Time-dependent density functional theory calculations to guide the development of modified organic scintillating materials

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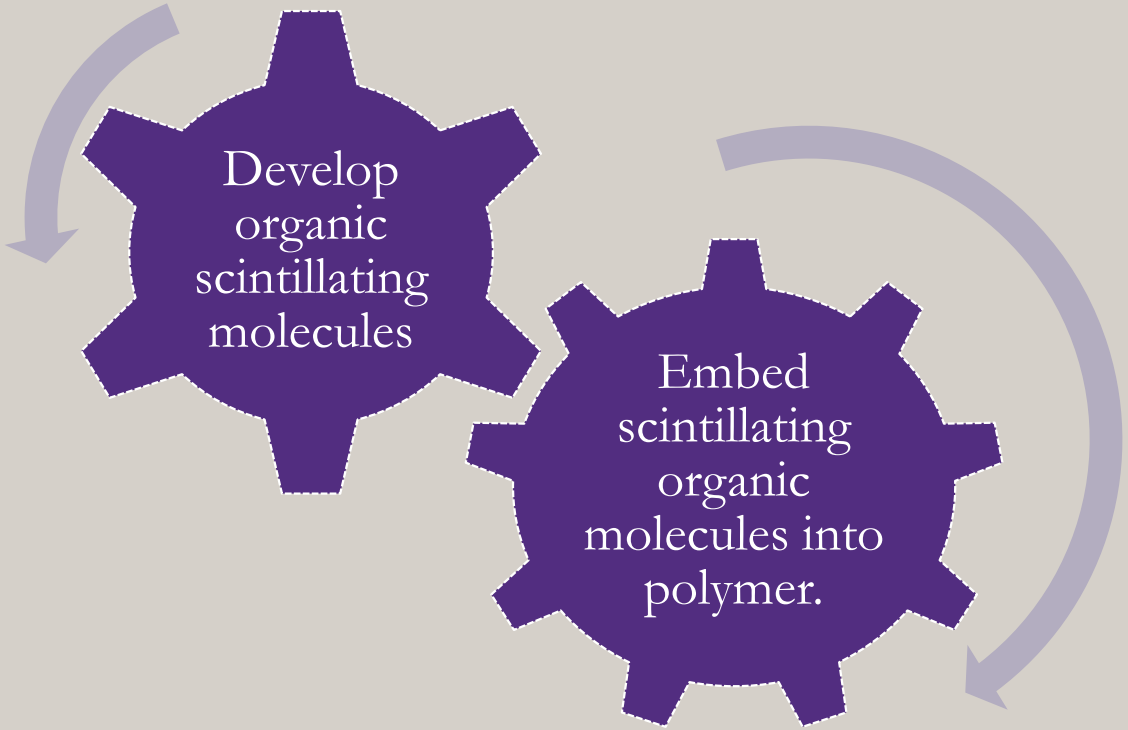
Objective

- Design highly selective and sensitive sensors for online monitoring of radionuclides



Can quantum-mechanical calculations shed light on underlying material differences?

e^- → quantum mechanics

Density functional theory uses Kohn-Sham theorem to equate the density functional to the electronic wave function to solve:

The Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

$\hat{H}$: an operator that represents the interactions in the system
Ψ: describes the electron distribution
E: the total electron binding energy

Density Functional Theory

Hohenberg-Kohn Theorem **ground state density** can be used to describe a stationary electronic system

1964

Kohn-Sham Theorem electrons obey a **simple, one particle** Schrodinger equation with an effective potential $v_{KS}(r)$

$$v_{KS}(r) = v_{ext}(r) + v_{Ha}(r) + v_{xc}(r)$$

where $v_{ext}(r)$ = External pot.
$v_{Ha}(r)$ = Hartree (classical) e-e pot.;
$v_{xc}(r)$ = Exchange correlation pot.

1965

Generalized Gradient Approximation (GGA) next-generation functional beyond LDA, in which the xc energy density is a function of its density and gradient

1999

1984

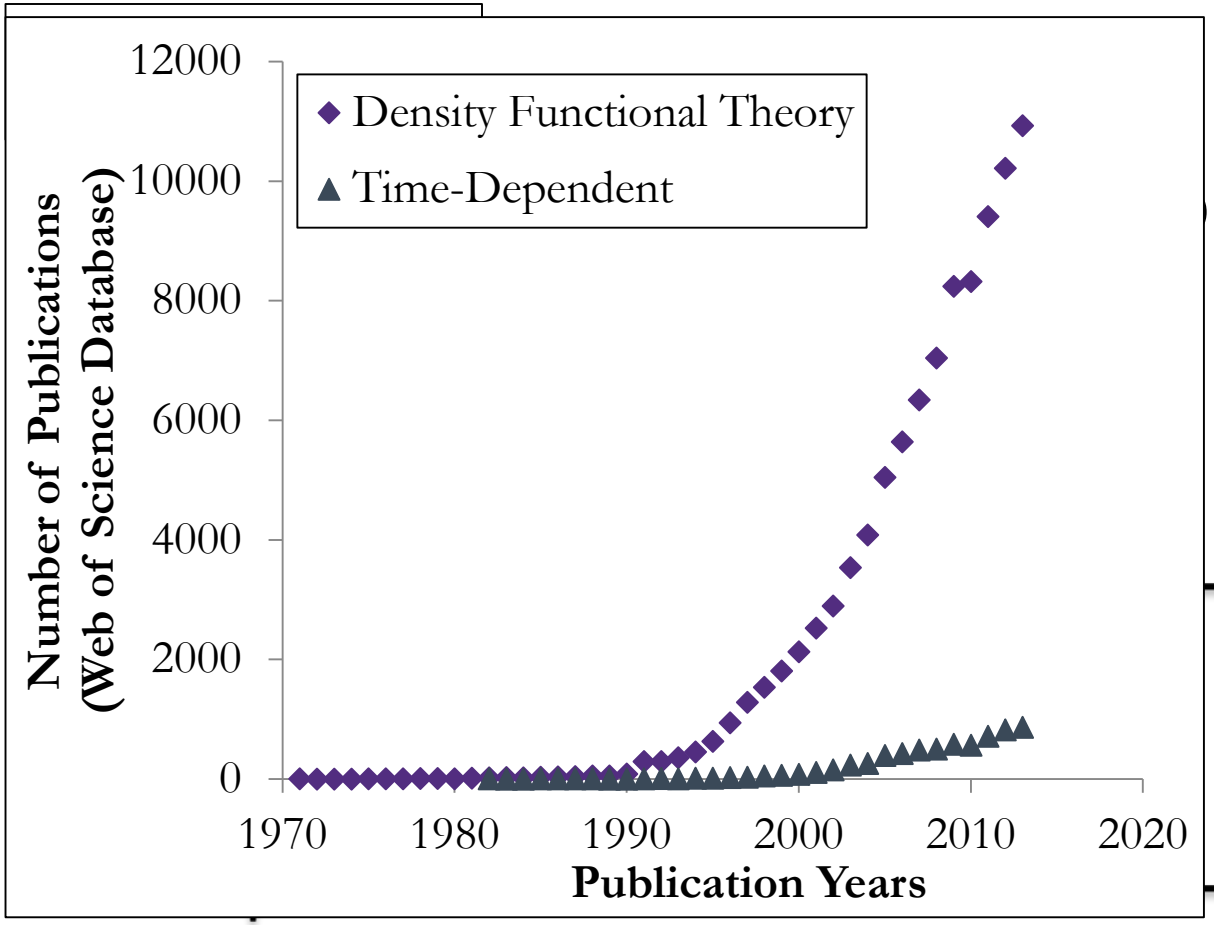
Runge and Gross Theorem **Hohenberg-Kohn-like** theorem for the **time-dependent** Schrodinger equation

$$i\frac{\delta}{\delta t}\Psi(\{r\},t) = \hat{H}(\{r\},t)\Psi(\{r\},t)$$

1998

Efficient implementation of TD-DFT Stratmann, Scuseria, and Frisch, J. Chemical Physics **109**: 8218-8224.

Time-Dependent Density Functional Theory



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Time-Dependent Density Functional Theory

Key deliverables for DFT and TD-DFT calculations

DFT

- Ground state energy
- Ground state geometry
- Vibrational frequencies
- Solvation energy

TD-DFT

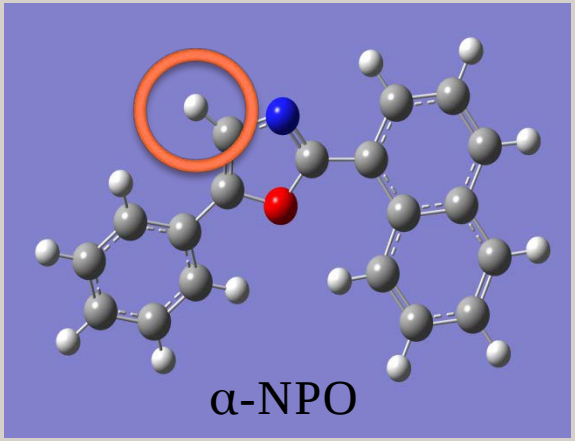
- Excited state energy
- Excited state geometry
- Excitation and relaxation wavelength
- Solvation effects

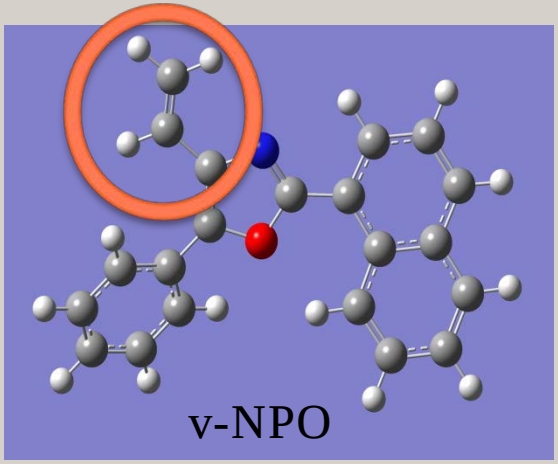
Key deliverables for DFT and TD-DFT calculations

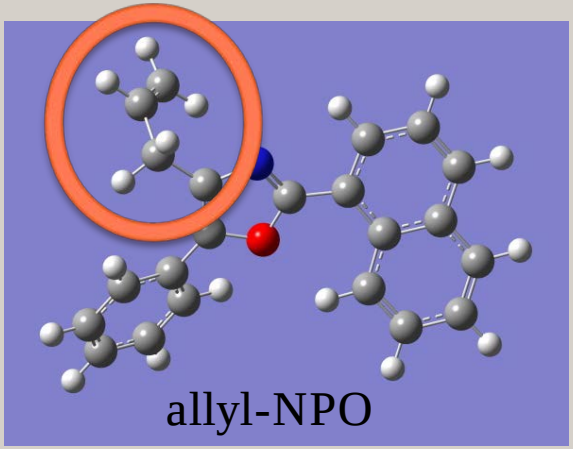
DFT	TD-DFT
• Ground state energy	• Excited state energy
• Ground state geometry	• Excited state geometry
• Vibrational frequencies	• **Excitation and relaxation wavelength**
• Solvation energy	• Solvation effects

Hypothesis

Targeted modifications to the 2-(l-naphthyl)-5-phenyloxazole (α-NPO) molecule will shift absorption/emission wavelengths, leading to improved solid scintillating materials.



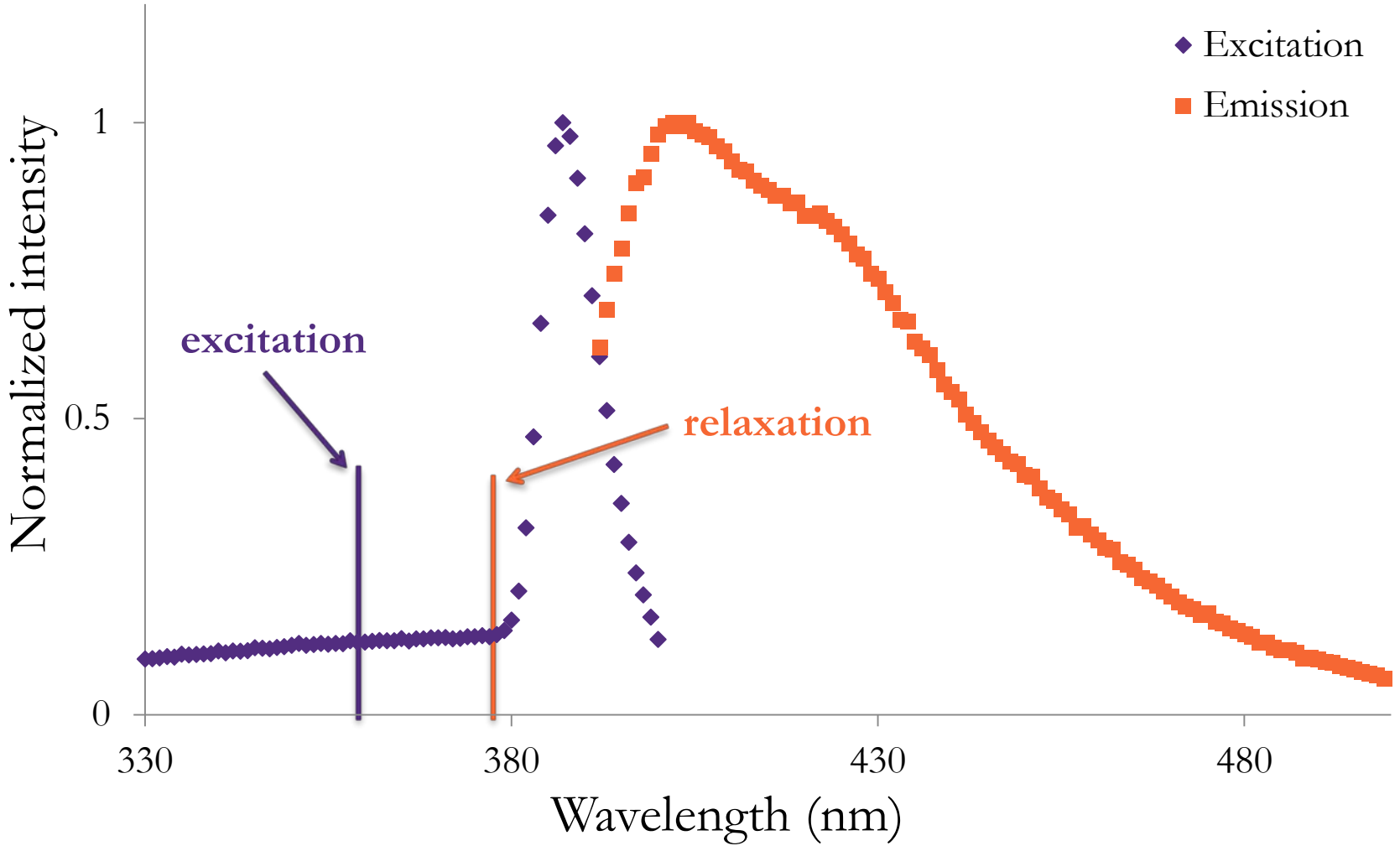




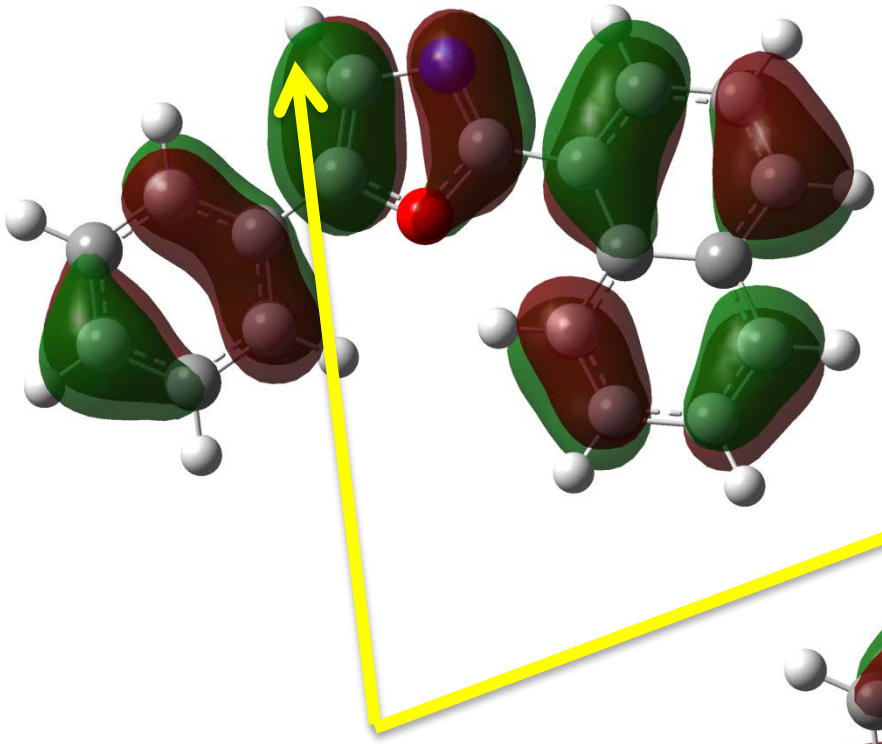
Methodology

- Ground state geometry optimizations
  - Vibrational frequency calculations
- Vertical excitation calculations
  - Determination of excited state geometry
- Relaxation calculations
- Addition of solvation

Excitation and emission of α-NPO in toluene (experimental) and gas (computational)

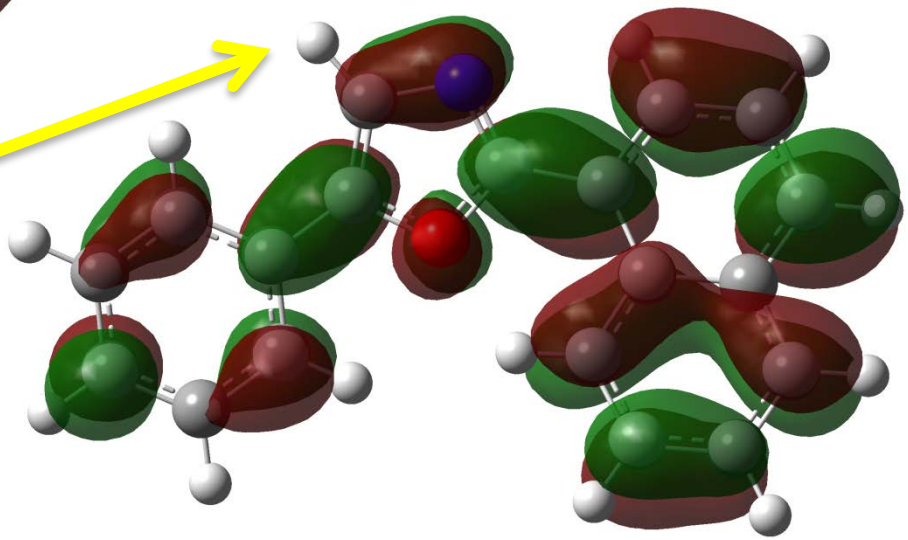


Projection of the HOMO and LUMO for α-NPO Excitation



Highest occupied molecular orbital (HOMO)

Lowest unoccupied molecular orbital (LUMO)

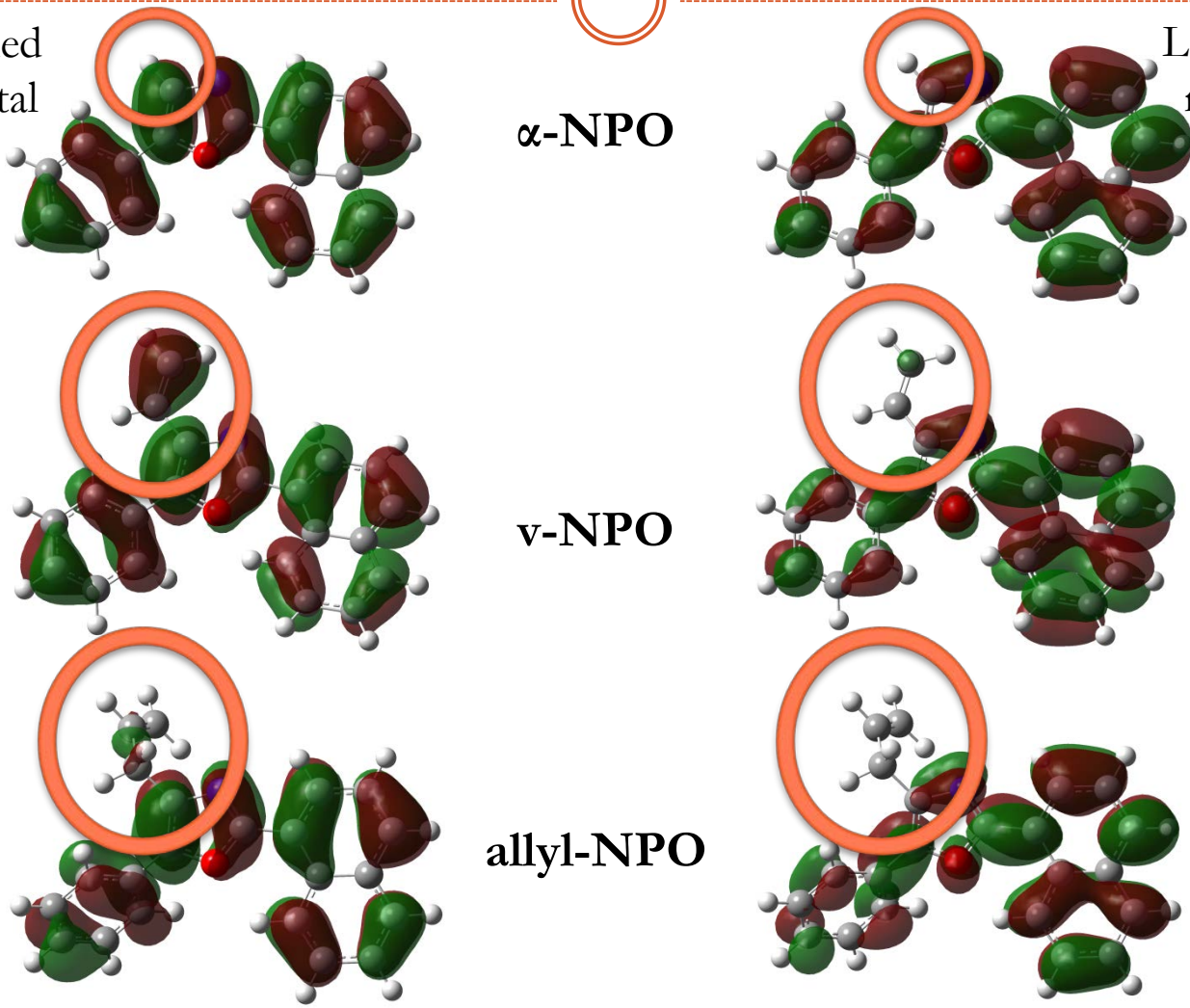


Highlights role of the α site.

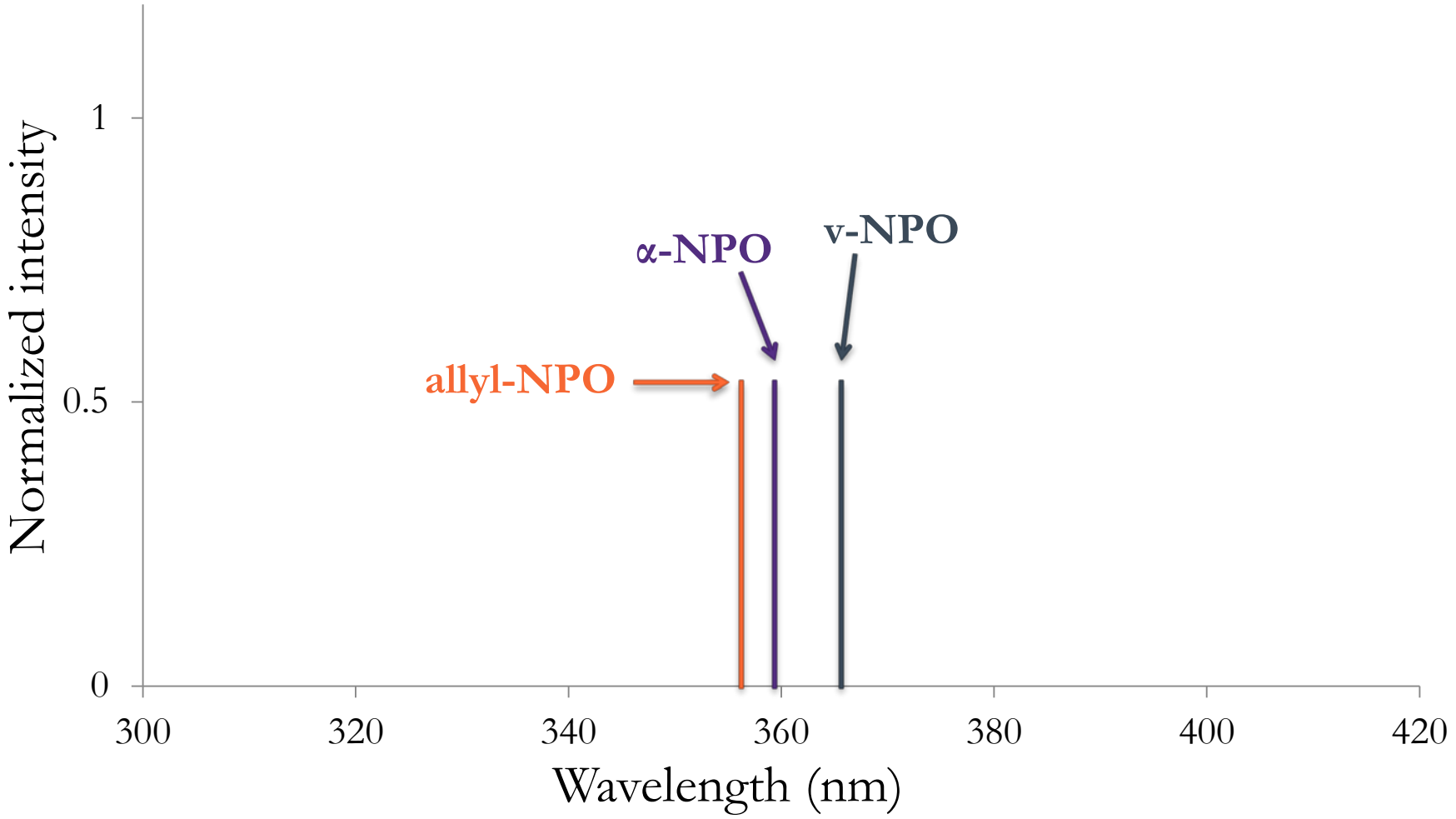
Projection of the HOMO and LUMO for x-NPO Excitation

Highest occupied molecular orbital (HOMO)

Lowest unoccupied molecular orbital (LUMO)



Excitation spectra for α-NPO, v-NPO, and allyl-NPO



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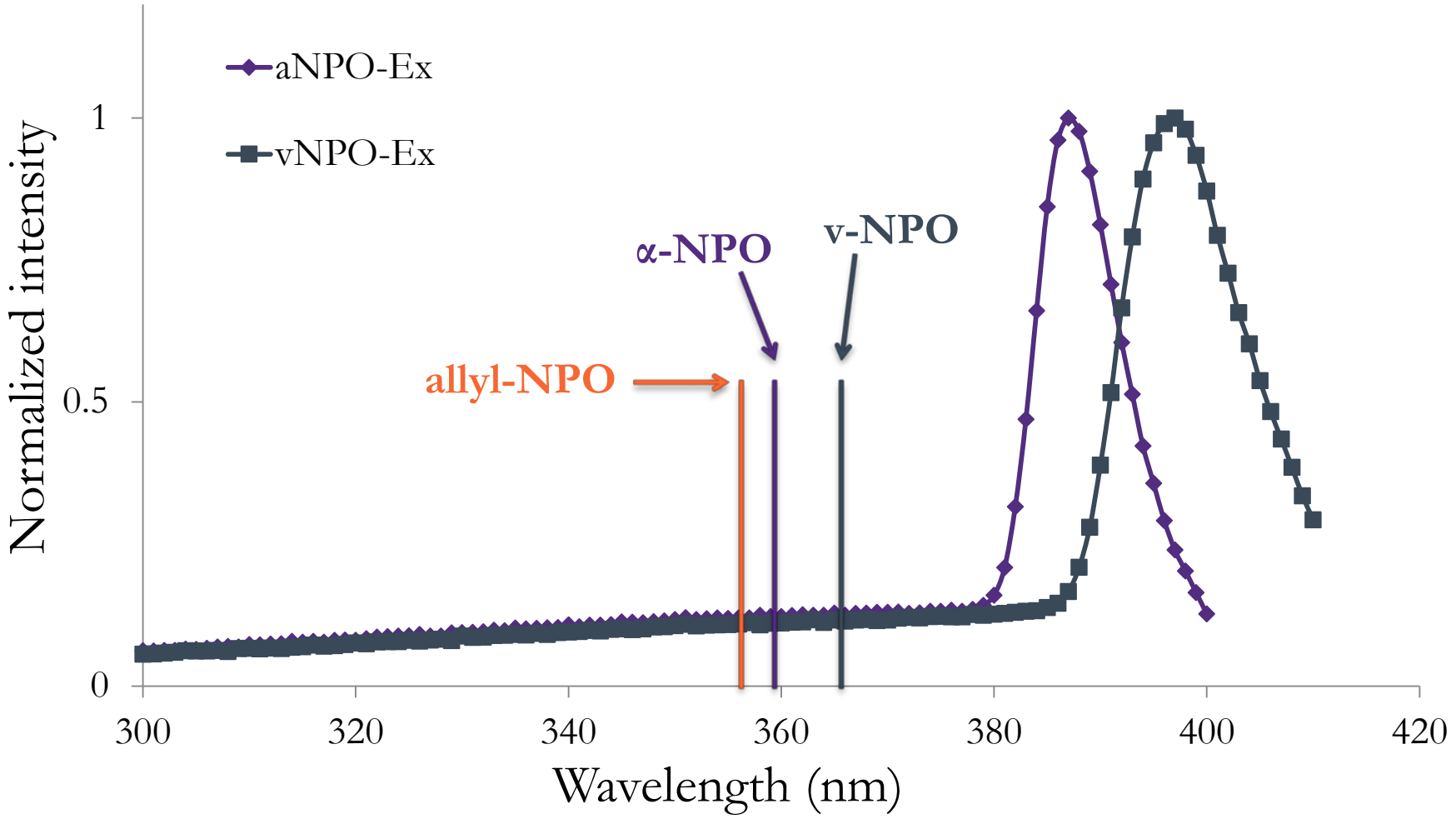

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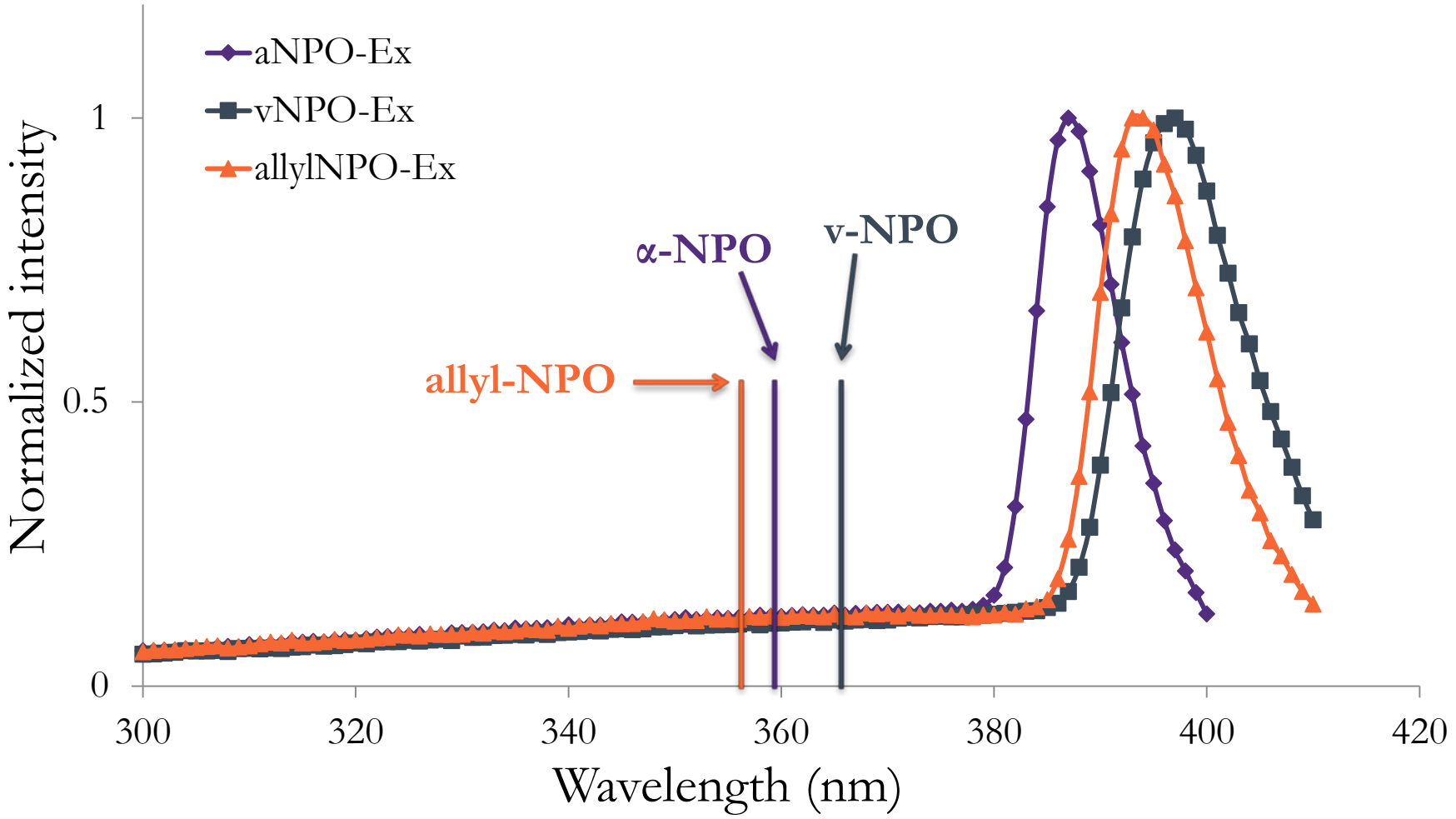
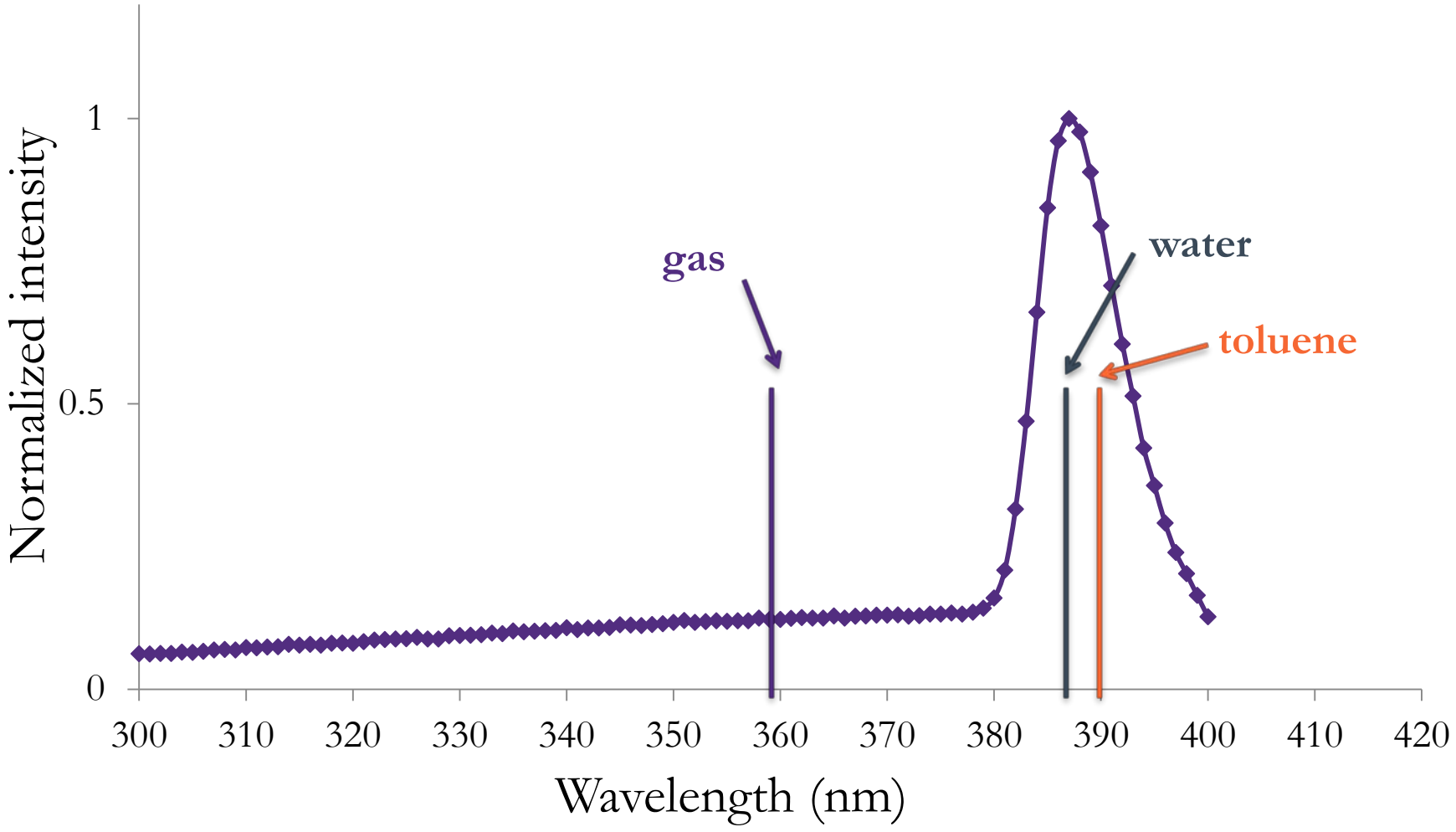
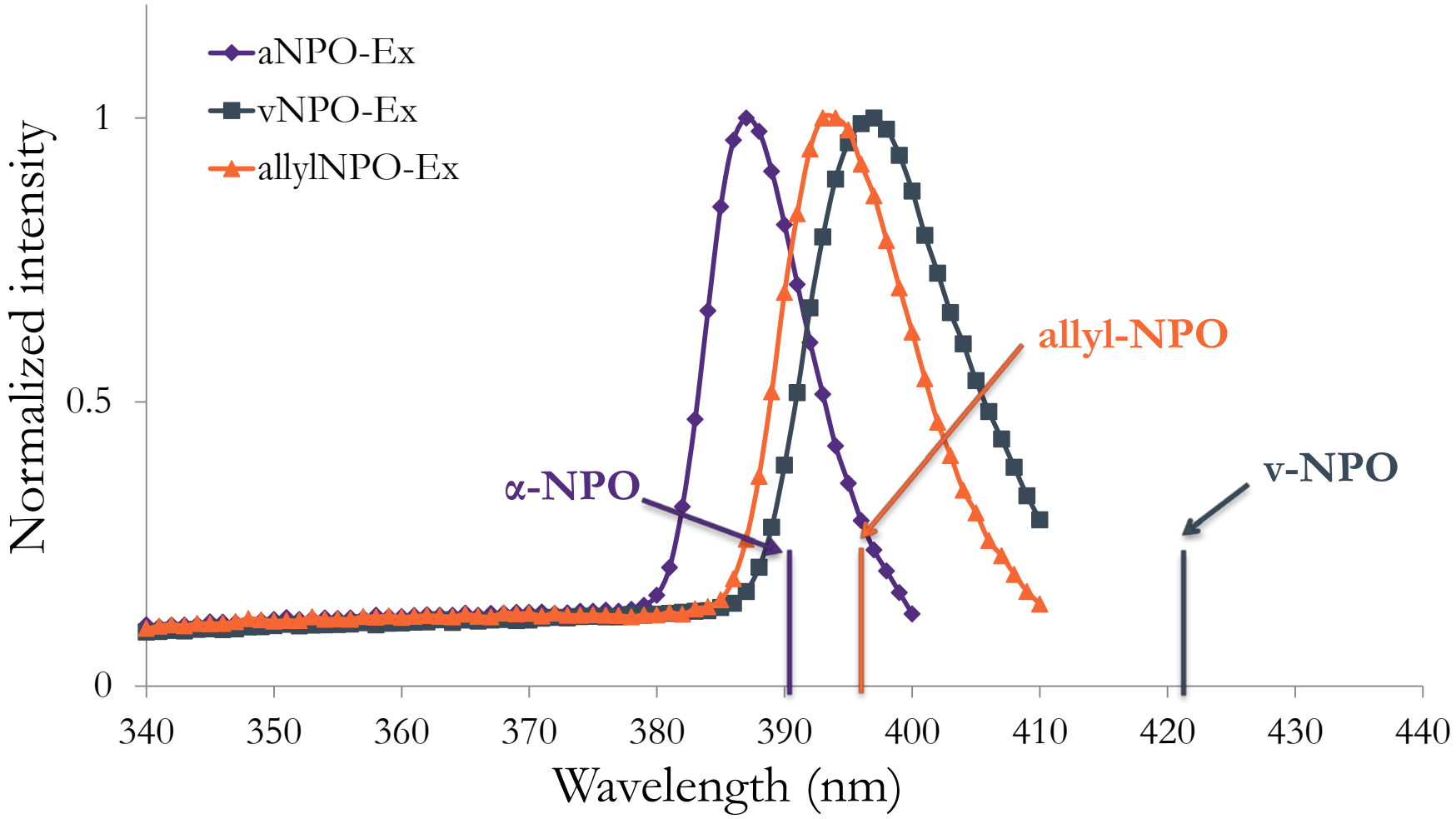


Effect of solvation on excitation spectra for α-NPO



Effect of solvation (toluene) on α-NPO, v-NPO, and allyl-NPO Excitation Wavelength



Conclusions

- The **absorption wavelength increases** from α-NPO to allyl-NPO to vinyl-NPO.
- **Environment** (solvation/crosslinking) directly affects absorption/emission and is important to consider for accurate calculations.
- **Refined calculations** (e.g., range-separated hybrid functionals) are necessary for more accurate results.

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