Electronic transitions of paranitrophenol in different pH conditions I

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Motivation: Electronic Transition of Molecules in Solution

Electronic Transitions are very sensitive to the conditions of the environment: solvent affects the energy of the transition; temperature affects the band intensity; pH affects the population ratio of moieties.
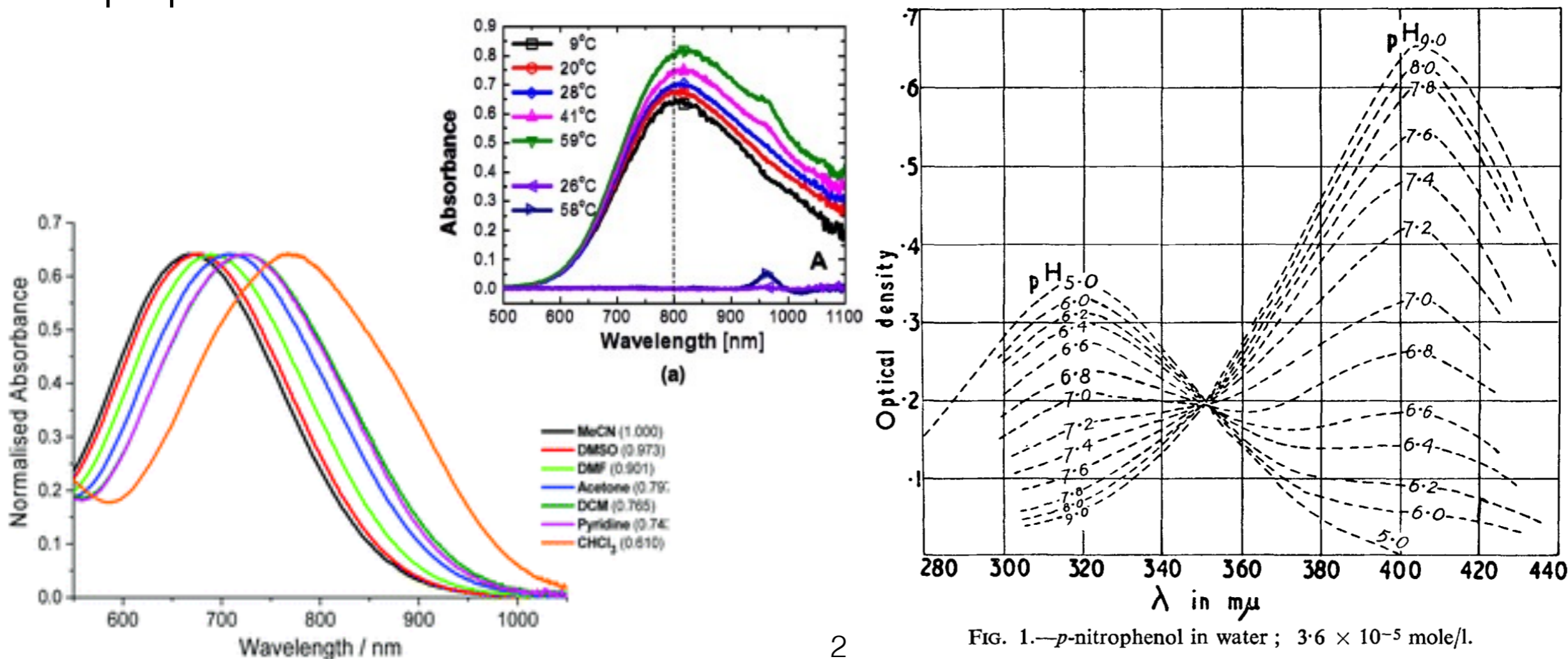

FIG. 1.—p-nitrophenol in water; $3 \cdot 6 \times 10^{-5}$ mole/l.

The last time I came here...

Table 1: Lowest π-π* transition of pNP and pNP⁻ in aqueous solution, calculated with CASPT2(12,10). Geometries obtained by using different methods. In order to include the solvent effect, the ASEC model was used. Values in eV.

Geometry	pNP	pNP⁻	Shift
GAS	4.51	-- [a]	
PCM	4.22	3.37	0.85
FEG	3.99	3.38	0.61/0.71[d]
EXP	3.90[b]	3.09[b,c]	0.81

a) In gas phase, the geometry of pNP⁻ has C2v symmetry, whereas the interaction with the solvent breaks this symmetry (C1 group);

b) Ando et al., *J. Phys Chem. A* **111** (2007) 7194;

c) Abe et al., *Bull. Chem. Soc. Jpn.* **35** (1962) 318.

d) We estimate a correction of -0.1 eV caused by non-electrostatic interaction between pNP⁻ and the solvent.

Table 2: Geometrical changes in the nitro group. Bond distances in Å and bond angle in degree.

	GAS	PCM	FEG
C4-N1	1.46557	1.45000	1.41231
N1-O2	1.23075	1.23967	1.25721
N1-O3	1.23111	1.23944	1.25442
∠O2-N1-O3	124.237	122.838	120.308

HOMO   **LUMO**

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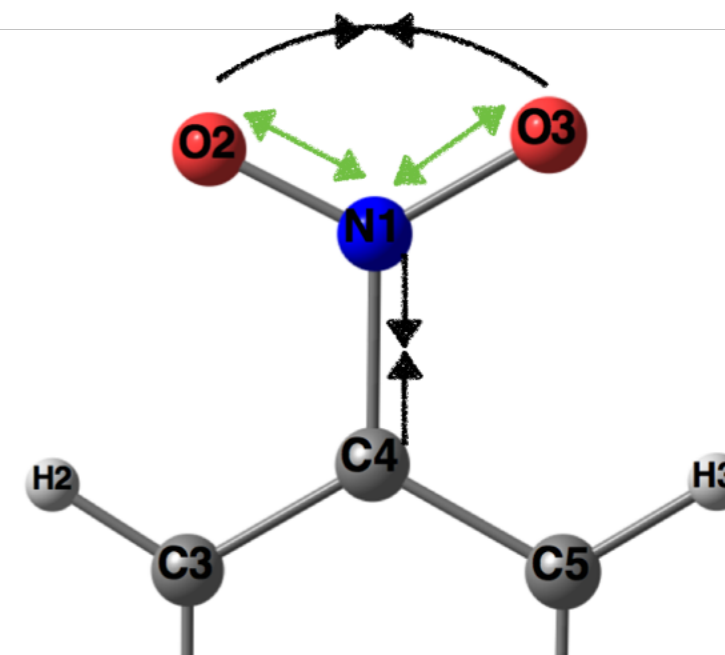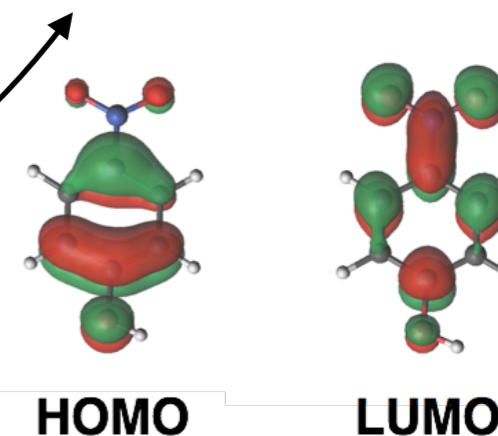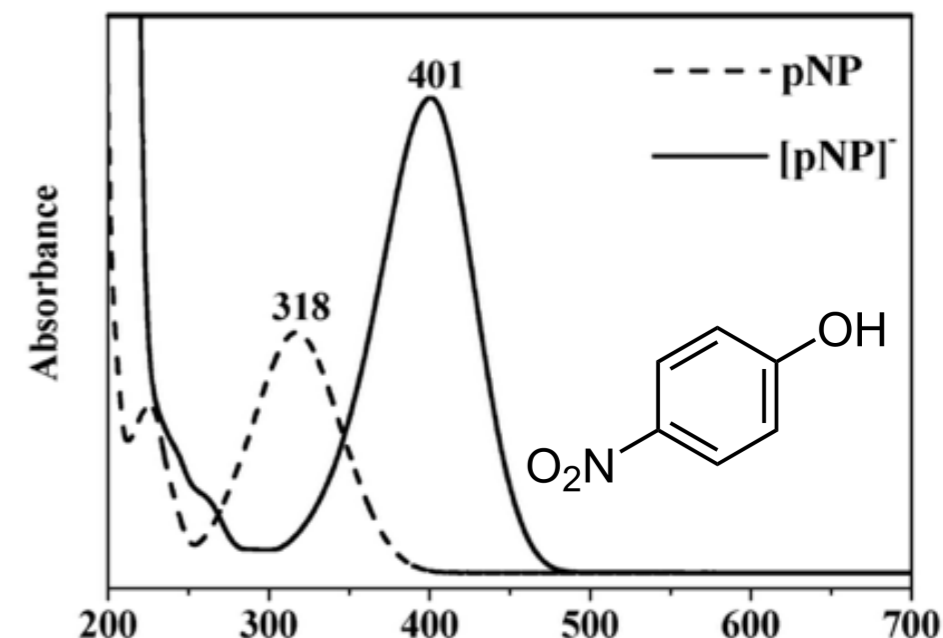
MD Simulation -> ASEC
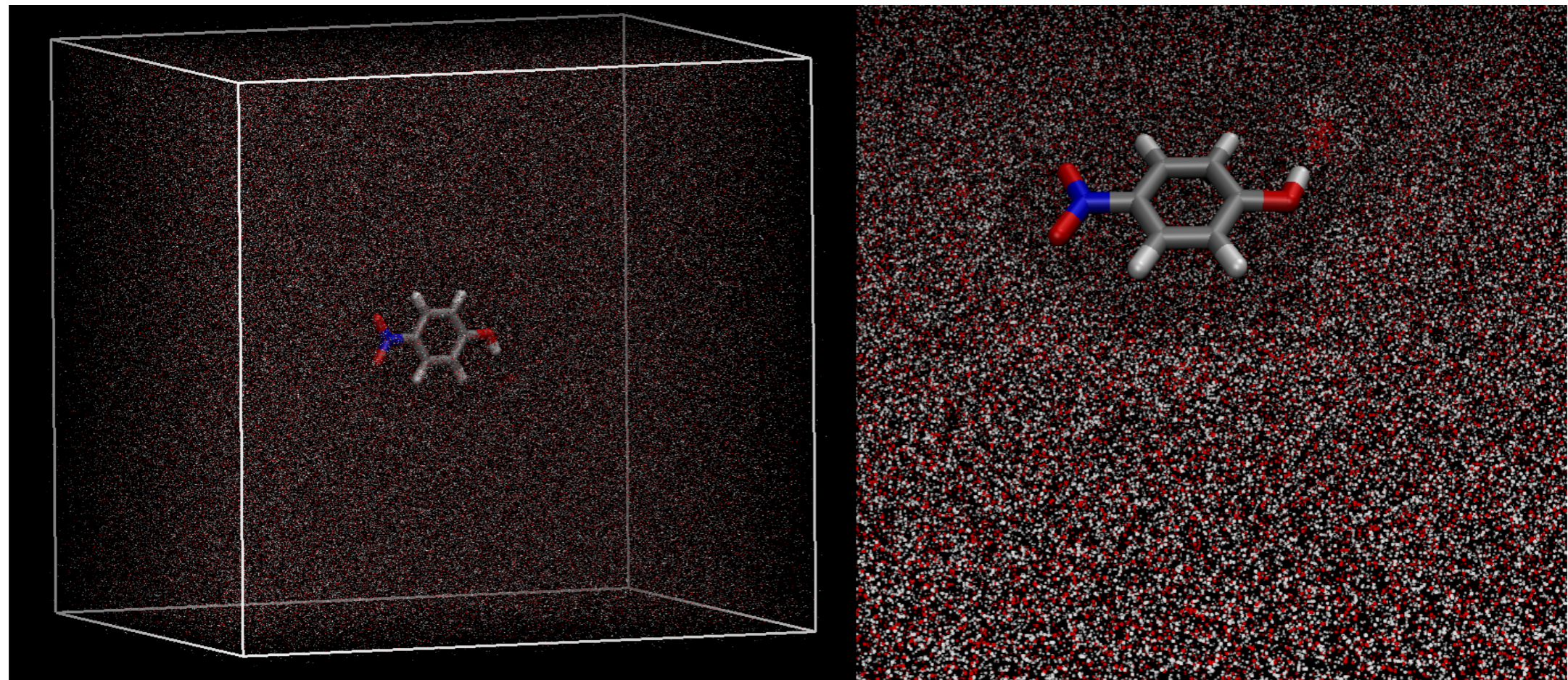
Left) The average solvent electrostatic configuration (ASEC) model. The solute molecule is treated by a QM method, but the solvent molecules are represented by the point charges localized in the atomic sites. Several snapshots are overlapped to construct an average configuration and the charge values are normalized by the number of snapshots used. This model is used in a CASPT2 calculation to obtain the electronic transition. Right) a zoom in the region of the solute shows the cavity formed by the solute-solvent interaction, as also the formation of hydrogen bonds.

What's next???

- **Achievement:** description of the electronic transition of the two different moieties in solution (paper in near future)

- **Next Stage:** a theoretical method to obtain the spectrum depending on the pH condition.

Method

For both moieties:

- Classical Simulation -> Generate several configurations

- Calculate the electronic transitions in selected configurations

- Convolute the spectrum by adjusting a Lorentzian function
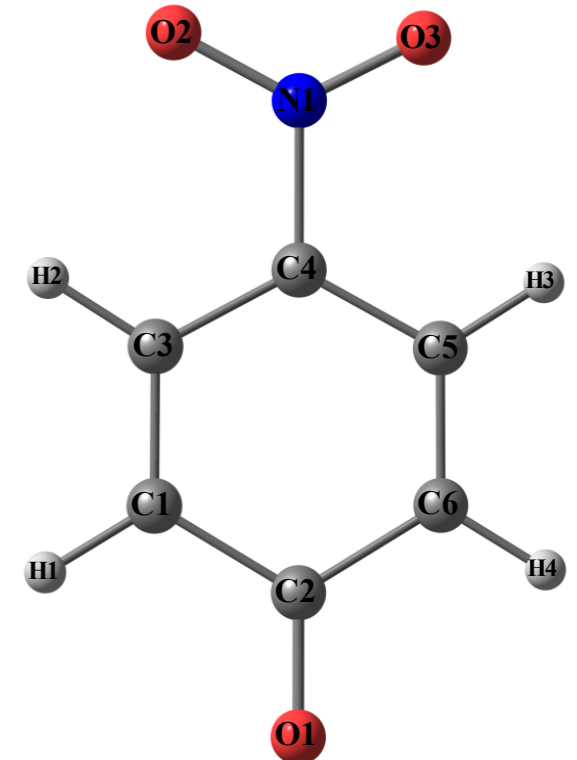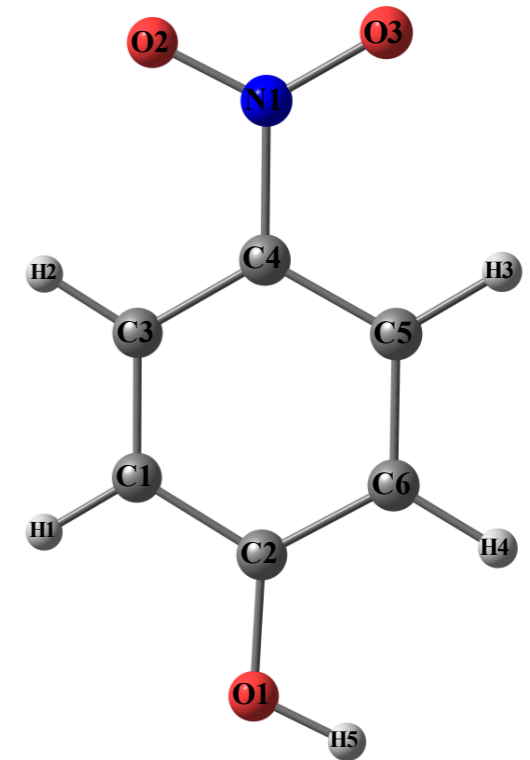
Test:TD-DFT & CASPT2

Table 3: The 7 lowest-lying electronic transition energies of pNP and pNP-, obtained at TD-B3LYP/aug-cc-pVDZ level of calculation. Solvent is represented by ASEC. CASPT2 and experimental results for the most intense transition are also showed.

Transition	pNP			pNP-		
	E (eV)	λ(nm)	f	E (eV)	λ(nm)	f
1	3.25	381	0.000	2.95	420	0.001
2	**4.09**	**303**	**0.198**	**3.42**	**362**	**0.460**
3	4.11	302	0.128	3.71	334	0.000
4	4.44	279	0.004	3.78	328	0.005
5	5.25	236	0.012	4.04	307	0.001
6	5.43	228	0.000	4.22	294	0.019
7	5.54	224	0.130	4.35	285	0.001
CASPT2	**3.99**	**311**	**0.624**	**3.39**	**367**	**0.665**
EXP	**3.88[a],3.90[b]**	**318**		**3.09[a,b]**	**401**	

a) Abe, *Bull. Chem. Soc. Jpn.* **35** (1962) 318;
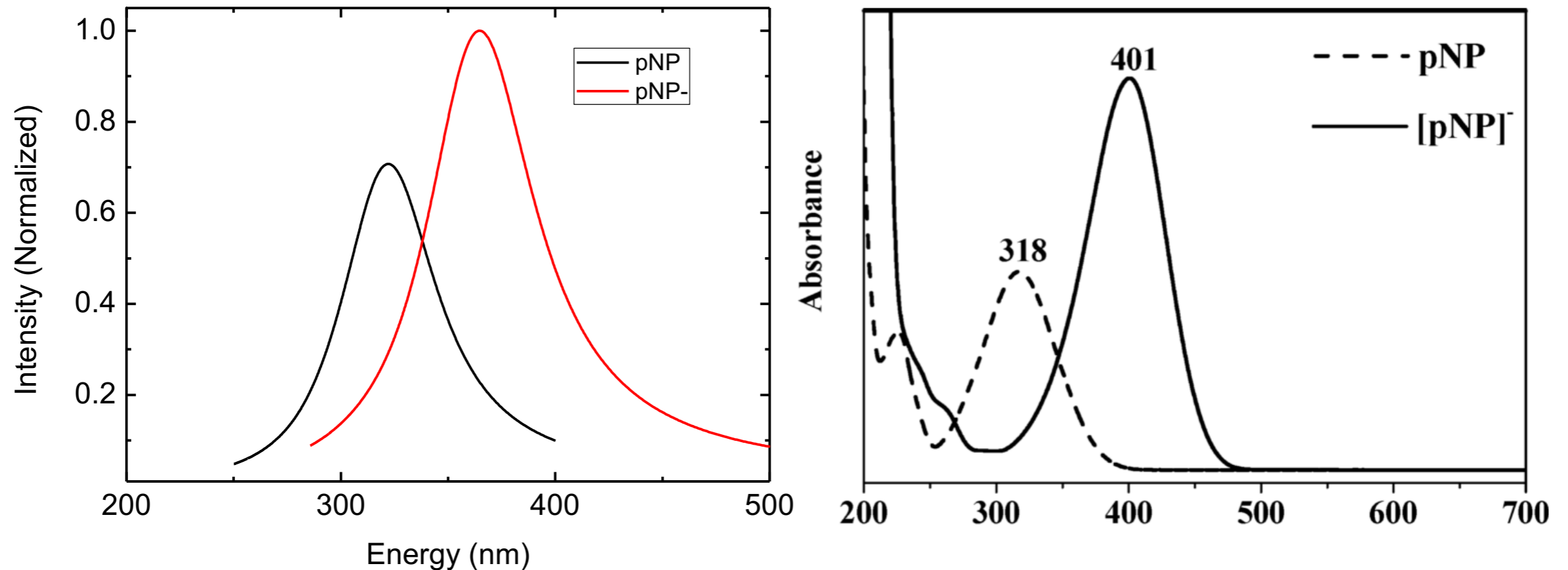b) Ando et al, *J. Phys. Chem. A* **111** (2007) 7194.

Configurations
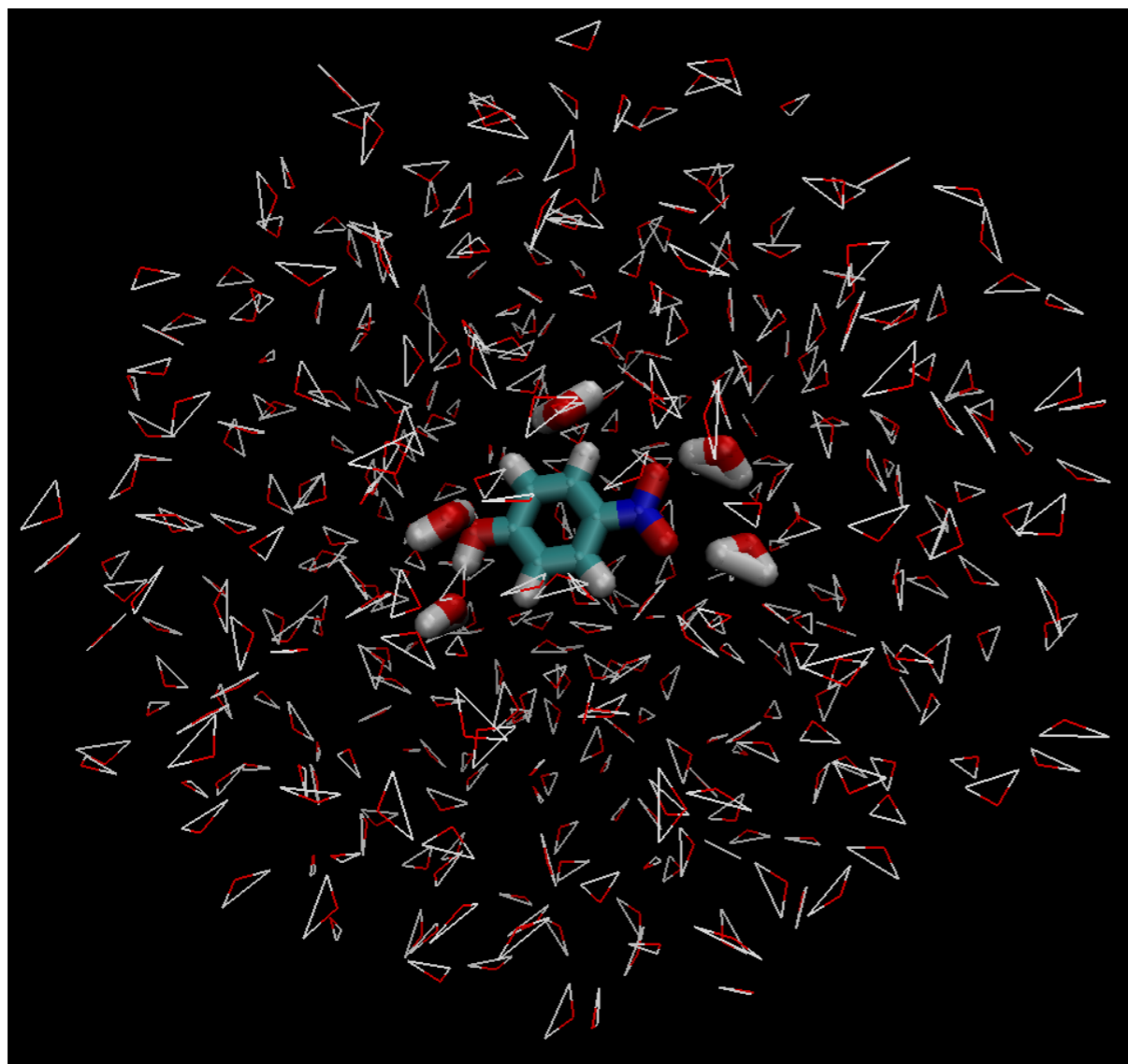
x 100

One of the configurations used in the TD-DFT calculations. The solute molecule and the 5 nearest water molecules (thick) were treated quantum mechanically, whereas the remaining water molecules (thin) were treated as point charges.

Theoretical Spectrum

Left) The theoretical spectrum obtained from the electronic transitions convoluted by a Lorentzian function. Electronic transitions obtained at the TD-B3LYP/aug-cc-PDVZ level of calculation; Right) the experimental spectrum [Ando et al., *JPCA* **111** (2007) 7194].

$$\pounds\left(x; x_0, \gamma\right) = \frac{1}{\pi}\left[\frac{\gamma}{\left(x - x_0\right)^2 + \gamma^2}\right]$$

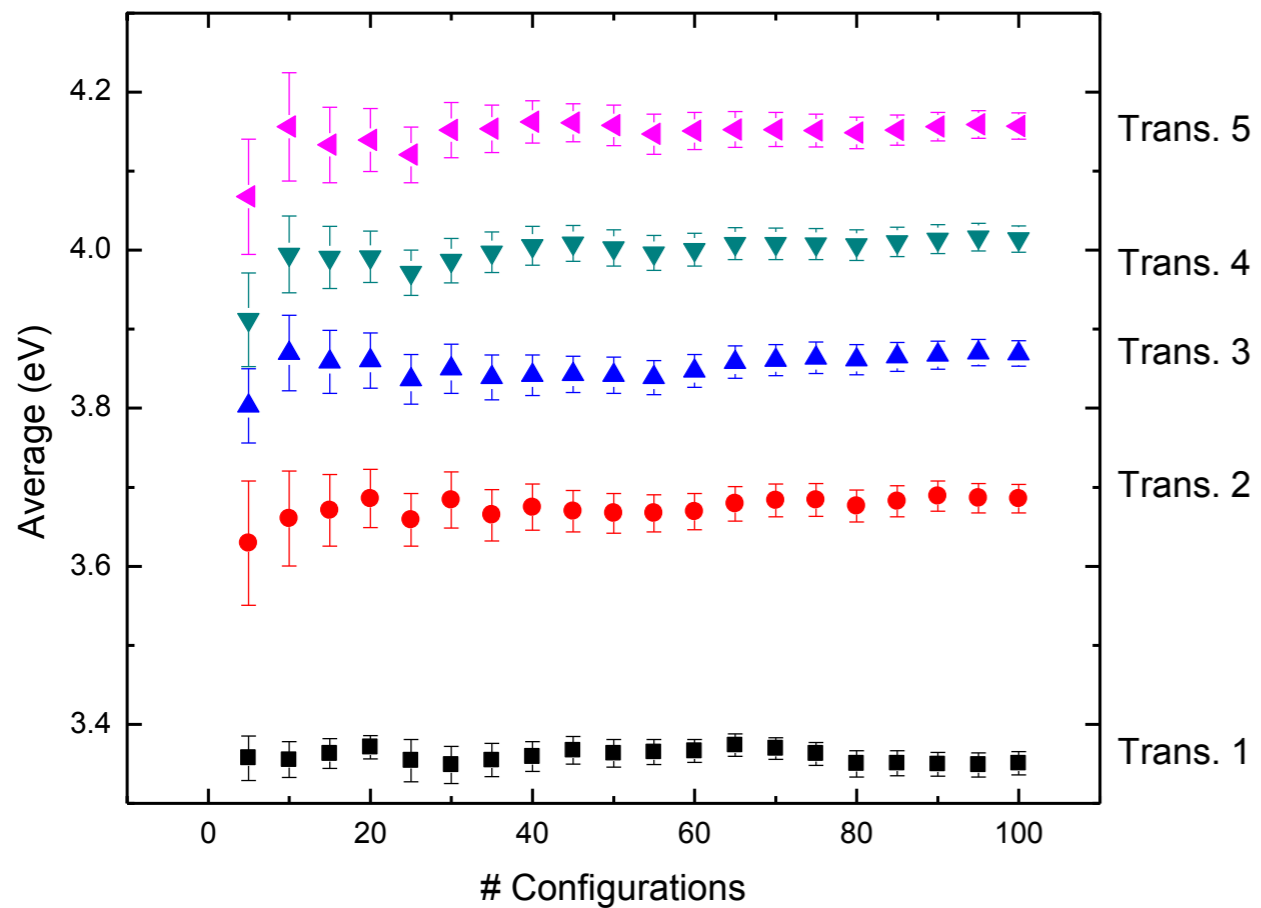$\gamma =$ half-width at half-maximum (HWHM)

$x_0 =$ center of the distribution

Theoretical Spectrum
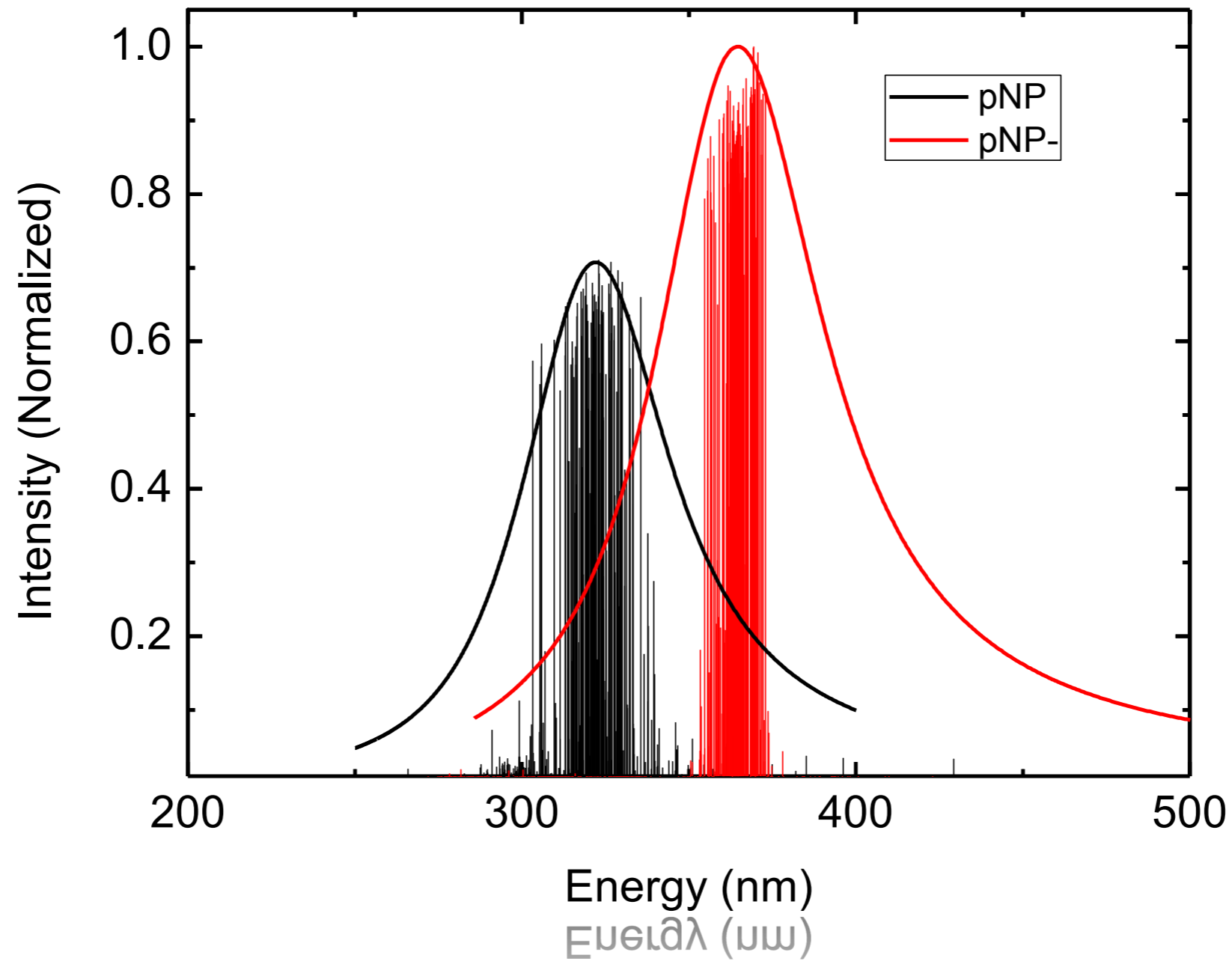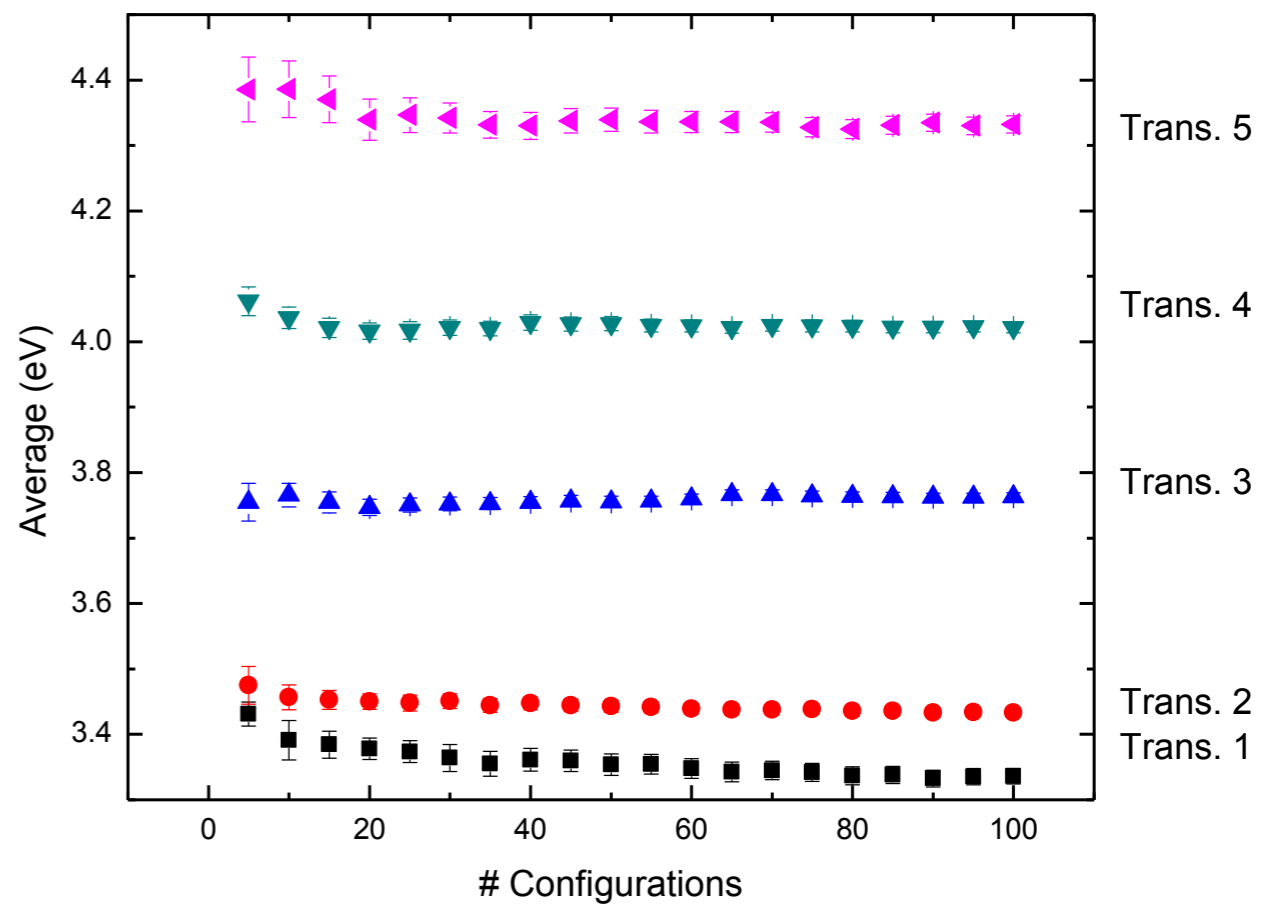

The same spectra, but also showing
the electronic transitions used in the convolution.

Converged? YES!

Test: B3LYP and CAM-B3LYP

Table 1: Comparison between B3LYP and CAM-B3LYP results for the most intense electronic transition of pNP and pNP-. The values are average of 100 calculations. Values in **eV**. Basis set used: aug-cc-pVDZ. Statistical error is less than 0.01 eV.

	B3LYP	CAM-B3LYP	EXP[a,b]
pNP	4.01	4.12	3.88, 3.90
pNP-	3.34	3.53	3.09
shift	0.68	0.58	0.79, 0.81

a) Abe, *Bull. Chem. Soc. Jpn.* **35** (1962) 318;
b) Ando et al, *J. Phys. Chem. A* **111** (2007) 7194.

H2O Molecules?

Table: B3LYP/aug-cc-pVDZ calculations with different quantities of QM water molecules. Just one configuration was used.

All the transitions concern occupied orbitals mainly localized in water molecules.

pNP	5 H2O		10 H2O		35 H2O	
Transition	E(eV)	f	E(eV)	f	E(eV)	f
1	3.25	0.005	2.82	0.004	2.39	0.001
2	3.43	0.000	3.35	0.001	2.76	0.000
3	3.86	0.280	3.67	0.005	2.84	0.000
4	3.91	0.114	3.84	0.028	2.88	0.000
5	4.16	0.001	3.93	0.353	3.14	0.000

| *pNP-*	5 H2O		10 H2O		35 H2O	
Transition	E(eV)	f	E(eV)	f	E(eV)	f
1	3.42	0.503	3.37	0.493	2.03	0.001
2	3.46	0.009	3.51	0.000	2.27	0.000
3	3.70	0.000	3.73	0.000	3.38	0.428
4	4.07	0.003	3.89	0.004	3.58	0.000
5	4.42	0.001	4.31	0.001	3.61	0.000
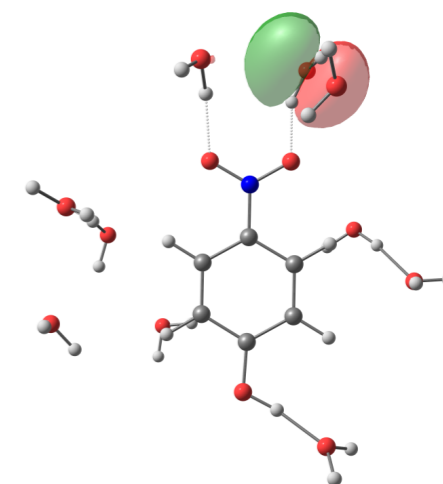
Occupied
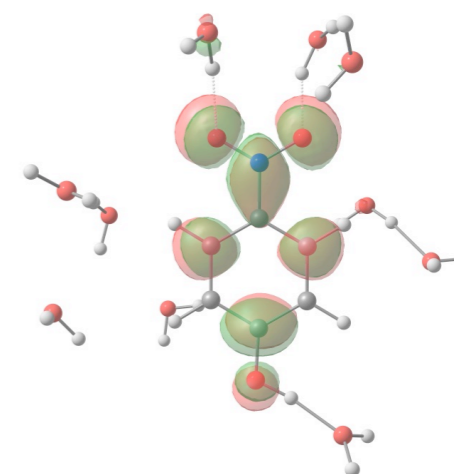
Virtual

Red color is used to indicate the same electronic transition in different calculations. As an example, the molecular orbitals involved in the blue-indicated transition are showed.
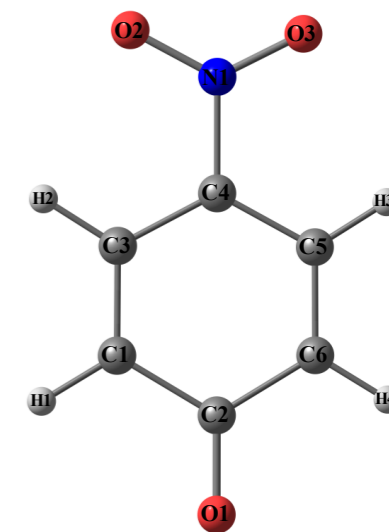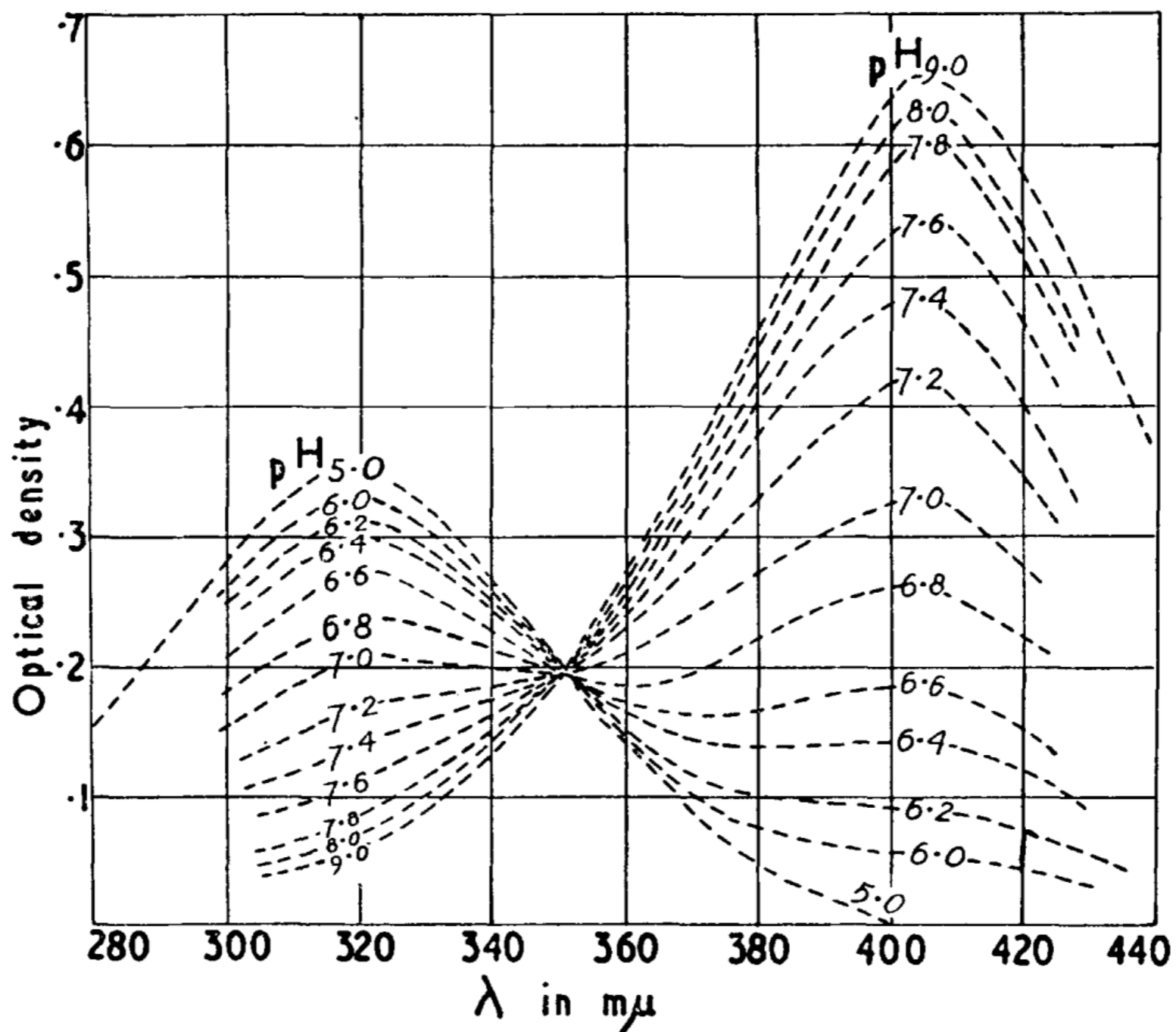
Conclusion

- It is possible to use MD simulations and TD-DFT calculations in order to describe theoretically the spectrum of both moieties, pNP and pNP-, in solution, with an acceptable accuracy.

Next Stage
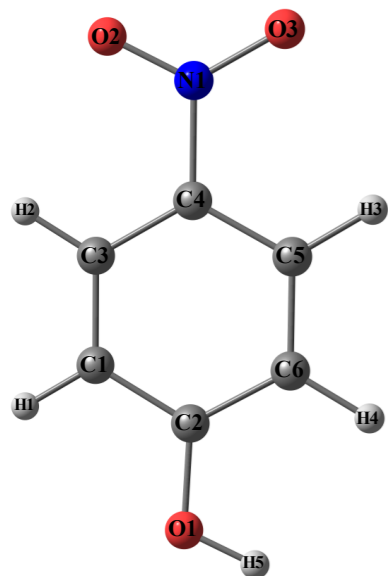
Acid pH

Basic pH

FIG. 1.—*p*-nitrophenol in water; $3 \cdot 6 \times 10^{-5}$ mole/l.

Biggs, *Trans. Faraday Soc.* **50** (1954) 800

Plan:

- To use Constant pH simulation to obtain information about the population ratio of the two moieties in different pH conditions;

- Construct the spectra, with intensities proportional to the population ratio, aiming to reproduce the experimental behavior.