

Computational Modeling of Organic Fluor Molecules

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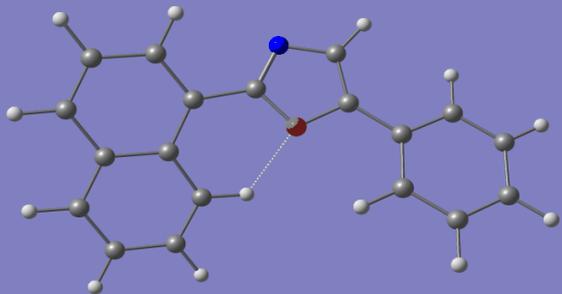
Motivations

- 2-(1-naphthyl)-5-phenyloxazole (**α NPO**)
- 2-(1-naphthyl)-4-vinyl-5-phenyloxazole (**vNPO**)
- 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (**PBD**)
- 2-[4-(4'-vinylbiphenyl)]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole monomer (**vPBD**)
- 5-(4-Bromophenyl)-3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (**PZ1**)
- 3-(4-Ethylphenyl)-5-(4-vinylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (**vPZ1**)
- 3-(4-Ethylphenyl)-5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (**PZ2**)

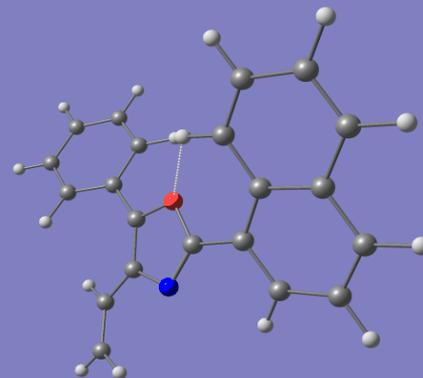
Motivations

- Synthesis of new organic scintillators can be expensive.
 - Is the chemical structure stable?
 - Does the scintillator fluoresce around 420 nm?
- Modeling organic scintillating molecules can be a cost effective method for studying photo physical behavior.

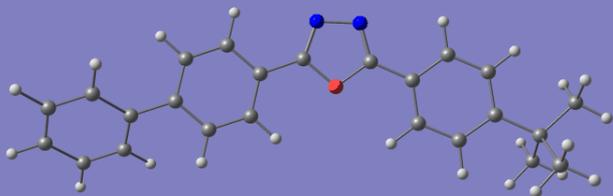
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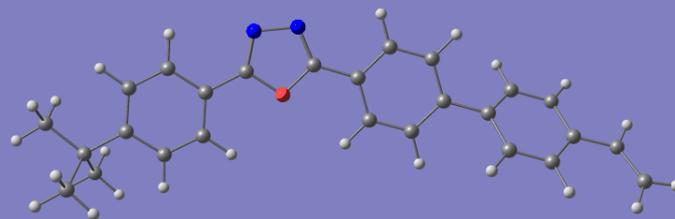
α NPO



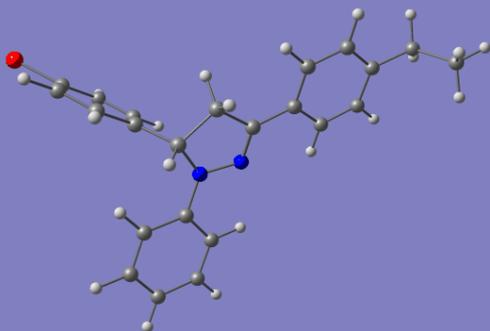
vNPO



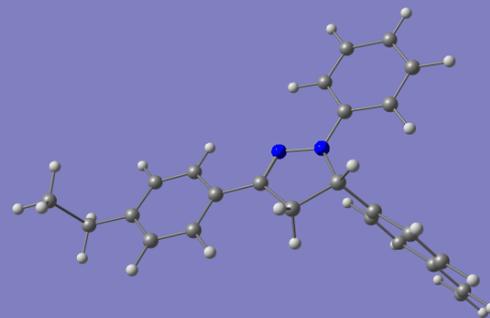
PBD



vPBD

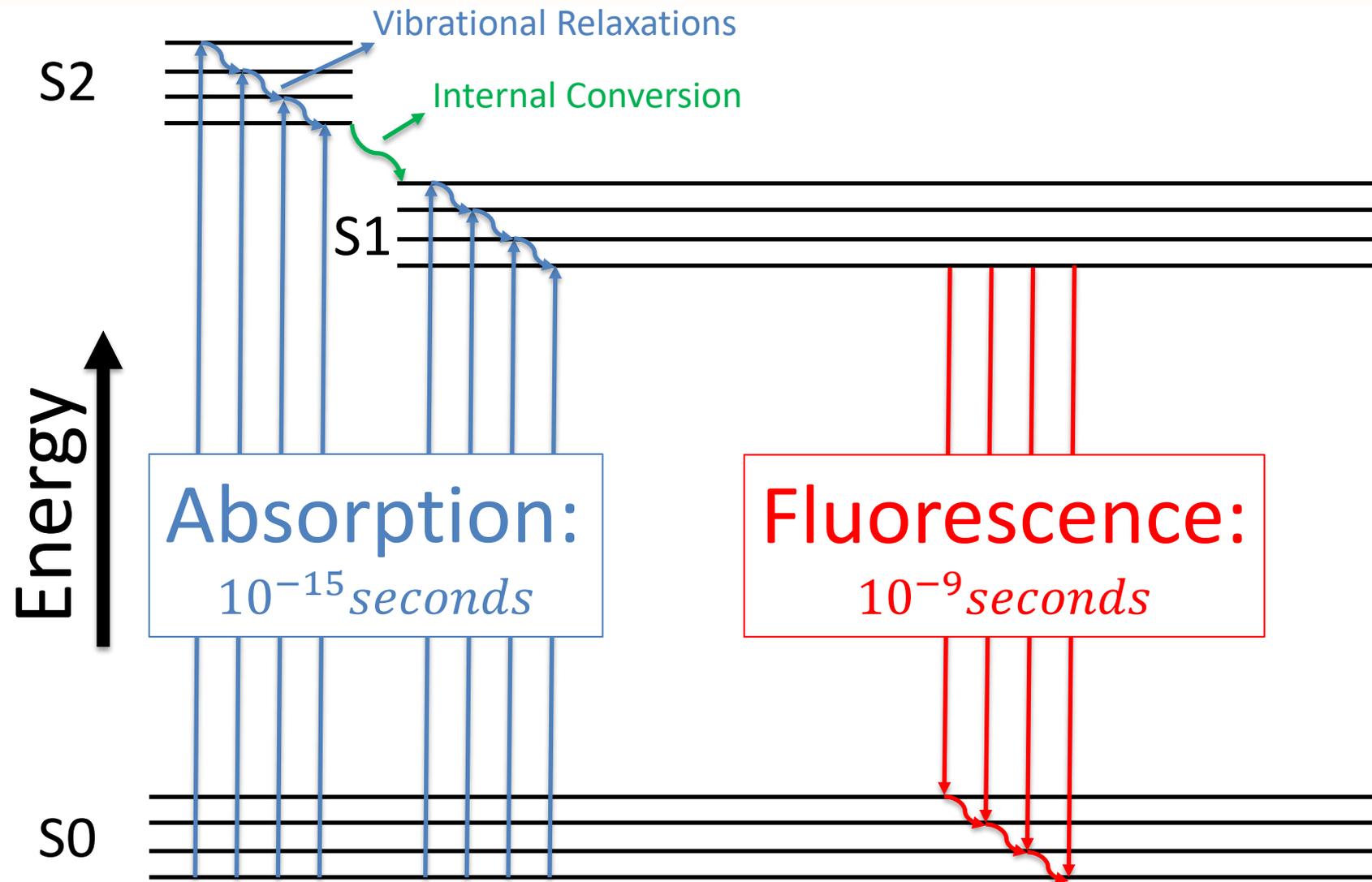


PZ1*



vPZ1

Jablonski Diagram



Computational Theory

- To model electron transfer processes we need to solve the Schrödinger equation:

$$\hat{H}(\{\mathbf{r}\}, t) \Psi(\{\mathbf{r}\}, t) = E(\{\mathbf{r}\}, t) \Psi(\{\mathbf{r}\}, t)$$

\hat{H} : An operator that represents the interactions in the system

Ψ : Describes the electron distribution

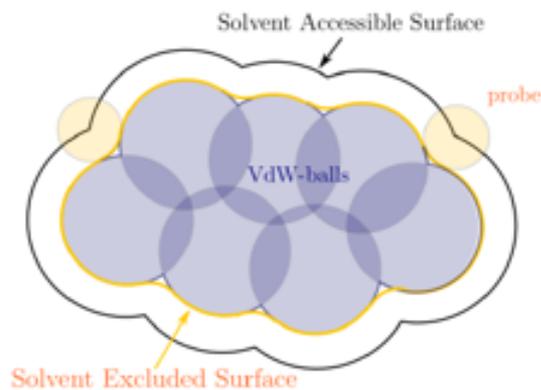
E : The total electron binding energy

- **Energy functionals** are used to complete the Hamiltonian.
- **Basis sets** approximate the wave function by generating the atomic orbitals in the system.

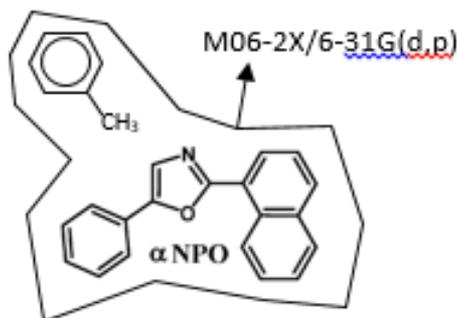
Computational Theory

Implicit Solvation

- Polarized Continuum Model (PCM): Treats the bulk solvent environment as a continuum of dielectric medium.



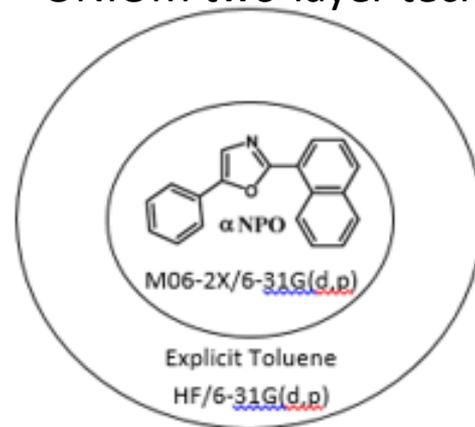
Implicit PCM Cavity



PCM-Hybrid

Hybrid Solvation

- Hybrid methods adopt explicit solvent molecules in addition to implicit models.
 - PCM with single explicit solvent.
 - ONIOM two-layer technique



Two-layer ONIOM

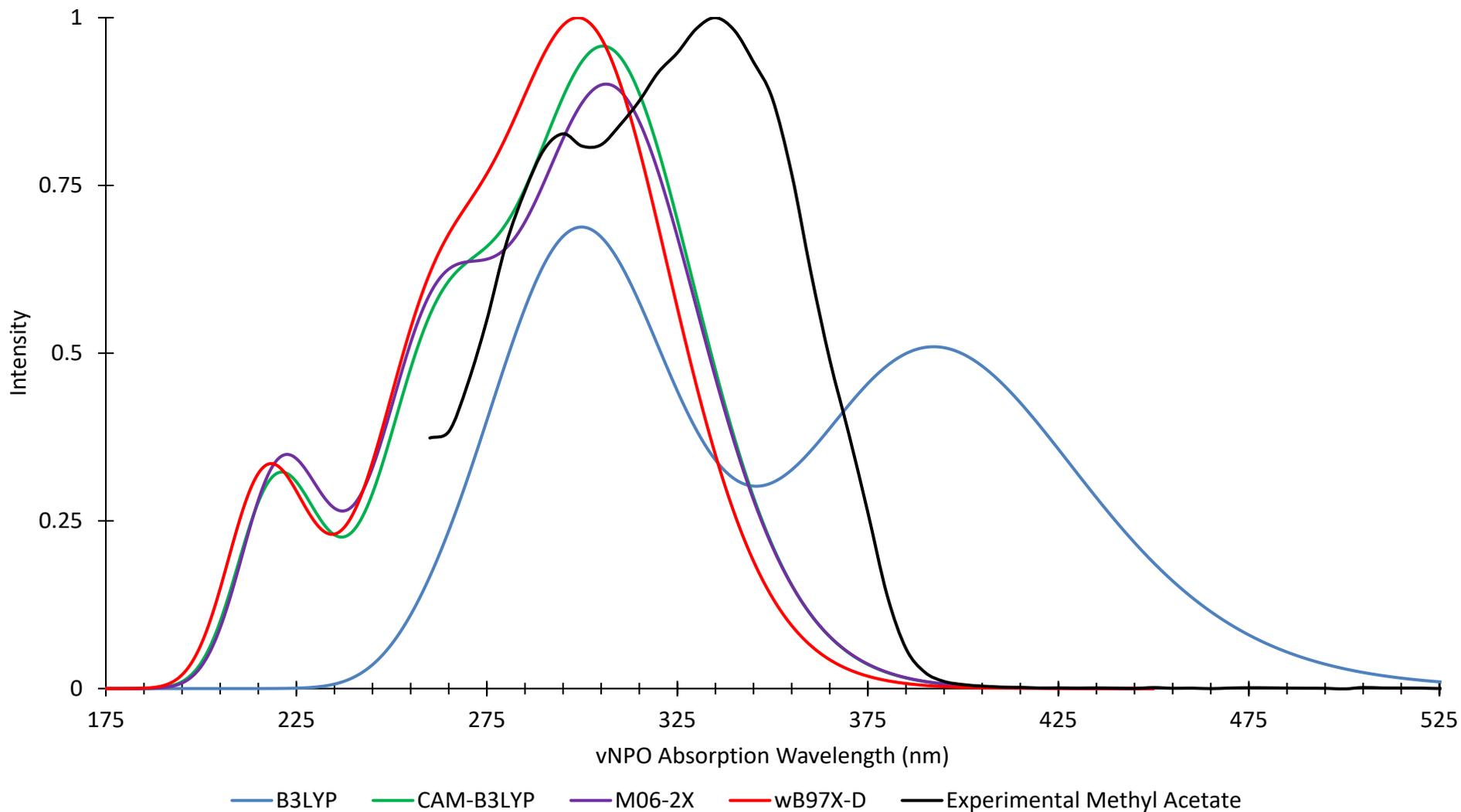
Hypotheses

- **Time Dependent Density Functional Theory (TD-DFT) can be used to predict the fluorescent behavior of organic fluorophores using appropriate computational parameters.**
 - The incorporation of long-range energy functionals will produce better results than traditional functionals (B3LYP).
 - Implicit solvent environments will correctly predict general trends shown in experiments.
 - The addition of explicit solvent molecules will further enhance the predictability of the model.

Tasks

- **Part 1: Energy Functional Effects**
 - **Compare traditional B3LYP with long range corrected functionals.**
- **Part 2: Impacts of Solvation**
 - Implicit (PCM) Solvent Effects.
 - Hybrid Solvation (α NPO and vNPO in toluene).

vNPO Absorption



vNPO: Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO)

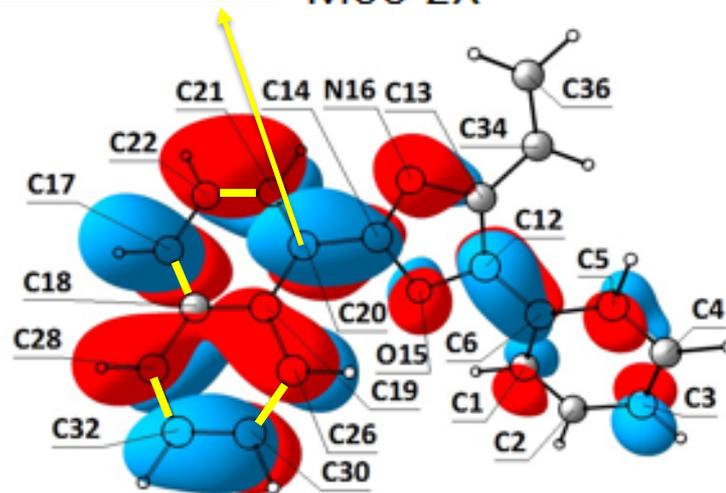
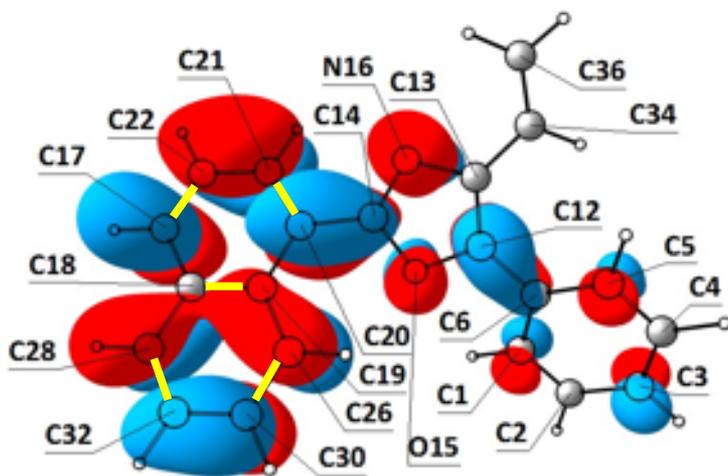
— Double Bond

B3LYP

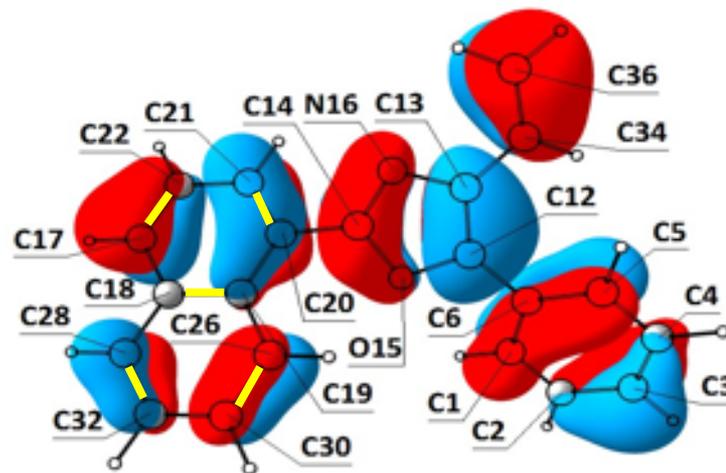
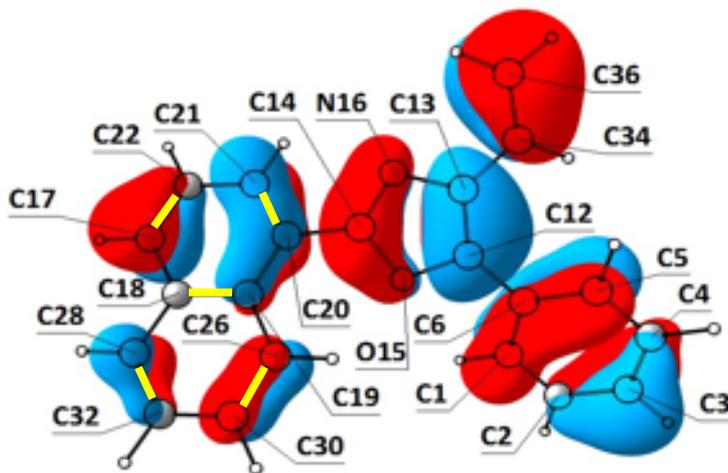
Lone Pair

M06-2X

LUMO



HOMO



Orbital Analysis: Energetics

Calculated Energy (eV)

Functional	HOMO	LUMO	HOMO-LUMO Gap	Optical Gap
B3LYP	-5.36	-1.82	3.54	3.15
M06-2X	-6.68	-0.86	5.82	4.02

Tasks

- Part 1: Energy Functional Effects
 - Compare traditional B3LYP with long range corrected functionals.
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 - **Implicit Solvation (PCM) Solvent Effects.**
 - Hybrid Solvation (α NPO and vNPO in toluene).

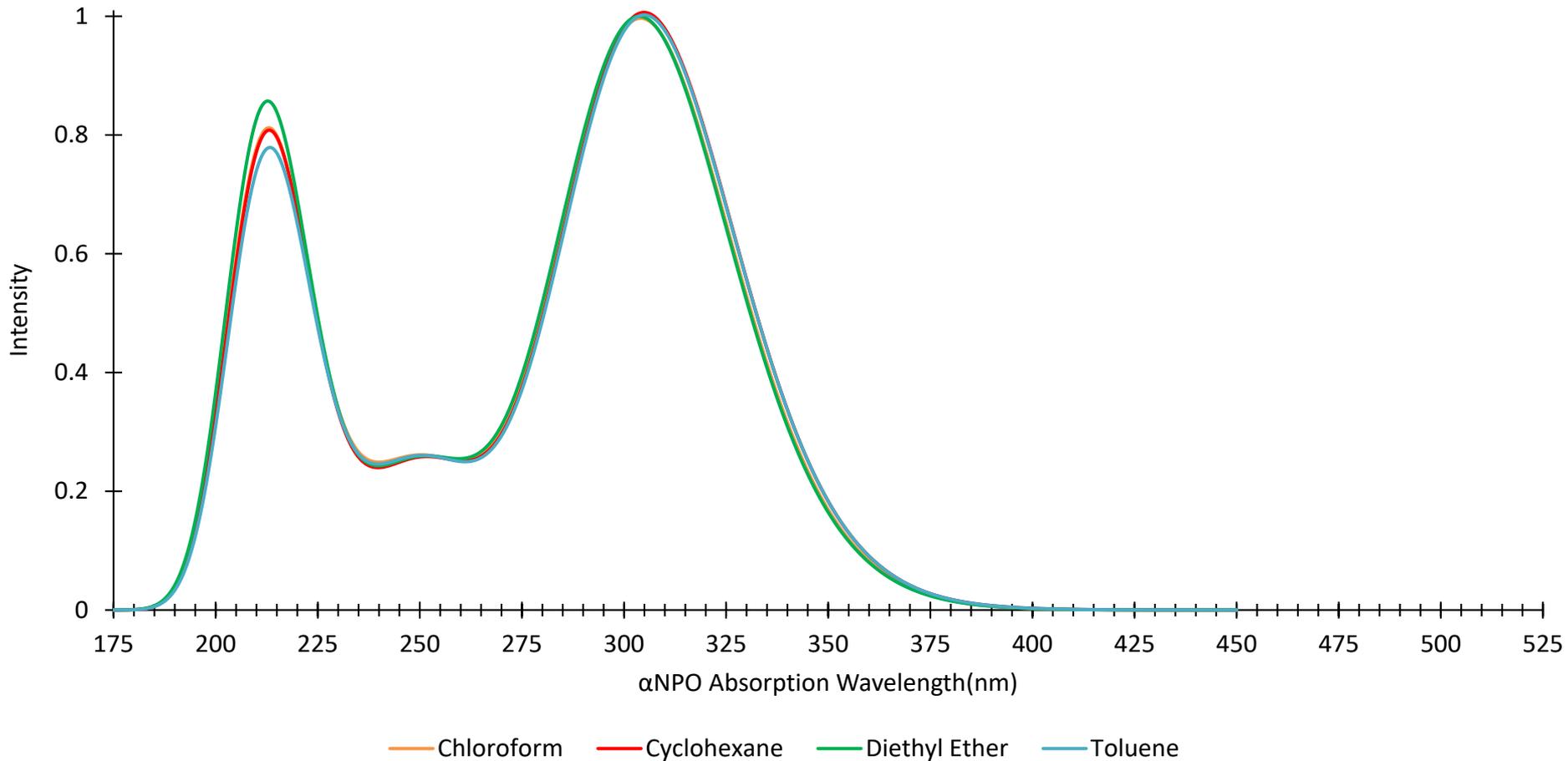
α NPO Absorption

Chloroform ($\epsilon = 4.7113$)

Diethyl ether ($\epsilon = 4.2400$)

Toluene ($\epsilon = 2.3741$)

Cyclohexane ($\epsilon = 2.0165$)



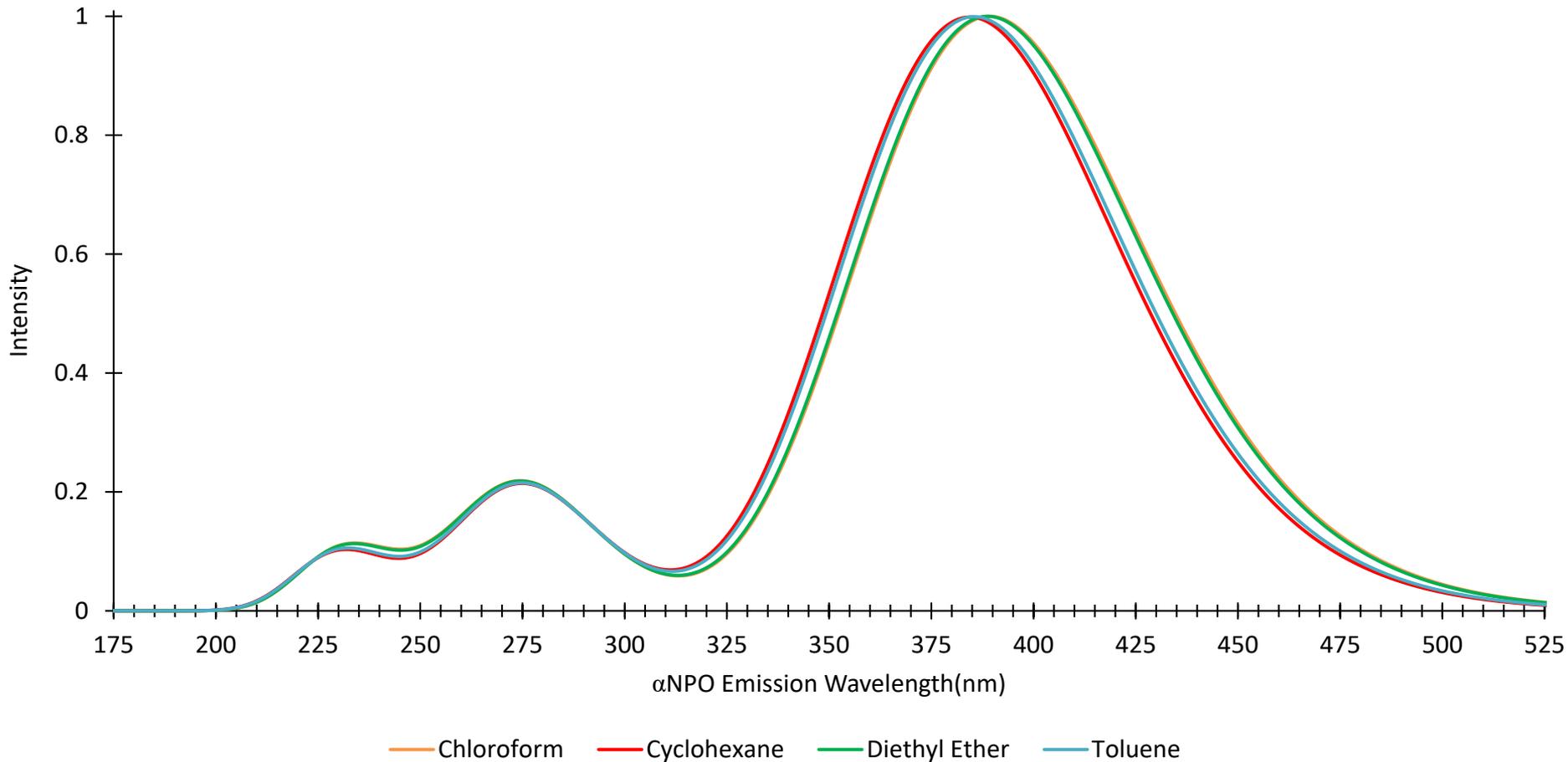
α NPO Emission

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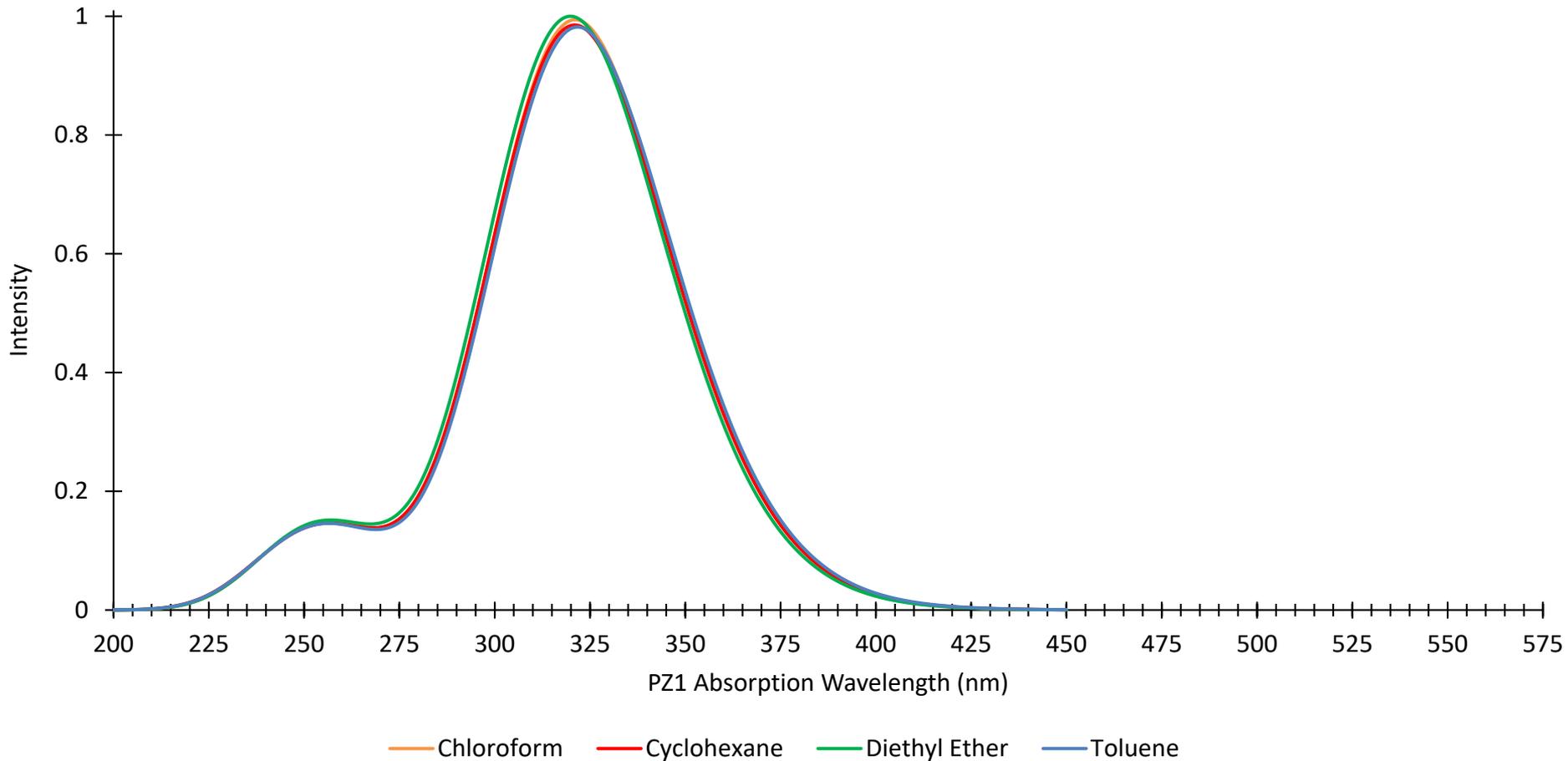
PZ1 Absorption

Chloroform ($\epsilon = 4.7113$)

Diethyl ether ($\epsilon = 4.2400$)

Toluene ($\epsilon = 2.3741$)

Cyclohexane ($\epsilon = 2.0165$)



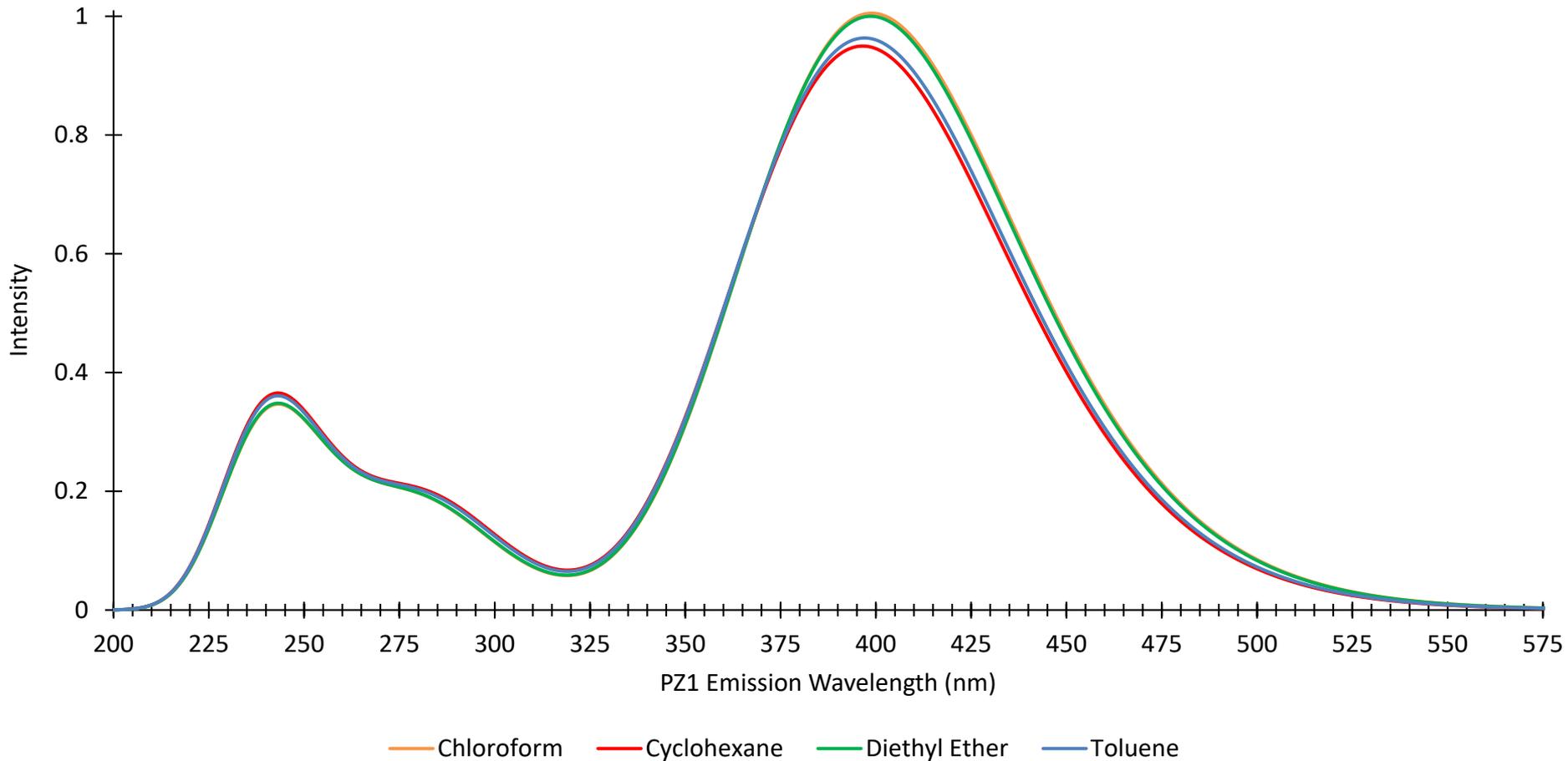
PZ1 Emission

Chloroform ($\epsilon = 4.7113$)

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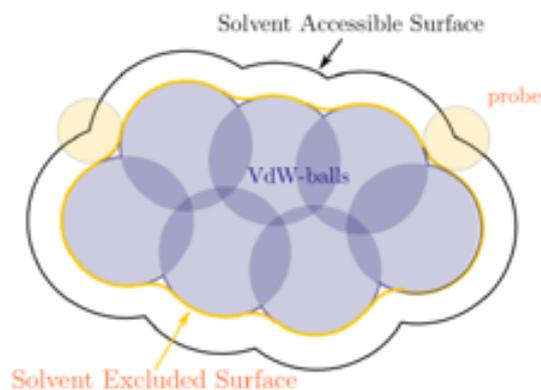
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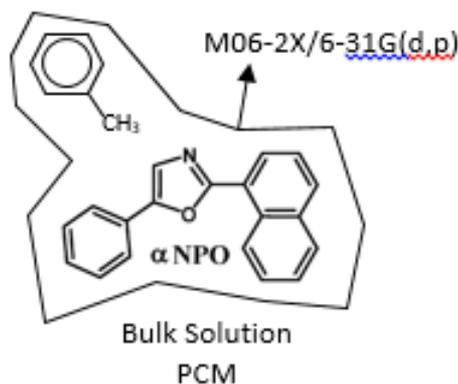


Implicit Solvation \rightarrow Explicit Solvation

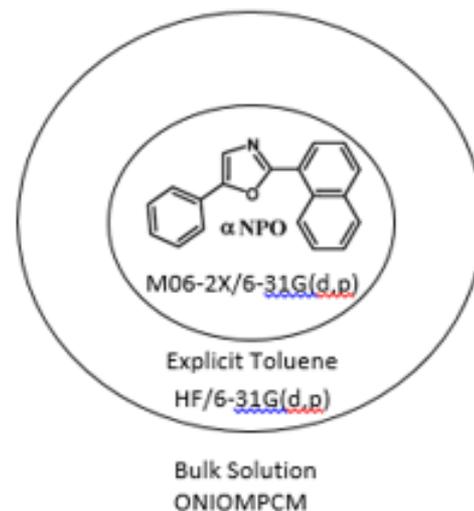
- PCM model could predict electrostatic differences in solvents.
- PCM model could not predict specific solute-solvent interactions.



Implicit PCM Cavity



PCM-Hybrid



Two-layer ONIOM

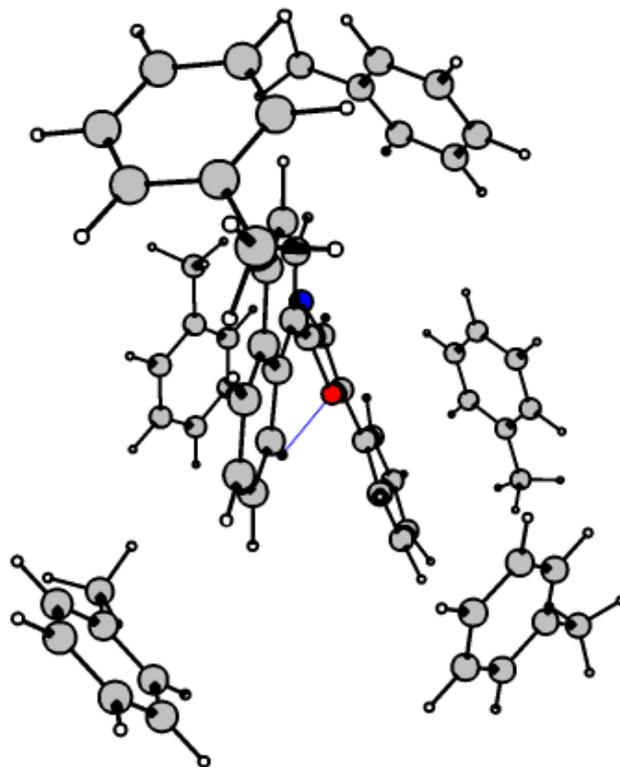
Tasks

- Part 1: Energy Functional Effects
 - Compare traditional B3LYP with long range corrected functionals.
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 - **Hybrid Solvation (α NPO and vNPO in toluene).**

α NPO ONIOM two-layer

Two approximations made:

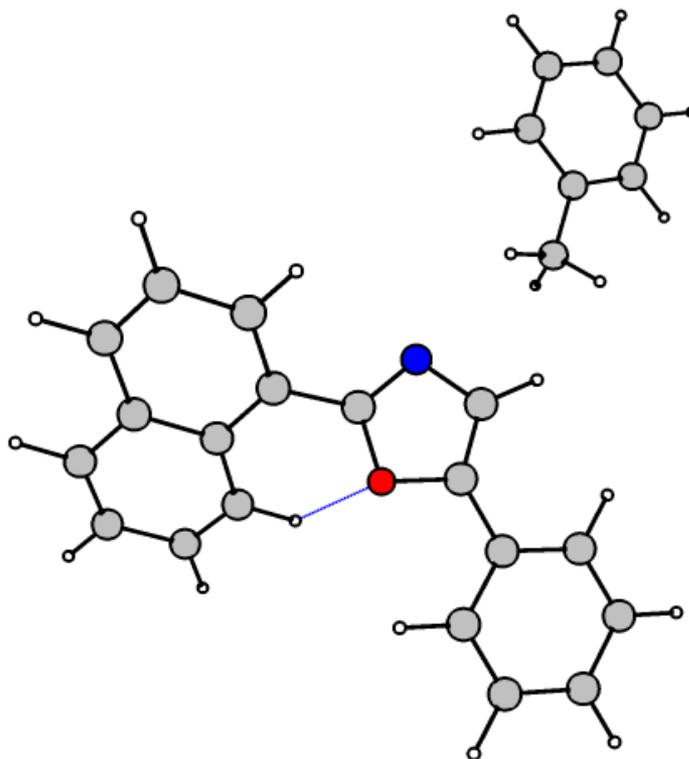
1. Hold the fluor static during optimization.
2. Hold explicit toluene static during optimization.



α NPO PCM-Hybrid Ground State Optimization

Approximation made:

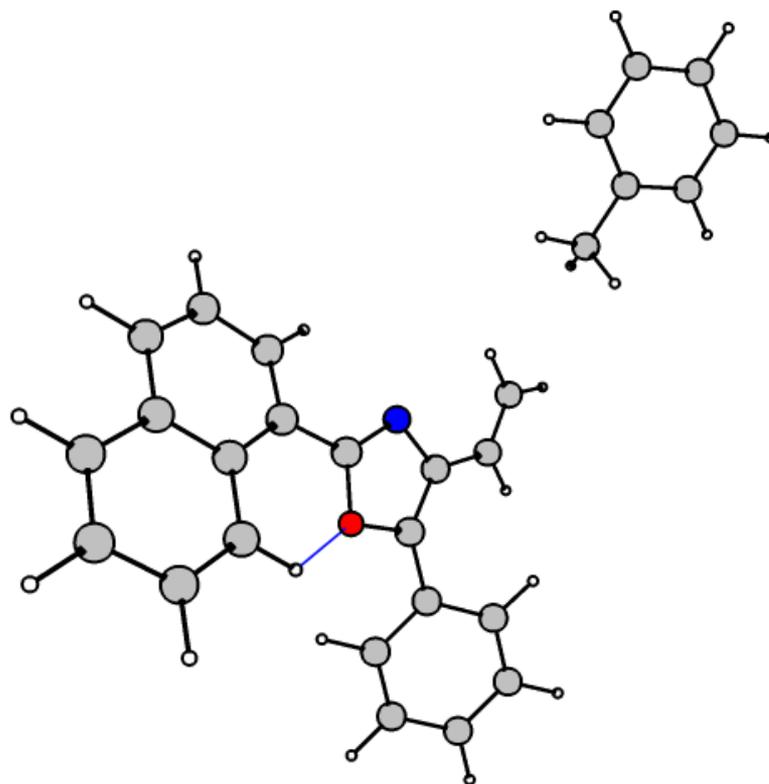
1. Where to coordinate the toluene before optimization.



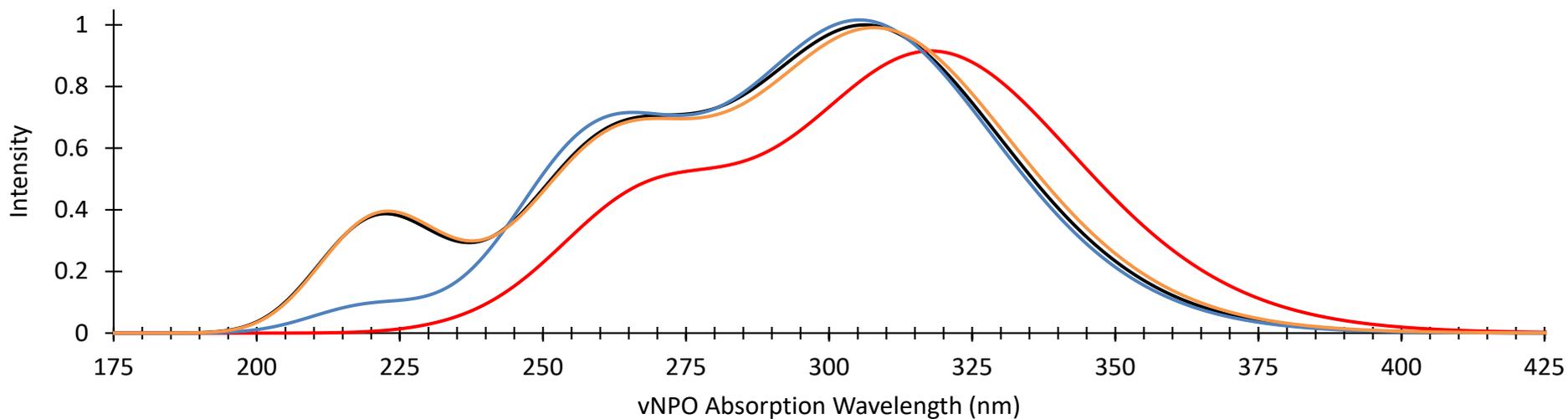
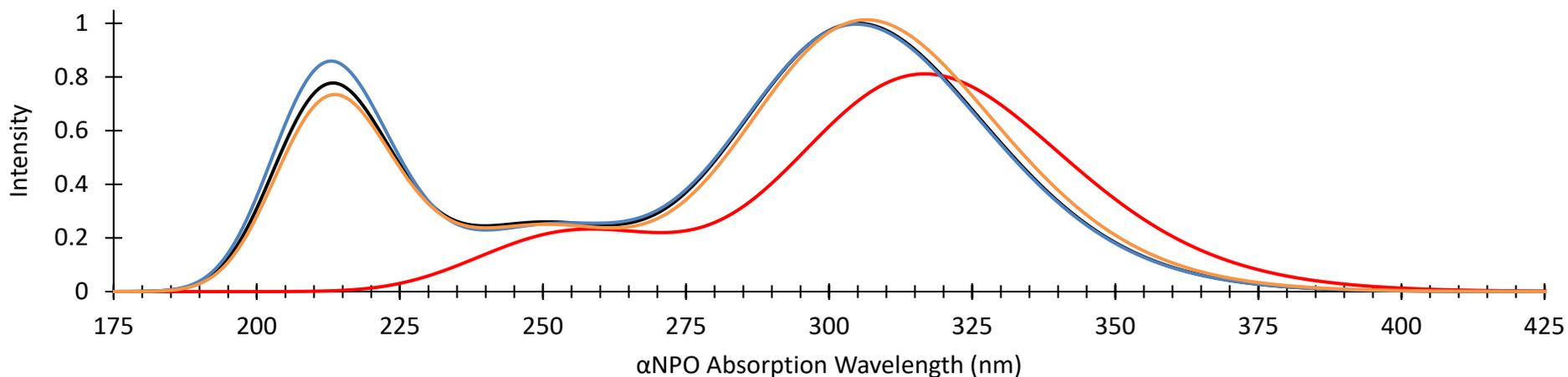
vNPO PCM-Hybrid Ground State Optimization

Approximation made:

1. Where to coordinate the toluene before optimization.



Hybrid Solvation vs. Implicit: α NPO and vNPO Absorption



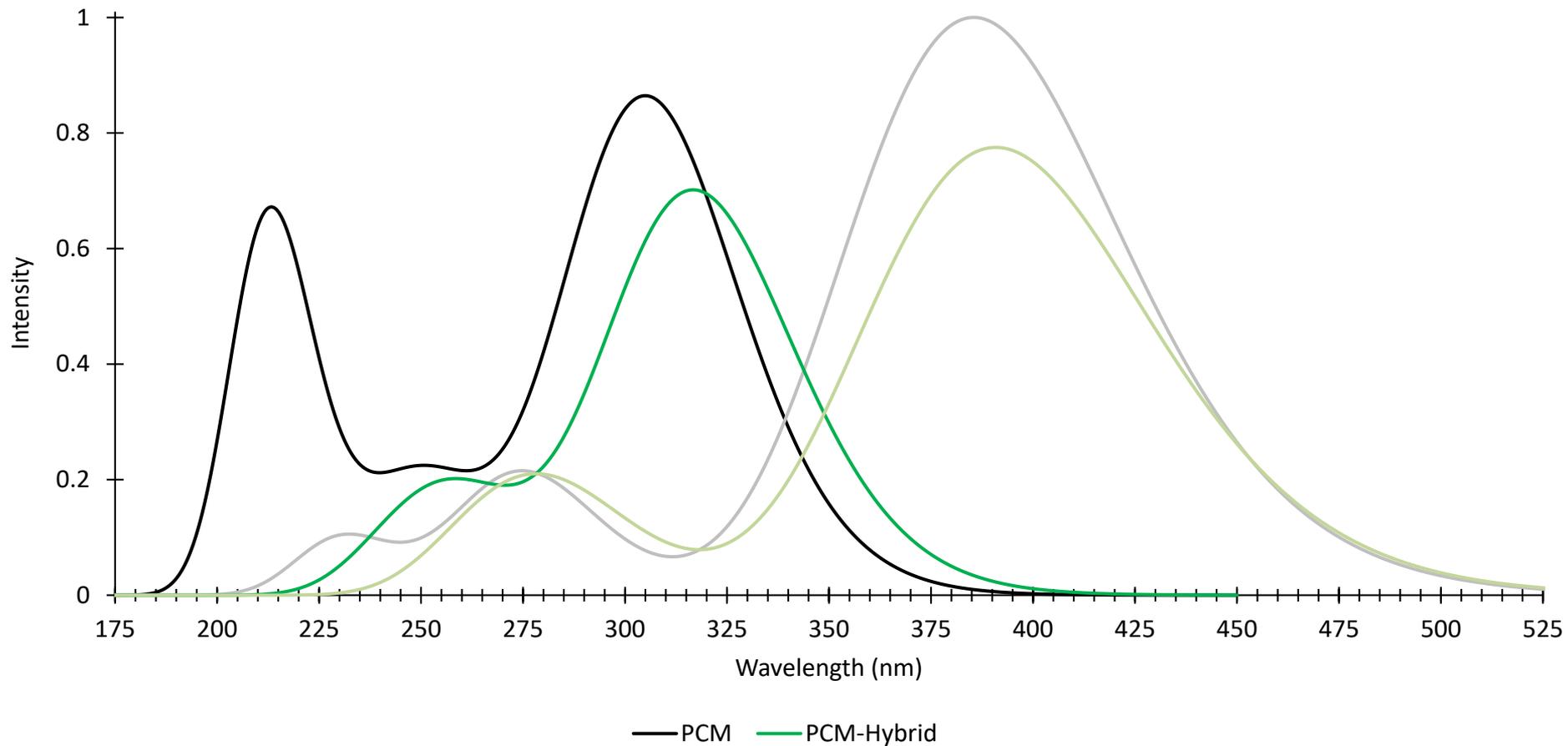
— PCM — PCM-Hybrid — Static Fluor — Static Toluene

α NPO PCM-SS vs. PCM-Hybrid

Stokes Shifts

PCM-implicit: 80.35 nm

PCM-hybrid: 73.96 nm

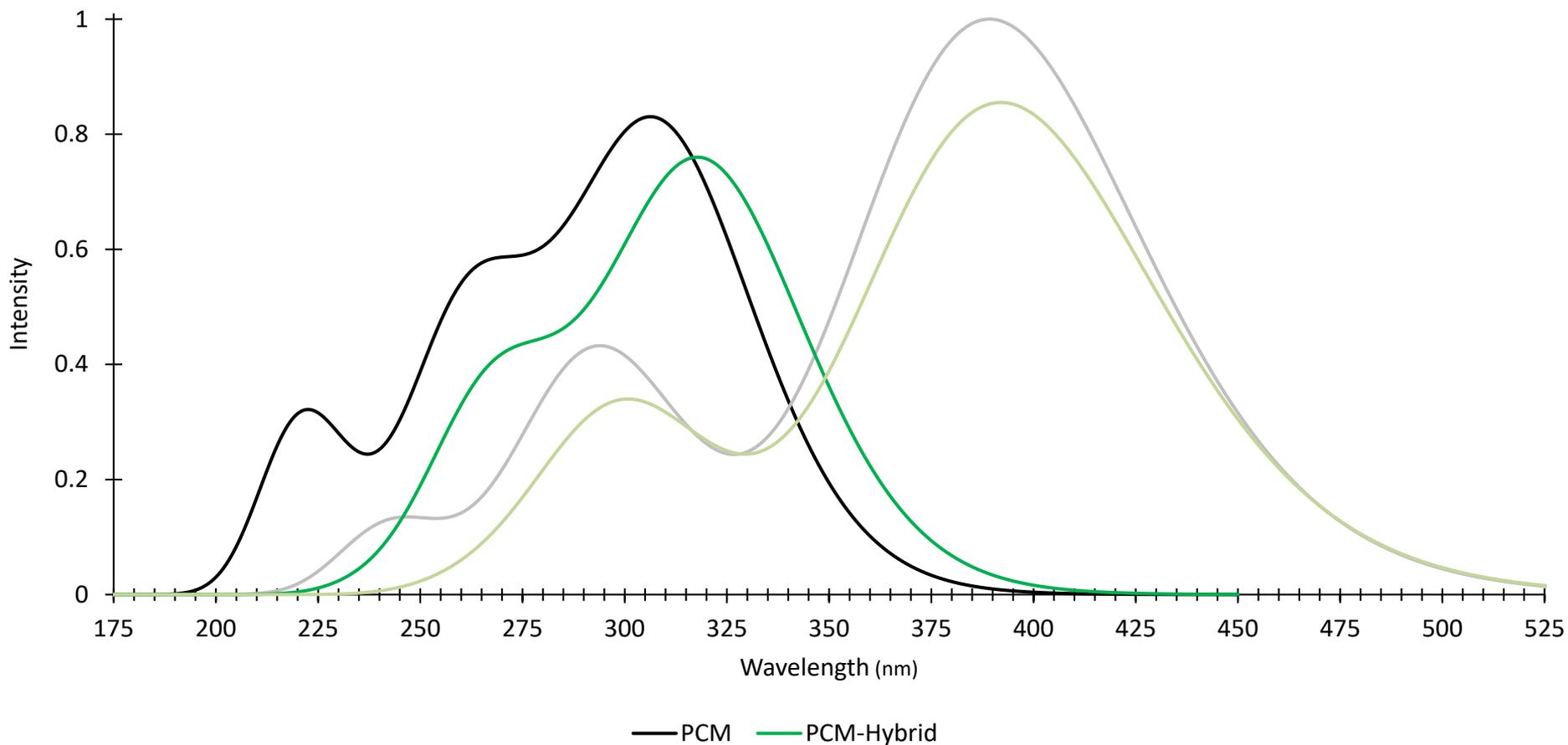


vNPO PCM-SS vs. PCM-Hybrid Absorption and Emission

Stokes Shifts

PCM-implicit: 80.77 nm

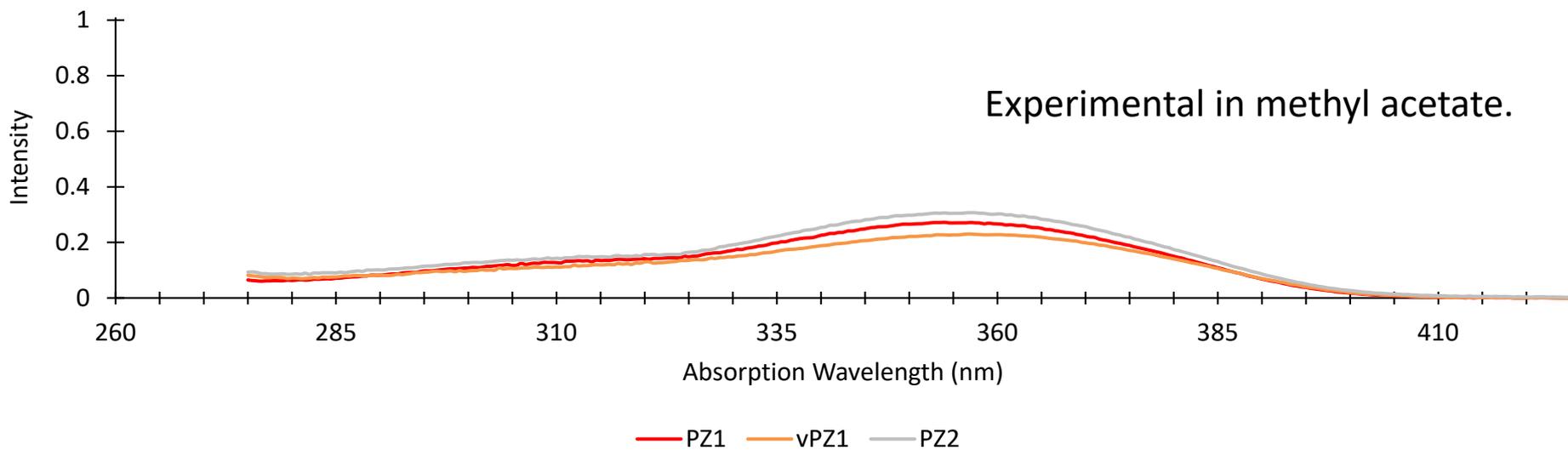
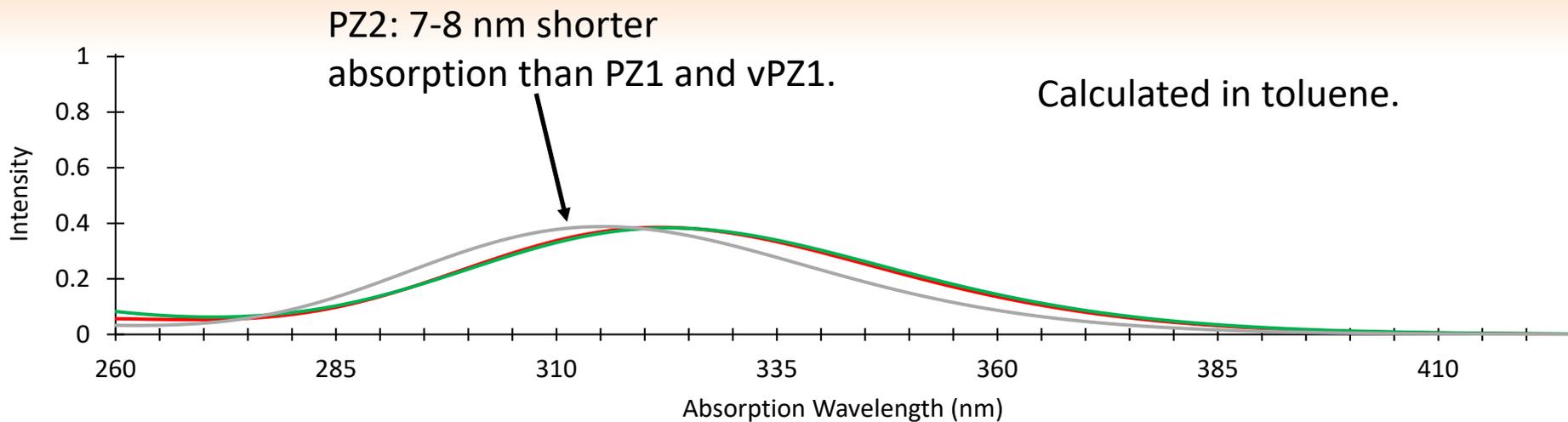
PCM-hybrid: 72.76 nm



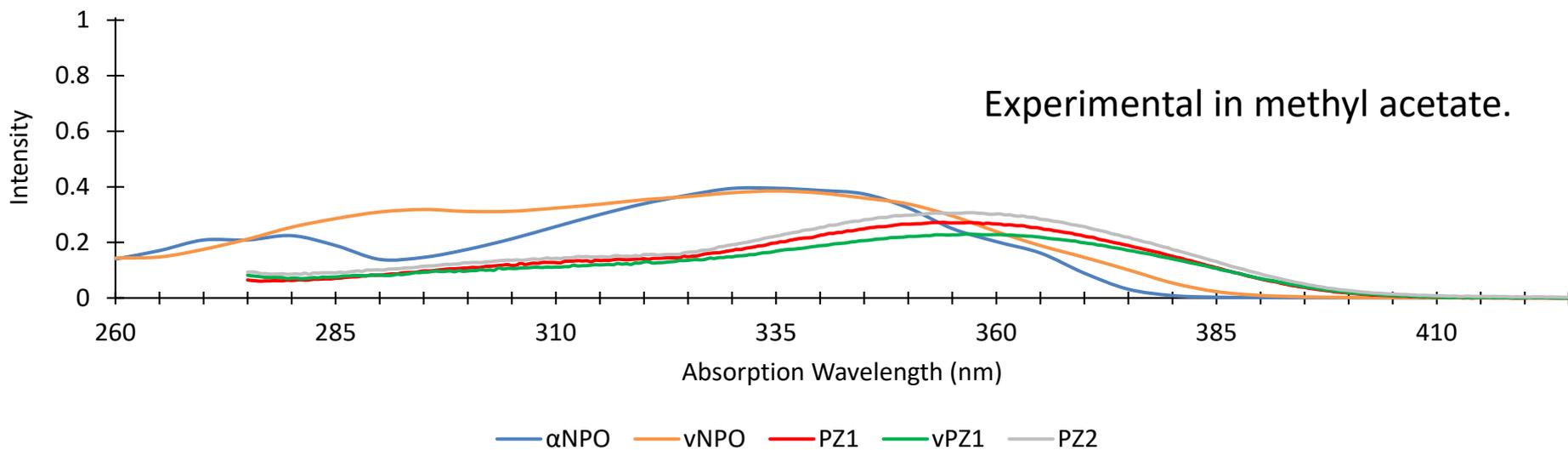
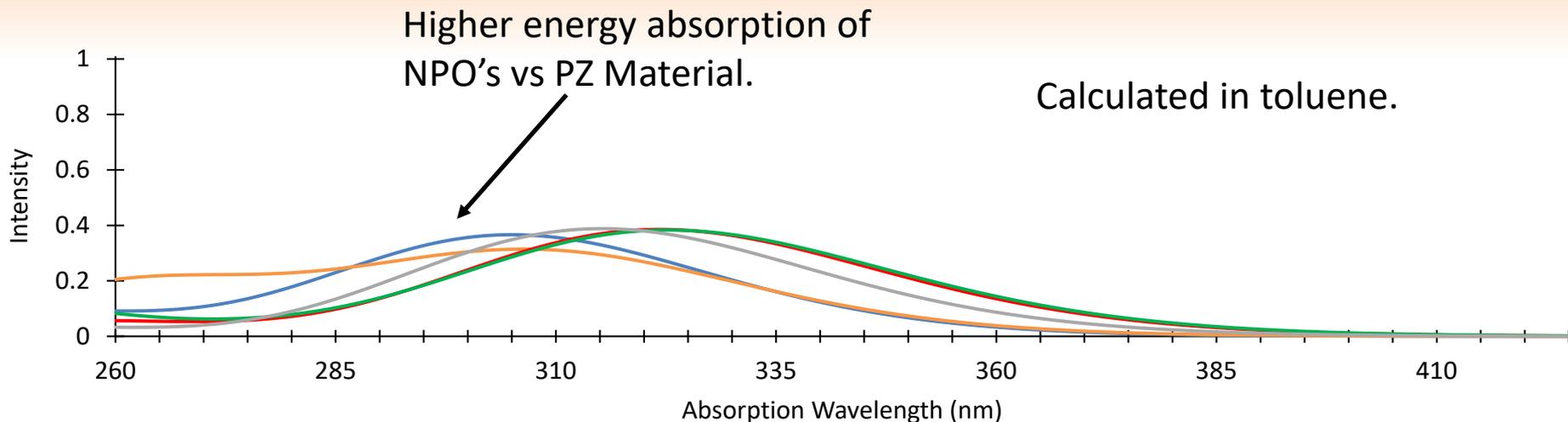
Hybrid Solvation

- ONIOM hybrid technique has flaws.
 - Approximations make system non-real.
 - Only LR excitations are possible.
 - Currently not able to produce emission spectra in G09.
- PCM-hybrid technique need additional work.
 - Returns spectra that differ from the PCM SS and ONIOM results.
 - No drastic approximations.
 - Can produce emission spectra.
 - Unknown coordination of explicit solvent can lead to misleading results.

27 PCM vs Experimental Chemical Effects



28 PCM vs Experimental Chemical Effects

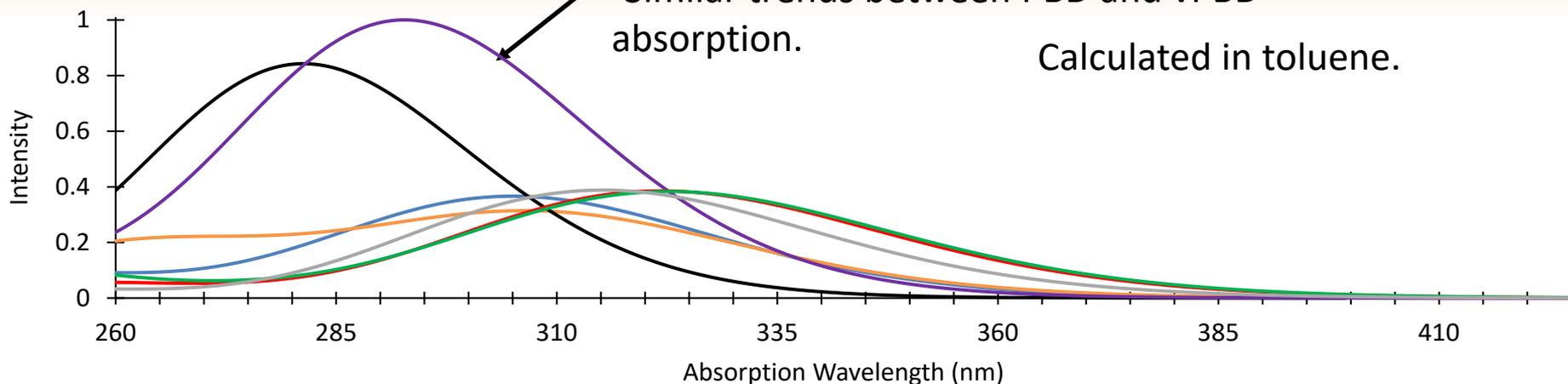


PCM vs Experimental Chemical Effects

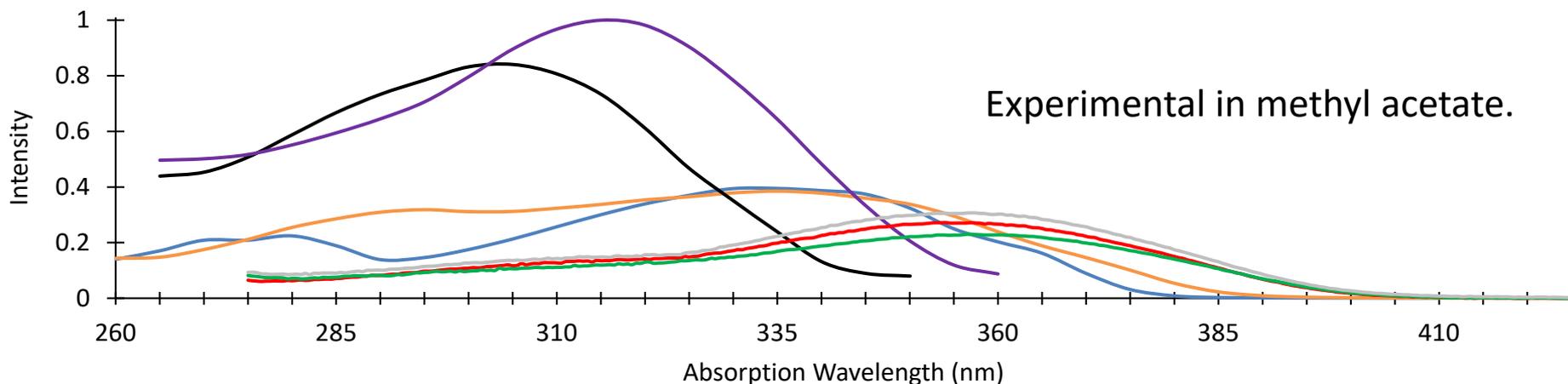
-Higher energy absorption PBD and vPBD than NPO's and PZ Material.

-Similar trends between PBD and vPBD absorption.

Calculated in toluene.



— αNPO — vNPO — PBD — vPBD — PZ1 — vPZ1 — PZ2



Experimental in methyl acetate.

— αNPO — vNPO — PBD — vPBD — PZ1 — vPZ1 — PZ2

PCM vs Experimental-Toluene

30

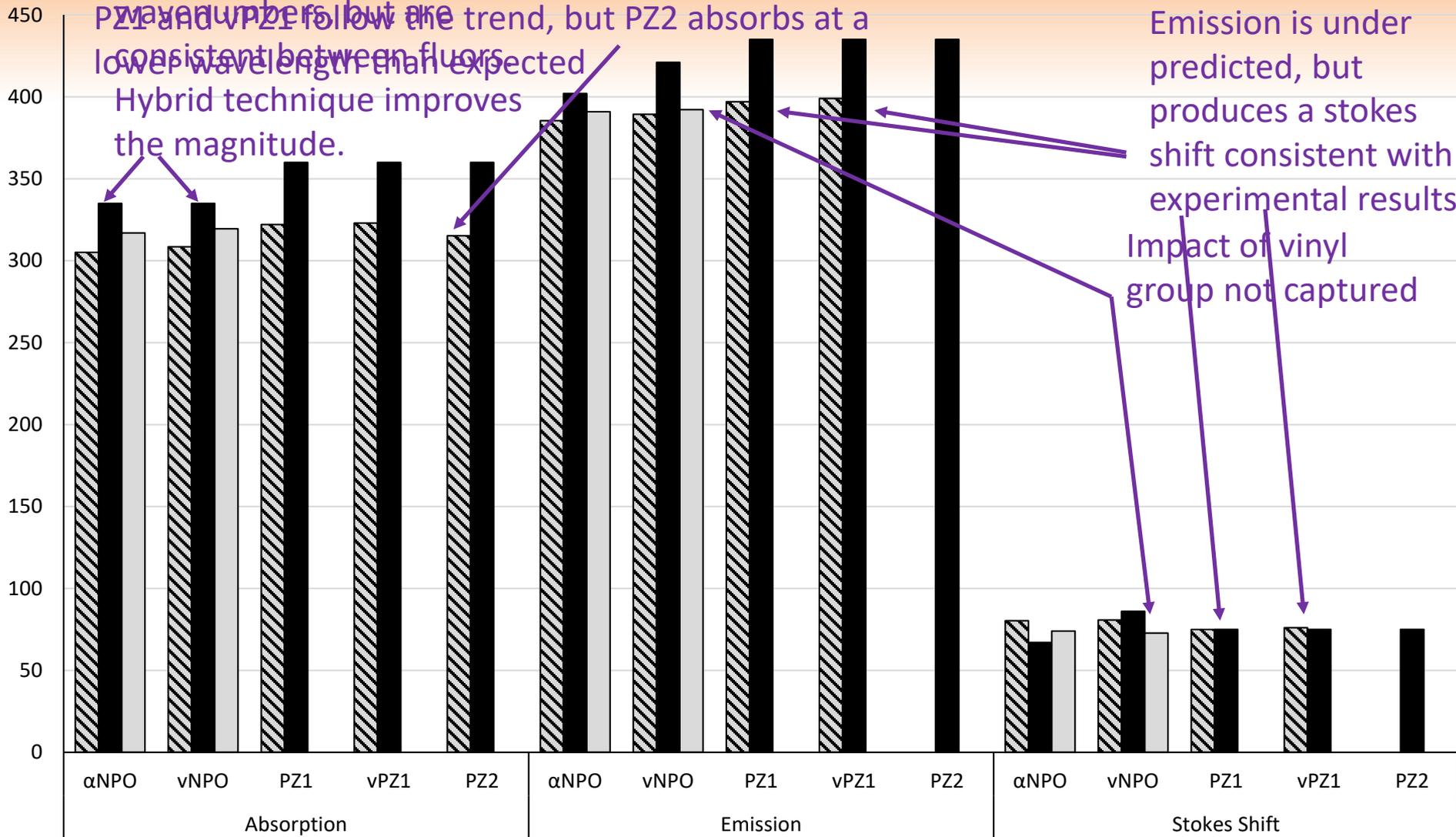
Both models under predict wave numbers.

PCM-SS under predicts wave numbers but are consistent between fluors

Hybrid technique improves the magnitude.

Emission is under predicted, but produces a stokes shift consistent with experimental results

Impact of vinyl group not captured



PCM-SS Experimental PCM-hybrid

Summary

- Energy Functional Effects
 - Need long range corrected functional.
- Solvation Effects
 - PCM model can predict general trends.
 - Could predict electrostatic differences in solvents, but not solute-solvent interactions.
 - Correctly identified reactivity between fluor molecules
 - Did not produce the experimental stokes shift observed between α NPO that vNPO.
 - PCM-hybrid technique need additional work.
 - Returns spectra that differ from the PCM SS and ONIOM results.
 - Improved values of absorption and emission wavelength.
 - Did not produce the experimental stokes shift observed between α NPO that vNPO.
 - Unknown coordination of explicit solvent can lead to misleading results.
 - ONIOM hybrid technique has flaws.
 - Approximations make system non-real.
 - Only LR excitations are possible.
 - Currently not able to produce emission spectra in G09.

Acknowledgements

- My advisor, Dr. Shuller-Nickles, for invaluable support and guidance.
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- CCIT for their generous access to the Palmetto Cluster Supercomputer.
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References

1. Seliman, Ayman F., et al. "Development of Polymerizable 2-(1-Naphthyl)-5-Phenyloxazole Scintillators for Ionizing Radiation Detection" *Journal of Materials Chemistry C* 3 (2015): 7053. Print.
2. Bliznyuk, Valery N., et al. "New Efficient Organic Scintillators Derived from Pyrazoline." *American Chemical Society Applied Materials and Interfaces* 8.20 (2016): 12843-51.

Questions?

Future Work

- Increase the number of explicit toluene in PCM-hybrid technique from 1 to 2-3 in order to address toluene coordination issues.
- Basis Set Effects
 - Incorporate Diffuse Functions.
- Gaussian 16 software upgrade
 - Electronic Energy Transfer (EET): Energy transfer from an explicit solvent to the fluor is coupled.
 - Updates on ONIOM for emission spectra and computational time improvements.

Initial Results – Basis Set Effects

