

DFT project

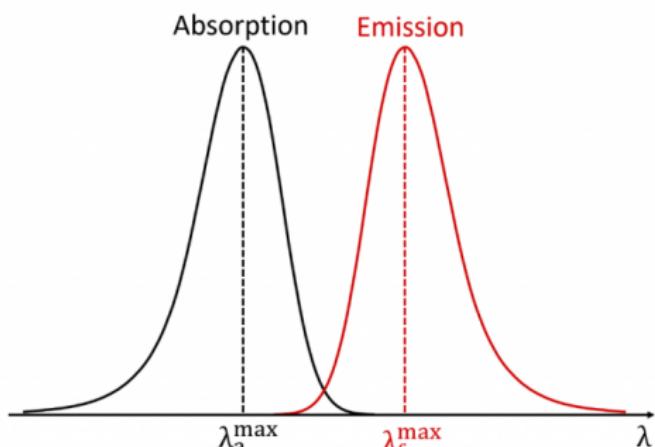
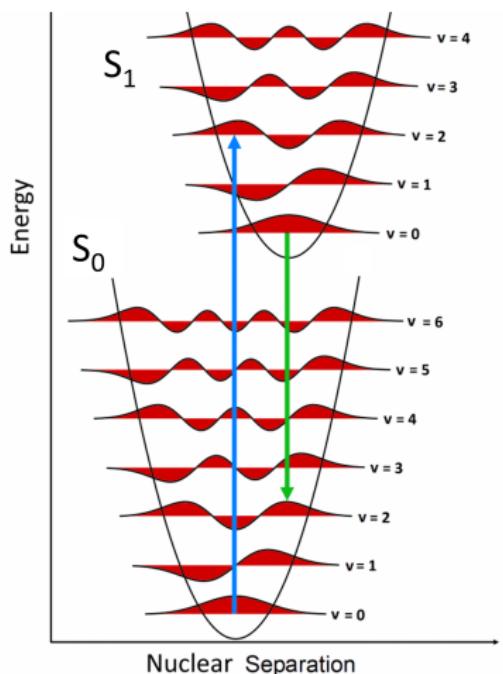
Calculation of the Stokes shift of 4-Nitroaniline

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Overview

- ① Introduction
- ② Computational Setup
- ③ Structural Analysis
- ④ Absorption Spectra
- ⑤ Stokes Shift

Stokes shift

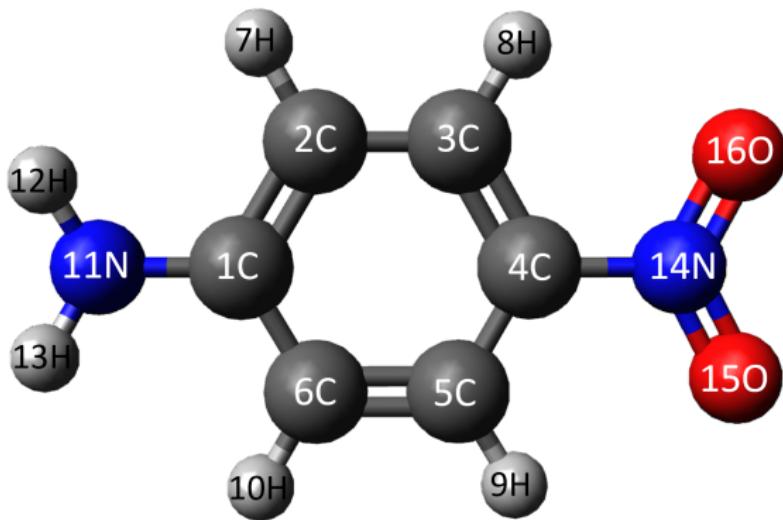


$$\text{Stokes shift} = \lambda_f^{\max} - \lambda_a^{\max}$$

Computational Setup

- Ground state structure optimization:
 - Functional: B3LYP
 - Basis sets: 6-31G(d), 6-311++G(d,p)
- TD-DFT calculations:
 - Functional: B3LYP
 - Basis sets: 6-311++G(d,p)

Structure of 4-Nitroaniline (PNA)



Structural comparison

Bonds Å	B3LYP/ 6-311++G(d,p)	B3LYP/ 6-31G(d)	B3LYP/ 6-311++G(d,p) ²	XRDa 4-nitroaniline ³
C1-C2	1.409	1.412	1.408	1.408
C1-C6	1.409	1.412	1.409	1.415
C1-N11	1.378	1.381	1.378	1.371
C2-C3	1.384	1.386	1.383	1.377
C2-H7	1.085	1.087	1.085	0.950
C3-C4	1.395	1.398	1.395	1.390
C3-H8	1.082	1.083	1.081	0.810
C4-C5	1.395	1.398	1.395	1.395
C4-N14	1.462	1.457	1.461	1.460
C5-C6	1.384	1.386	1.383	1.373
C5-H9	1.082	1.083	1.081	0.830
C6-H10	1.085	1.087	1.085	0.830
N11-H12	1.008	1.011	1.007	0.960
N11-H13	1.008	1.011	1.007	0.750
N14-O15	1.229	1.235	1.229	1.247
N14-O16	1.229	1.235	1.229	1.246

²Esakimuthu et al. (2010). Molecular structure, vibrational spectroscopic and HOMO, LUMO studies of 4-nitroaniline by density functional method.

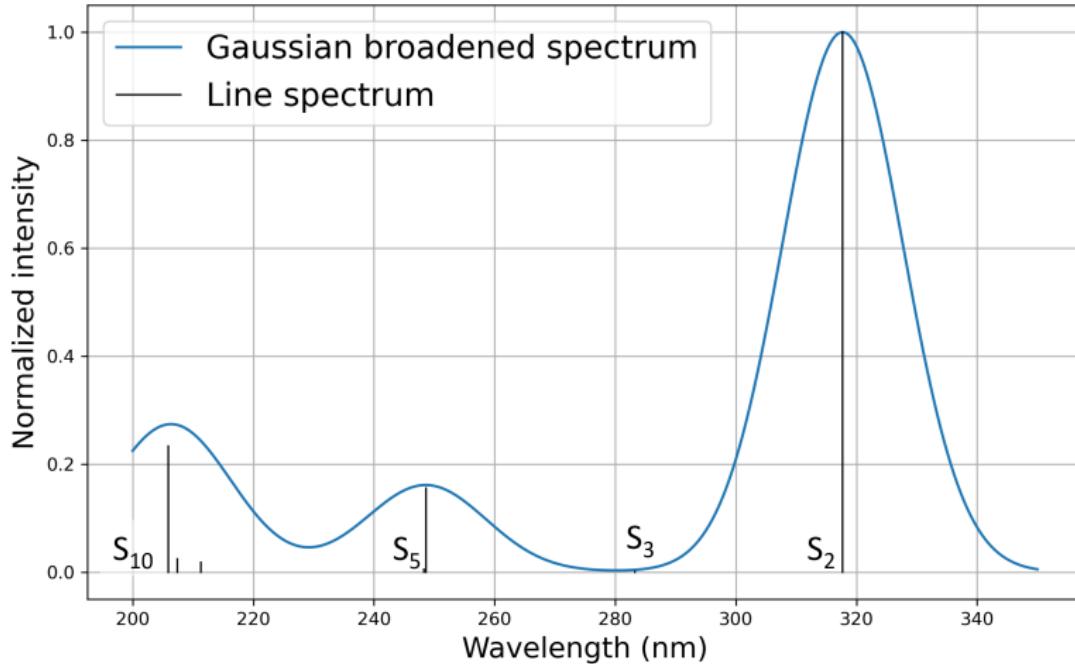
³Trueblood et al. (1961). A three-dimensional refinement of the crystal

Structural comparison

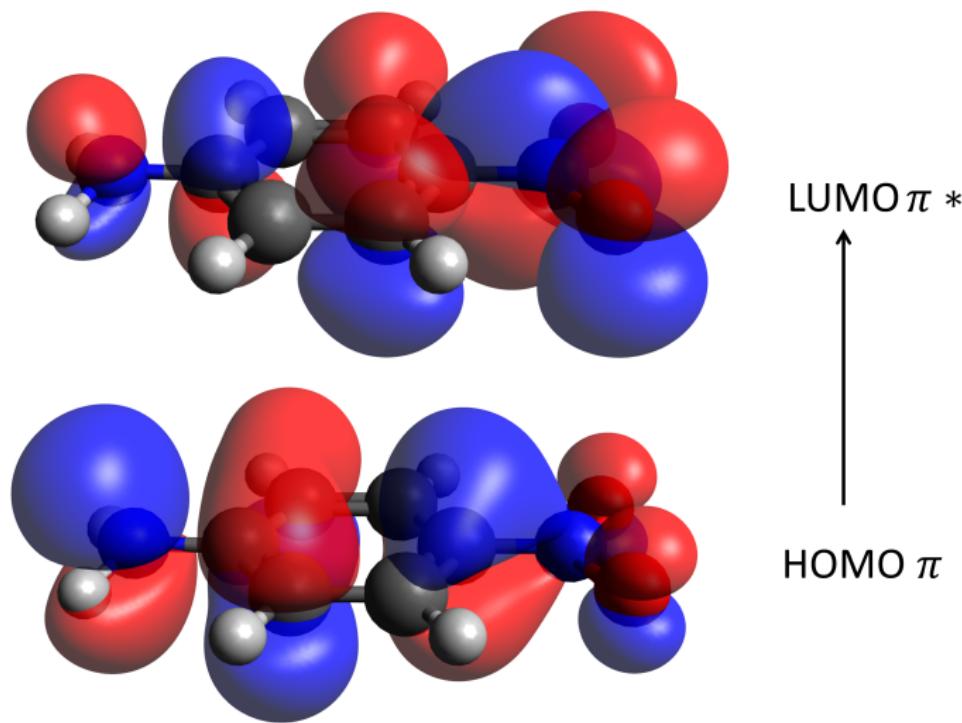
	This project	
	6-311++G(d,p)	6-31G(d)
Reference theory	$\sum_{\text{errors}} = 0.0070$ RMSD = 0.0006	$\sum_{\text{errors}} = 0.0451$ RMSD = 0.0035
Reference experiment	$\sum_{\text{errors}} = 1.2110$ RMSD = 0.1346	$\sum_{\text{errors}} = 1.2491$ RMSD = 0.1359
This project 6-31G(d)	$\sum_{\text{errors}} = -0.0381$ RMSD = 0.0033	

Table: Bond lengths comparison for 4-nitroaniline in Å

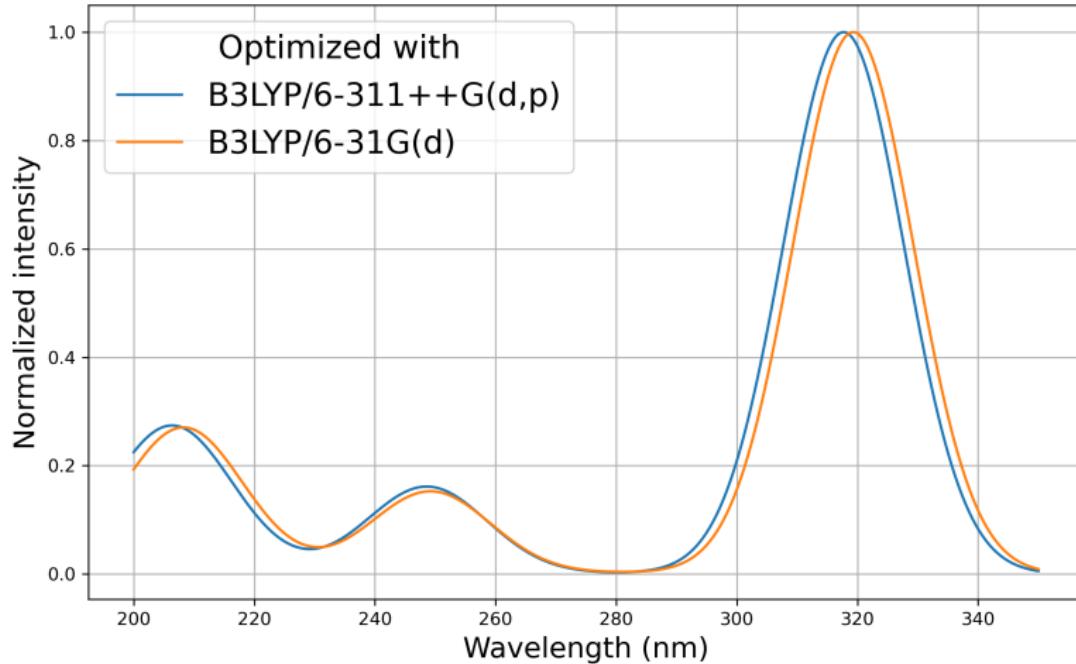
Absorption spectra



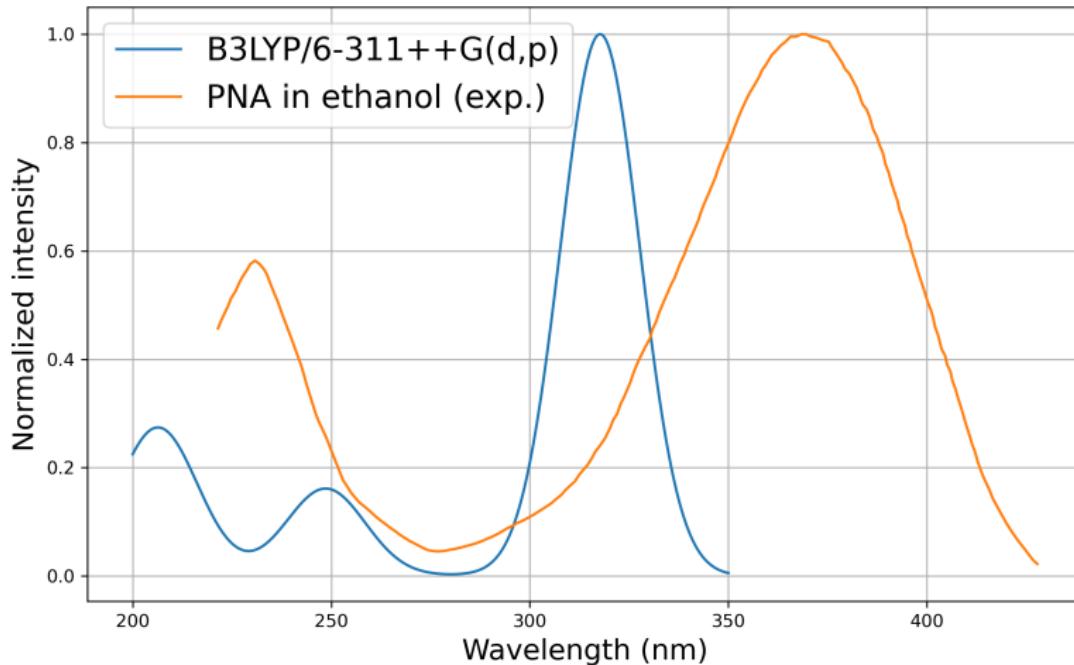
S_0 - S_2 Transition



Absorption spectra



Absorption spectra

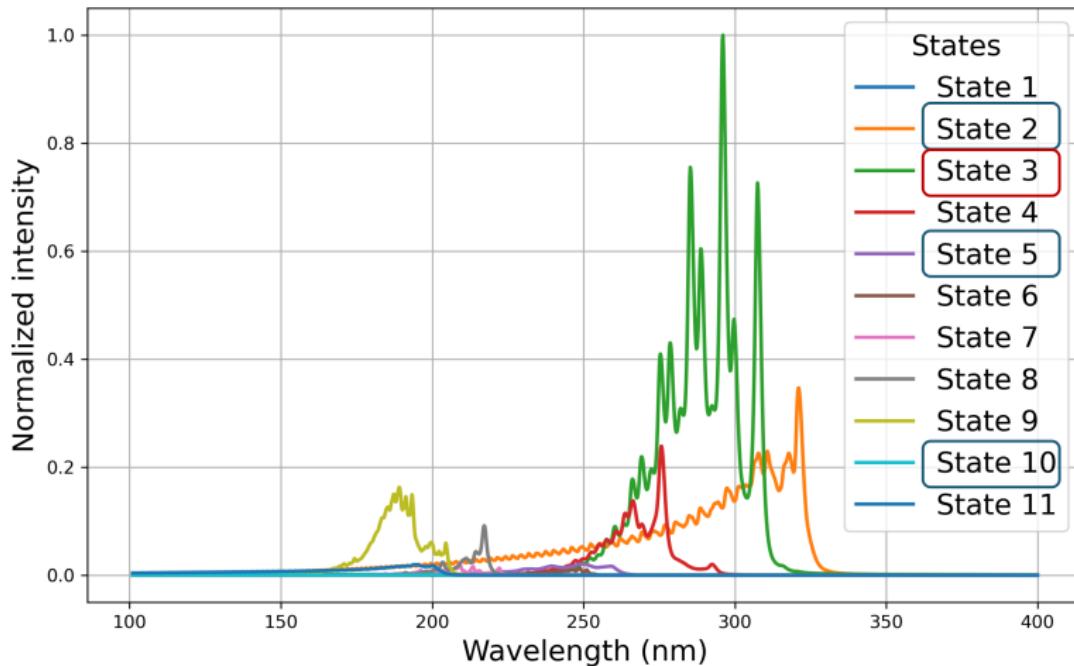


Excited State Dynamics

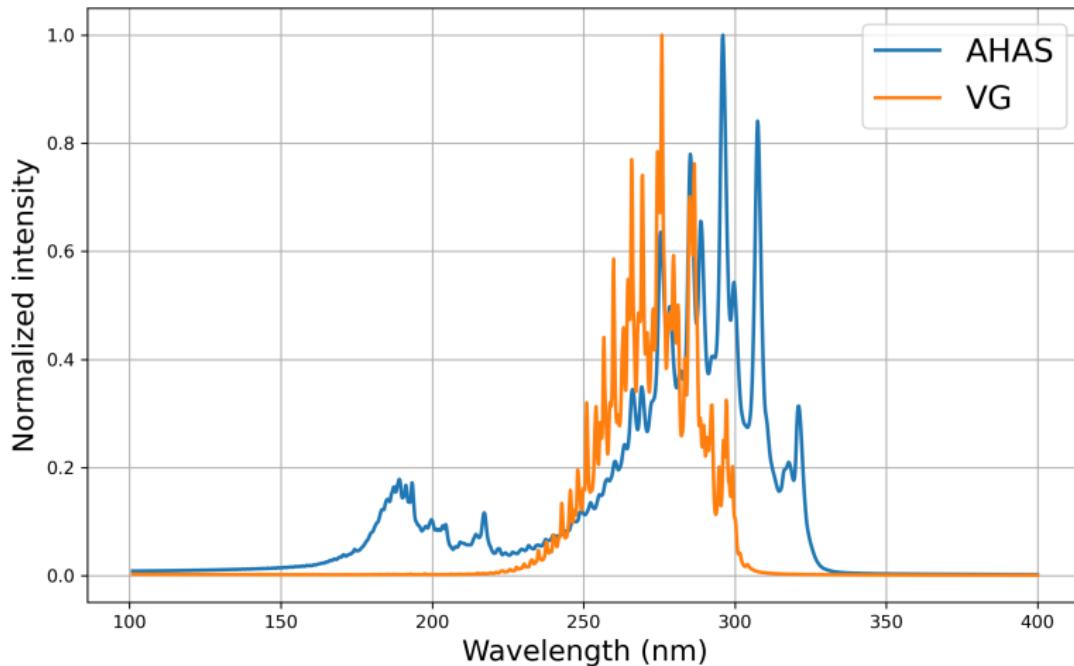
Orca module to calculate excited state (ES) properties (ORCA_ESD)

- Considers vibronic coupling
- Approximation of excited state PES
 - Vertical Gradient (VG):
Hessian equal to ground state Hessian
 - Adiabatic Hessian After a Step (AHAS):
Hessian calculated on the ES geometry

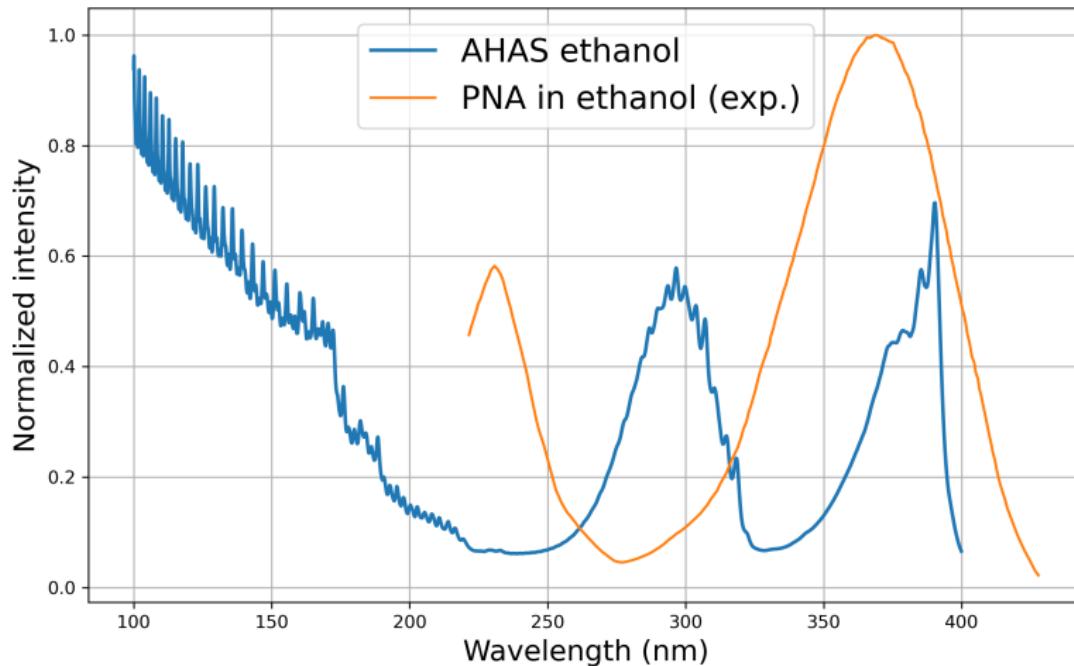
Absorption spectra - AHAS



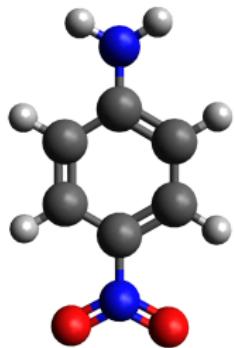
Absorption spectra



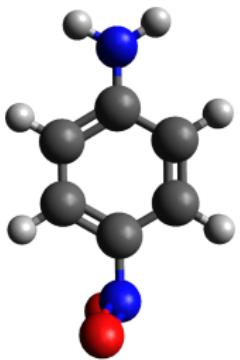
Absorption spectra



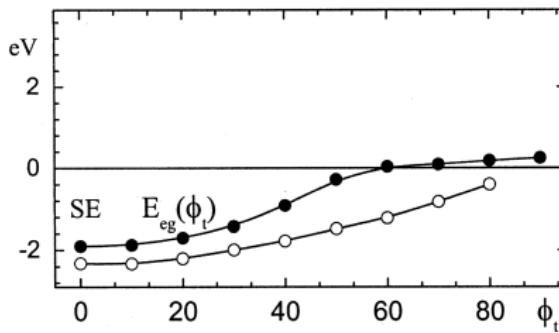
Excited state optimization (S_2)



Ground state



Excited state

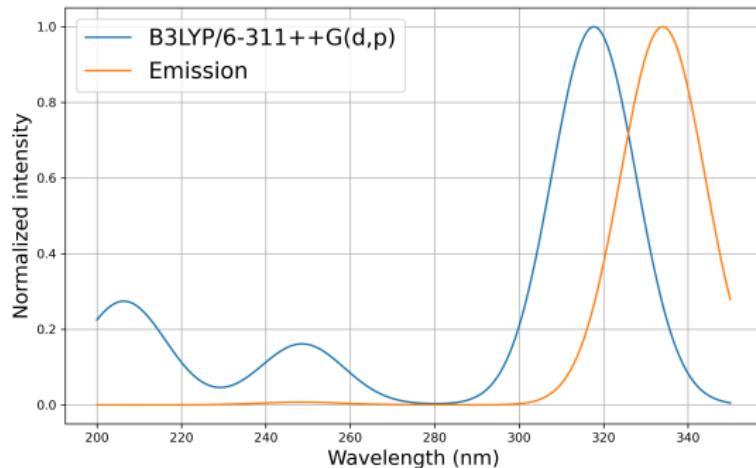


SE: Stimulated emission energy
 Φ : Angle around C- NO_2 bond

4

⁴Modified from: Kovalenko et al. (2000). Femtosecond relaxation of photoexcited para-nitroaniline.

Stokes shift

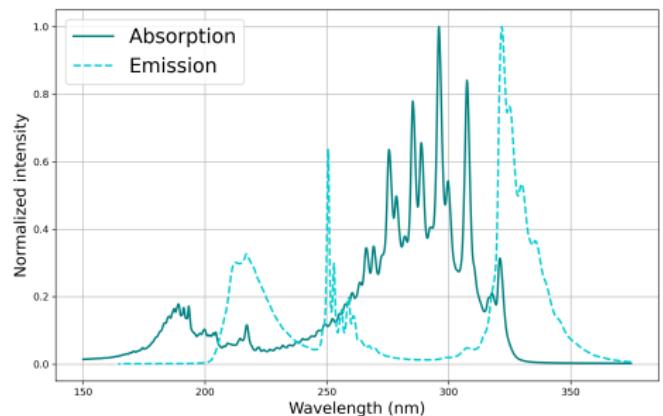


$$\lambda_a^{\max} = 317.72 \text{ nm}$$
$$\lambda_f^{\max} = 333.93 \text{ nm}$$

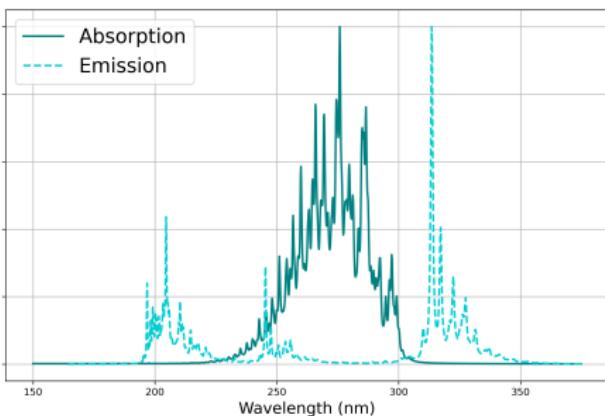
$$\text{Stokes shift} \\ = 16.21 \text{ nm}$$

Stokes shift - ESD

AHAS



VG



$$\lambda_a^{\max} = 296.01 \text{ nm}$$

$$\lambda_f^{\max} = 321.74 \text{ nm}$$

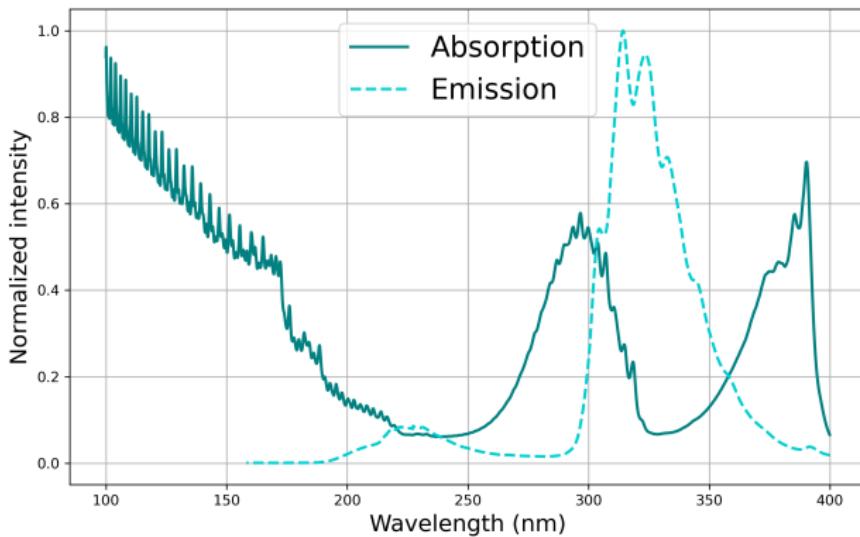
$$\text{Shift} = 25.73 \text{ nm}$$

$$\lambda_a^{\max} = 275.83 \text{ nm}$$

$$\lambda_f^{\max} = 313.50 \text{ nm}$$

$$\text{Shift} = 37.67 \text{ nm}$$

Stokes shift - solvent



Stokes shift: 17.76 nm
Anti-Stokes shift: -76.07 nm

Summary

- Optimized structure in agreement with experimental structure
- Comparison of methods for UV/Vis and fluorescence spectra
- Calculation of Stokes shifts:

Vertical excitation: ~16 nm

AHAS: ~26 nm

VG: ~38 nm

AHAS in ethanol: (~18 nm)

Thank you

