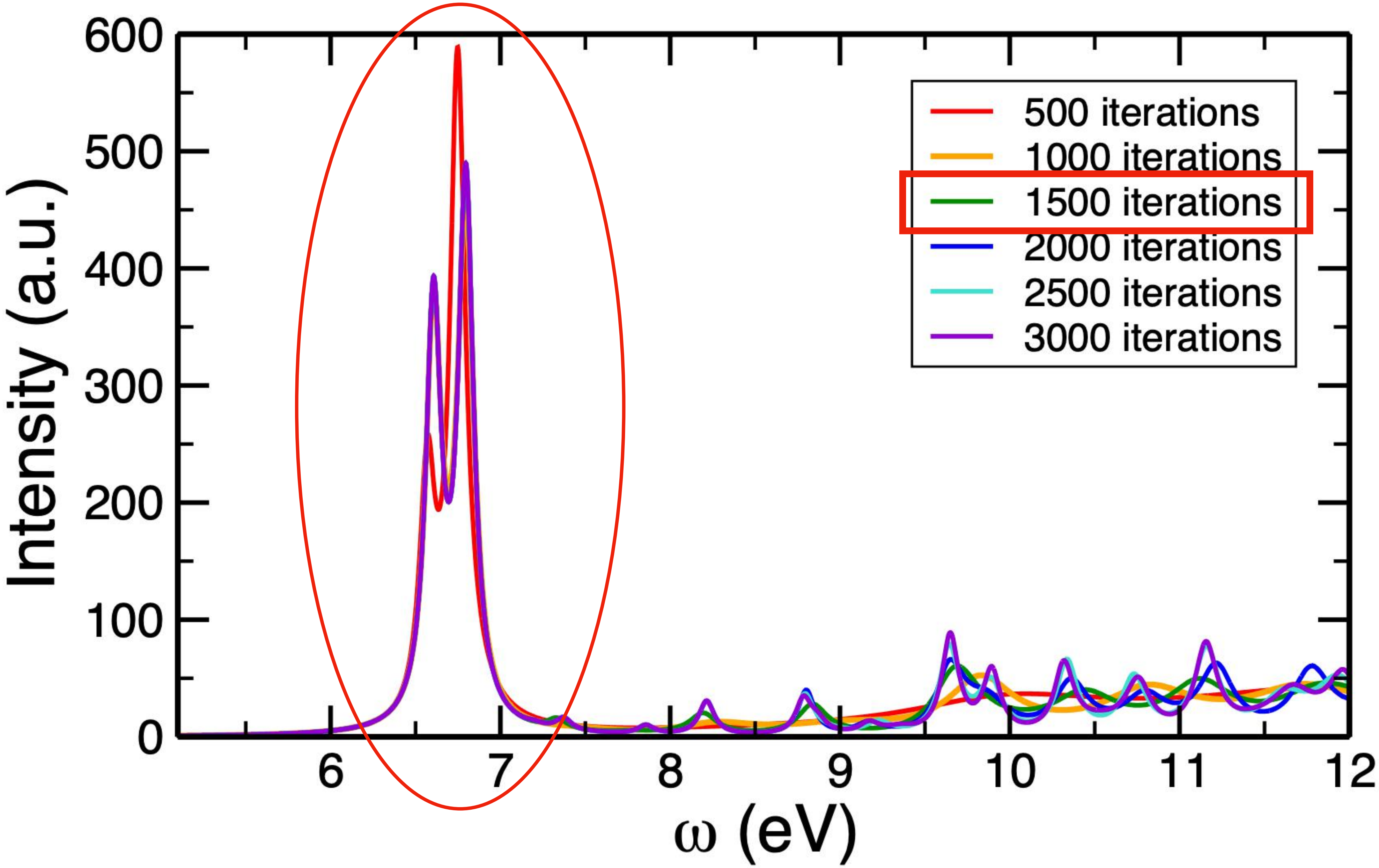


```
&lr_input
  prefix = 'C6H6',
  outdir = './tmp',
  itermax0 = 500,
  itermax   = 20000,
  extrapolation = "osc",
  epsil = 0.004,
  start = 0.0d0,
  end   = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

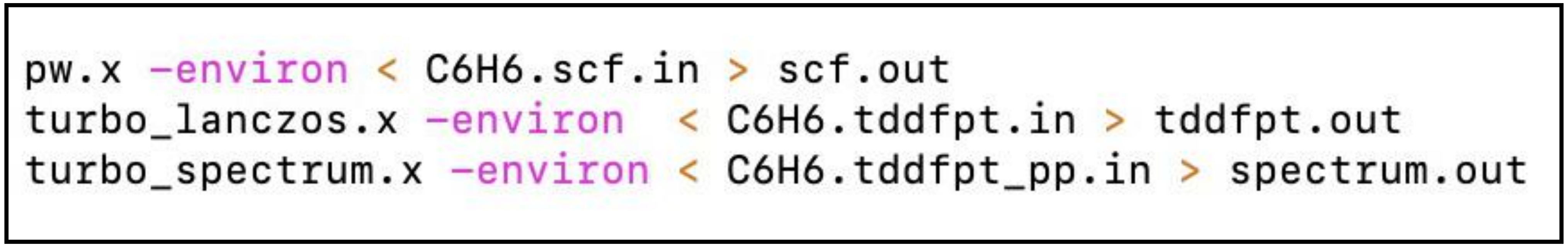
- Plot your results together. Your output is in Ry. Feel free to plot as is, or convert your files to eV.

- How many steps are necessary for your calculation to converge?

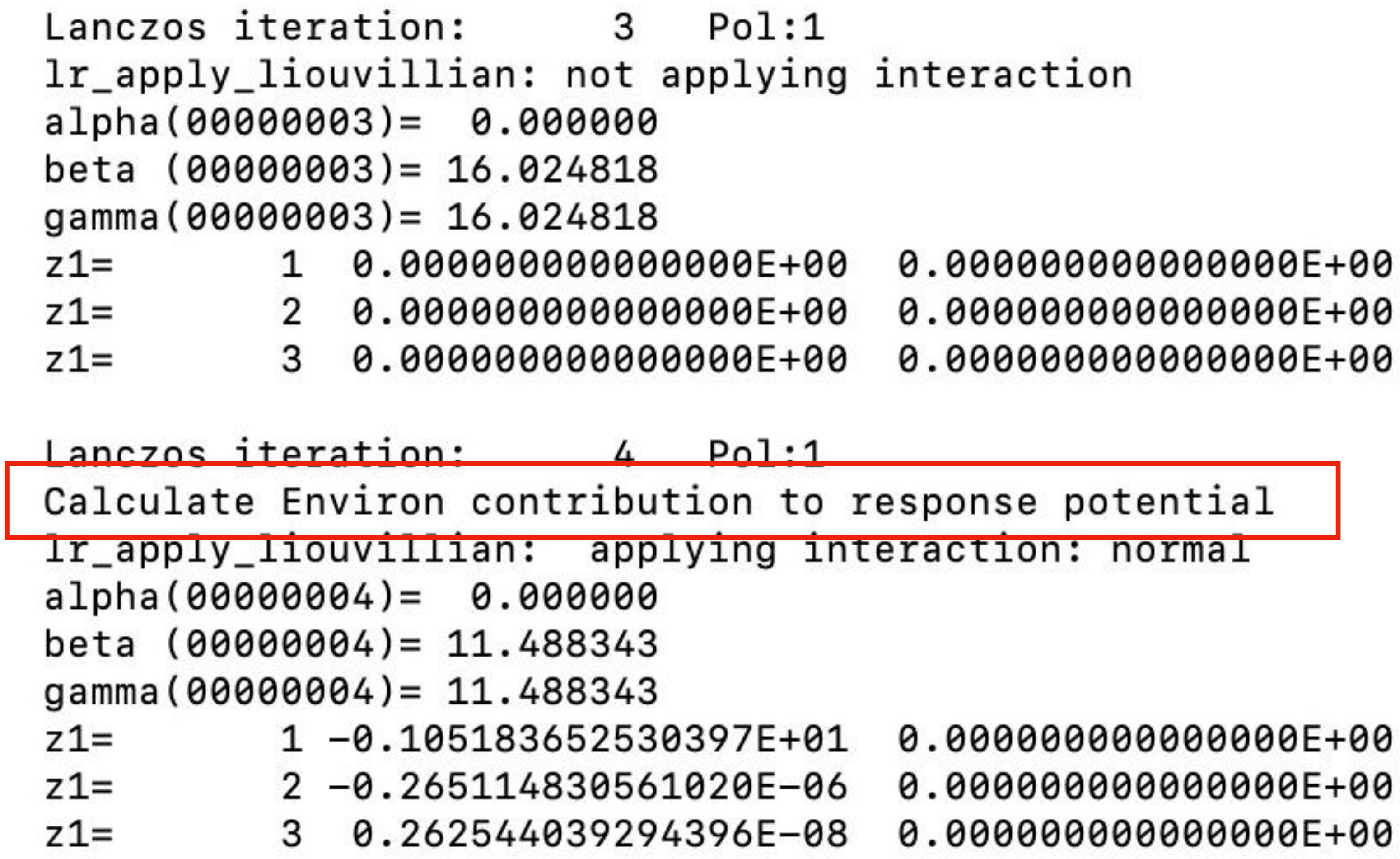
2. Absorption spectra convergence - Lanczos steps



3. Absorption spectra calculations with Environ

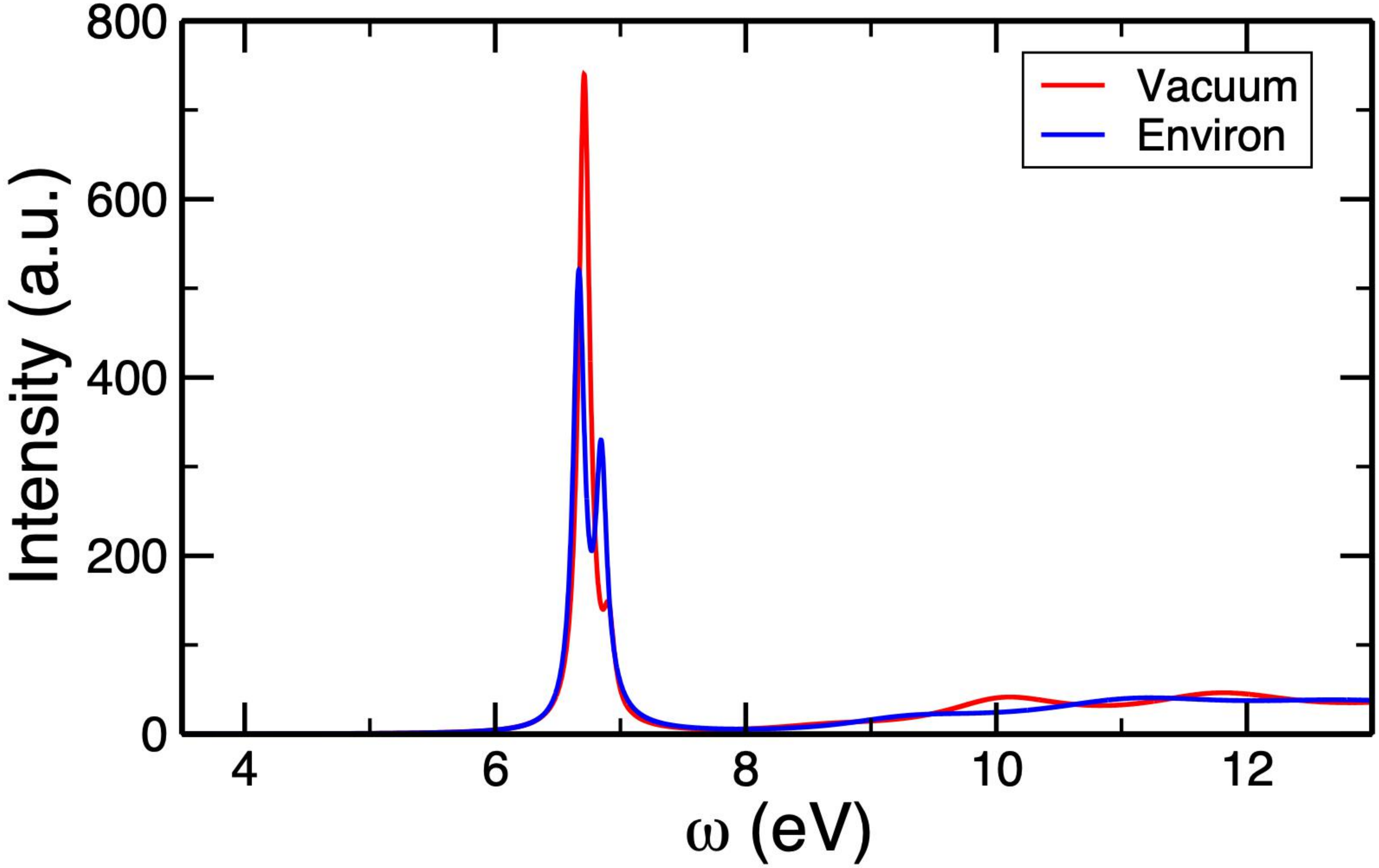


```
pw.x -environ < C6H6.scf.in > scf.out
turbo_lanczos.x -environ  < C6H6.tddfpt.in > tddfpt.out
turbo_spectrum.x -environ < C6H6.tddfpt_pp.in > spectrum.out
```



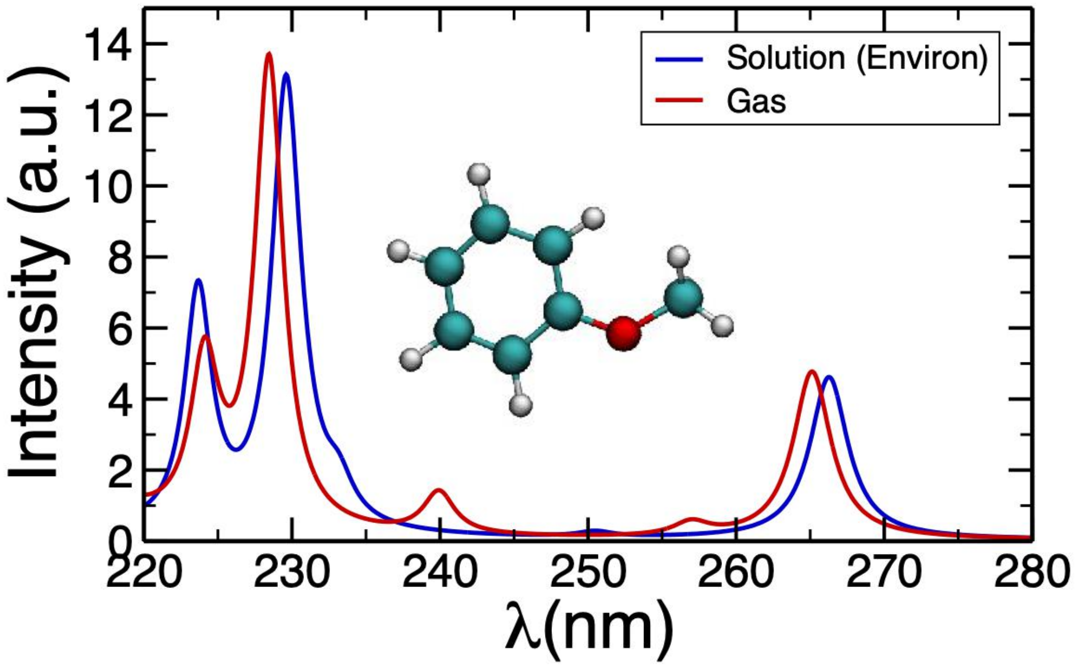
```
Lanczos iteration:      3   Pol:1
lr_apply_liouvillian: not applying interaction
alpha(00000003)=  0.000000
beta (00000003)= 16.024818
gamma(00000003)= 16.024818
z1=         1  0.000000000000000E+00  0.000000000000000E+00
z1=         2  0.000000000000000E+00  0.000000000000000E+00
z1=         3  0.000000000000000E+00  0.000000000000000E+00

Lanczos iteration:      4   Pol:1
Calculate Environ contribution to response potential
lr_apply_liouvillian:  applying interaction: normal
alpha(00000004)=  0.000000
beta (00000004)= 11.488343
gamma(00000004)= 11.488343
z1=         1 -0.105183652530397E+01  0.000000000000000E+00
z1=         2 -0.265114830561020E-06  0.000000000000000E+00
z1=         3  0.262544039294396E-08  0.000000000000000E+00
```

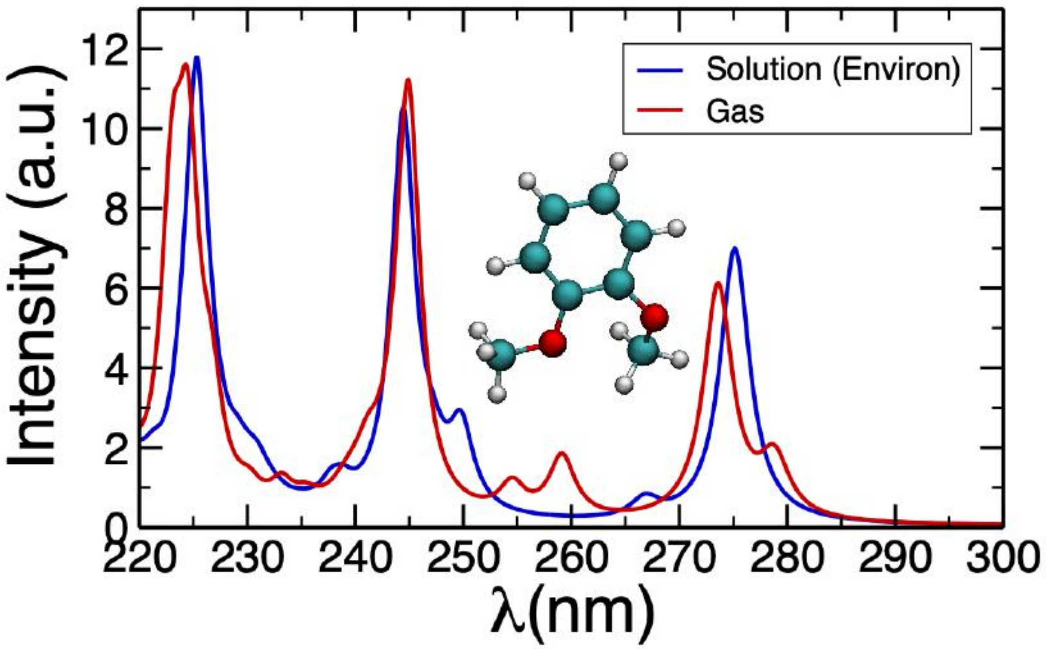
3. Absorption spectra calculations with Environ

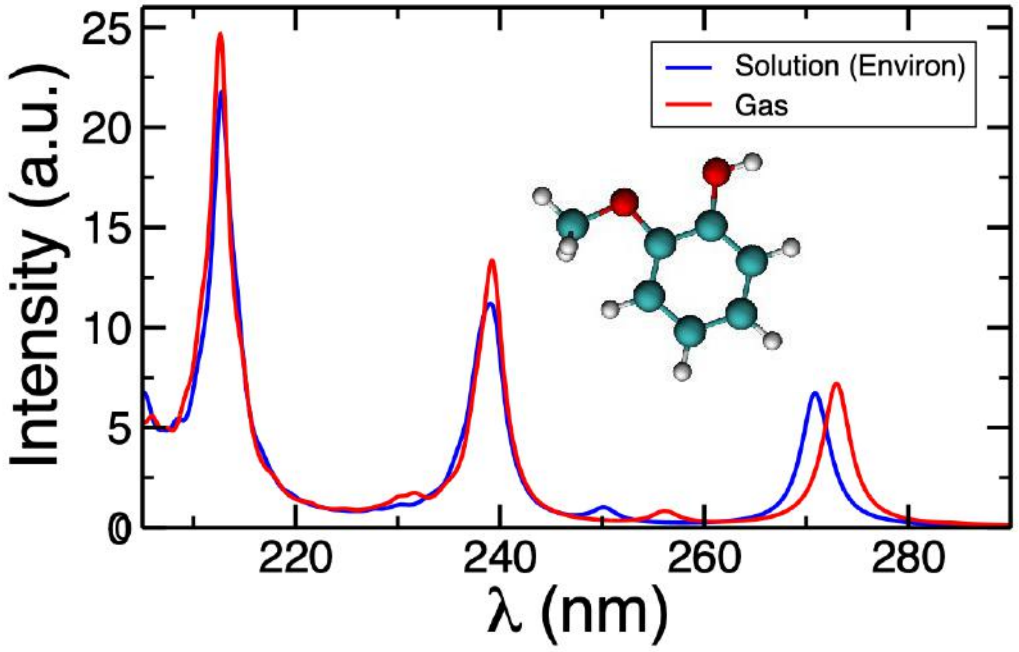


3. Absorption spectra calculations with Environ

Different molecules (functional groups) will show different environment interference







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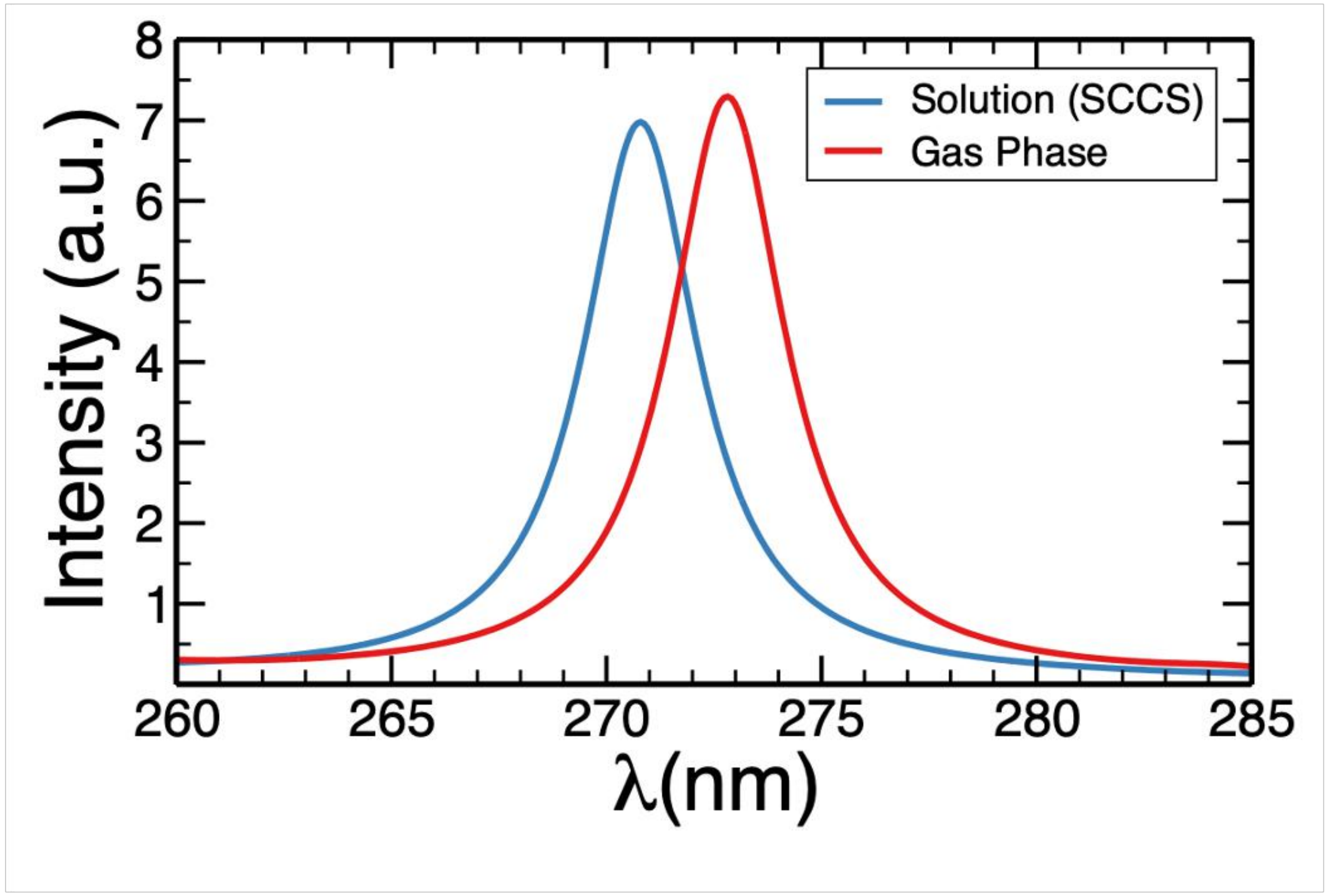
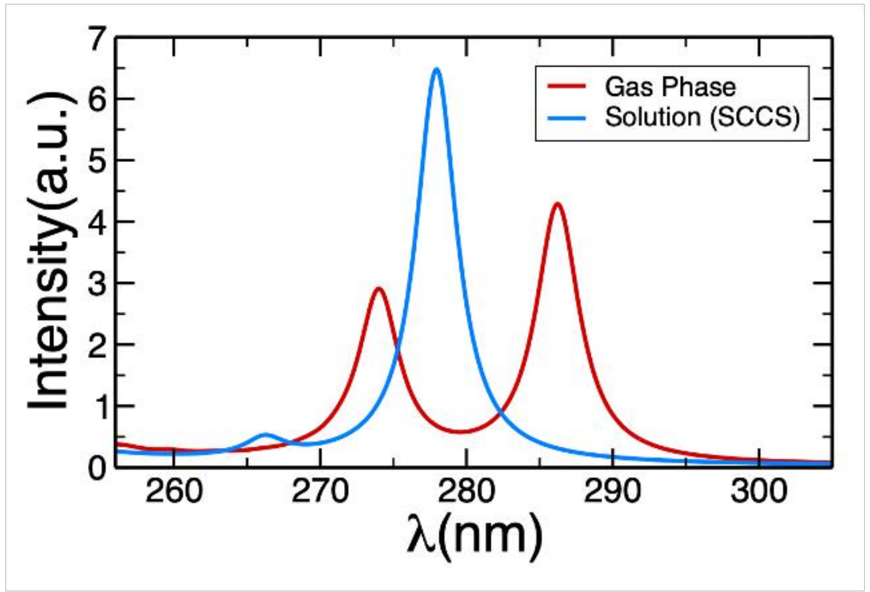
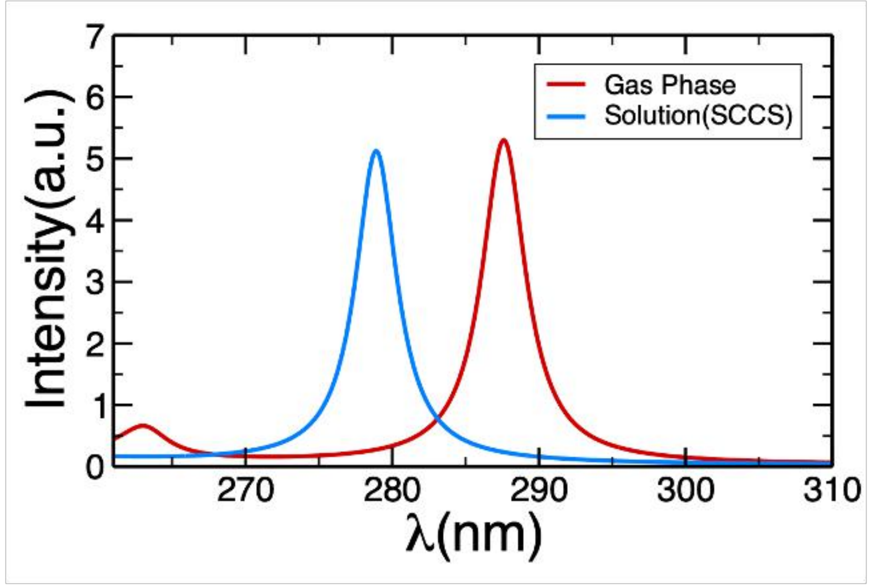
Importance of Environment Effects

Single Frame Optimized in gas phase

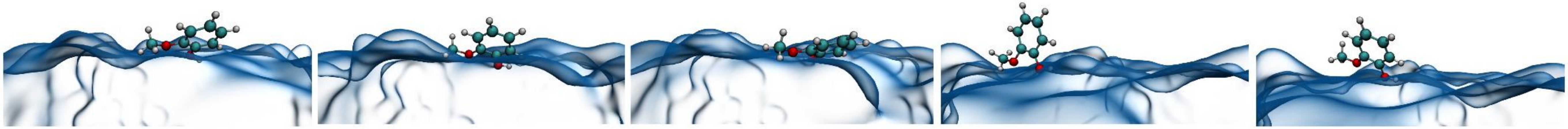


Random frames obtained from FPMD trajectory



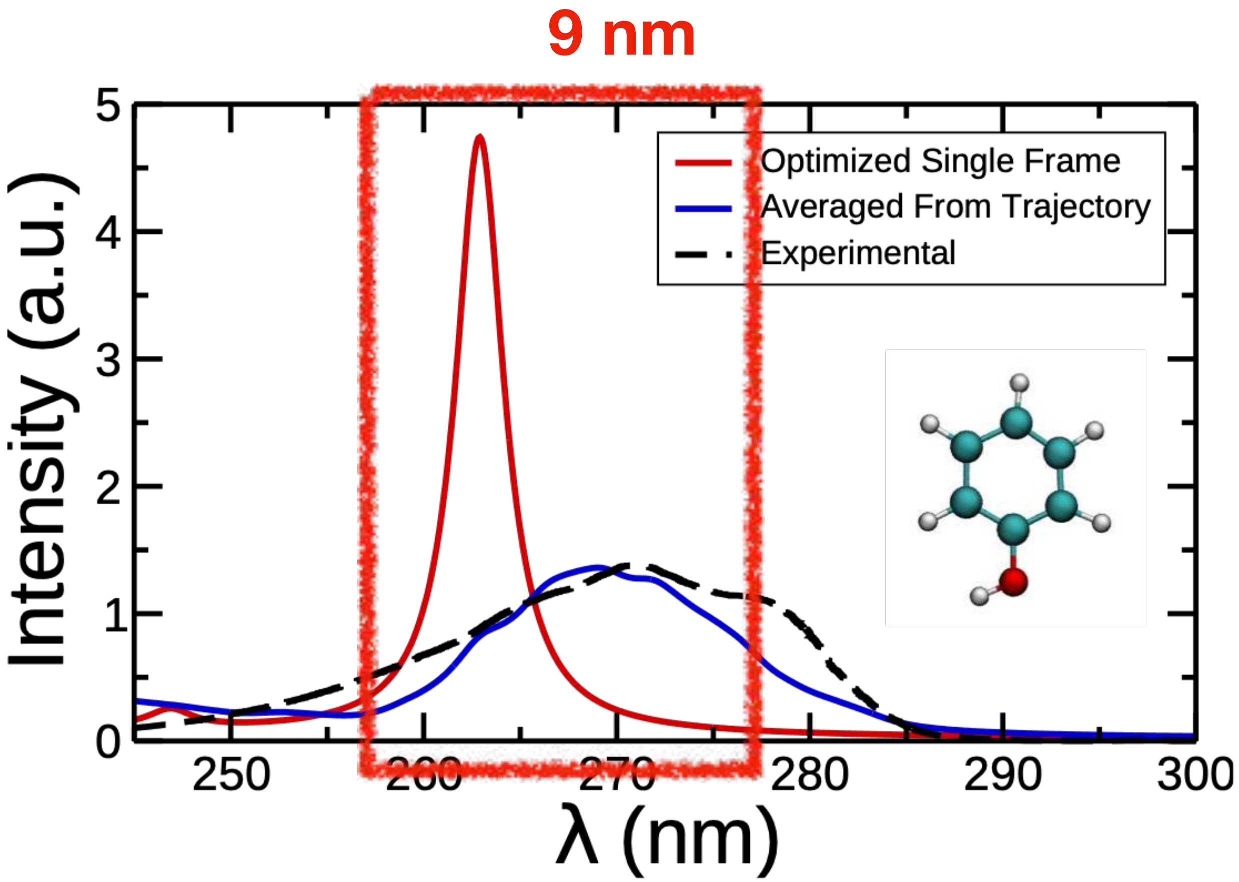


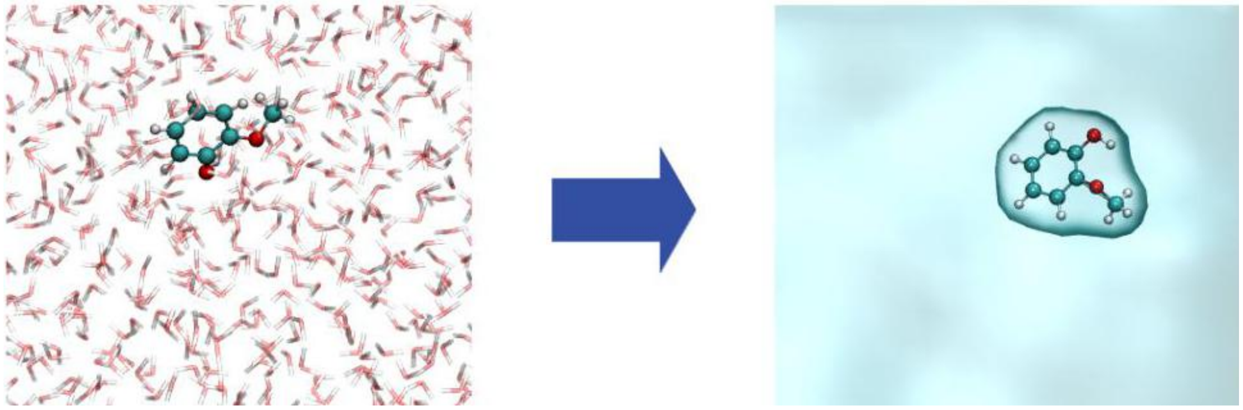
Ensemble Averaging



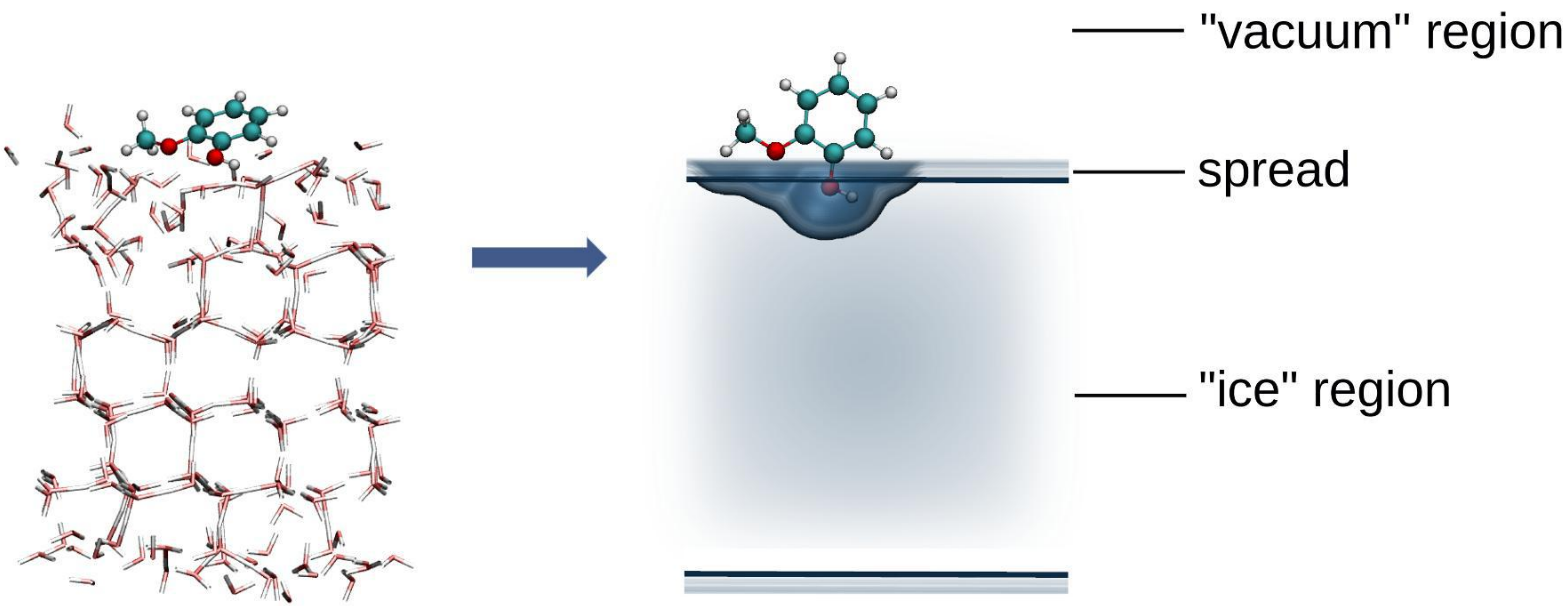
Absorption spectra obtained as an **average** of multiple frames of a trajectory and not from a single (structure-optimized) configuration

Optimized structure (single calculation) versus averaged calculation obtained from ab initio trajectory in solution





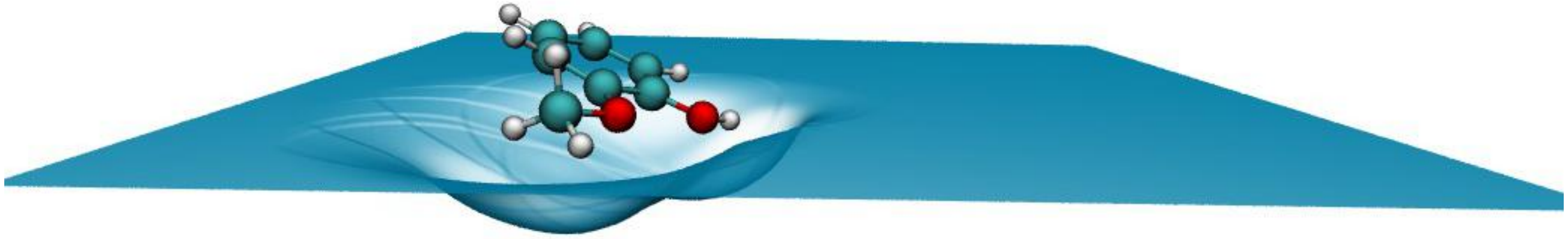
4. Absorption Spectra for Molecules on Surfaces



Important Parameters

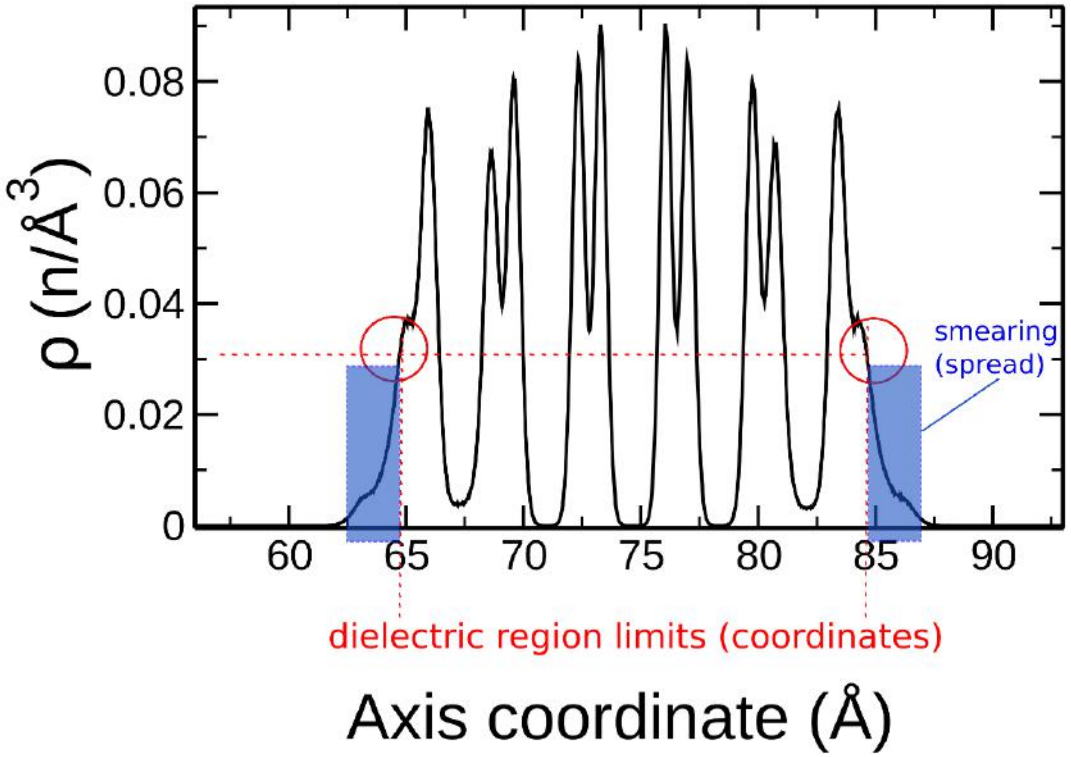
- Size of the simulation box
- Spread region (Δ)
- Thickness of the ice and vacuum region
- Static (ε_0) and optical (ε_{opt}) permittivities

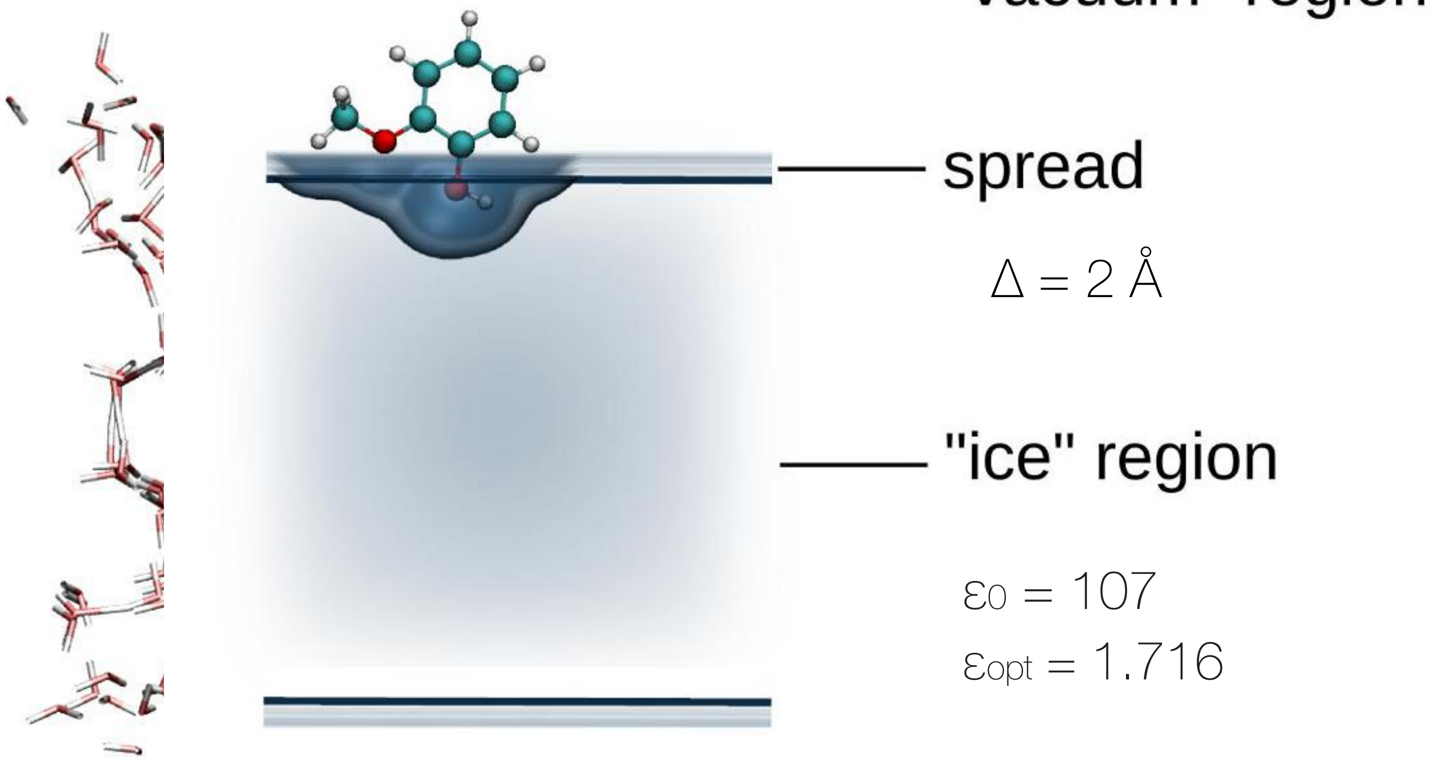
Setting up the correct parameters



Important Parameters

- Size of the simulation box
- Spread region (Δ)
- Thickness of the ice and vacuum region
- Static (ε_0) and optical (ε_{opt}) permittivities





"vacuum" region

spread

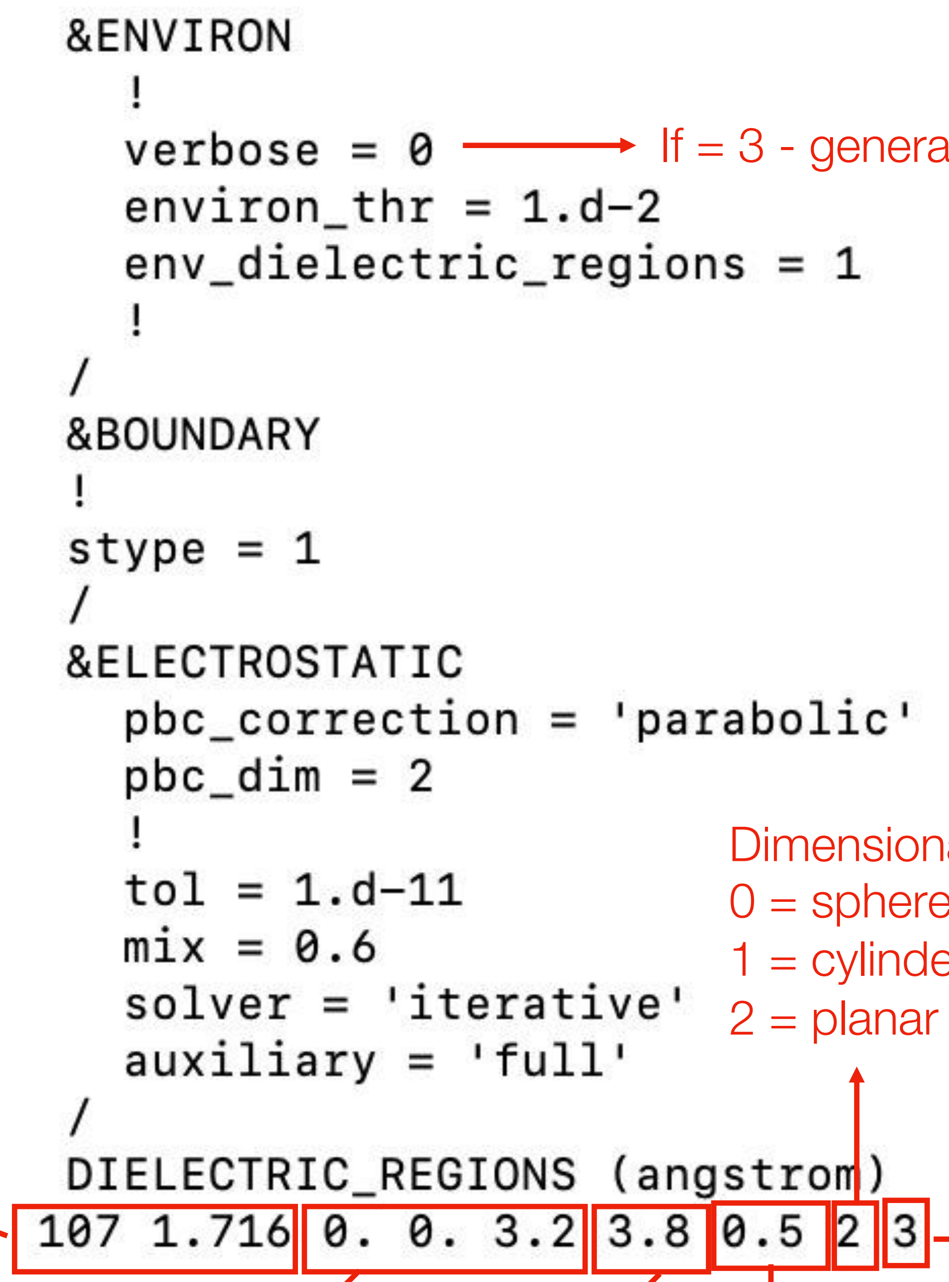
Δ = 2 Å

"ice" region

ε_0 = 107

ε_{opt} = 1.716

Environ input file



```
&ENVIRON
  !
  verbose = 0
  environ_thr = 1.d-2
  env_dielectric_regions = 1
  !
/
&BOUNDARY
!
stype = 1
/
&ELECTROSTATIC
  pbc_correction = 'parabolic'
  pbc_dim = 2
  !
  tol = 1.d-11
  mix = 0.6
  solver = 'iterative'
  auxiliary = 'full'
/
DIELECTRIC_REGIONS (angstrom)
 107 1.716 0. 0. 3.2 3.8 0.5 2 3
```

If = 3 - generates *.cube files (really cool!!)

Static (107) and optical (1.716) permittivity values inside dielectric region

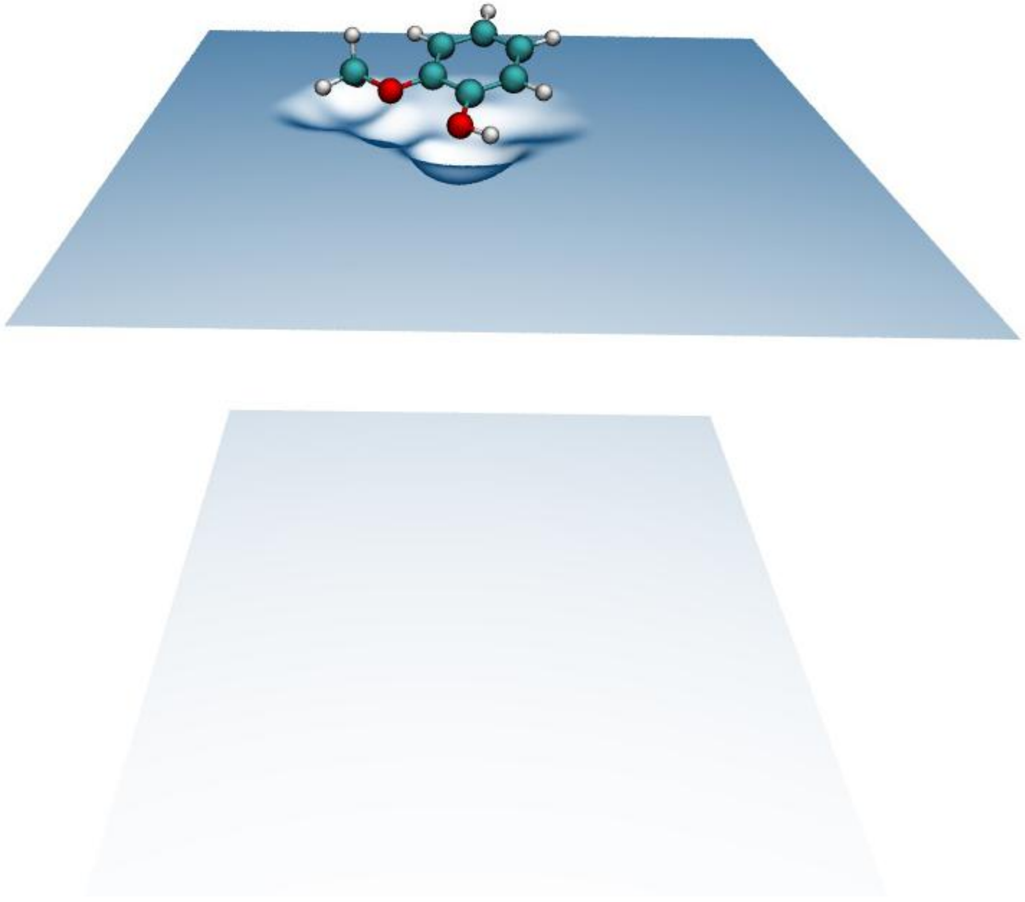
Dimensionality:
0 = sphere-like
1 = cylinder-like
2 = planar

Axis of the dielectric region (1,2,3 = x,y,z)

Spread

Positions (x, y, z) of center of region

Half of the width of the dielectric region



Phenol "Challenge"

- If you want to practice more of this, you can go to phenol/phenol_challenge and try to create your own input files for turbo_lanczos.x and turbo_spectrum.x based on the data presented on calculation convergence - try to set up a good enough number of iterations, a correct box size, etc.

- You may also want to play around with parameters on your post-processing file such as as start, end and increment. Remember that for experimental purposes, the range of interest in the absorption spectrum of phenol is between ~240-300 nm. ** Units in QE are Ry **