Electronic transitions of paranitrophenol in different pH conditions:
A review and new perspectives II

Dr. Carlos BISTAFA

1st CREST-WS, June 19th 2017

Electronic Transitions of Molecules in Solution

Electronic transitions are very sensitive to the environment:
- The interaction with the solvent affects the transition energy;
- The temperature affects the intensity of the band;
- The pH affects the population ratio.
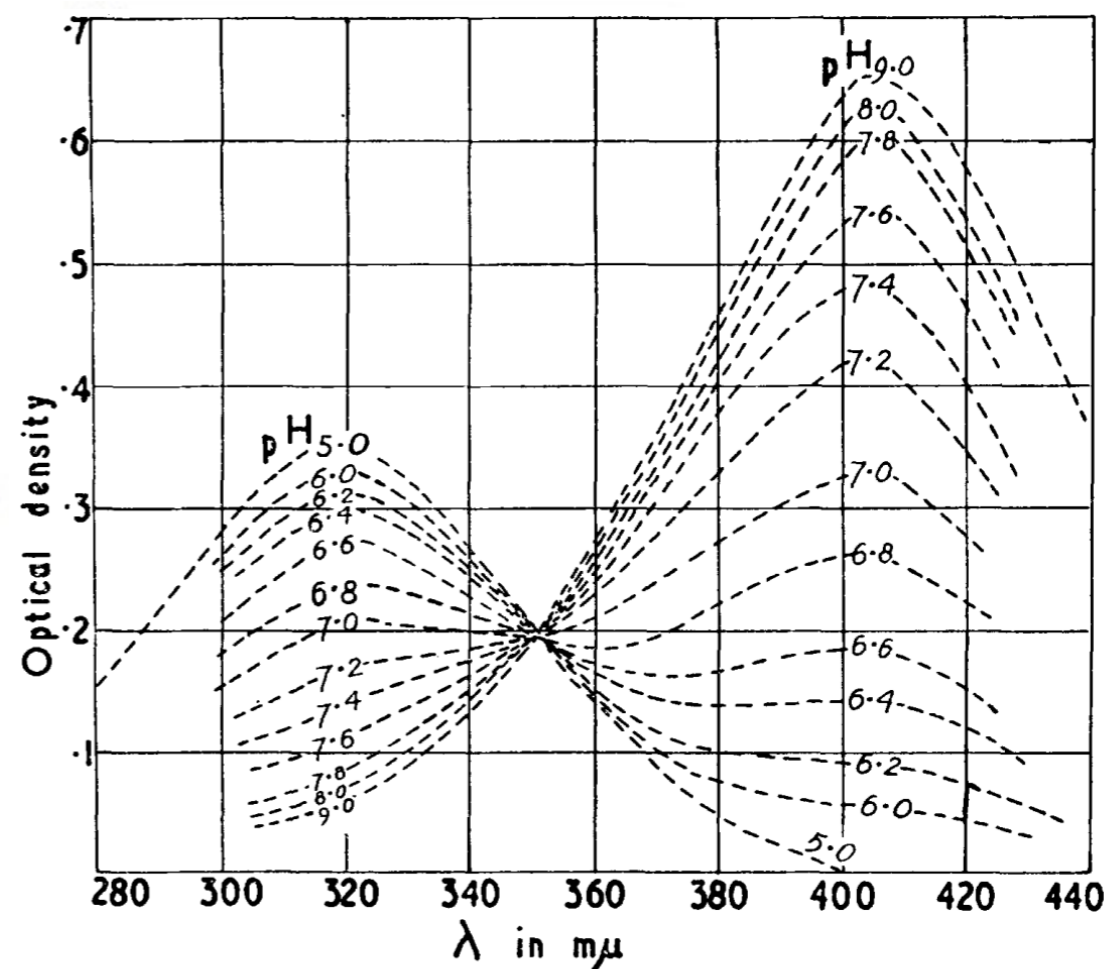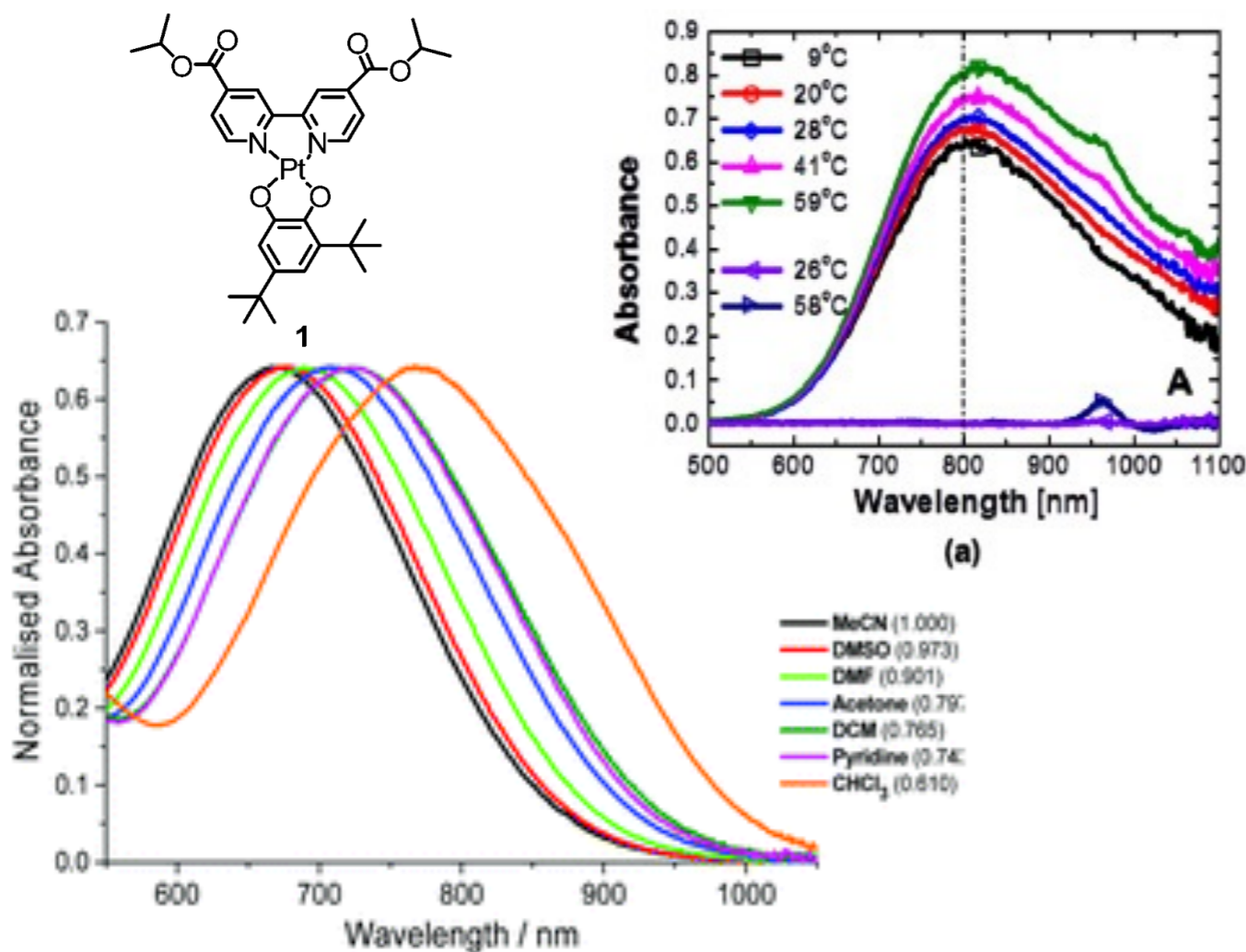
Pt(II) diimine catecholate

CuSO2 · 5H2O

Para-nitrophenol
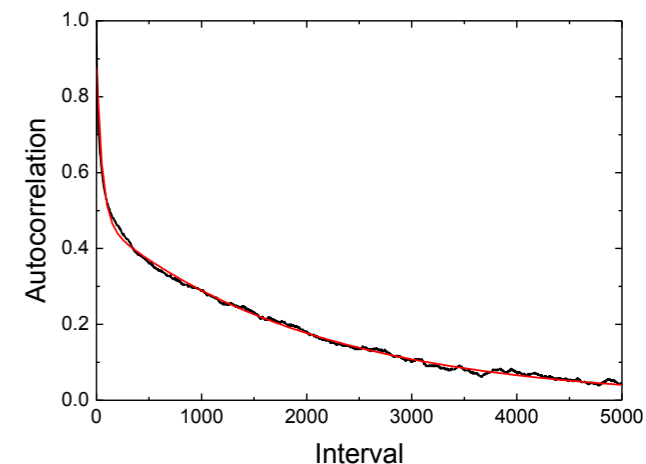

FIG. 1.—p-nitrophenol in water ; 3.6×10^{-5} mole/l.

2

Sequential-QM/MM (S-QM/MM)

1: Classical Simulation

2: Select Relevant Confs

Previous CREST-WS

$$C(t) = \frac{\langle \partial A_i \partial A_{i+t} \rangle}{\langle \partial A^2 \rangle} = \frac{\langle A_i A_{i+t} \rangle_{L-t} - \langle A_i \rangle_{L-t} \langle A_{i+t} \rangle_{L-t}}{\langle A^2 \rangle_L - \langle A \rangle_L^2}$$
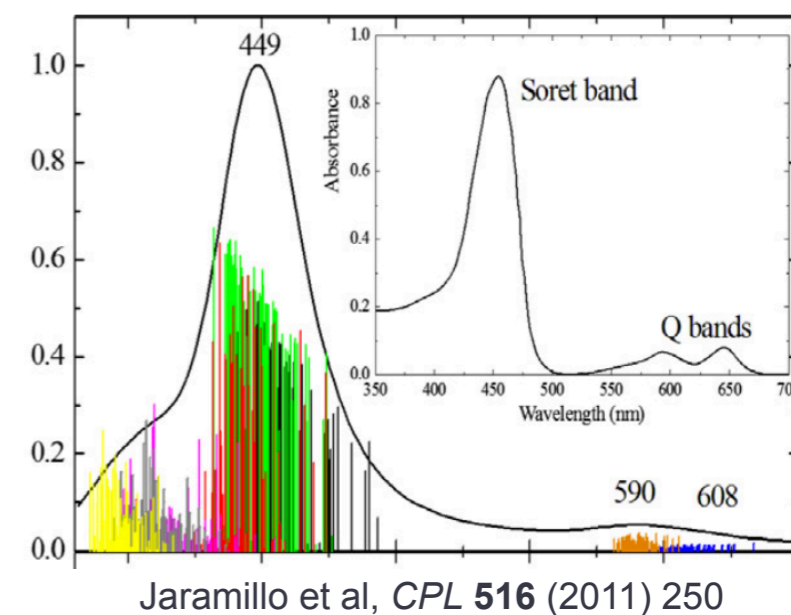
3: Select QM Region

4: Obtain QM Properties

QM

Steps

Jaramillo et al, *CPL* **516** (2011) 250

S. Canuto & K. Coutinho, *IJQC* **77** (2000)192
Solvent Effects on Molecules and Biomolecules, S. Canuto (ed.), Springer 2008 (chap. 6)

ASEC: Average Solvent Electrostatic Configuration

With a rigid solute, if all the solvent molecules can be taken as point charges, it is possible to overlap the snapshots in one single configuration:

$$\frac{1}{\cancel{N}}\underbrace{\sum_{j=1}^{N}H_{mol}^{(j)}}_{\cancel{N}H_{mol}} + \left(\underbrace{\frac{1}{N}\sum_{j=1}^{N}\sum_{i}^{m}\frac{q_i^{(j)}}{\left|r_i^{(j)}-r'\right|^2}\vec{e}_R}_{ASEC}\right) = H_{mol} + ASEC$$

ASEC has all the electrostatic contribution, and also preserves the statistical information of the ensemble and structural information, as HB.

Coutinho et al., Chem. Phys. Lett. 437 (2007) 148
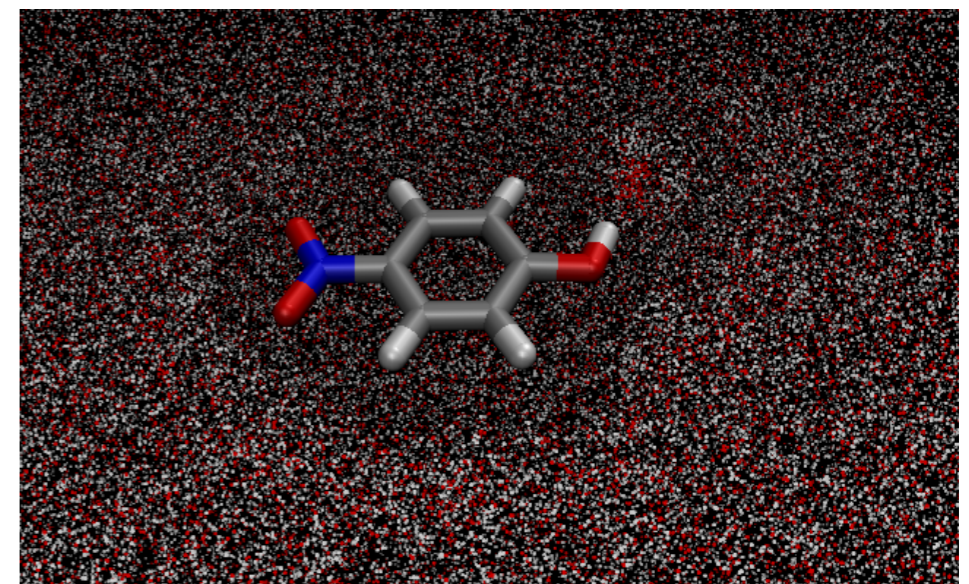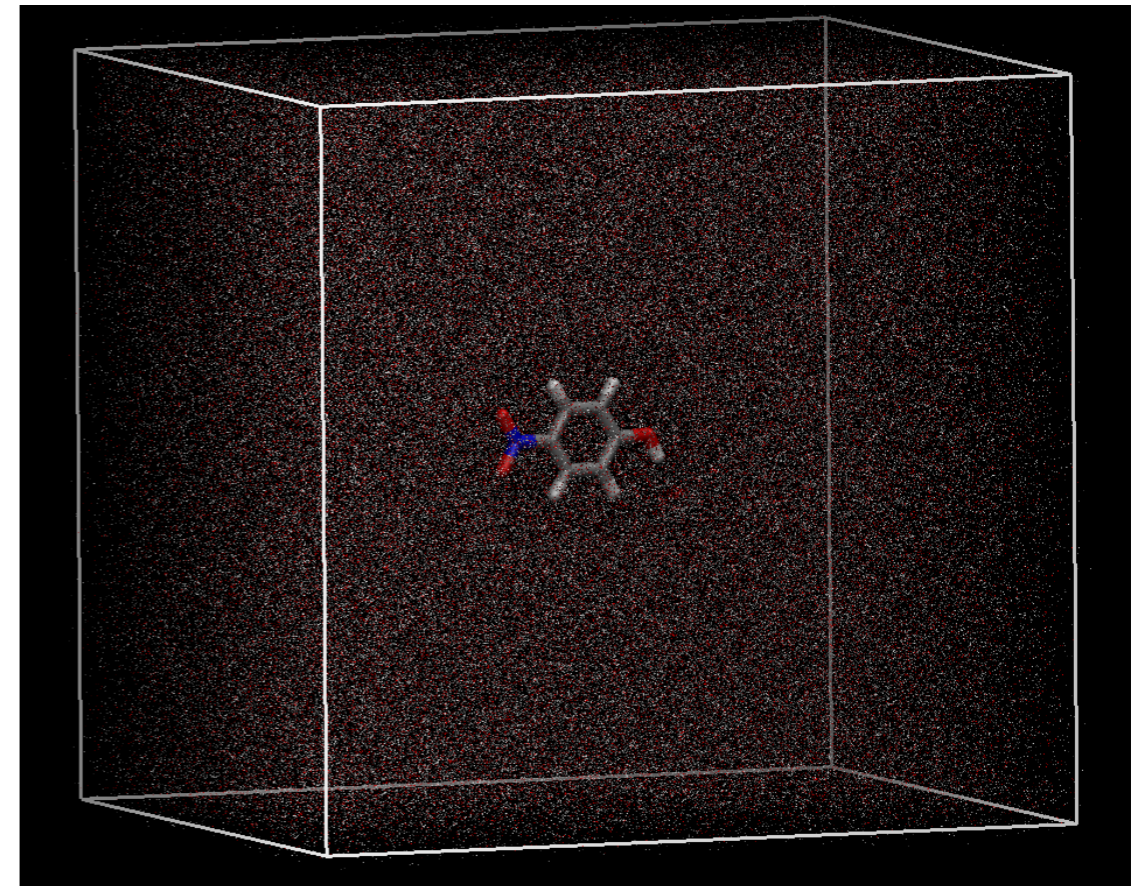
ASEC-FEG

1) M. Nagaoka & co-wks.,
IJQC 70 (1998) 95:

$$F(q) = -\frac{\partial G(q)}{\partial q} = -\left\langle \frac{\partial V(q)}{\partial q} \right\rangle$$

2) M. Aguilar & co-wks.,
J. Comp. Chem. 25 (2004) 1227:

$$F(q) \cong -\frac{\partial \langle V(q) \rangle}{\partial q}$$

3) H. C. Georg & S. Canuto,
JPCB 116 (2012) 11247.

4) C. Bistafa, H.C. Georg & S. Canuto,
   CTC 1040-1041 (2014) 312

Geom, Charges (GAS)

↓

Simulation

↓

ASEC

↓

Gradient → Geom.

↓

Charges

↓

Properties

Converged?

H. C. Georg, K. Coutinho &
S. Canuto,
Chem. Phys. Lett. 429 (2006) 119

The first time I came to Nagoya...

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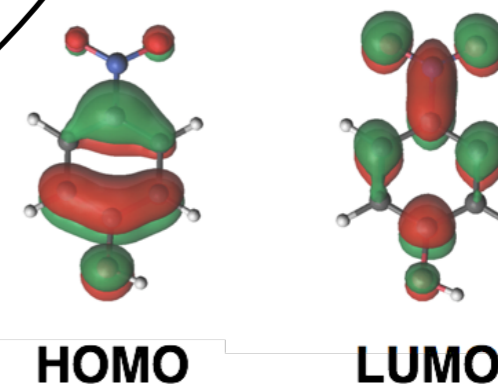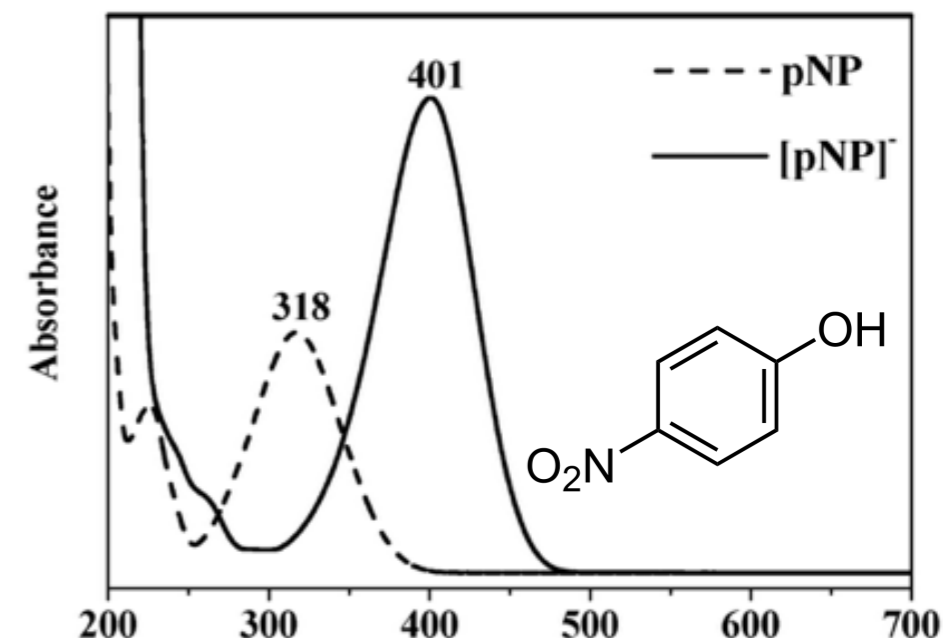
Table 2: Geometrical changes in the nitro group. Bond distances in Å and bond angle in degree.

	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

Bistafa, Kitamura, Nagaoka & Canuto (to be submitted)

HOMO   LUMO

6
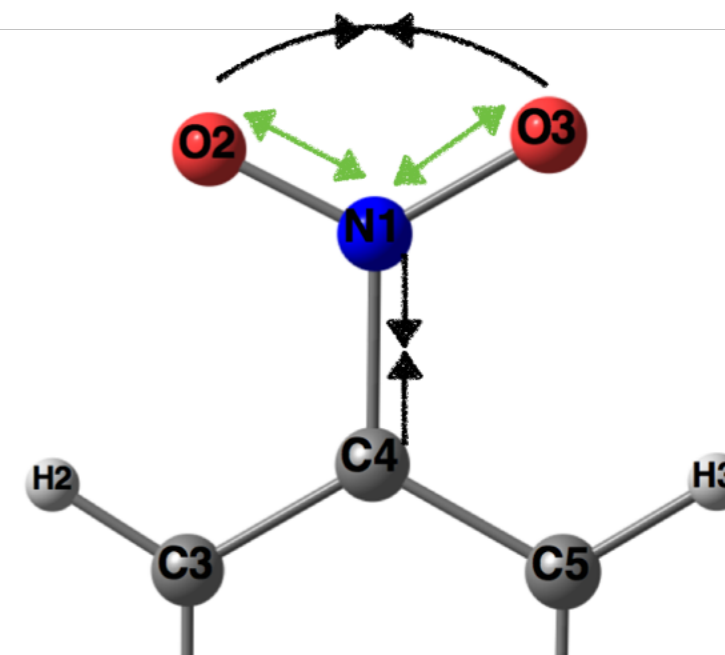
The spectrum in different pH conditions
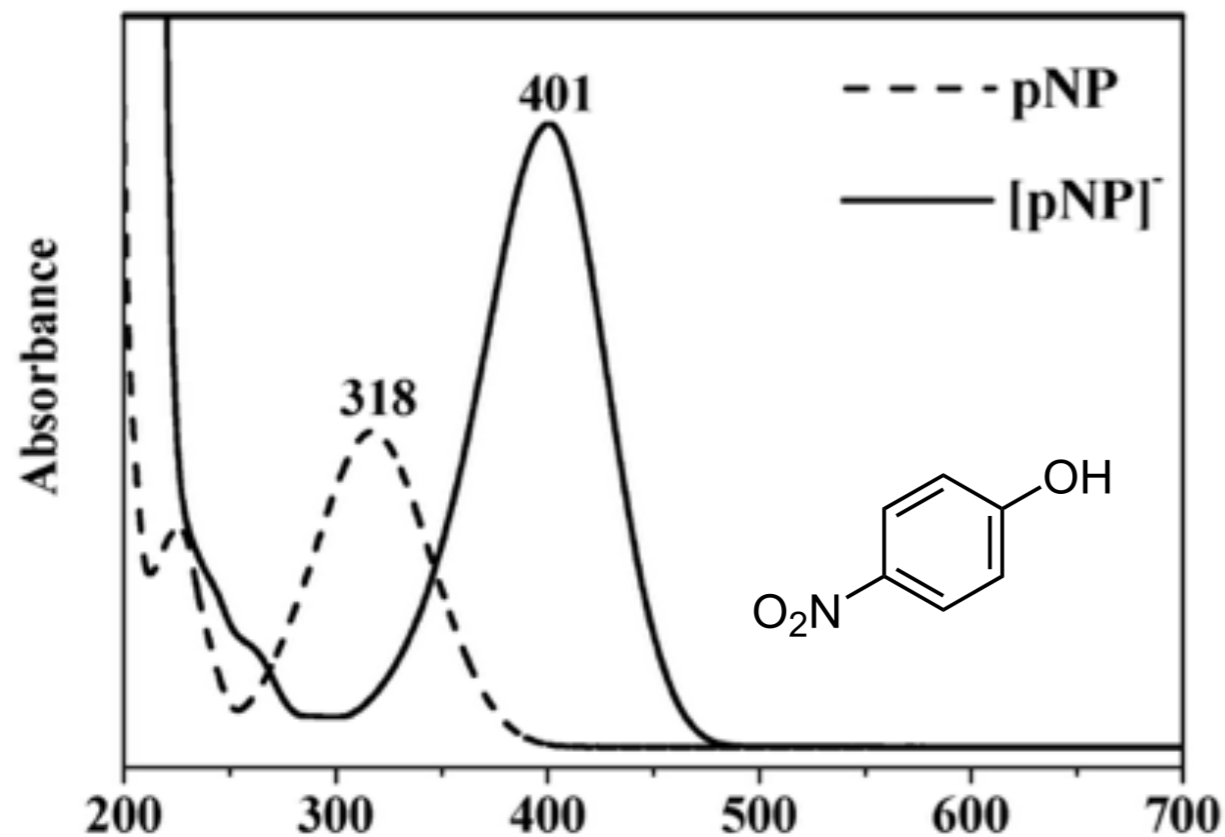
Ando et al, *J. Phys. Chem. A* **111** (2007) 7194

2. Experimental Section

All the reagents and solvents obtained from Aldrich were purified when necessary. The solutions of pNP, pNA, and their respective anions ([pNP]⁻ and [pNA]⁻) were prepared in suitable solvents. The neutral and anionic species of pNP (pK_a = 7.15) were studied in acidic and basic aqueous solution using 1 M HCl$_{(aq)}$ and 1 M KOH$_{(aq)}$, respectively. In the case of pNA (pK_a = 18.9), the deprotonation is achieved in an alkaline ([OH⁻] = 0.011 M) aqueous/dimethyl-sulfoxide (DMSO) solution (99.6% mol of DMSO and 0.4% mol water, pH = 26.2).[20,21]

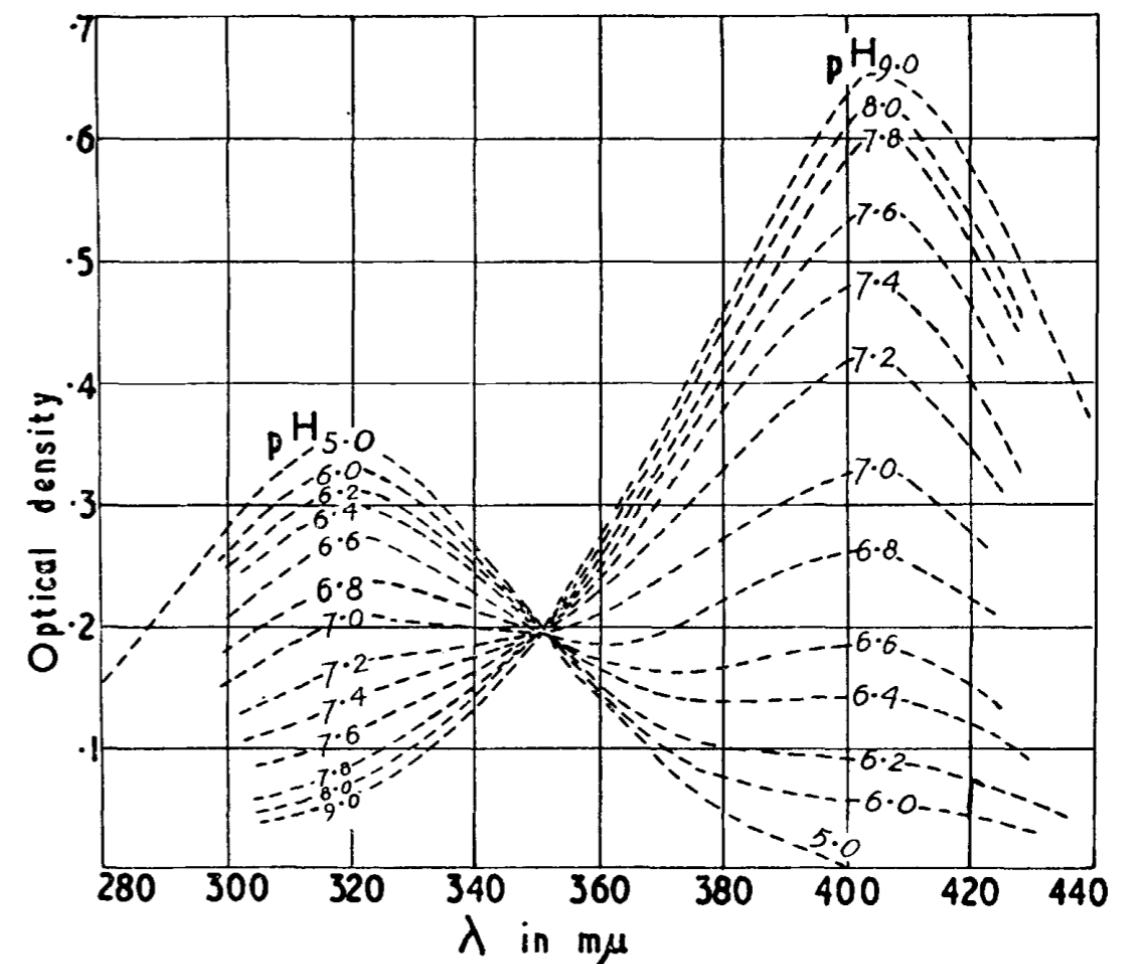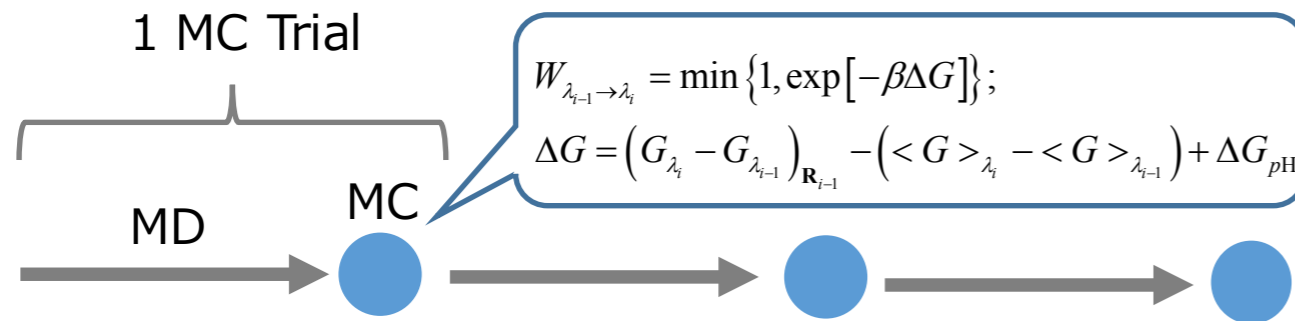FIG. 1.—*p*-nitrophenol in water ; 3.6×10^{-5} mole/l.

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

From a theoretical point of view, note that, at typical pH condition, a simulation box would include 1 H_3O^+/30,000 water molecules.

7

Constant pH Molecular Dynamics

Dr. Yukichi Kitamura

1 MC Trial

$$W_{\lambda_{i-1} \to \lambda_i} = \min\left\{1, \exp\left[-\beta \Delta G\right]\right\};$$
$$\Delta G = \left(G_{\lambda_i} - G_{\lambda_{i-1}}\right)_{\mathbf{R}_{i-1}} - \left(<G>_{\lambda_i} - <G>_{\lambda_{i-1}}\right) + \Delta G_{pH}$$

MD   MC
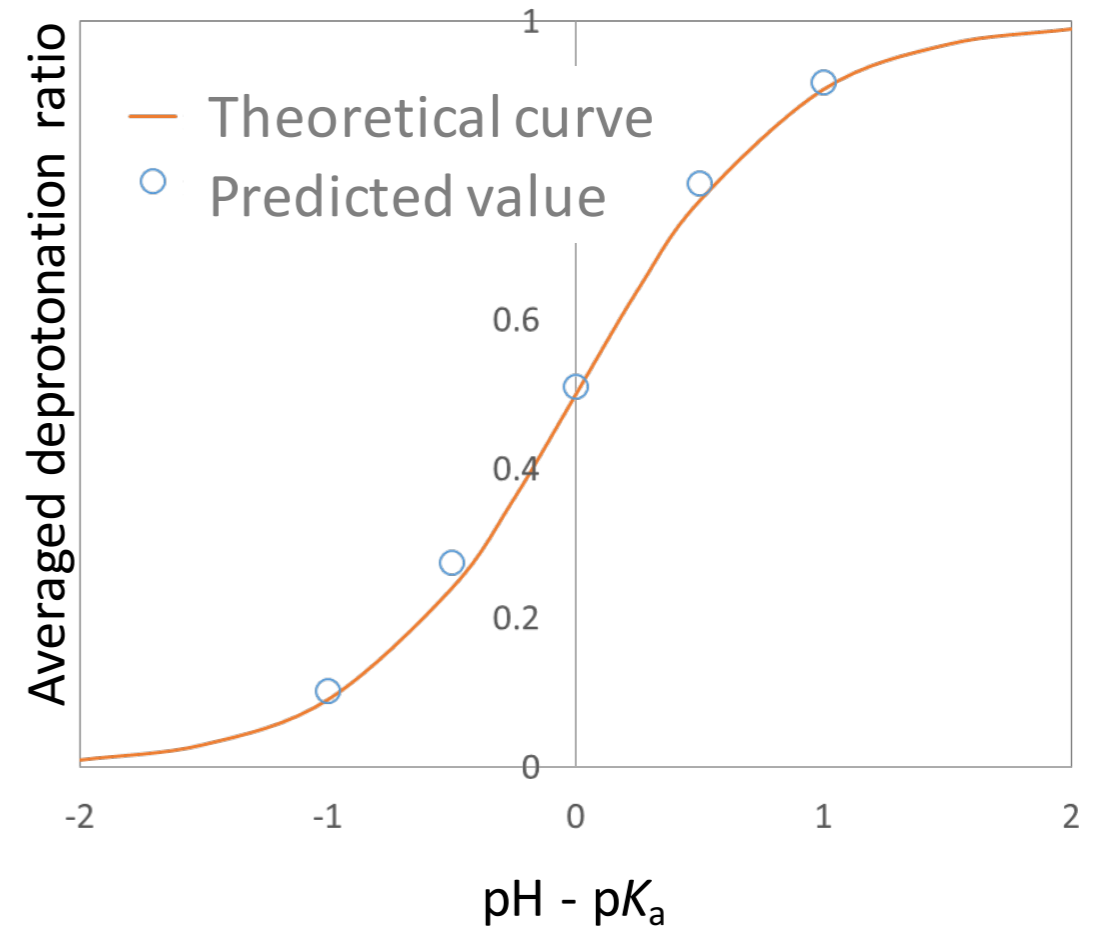
With explicit solvent model, a sudden change of titration site results in a large energy penalty, which leads to an improper MC trial.

Energy [kcal/mol]

State transition
λ=0 → λ=1

$\bar{E}_0$

$\Delta\bar{E}_{01}$

$\bar{E}_1$

<λ=0>   <λ=1>
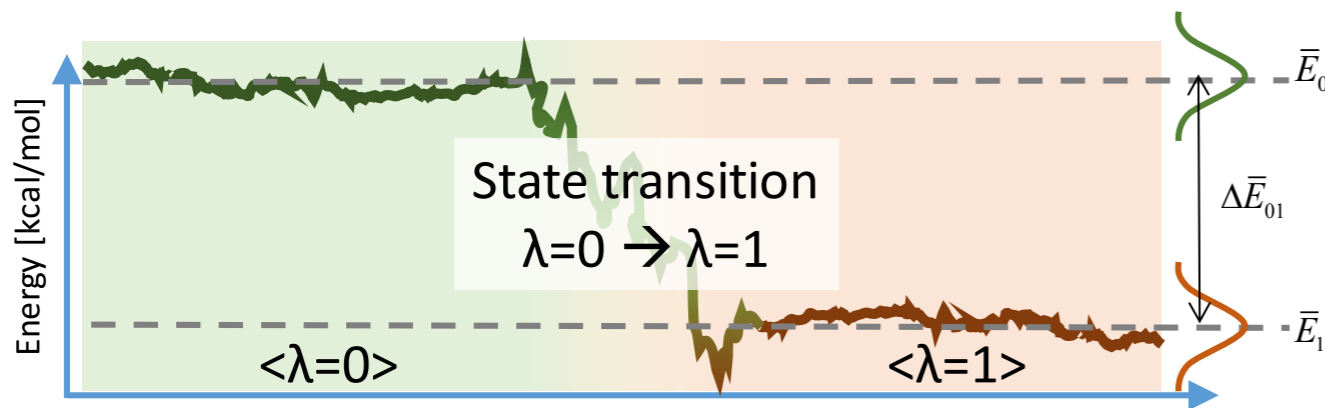
To avoid such large energy fluctuations, we introduced the **Gaussian filtering scheme** and the **correction term**.

Goal: Titration curves

Averaged deprotonation ratio

— Theoretical curve
○ Predicted value

1

0.6

0.4

0.2

0

-2   -1   0   1   2

pH - pK_a
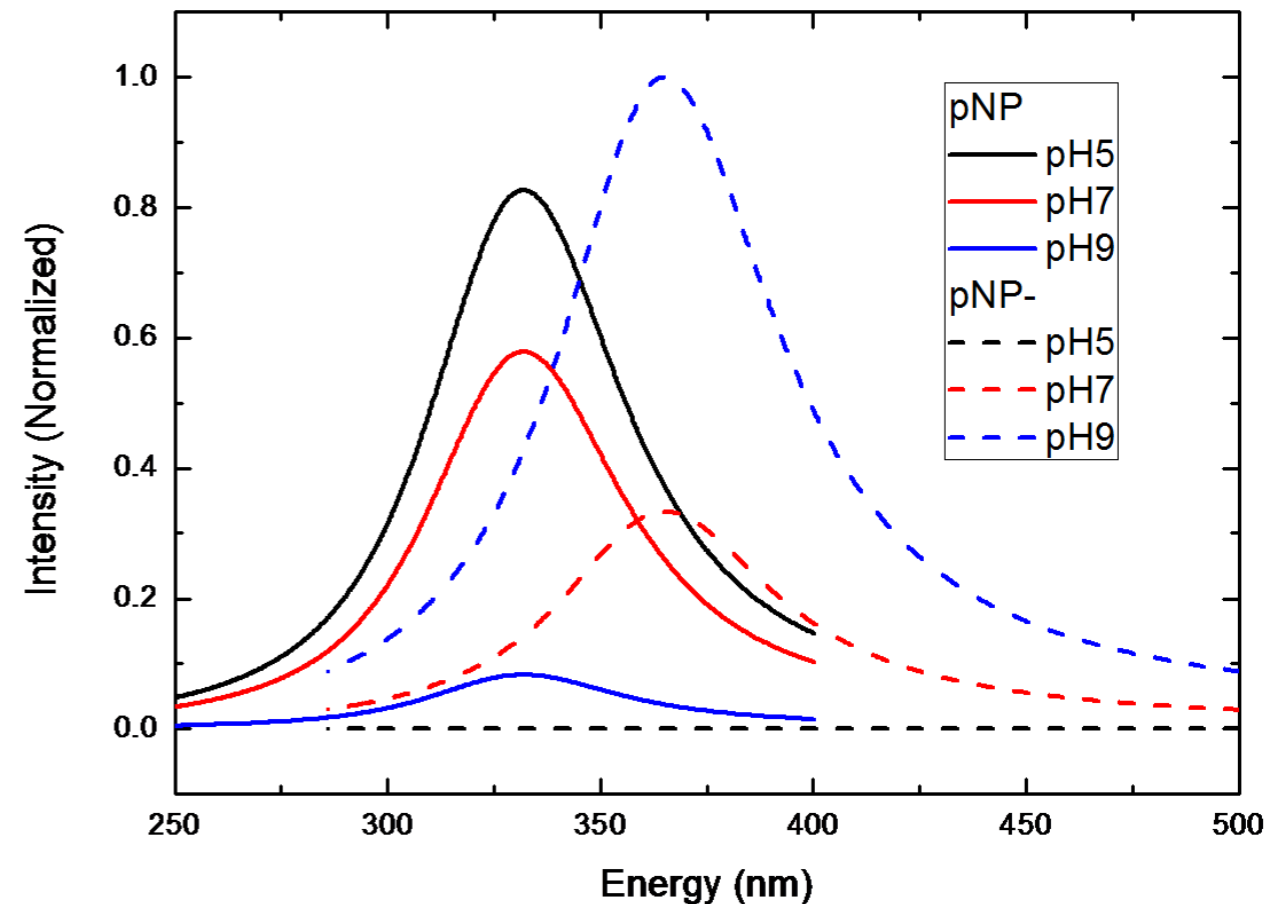
Sub-product: population ratio

Today's contents

In the previous workshop, I presented the theoretical spectra for 3 different pH conditions (pH= 5, 7, 9), obtained at B3LYP level of calculation. I could reproduce qualitatively the main aspects of the experimental data.

Today I will present:
- additional data for other two conditions (pH = 6.6, 7.4);
- their consistency with the Henderson-Hasselbalch equation;
- accurate electronic transitions at CISD level of calculation and the theoretical spectra.

Computational Details: CpH-MD

- Amber simulation: NPT ensemble, 1 atm, 298.15K;
- 1 solute molecule + counter-ion + 854 water molecules;
- solute geometry was determined previously with the Free Energy Gradient* method, at B3LYP/6-31G(d,p) level with no symmetry restrictions;
- Every 50ps, 1 trial to change the protonation state is done (1000 trials were done);
- 5 pH conditions were considered: 5, 6.6, 7, 7.4 and 9.

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*N. Okuyama-Yoshida, M. Nagaoka, T. Yamabe, *IJQC* **70** (1998) 95;
 N. Okuyama-Yoshida, K. Kataoka, M. Nagaoka, T. Yamabe, *JCP* **113** (1998) 3519.

Population ratio

pH	CpH-MD Simulation		Henderson-Hasselbalch	
	pNP	pNP-	pNP	pNP-
5	99.2	0.8	99.3	0.7
6.6	77.8	22.2	78.0	22.0
7	59.2	40.8	58.5	41.5
7.4	34.0	66.0	36.0	64.0
9	1.3	98.7	1.4	98.6

$$pH = pKa + \log\left(\frac{[A^-]}{[AH]}\right)$$

$$pH - pKa = \log\left(\frac{[A^-]}{[AH]}\right)$$

$$10^{(pH-pKa)} = \left(\frac{[A^-]}{[AH]}\right) = \frac{\varepsilon}{1-\varepsilon}$$

$$10^{(pH-pKa)}(1-\varepsilon) = \varepsilon$$

$$10^{(pH-pKa)} = \left(1 + 10^{(pH-pKa)}\right)\varepsilon$$

$$\therefore \boxed{\varepsilon = \frac{10^{(pH-pKa)}}{1 + 10^{(pH-pKa)}}}$$

The population ration between the species (%) as obtained from CpH-MD simulation and from the Henderson-Hasselbalch

The relation with the spectrum

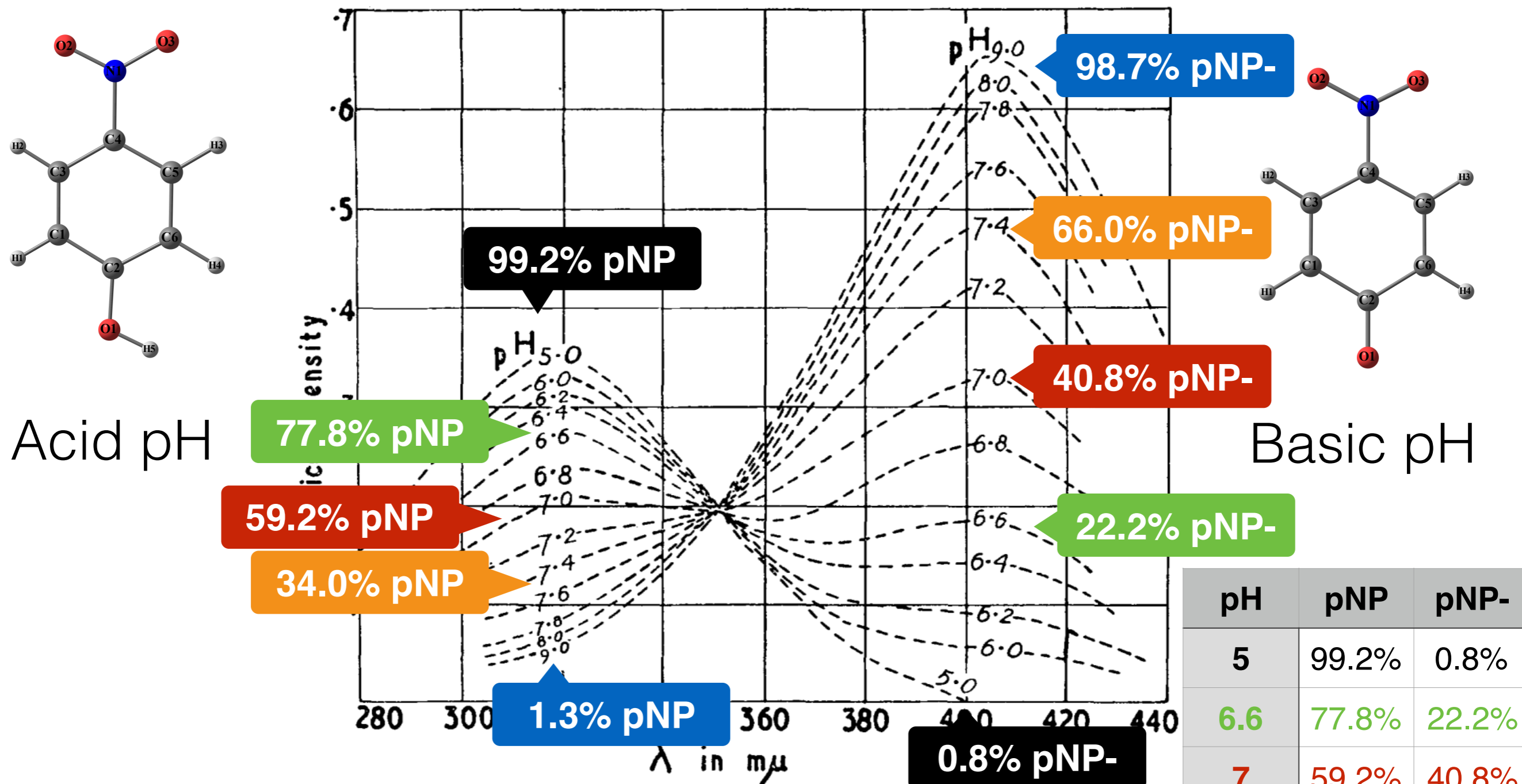- The results are consistent with the intensities observed in the experiments.

Acid pH

Basic pH

98.7% pNP-

66.0% pNP-

99.2% pNP

40.8% pNP-

77.8% pNP

59.2% pNP

22.2% pNP-

34.0% pNP

1.3% pNP

0.8% pNP-

FIG. 1.—*p*-nitrophenol in water ; $3\cdot6 \times 10^{-5}$ mole/l.

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

pH	pNP	pNP-
5	99.2%	0.8%
6.6	77.8%	22.2%
7	59.2%	40.8%
7.4	34.0%	66.0%
9	1.3%	98.7%

How can we obtain the spectrum?

A route for the theoretical pH-dependent spectrum

1) We obtain the electronic transitions in several configurations for both species;
2) We convolute the spectrum for both of them;
3) By assuming that intensity and population ratio are directly proportional, we multiply the intensity by the population ratio, and normalize with relation to the most intense.

Computational Details (QM/MM)

- <u>Geometry:</u> B3LYP/6-31G(d,p), with the Free Energy Gradient method, no symmetry restrictions;

- <u>MD Simulation:</u> AMBER (1+854), 298 K, NVT, Solute Rigid —> ASEC;

- <u>Electronic Transitions:</u> See next.

Tests with ASEC

Method	pNP		pNP-	
	E(eV)	f	E(eV)	f
CASPT2(12,10)/ANO-L	3.99	0.624*	3.38	0.665*
TD-B3LYP/aug-cc-pVDZ	3.82	0.364	3.47	0.474
TD-CAM-B3LYP/aug-cc-pVDZ	4.06	0.404	3.57	0.525
CIS(D)/aug-cc-pVDZ	4.04	0.541**	3.08	0.823**
Experimental value	3.88[a], 3.90[b]	—	3.09[a,b]	~ 2x pNP

* The Oscillator Strength is obtained at CASSCF level
** The Oscillator Strength is obtained at CIS level

a) Abe, *Bull. Chem. Soc. Jpn.* **35** (1962) 318-322
b) Ando et al, *J. Phys. Chem. A* **111** (2007) 7194
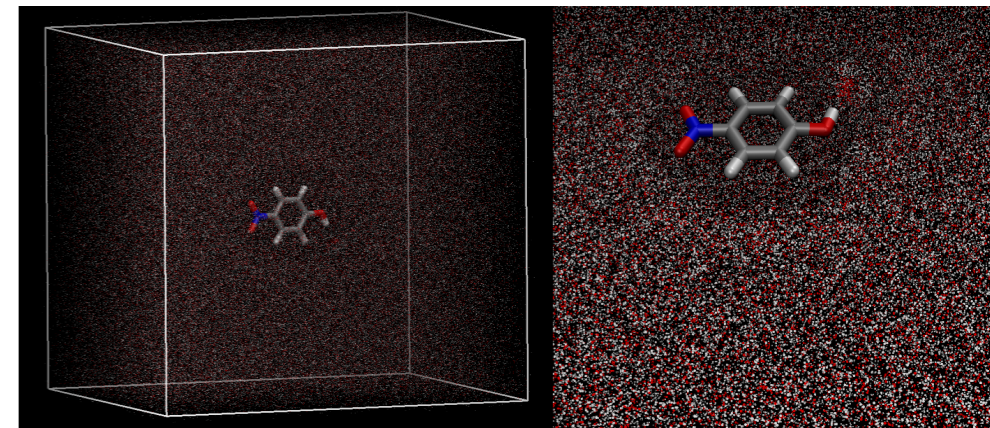
# CIS(D) Calculations with explicit water molecules
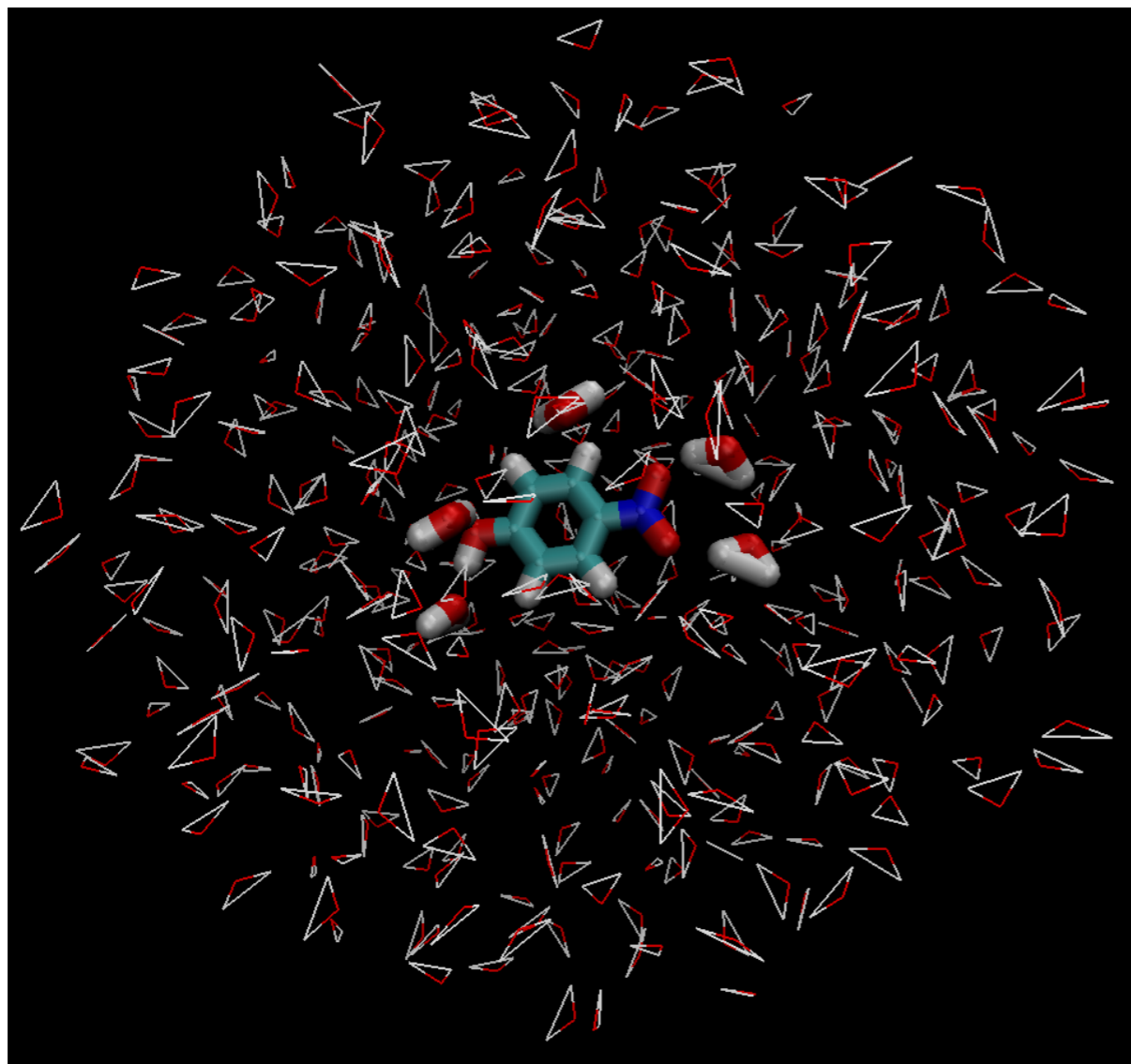
x 100

One of the configurations used in the CIS(D) 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.

In order to **reduce the computational cost***, we compromised, keeping the **aug-cc-pVDZ** basis set for the **solute**, but using **6-31G** for the **5 water molecules**.

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*Bistafa, Modesto-Costa, Canuto, *TCA* **135** (2016) 129.

CIS(D) Calculations with explicit water molecules
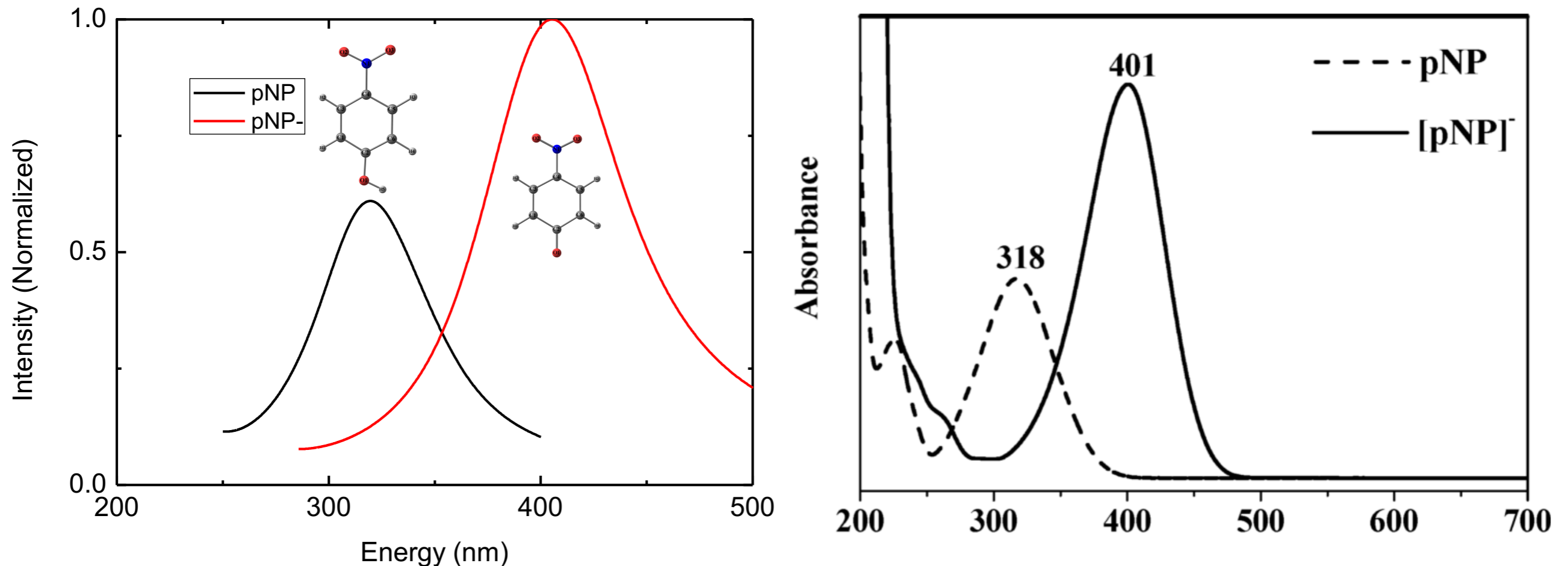
Left) Theoretical spectrum of pNP and pNP- in aqueous solution.
Method used: CIS(D); Basis set: aug-cc-pVDZ (pNP/pNP-), 6-31G (water molecules)
Solvent Model: 5 explicit water molecules + half of the solvation box as point charges.
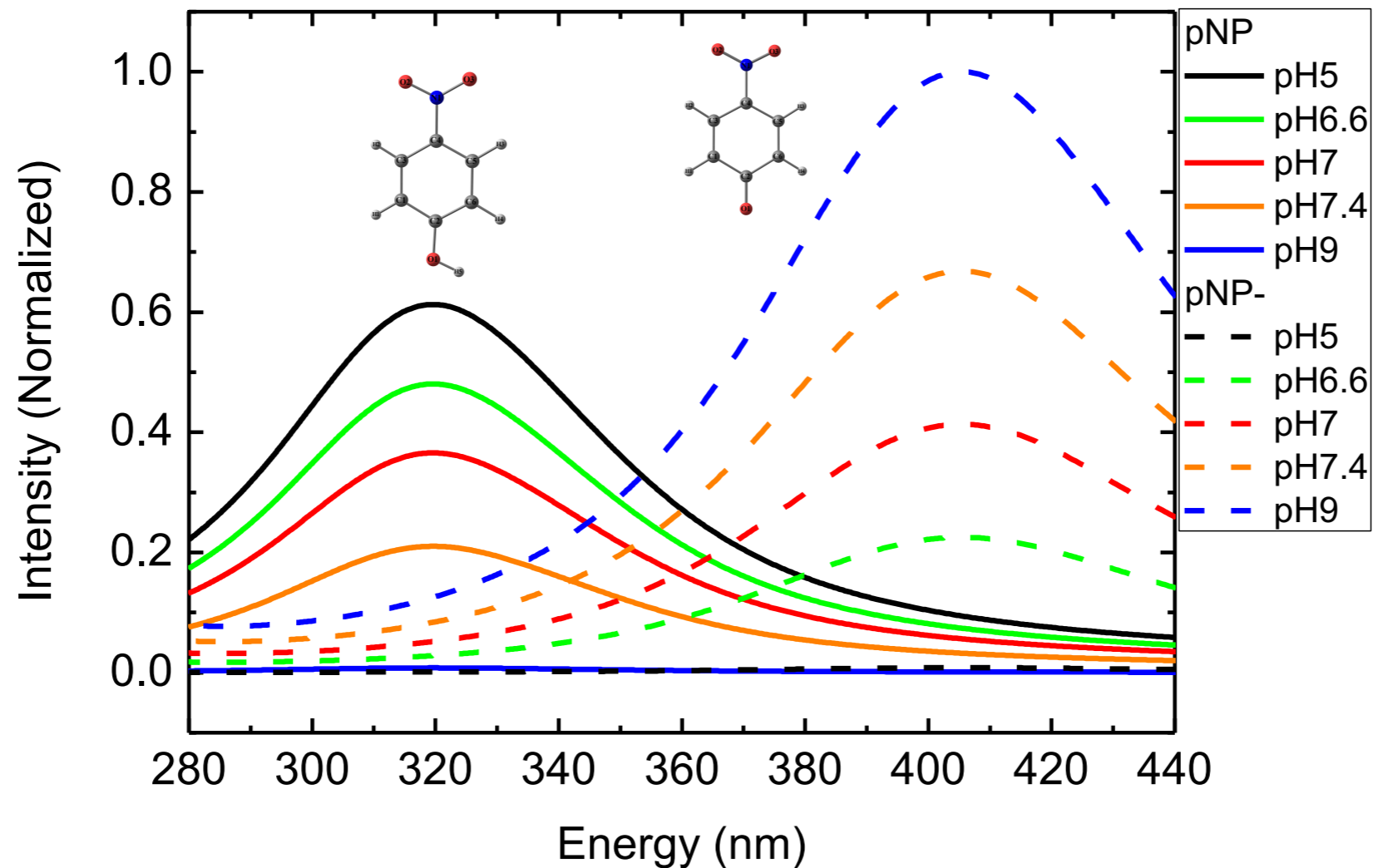
Right) Experimental Spectrum: Ando et al, *J. Phys. Chem. A* **111** (2007) 7194

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

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

$x_0 =$ center of the distribution

17

CIS(D) Spectrum: Different pHs

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

γ = half-width at half-maximum (HWHM)

x_0 = center of the distribution

The theoretical electronic spectrum of pNP and pNP- in aqueous solution, considering 5 different pH conditions. To obtain the spectrum, we convoluted a Lorentzian function to the electronic transitions calculated in 100 uncorrelated configurations and multiplied the intensity by the population ratio.
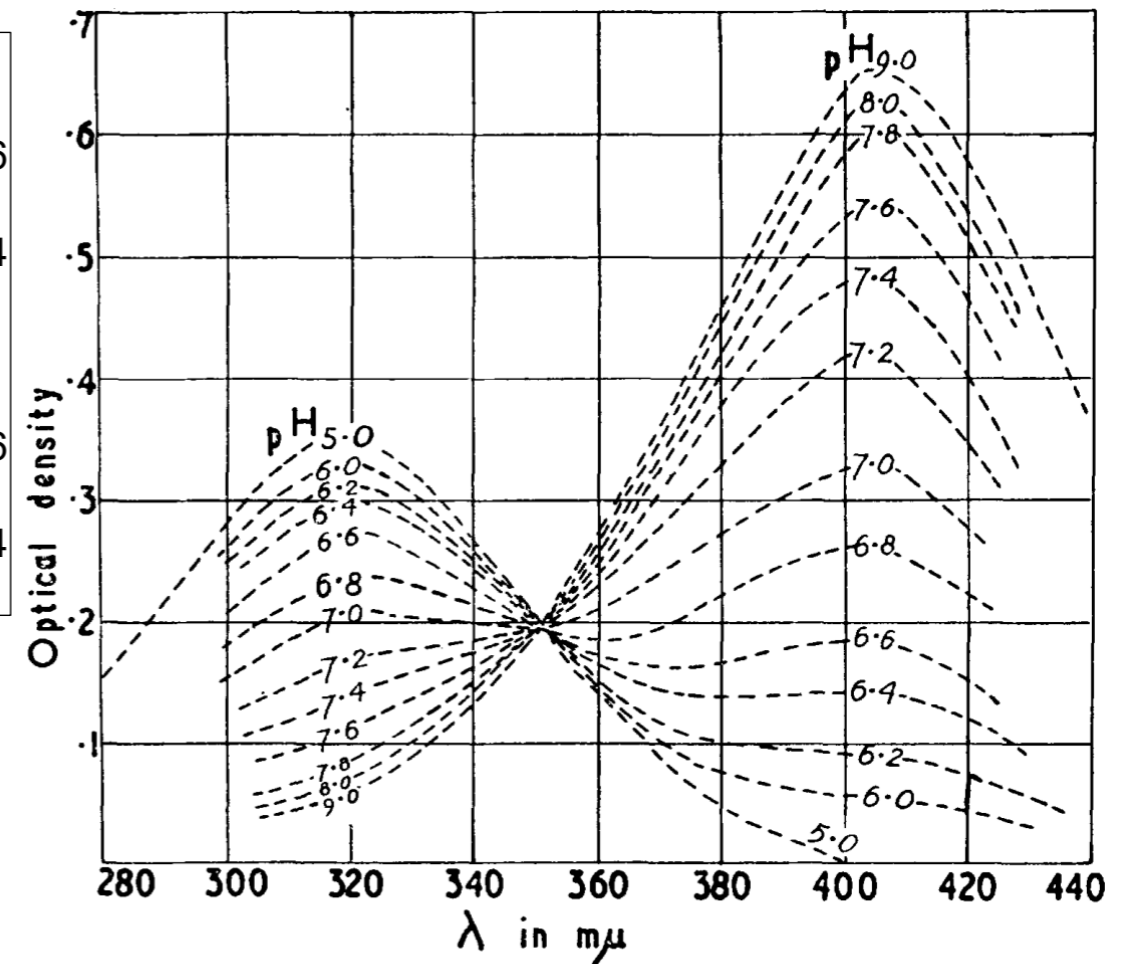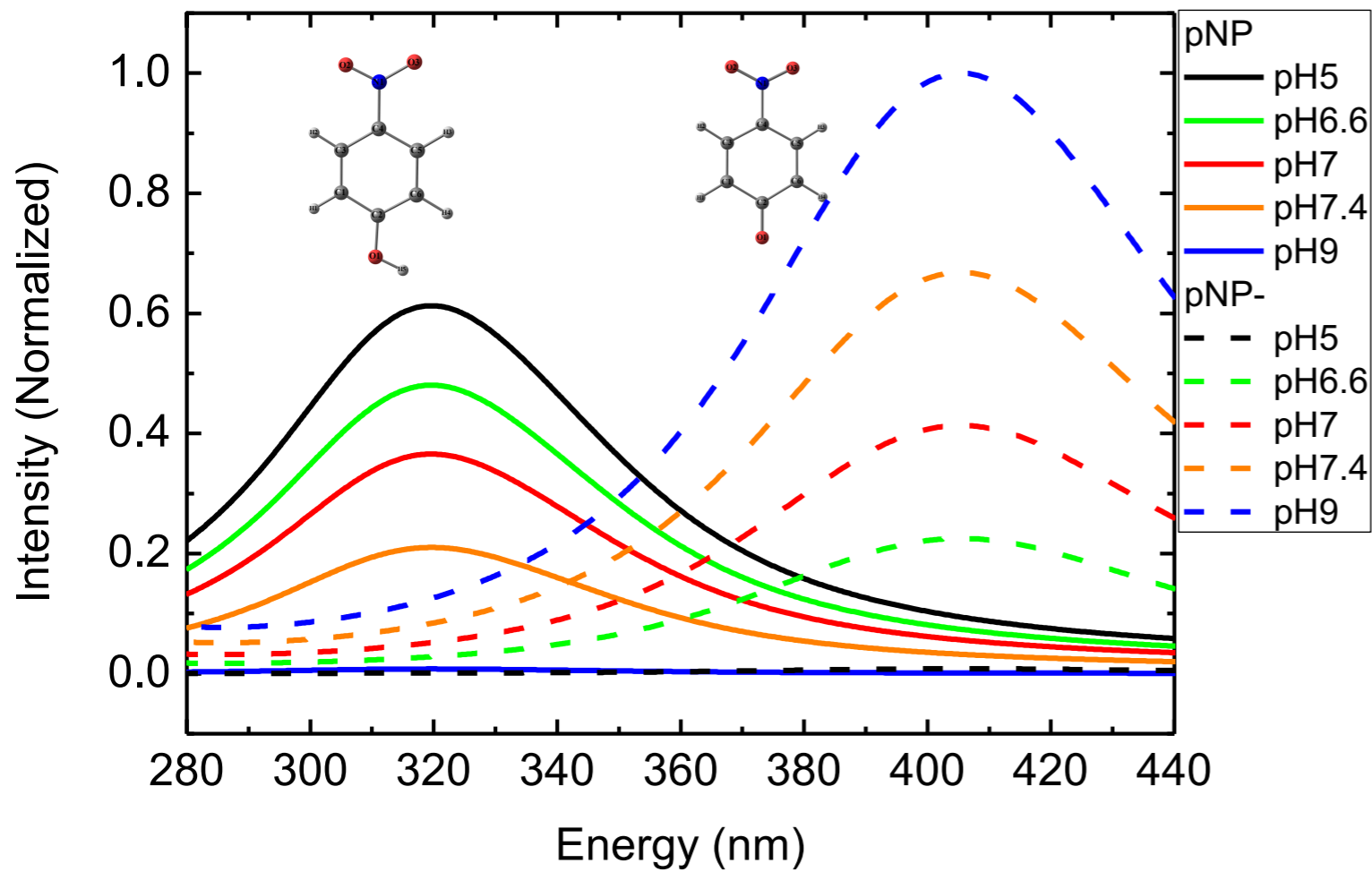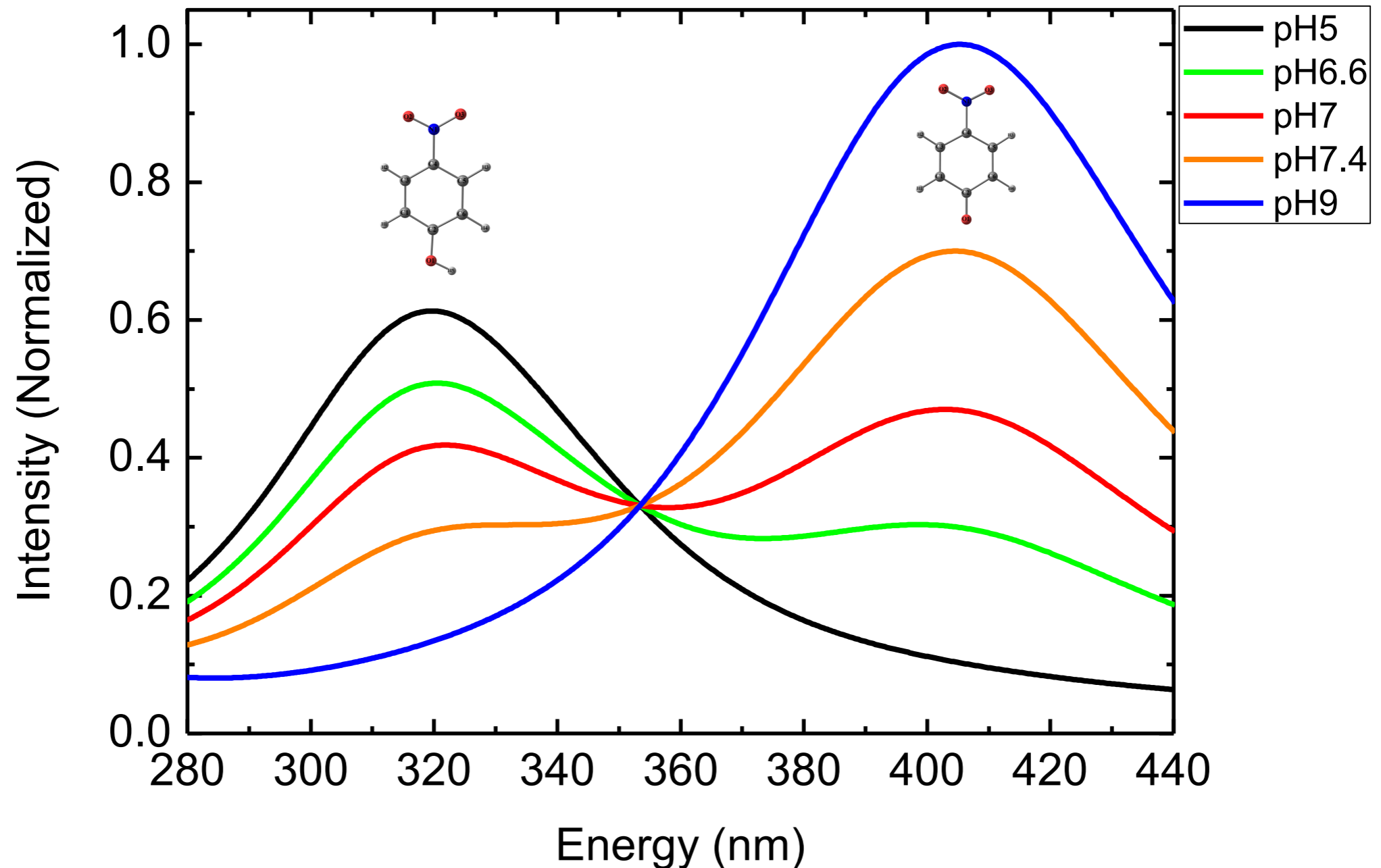
CIS(D) Spectrum: Different pHs

FIG. 1.—p-nitrophenol in water; 3.6×10^{-5} mole/l.

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

CIS(D) Spectrum: Combining the spectrum of both moieties

By summing and normalizing the previous spectra, it is possible to obtain a spectrum that present all the characteristics observed experimentally, including the **isosbestic point (等 吸収 点)**.

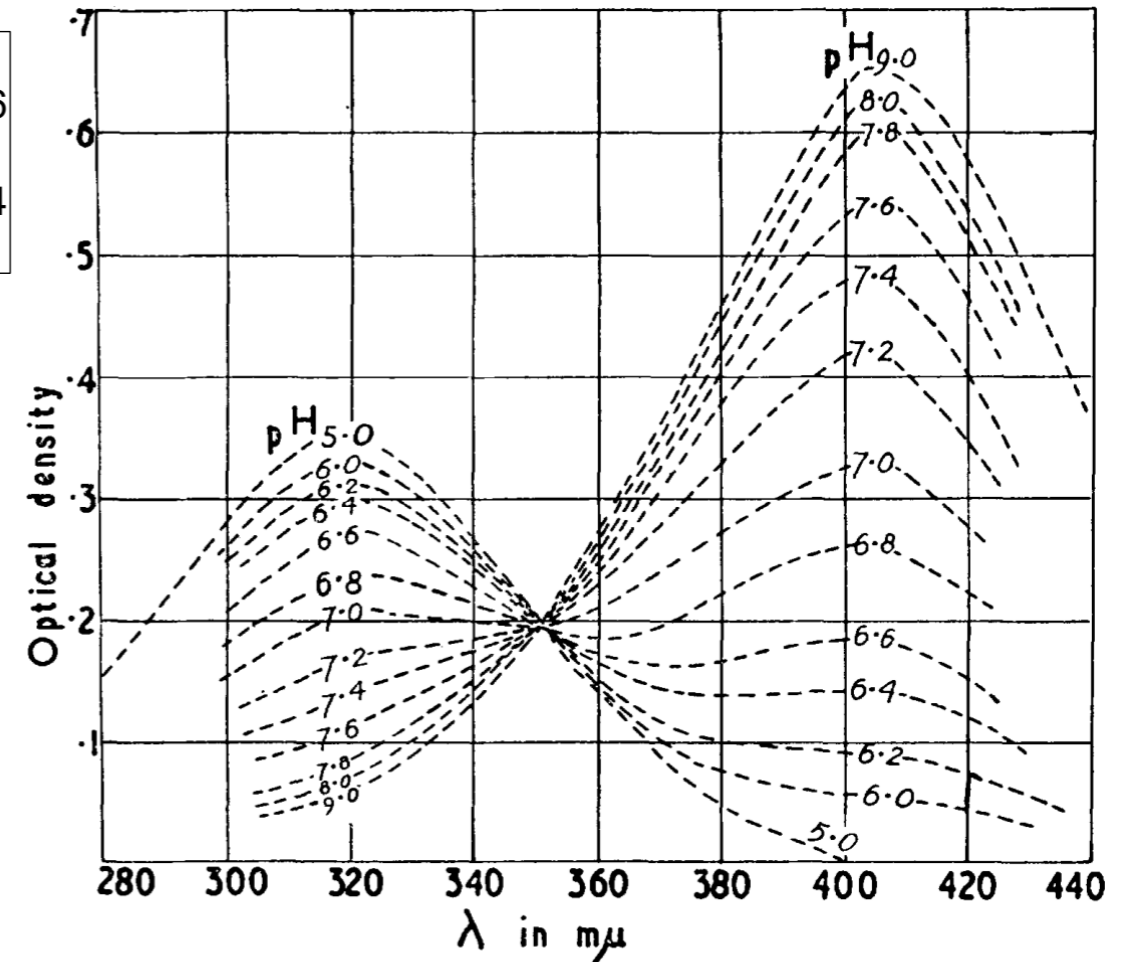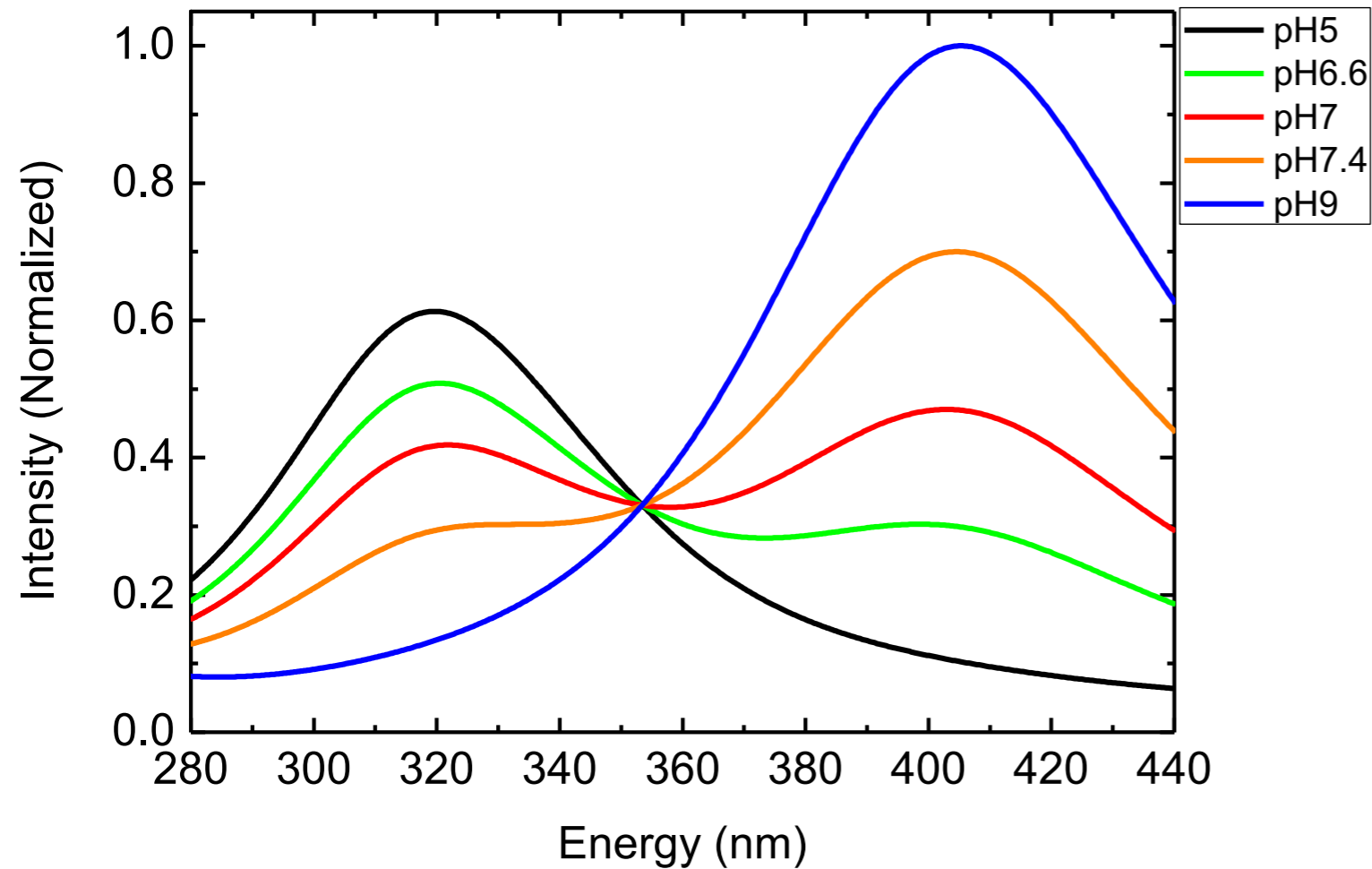# CIS(D) Spectrum: Combining the spectrum of both moieties

FIG. 1.—p-nitrophenol in water ; 3·6 × 10⁻⁵ mole/l.

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

Comparison between our theoretical spectrum and the experimental one. All the important characteristics have been successfully reproduced.

Conclusions & Perspectives

- It is possible to obtain theoretically a pH-dependent spectrum;
- This is possible by combining the population ratio from CpH-MD simulations with the electronic transitions obtained from S-QM/MM calculations.
- All the characteristics were well reproduced: peak positions, relative intensities and the isosbestic point.

- Apply our methodology in systems with more protonation sites.