Modeling the Absorption Spectra of Phenol and Guaiacol at the Ice-Air Interface

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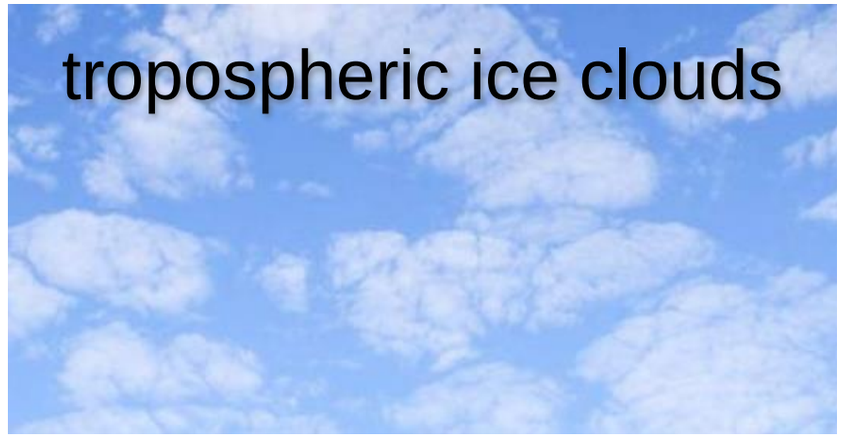
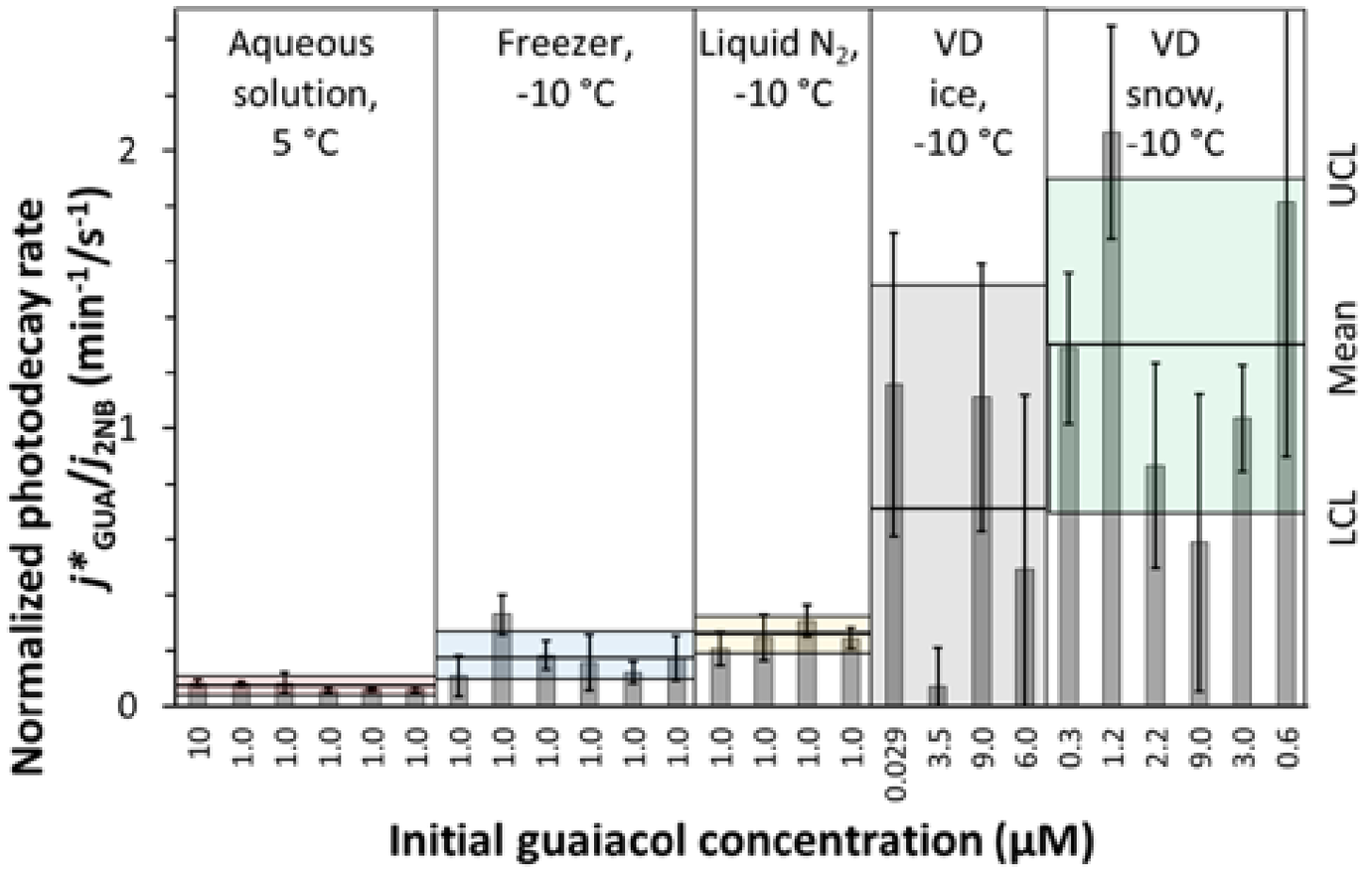
Ice surface in climate modeling:



- Snow: active location for chemical reactions
- Snow/ice crystals contain small areas of disordered water molecules, where most solutes are located:
  - QLL (quasi-liquid layer) - air-ice interface
  - LLR (liquid-like regions) - within the ice matrix

Ice surfaces and Atmospheric Chemistry

- Ice/snow foster photochemical reactions
- Only the rates of few photochemical reactions have been studied
- Research data shows reaction enhancement for certain molecules on ice and similar rates for others



Hullar, T., Anastasio, C. *Unpublished data*

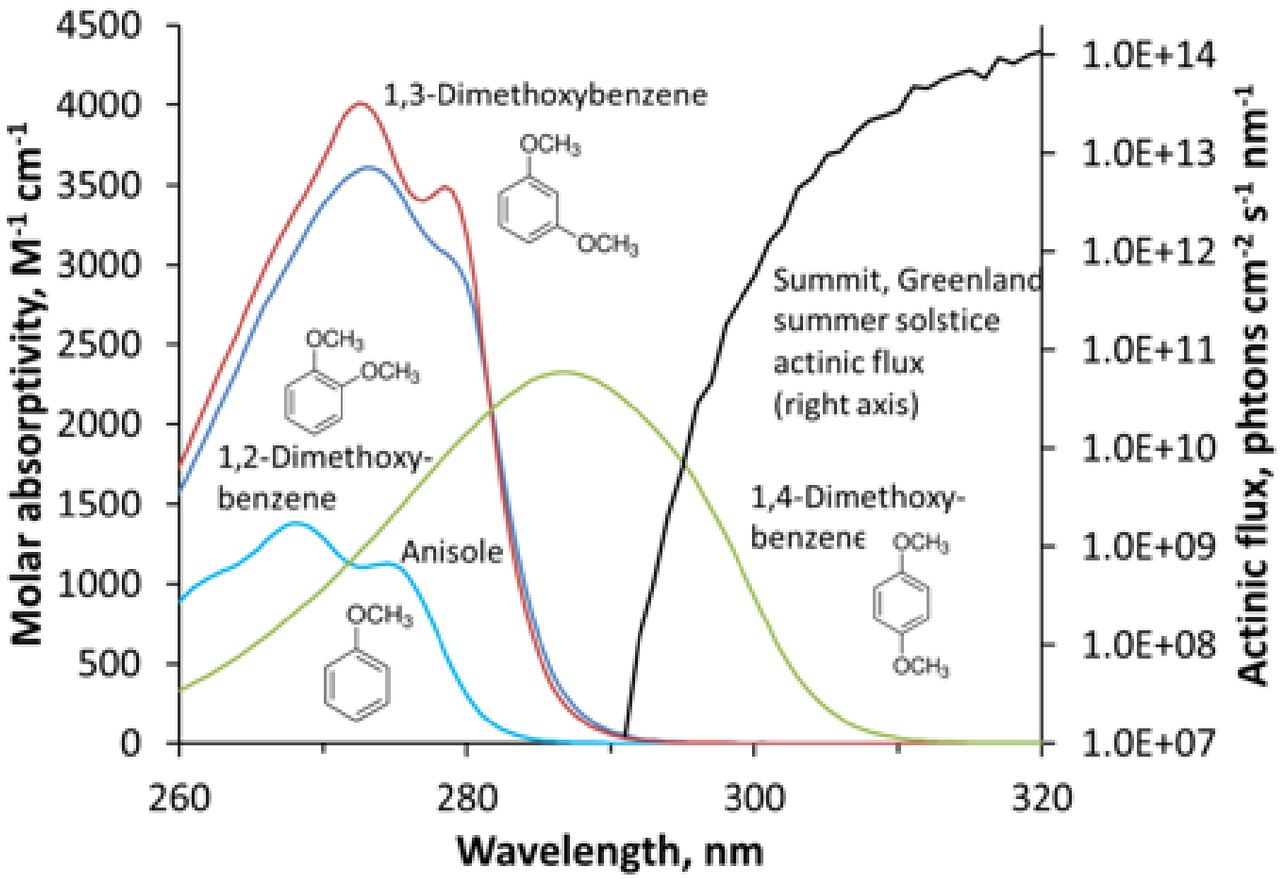
Photochemical Reactions are Enhanced on Ice

T ~ 250 - 270 K

Photochemistry in snow and tropospheric clouds

Could be due to:

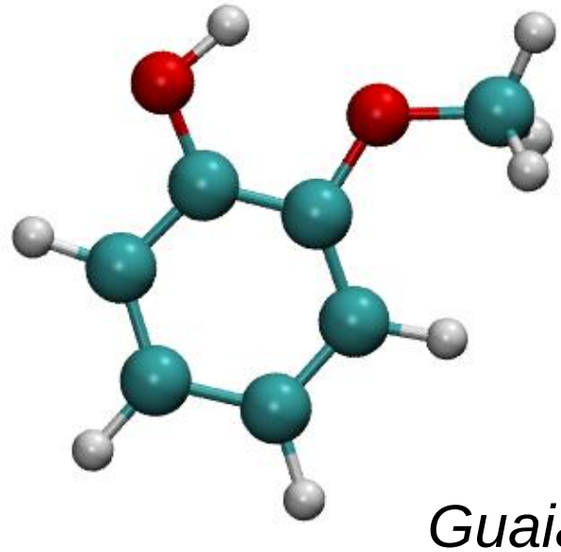
- Higher local photon fluxes
- Higher quantum yields
- A bathochromic shift in molar absorptivity



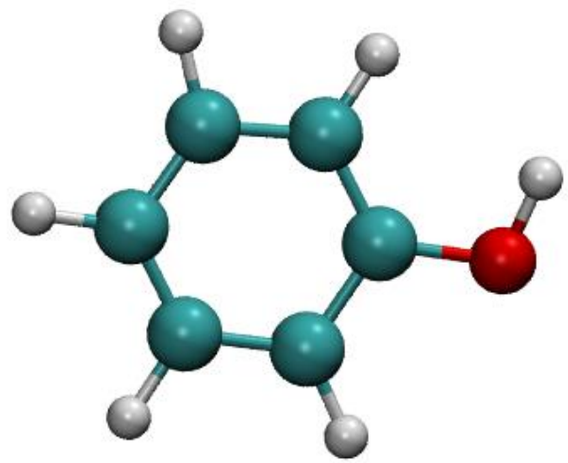
adapted from Madronich and Flocke, 1999

Modeling the Absorption Spectra of Organic Molecules

- Light absorption bands that tail off to zero between 280-320 nm
- Slightly soluble in water
- Vapor pressure between 0.001 and 10kPa



Guaiacol



Phenol

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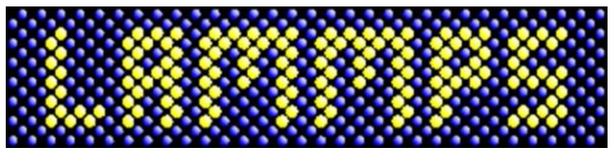
Modeling the Absorption Spectra of Organic Molecules

Multiscale/multimodel approach

- Large-scale classical Molecular Dynamics (MD) 
    - 1000s of atoms, 100s of nanoseconds
    - Equlibrate the QLL at the ice surface
        - characterization of solvation/adsorption of selected molecules
- First-principles Molecular Dynamics 
    - maximum of 100s of atoms, productions runs of a maximum of 100 picoseconds
- Absorption Spectra Calculations 
    - Using computer-intensive Time-Dependent Density Functional Theory calculations

Timrov, I. *et al. J Chem Theory Comp.* (2016)

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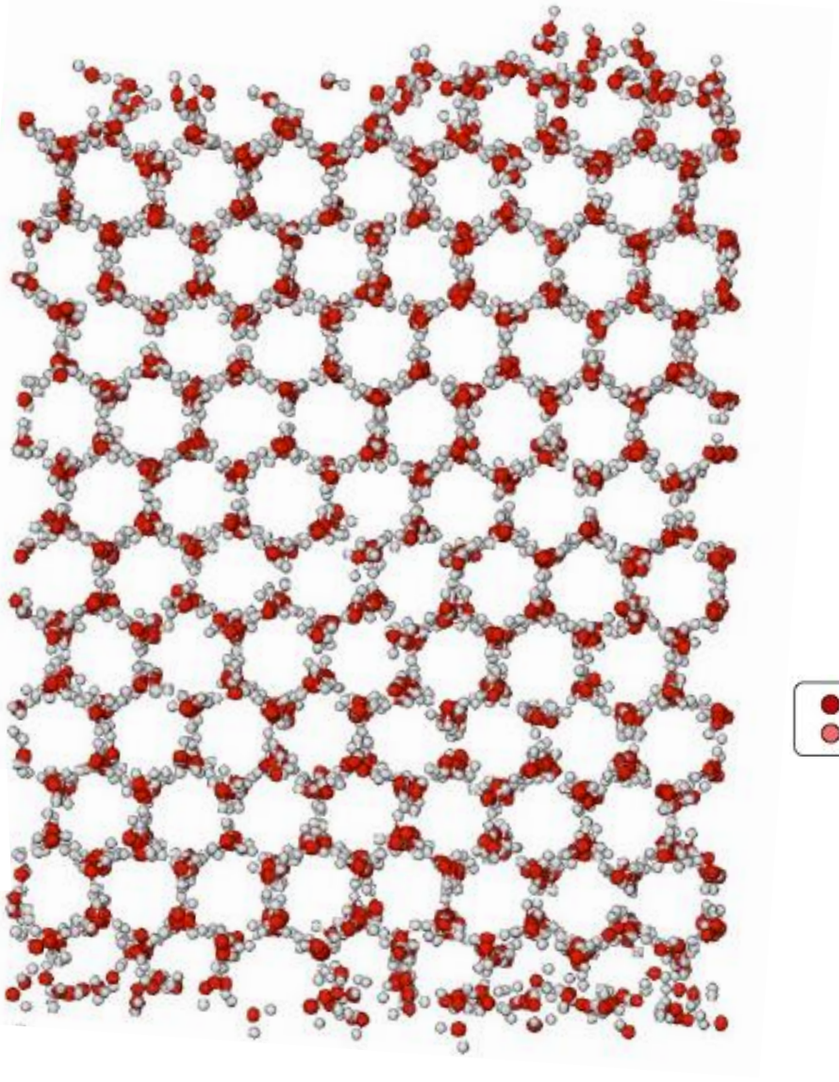
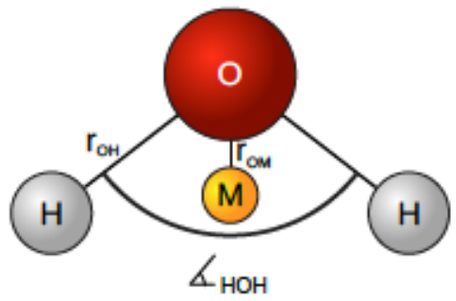
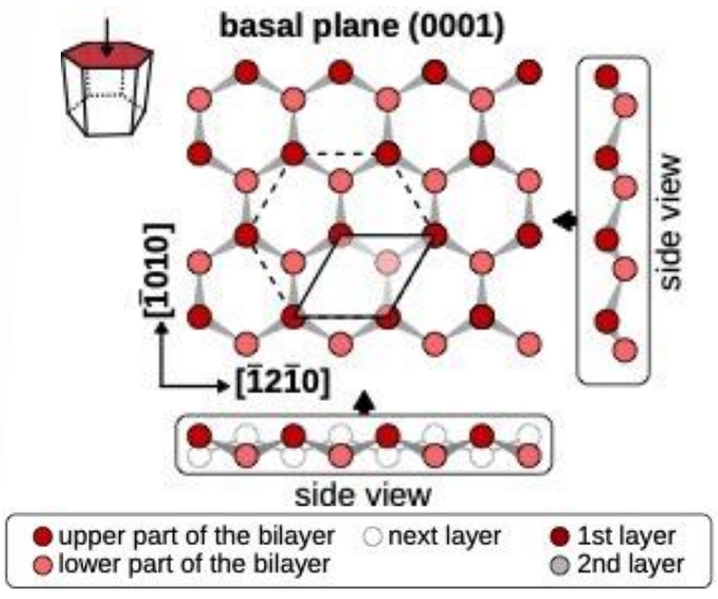
Characterization of ice surfaces

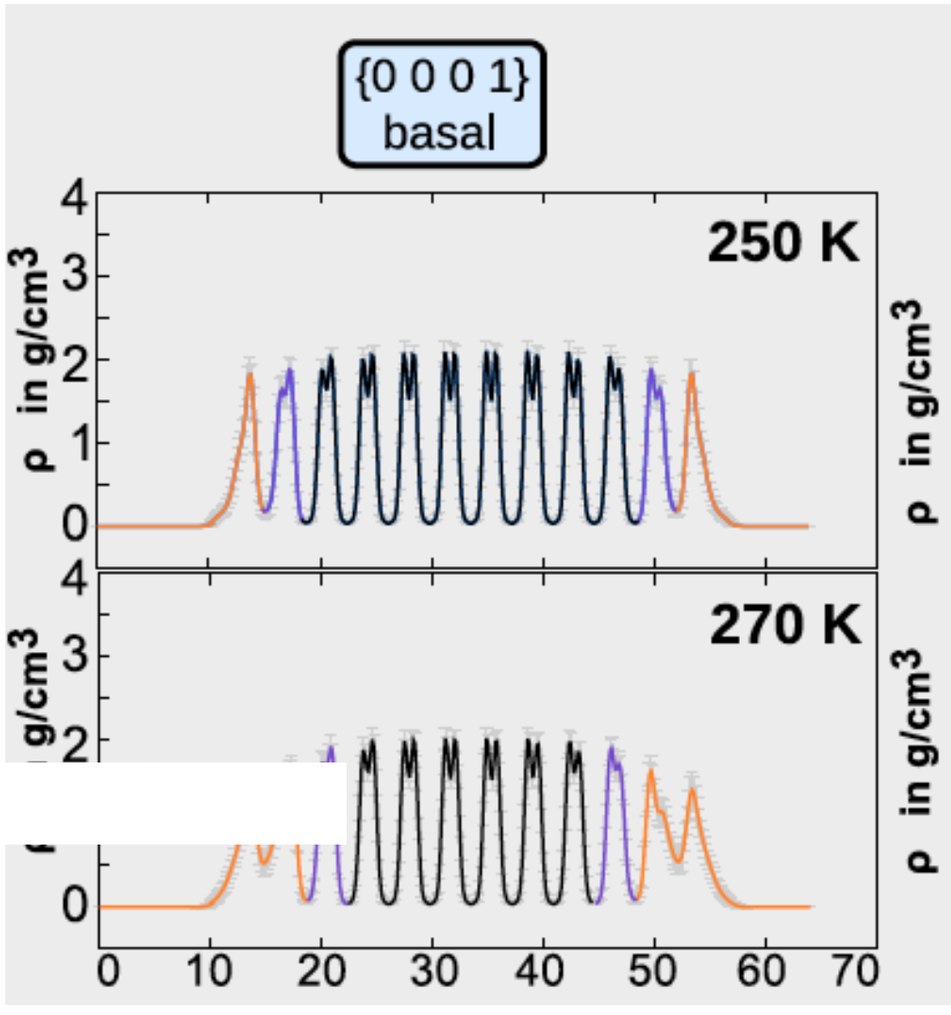
- TIP4P/Ice model
- Temperature: 200 to 270 K
- Total simulation time: 200 ns





TIP4P/Ice

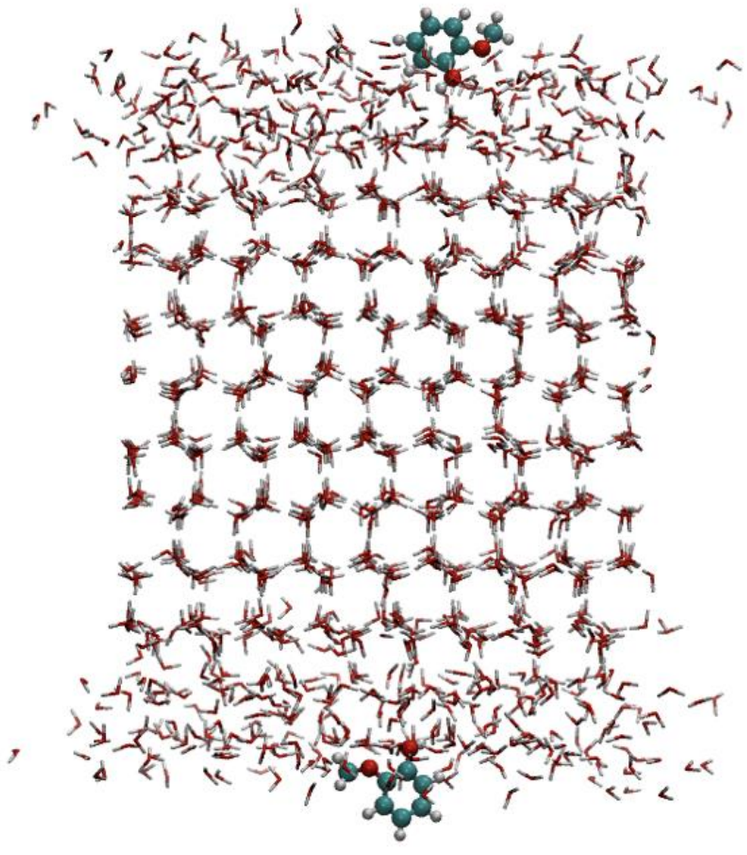


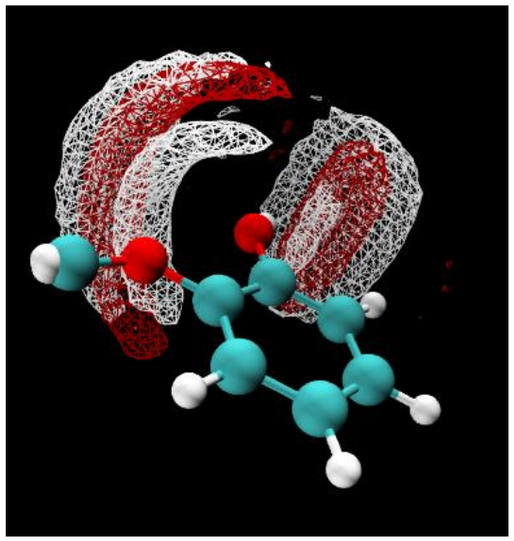


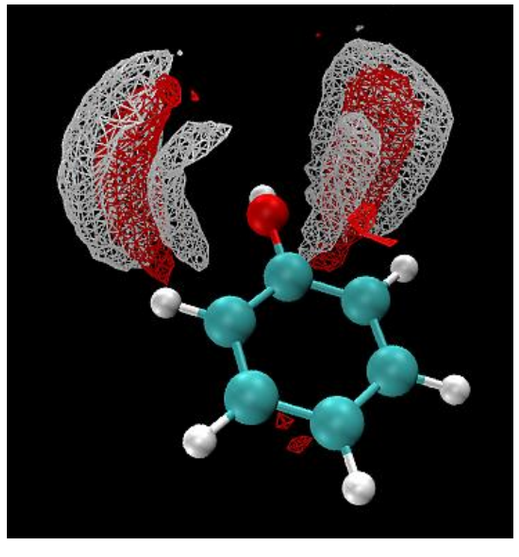
discrete melting

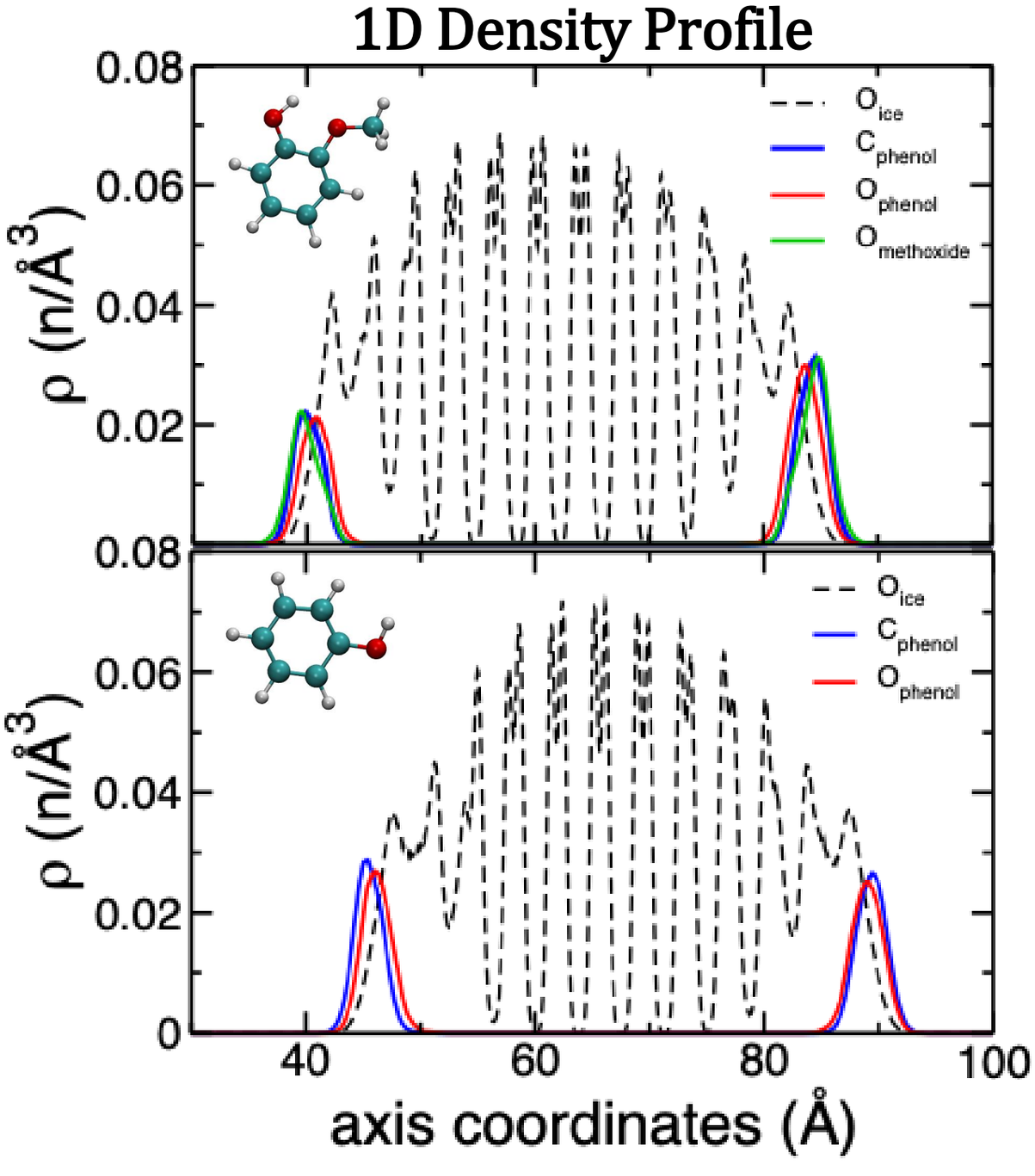
Molecules on Ice

- Temperature: 263 K
- Production run: 100 ns









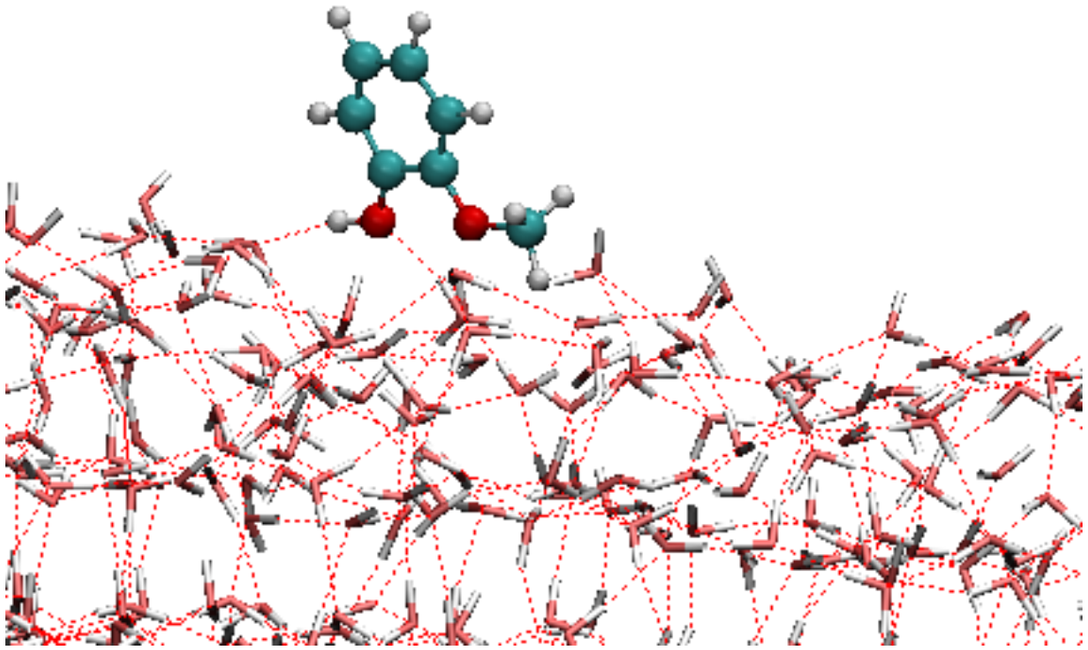
Free Energy of Solvation

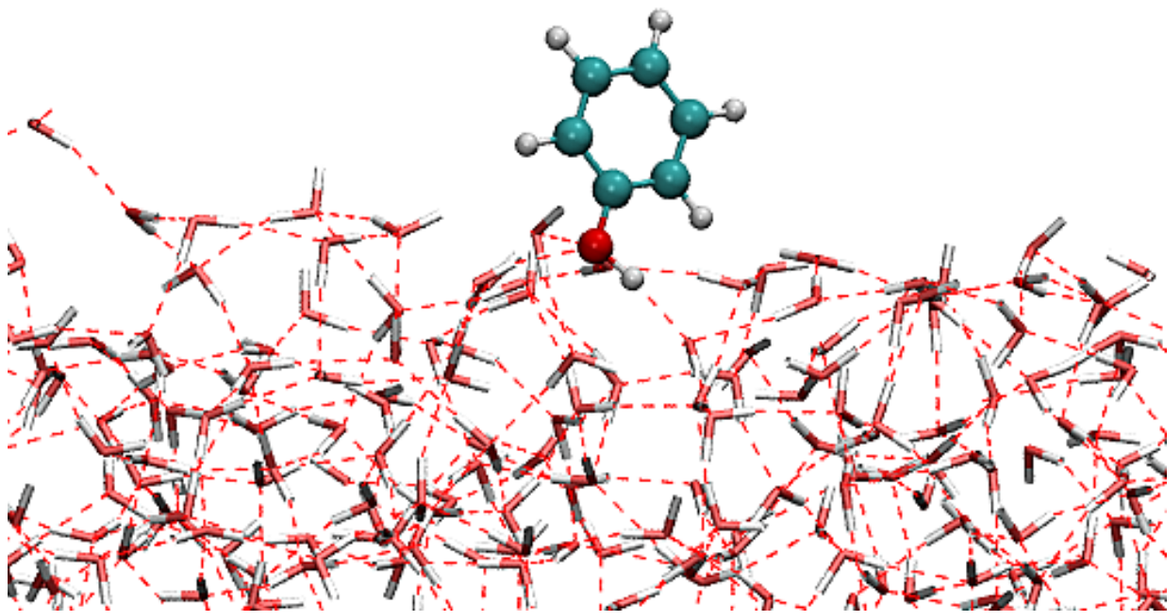
Guaiacol

Conditions	ΔGexp	ΔGcalc
300K (Water)	5.94	6.8
270K(Water)	-	7.63
270K (Ice Surface)	-	9.92

Phenol

Conditions	ΔGexp	ΔGcalc
300K (Water)	6.62	5.84
270K (Water)	-	6.52
270K (Ice Surface)	-	15.65





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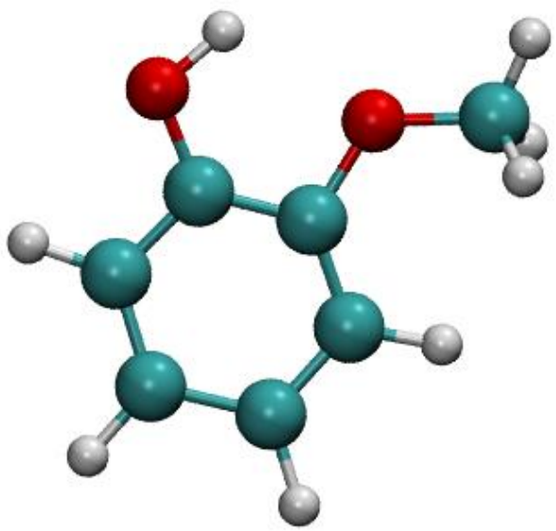
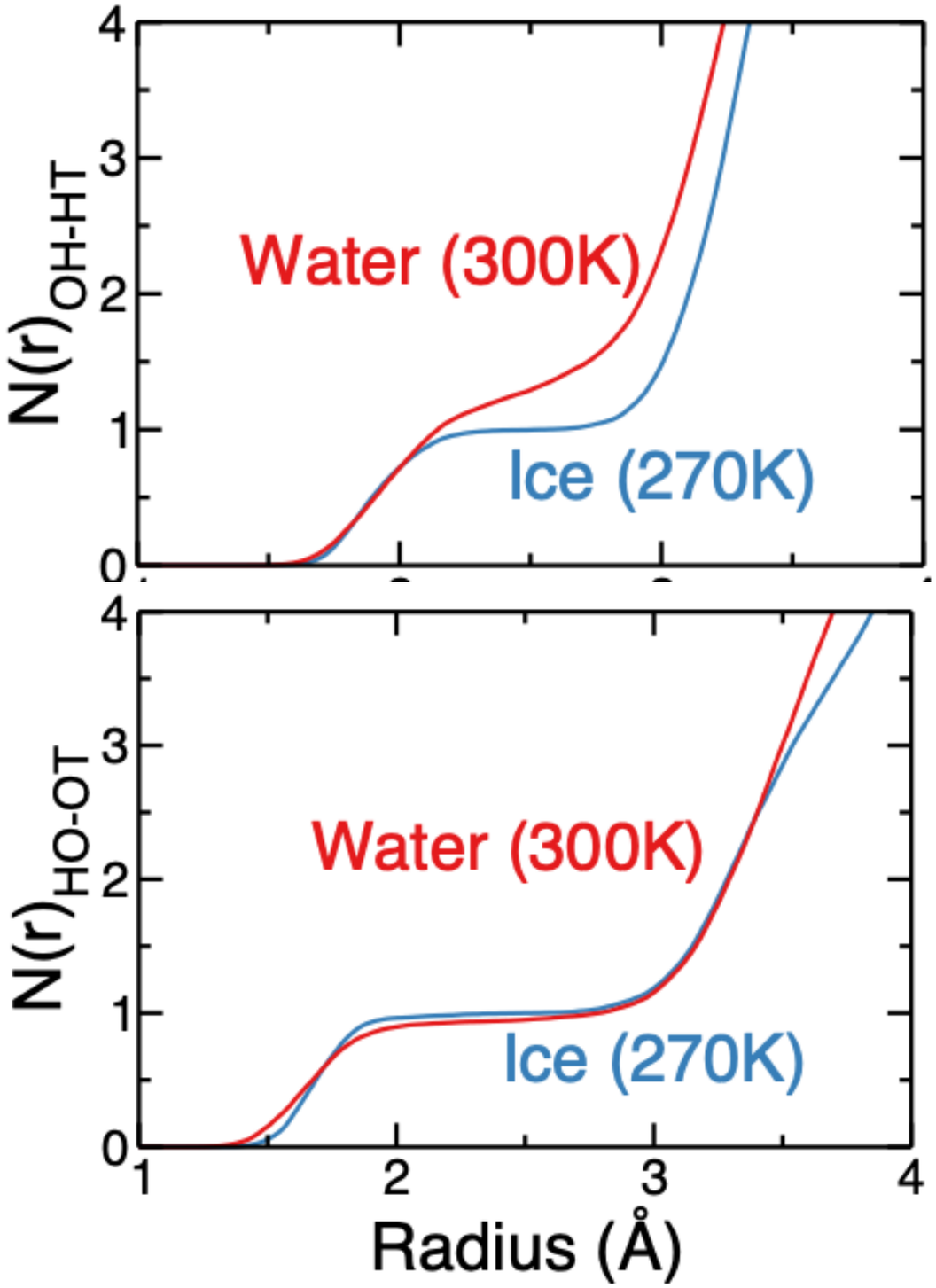
First-Principles Molecular Dynamics

- Gas phase, aqueous solution (300K) and on surface of ice (263K)
- Representative clusters will be used to comp[illegible] spectra





Absorption Spectra Calculations

Current approaches cannot predict bathochromic shifts

- do not incorporate the effect of temperature driven fluctuations of the solvation shell
- air-ice interface provides unique solvation environment

Absorbance Spectra are affected by:

- **Temperature-driven fluctuations of solvation shell**

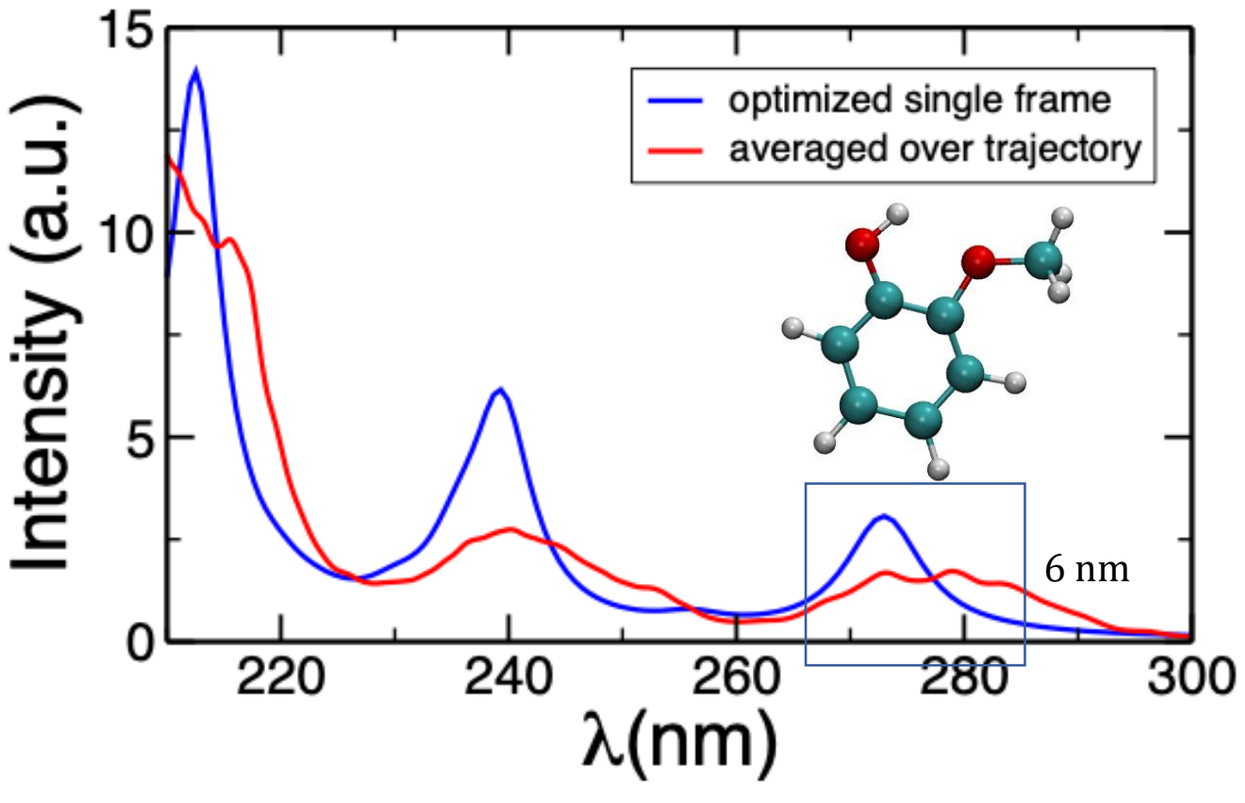
  - Determine width and shape of absorption bands

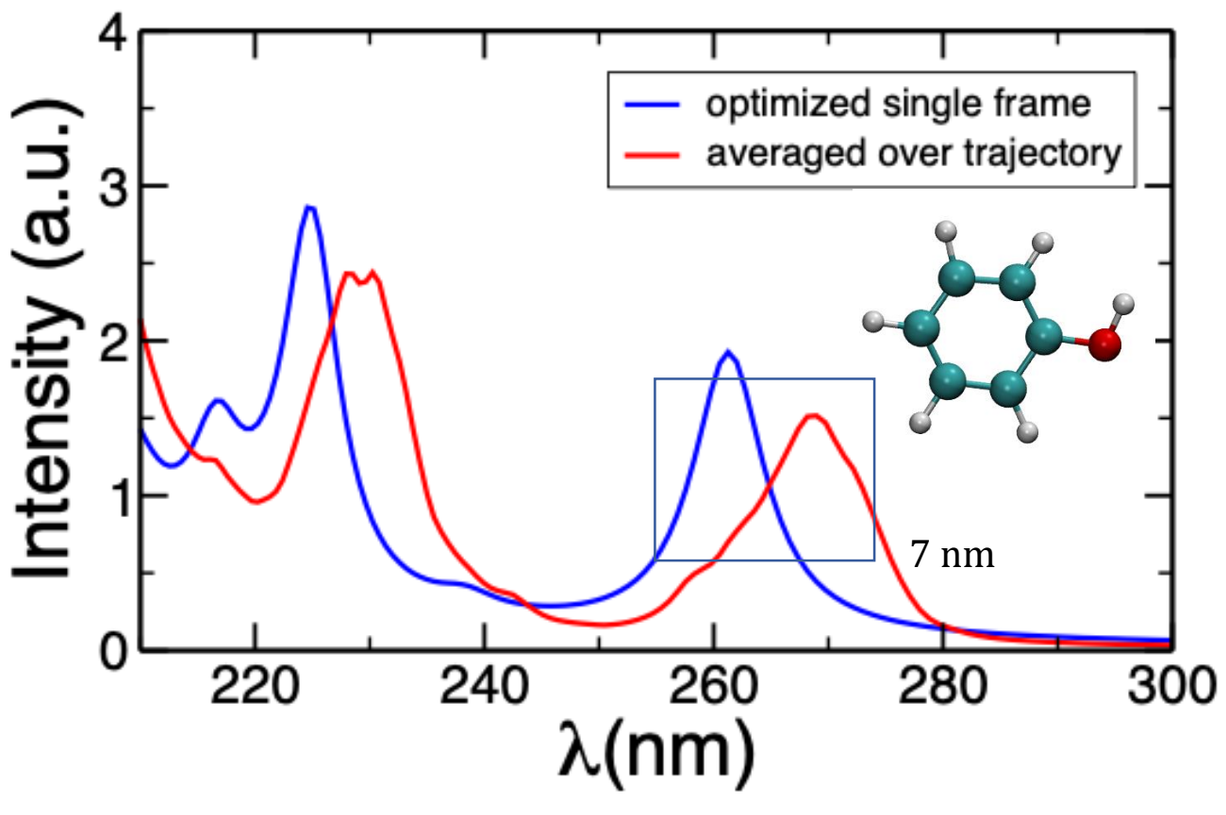
- Solvent-Solute/Solvent-Solvent interactions (short range and long range): **Hydrogen bonding** and **electrostatics**

Temperature-driven effects

Gas Phase (Finite Temperature - 300 K)

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

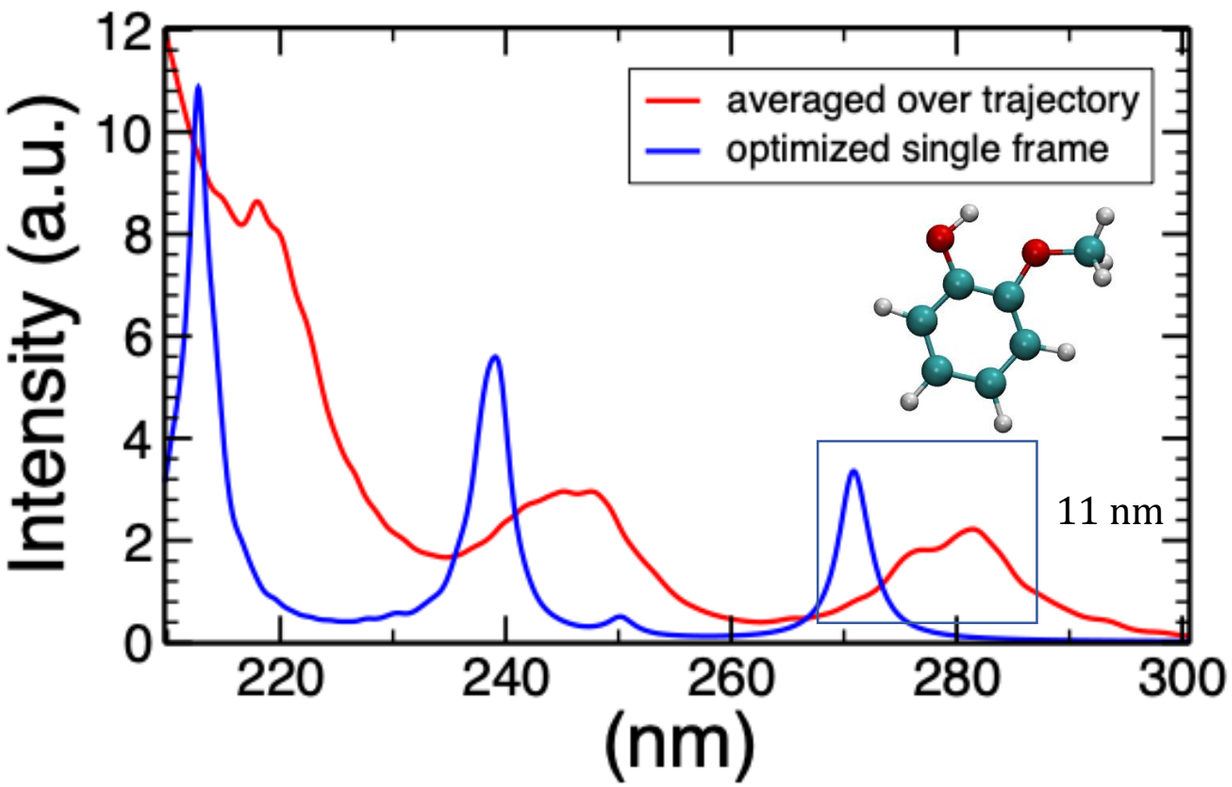


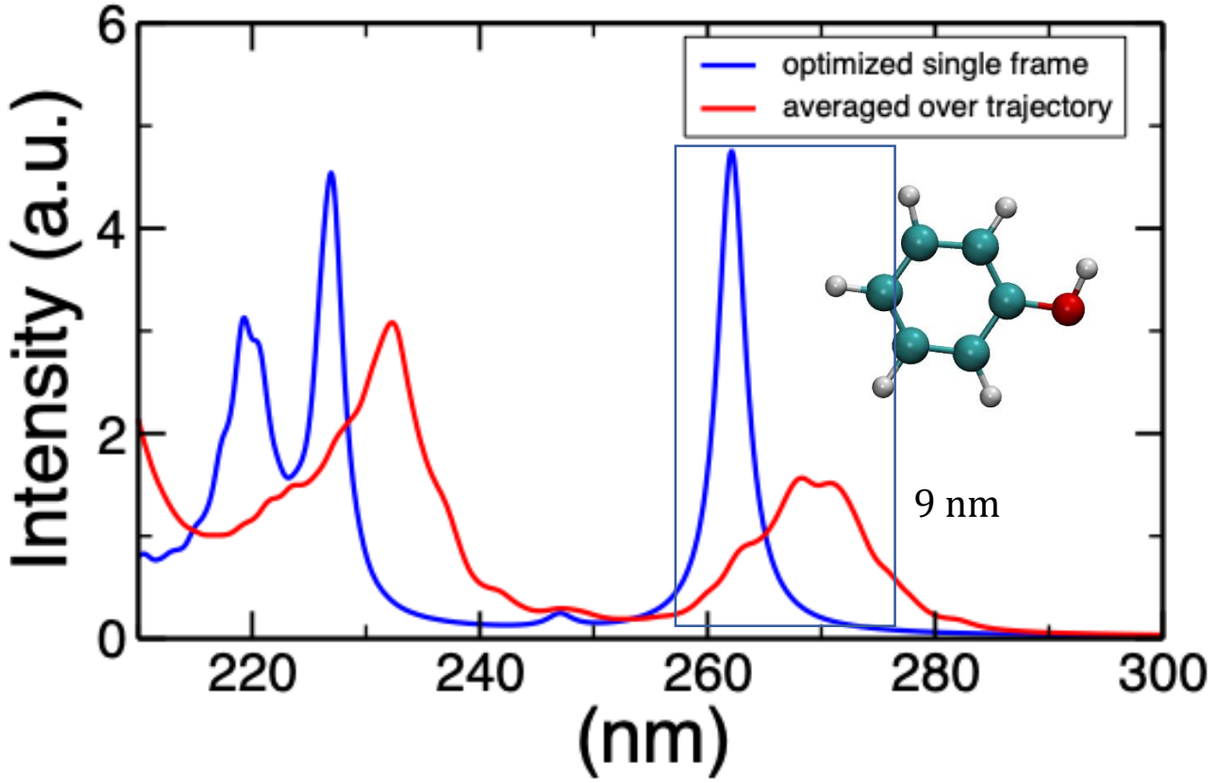


Temperature driven effects

- Optimized structure (single calculation) versus averaged calculation obtained from ab initial trajectory

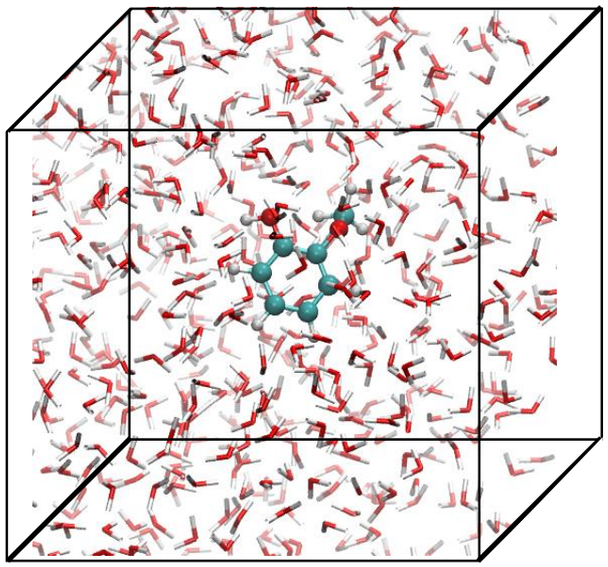
Aqueous solution (300 K)



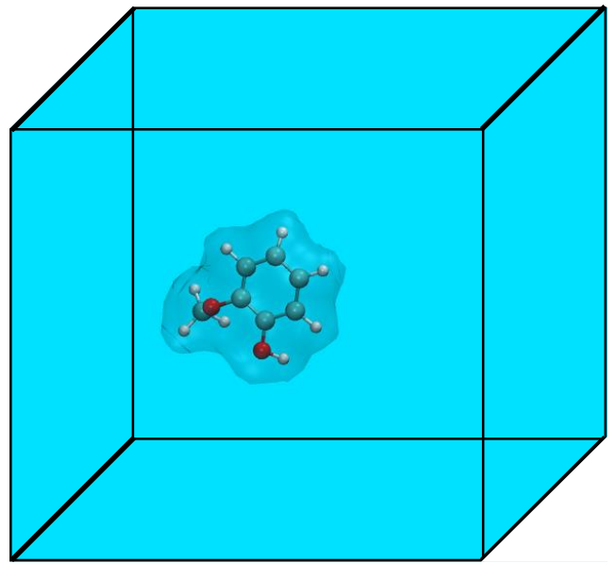


Effects of solvent-solute interactions

Multiscale/multimodel approach



QM water molecules replaced
by a Polarizable Continuum Model (PCM)



More expensive

More realistic picture of short-range solvent-solute interaction

Less expensive

Simplified approaches: less degrees of freedom, faster averaging, better representation of long-range interactions

O. Andreussi *et al. J. Chem. Phys.* (2012)

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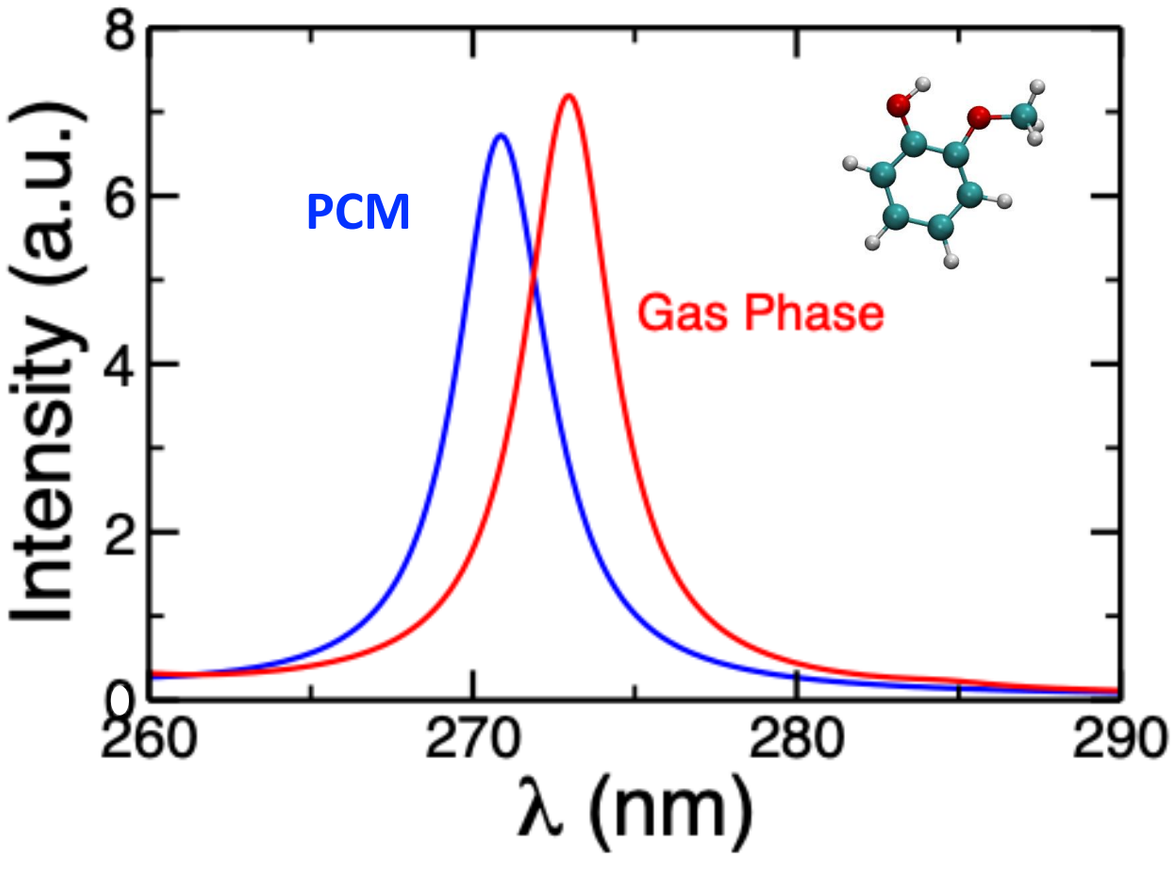
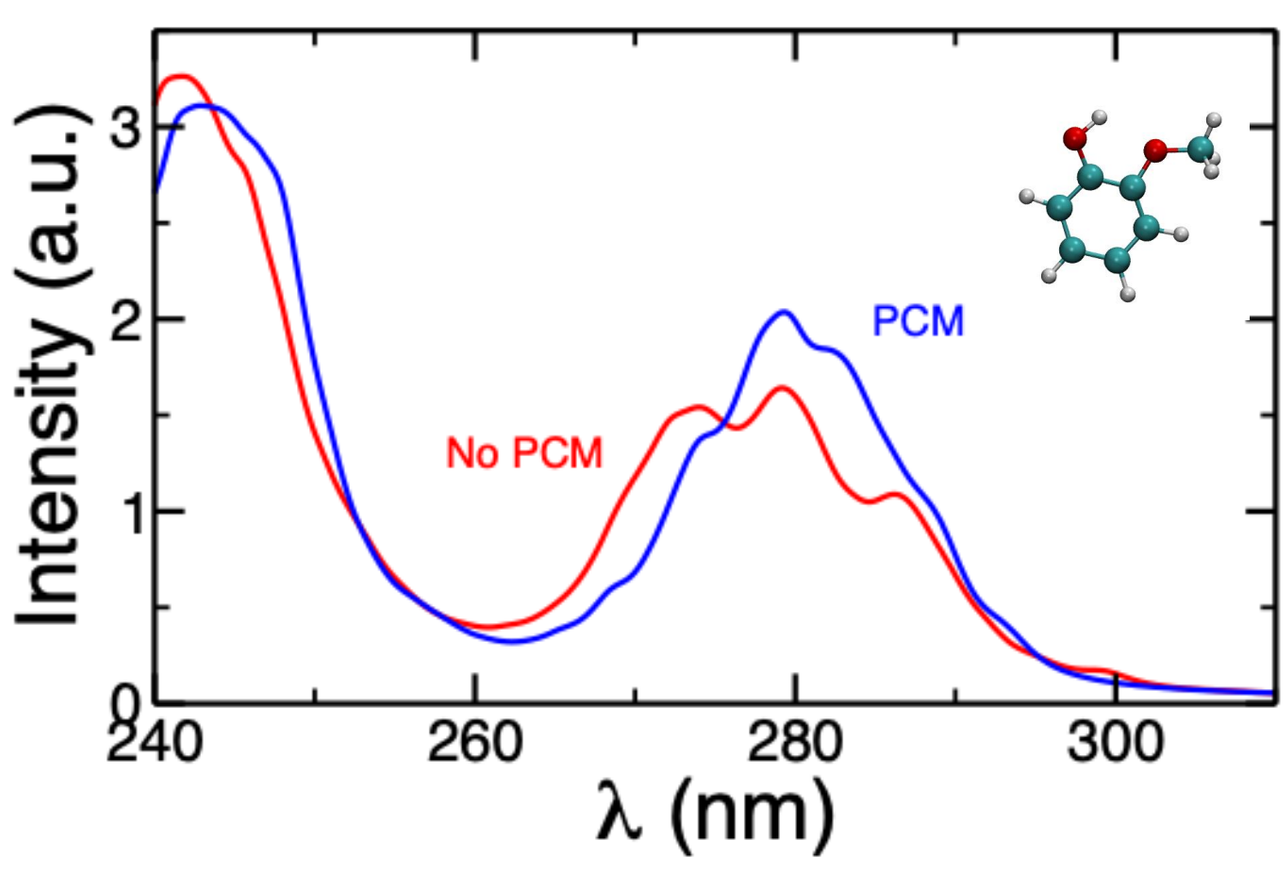
Effects of solvent-solute interactions

Optimized Frame



Averaged Trajectory



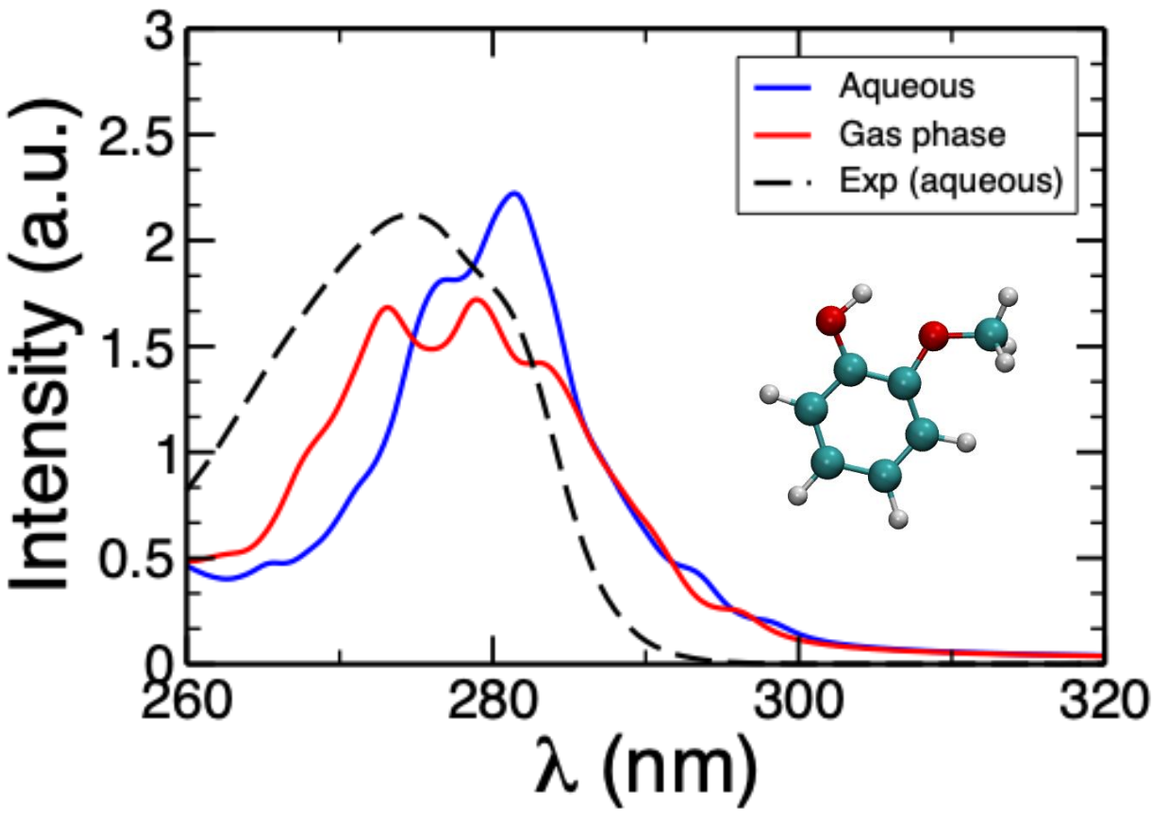
Absorption Spectra Calculations

Current Results for Gas and Solution (PCM)

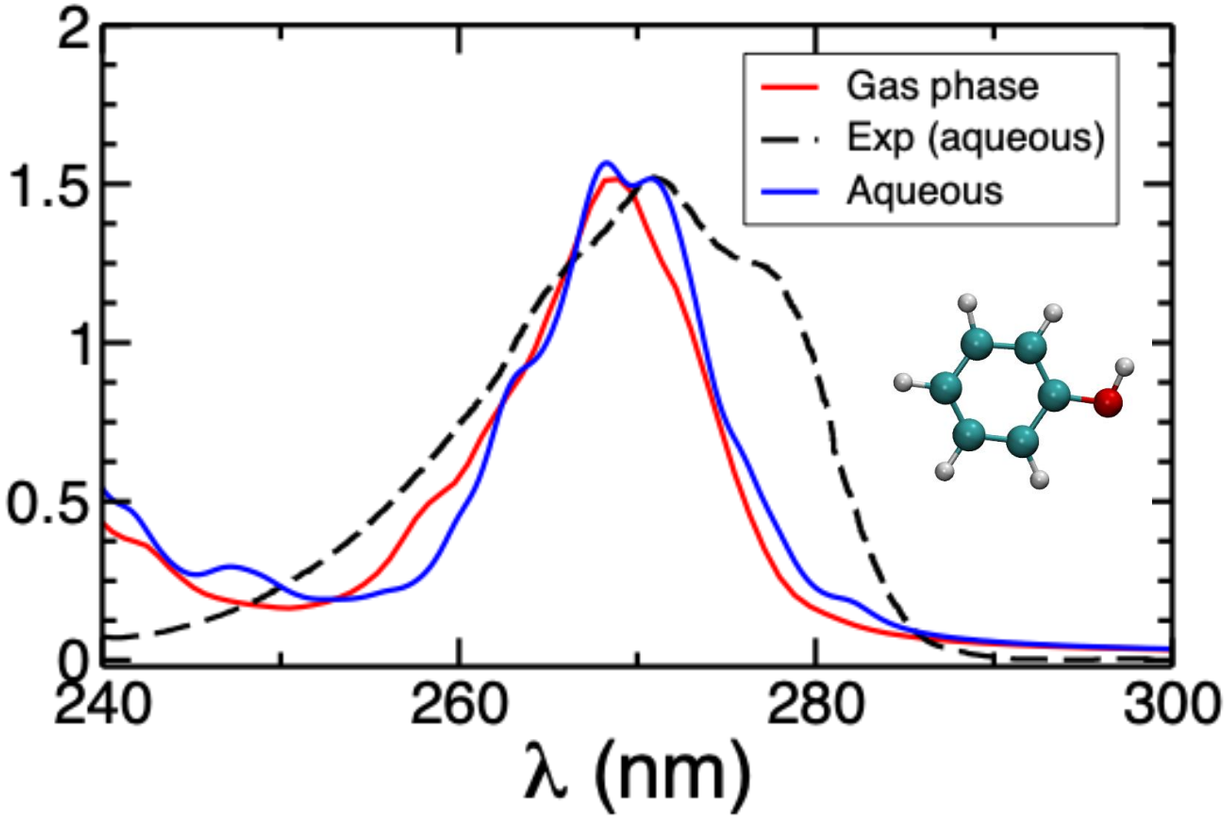
- 20 ps trajectories (40000 frames)

- Convergence achieved with 100 frames

Guaiacol

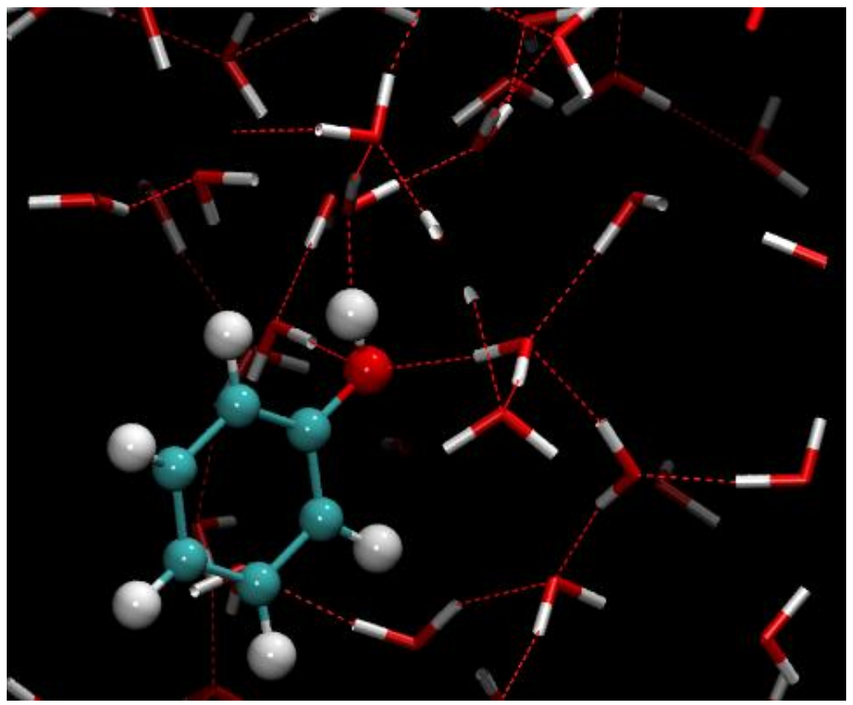


Phenol

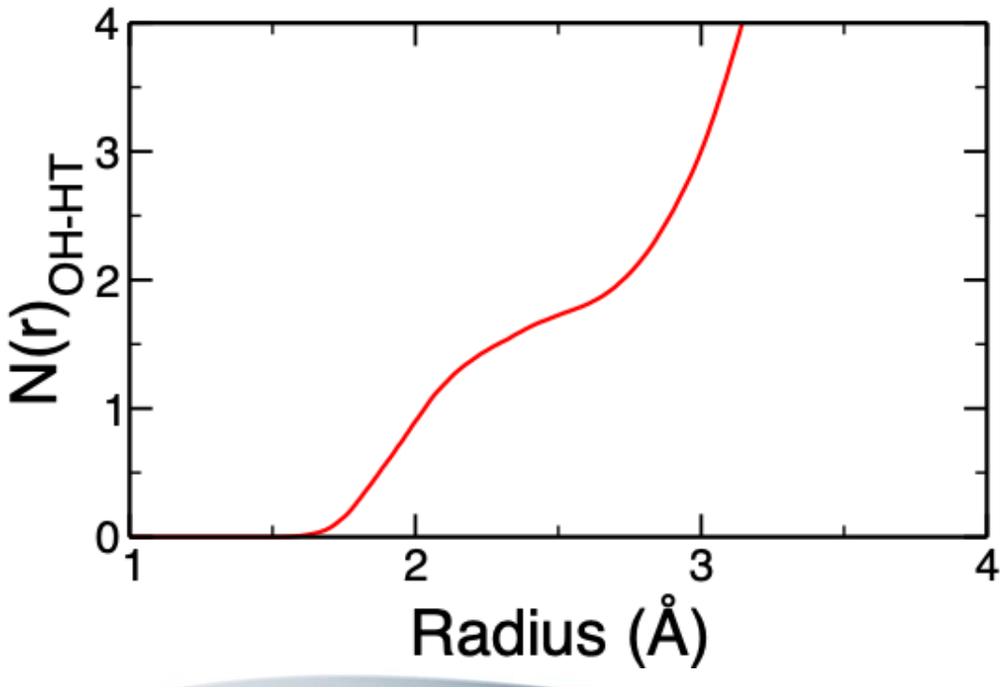


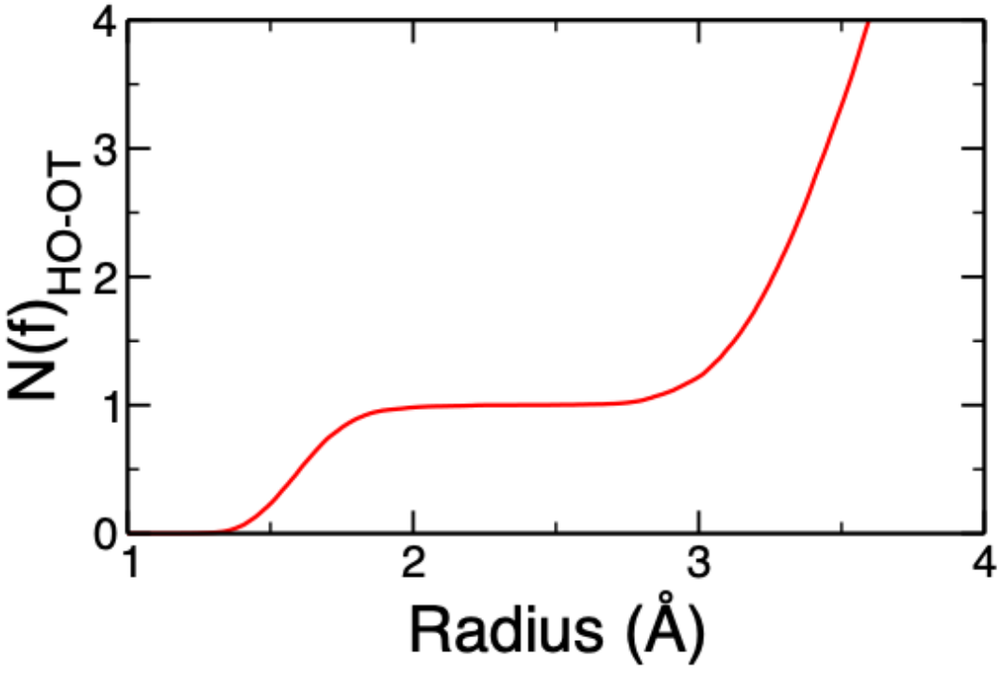
Effect of local environment - short-range interactions

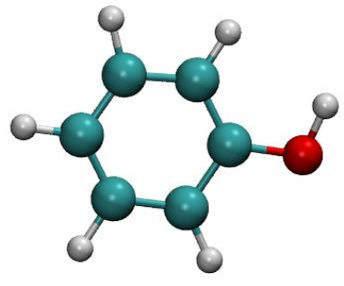
Hydrogen bonding network can interfere on absorption spectra



Coordination number for phenol oxygen (left) and phenol hydrogen (right) in relation to water hydrogens and oxygen

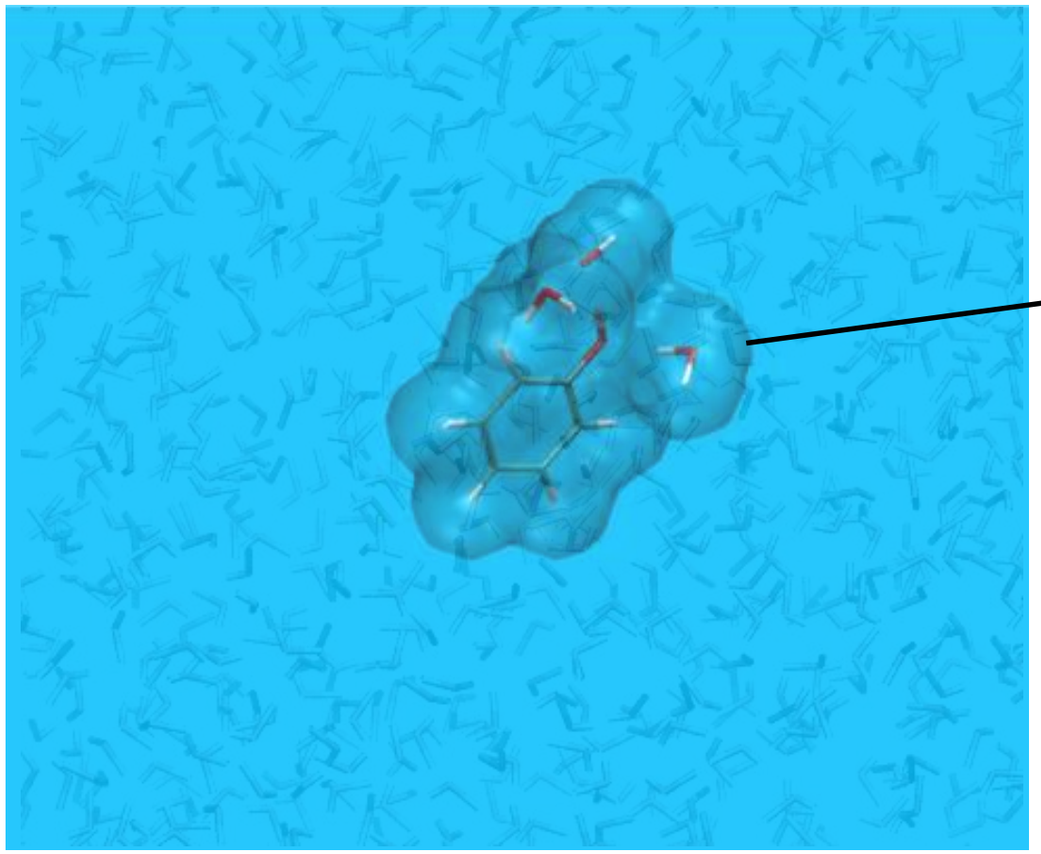






(in solution)

Effect of local environment - short-range interactions

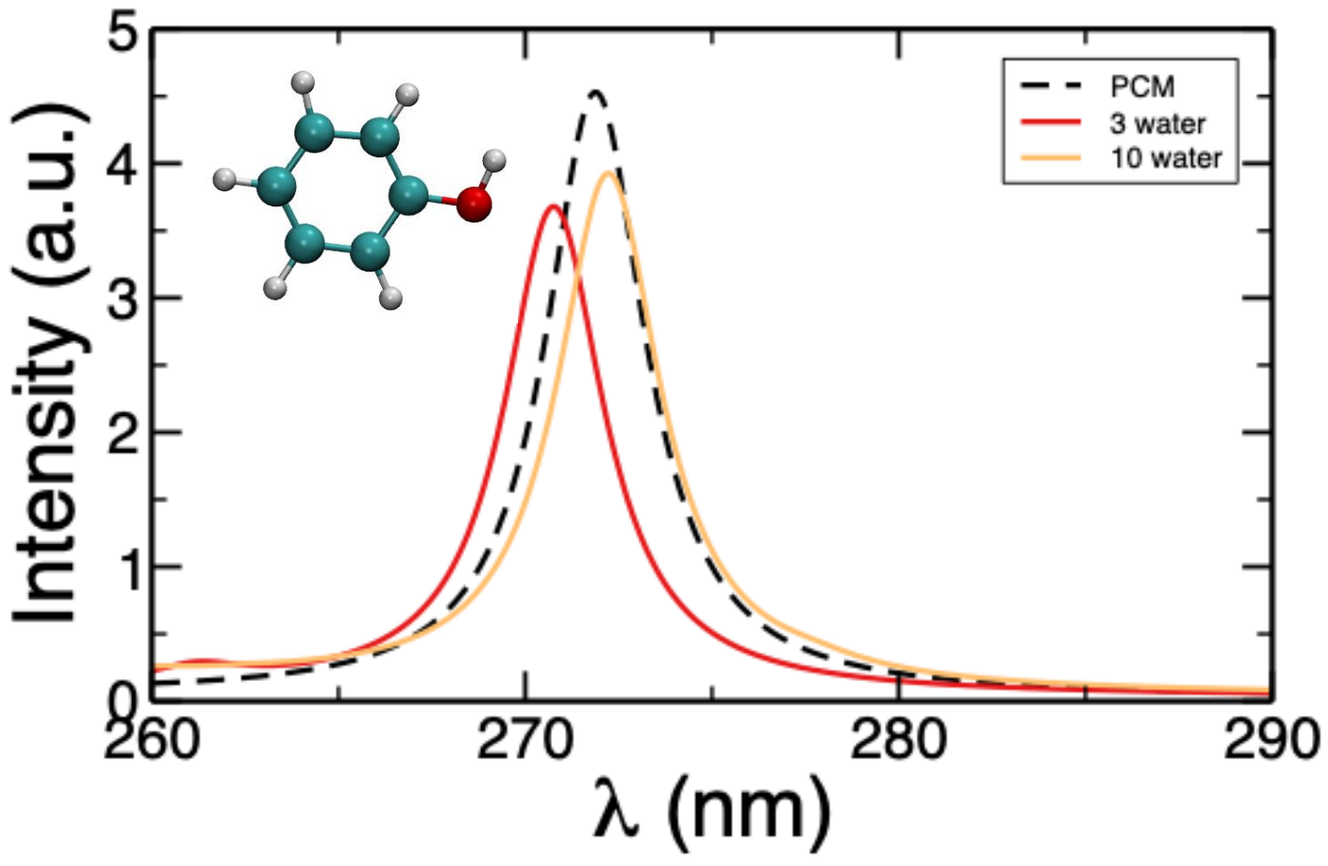


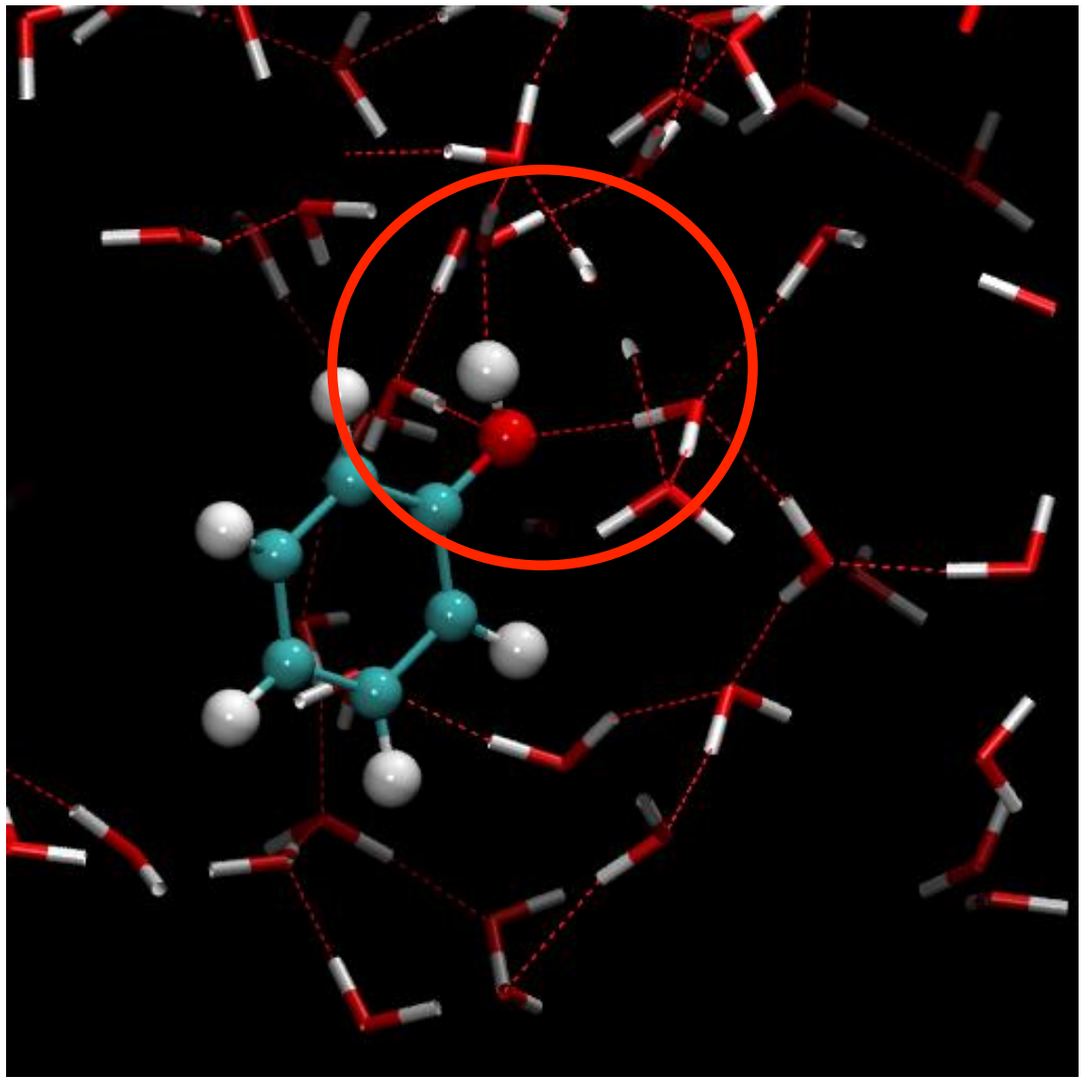
Treat these water molecules as “ explicit”?

Does that make a difference?
How many water molecules should be used?

Computation time x more accurate description

A first look at the local environment



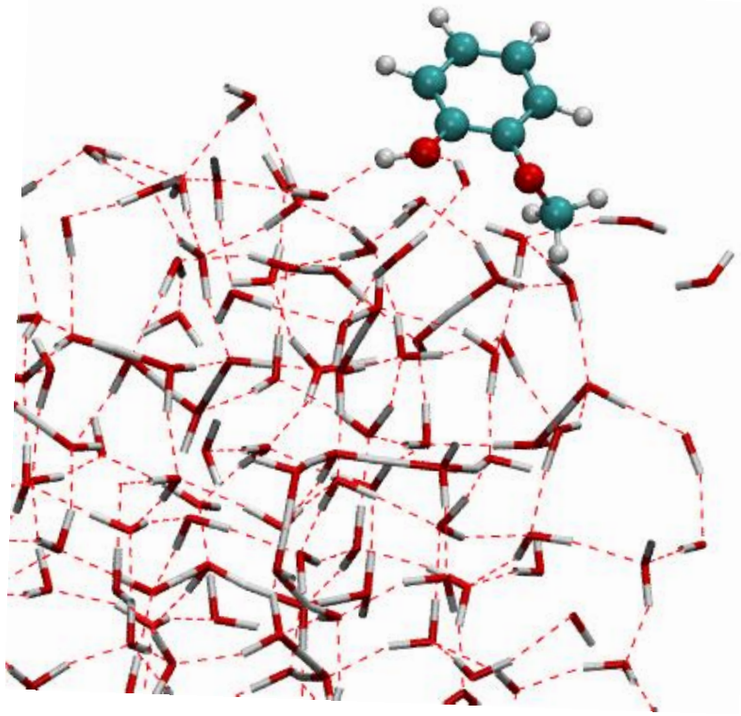


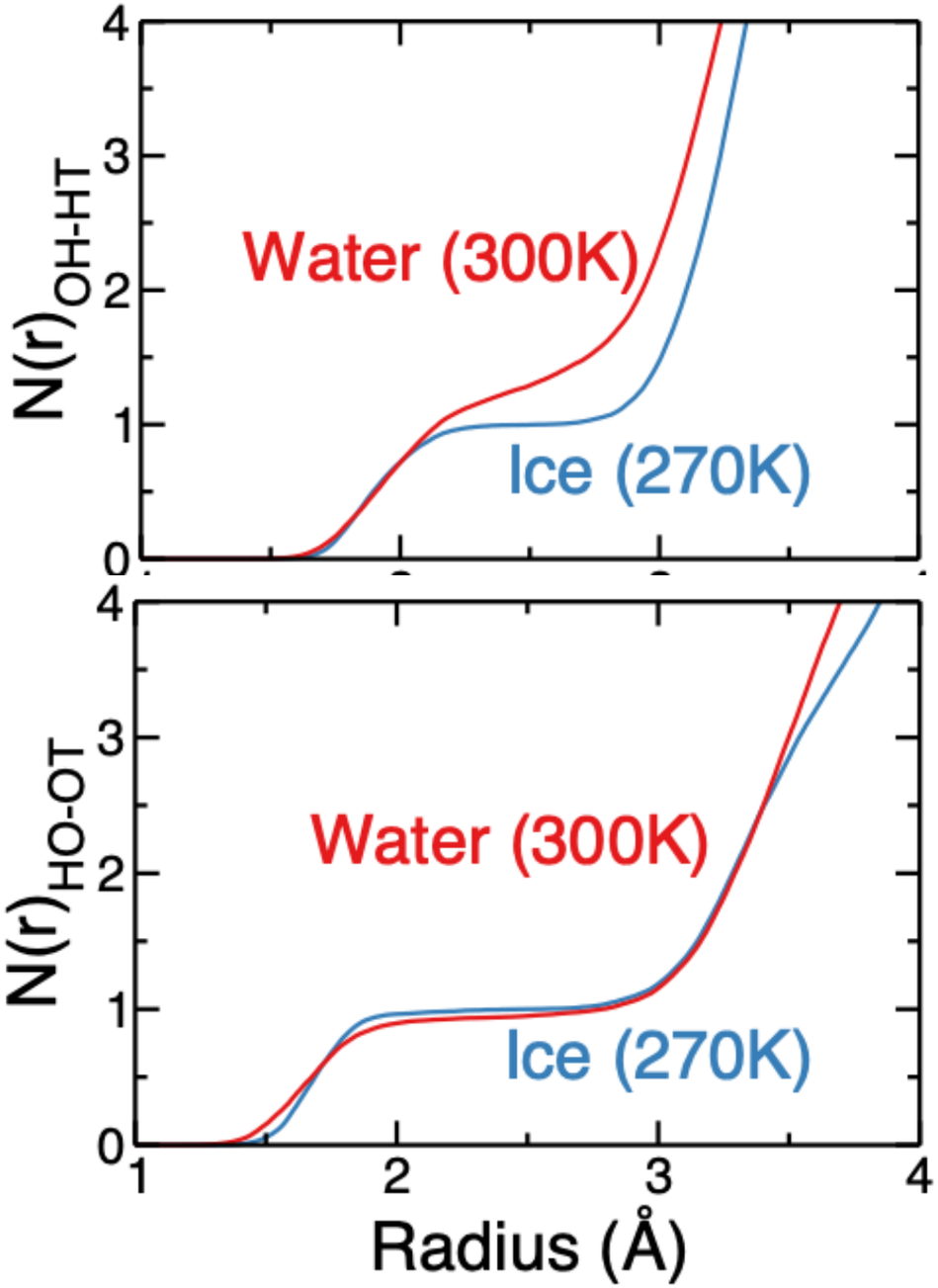
Conclusions

- Experiments show an increase in the photodecay rate for guaiacol
- We quantified temperature and water solvation effects on absorption spectra by utilizing a multimodel approach
- We are currently working on trying to improve the solvation picture for calculations in solution

Future Work - The Ice Model

- A simple PCM approach will not work - air-ice interface
- How does the hydrogen bonding network compare to solution?
- How to use the information from the solution spectra calculations to predict what happens on ice





Thank you!

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Donadio Group Members

Tanja Kling (Max Planck Institute for Polymer Research)

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