Electronic transitions of paranitrophenol in different pH conditions:

A review and new perspectives

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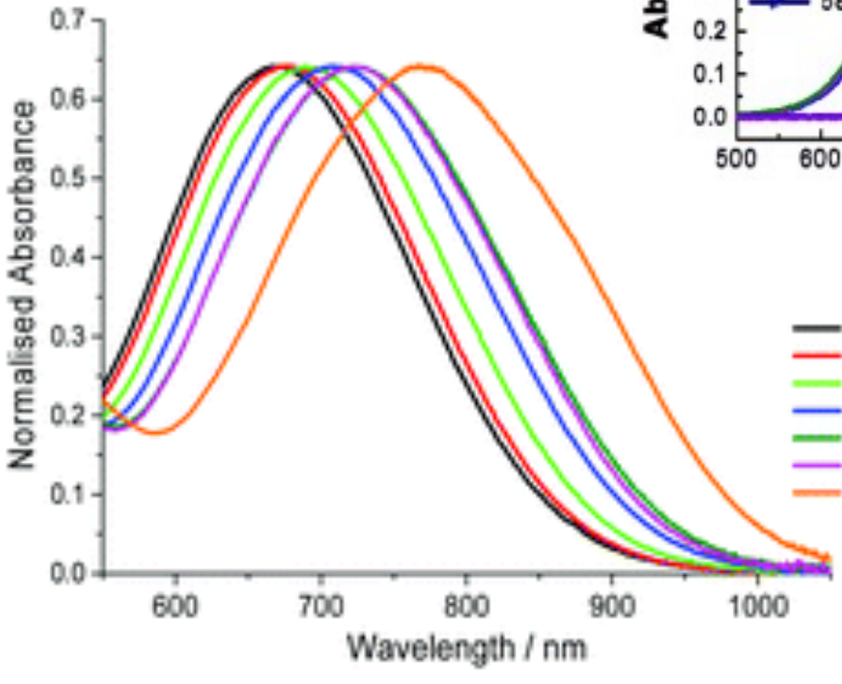
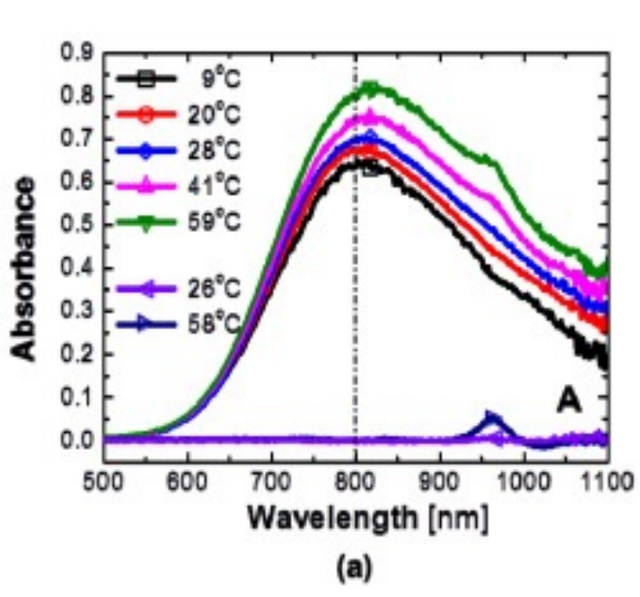
Motivation: Electronic Transition of Molecules in Solution

Previous CREST-WS

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.





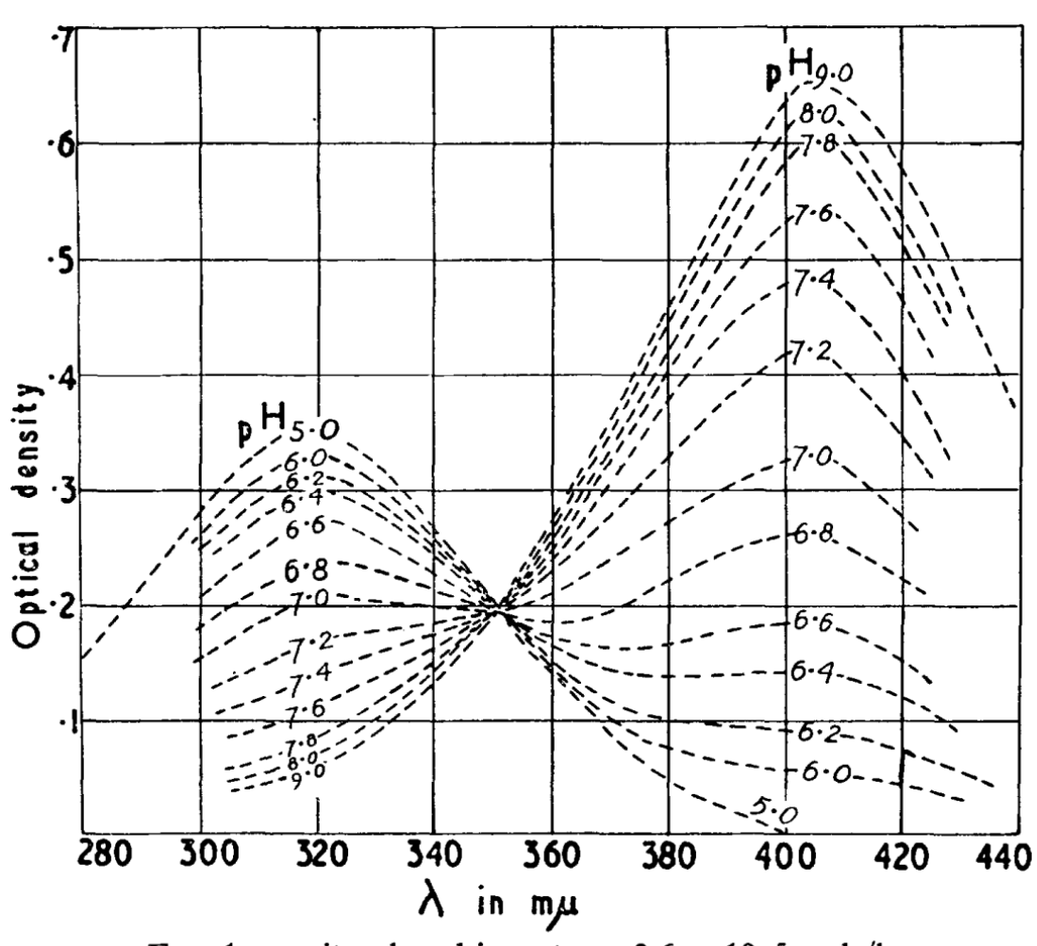
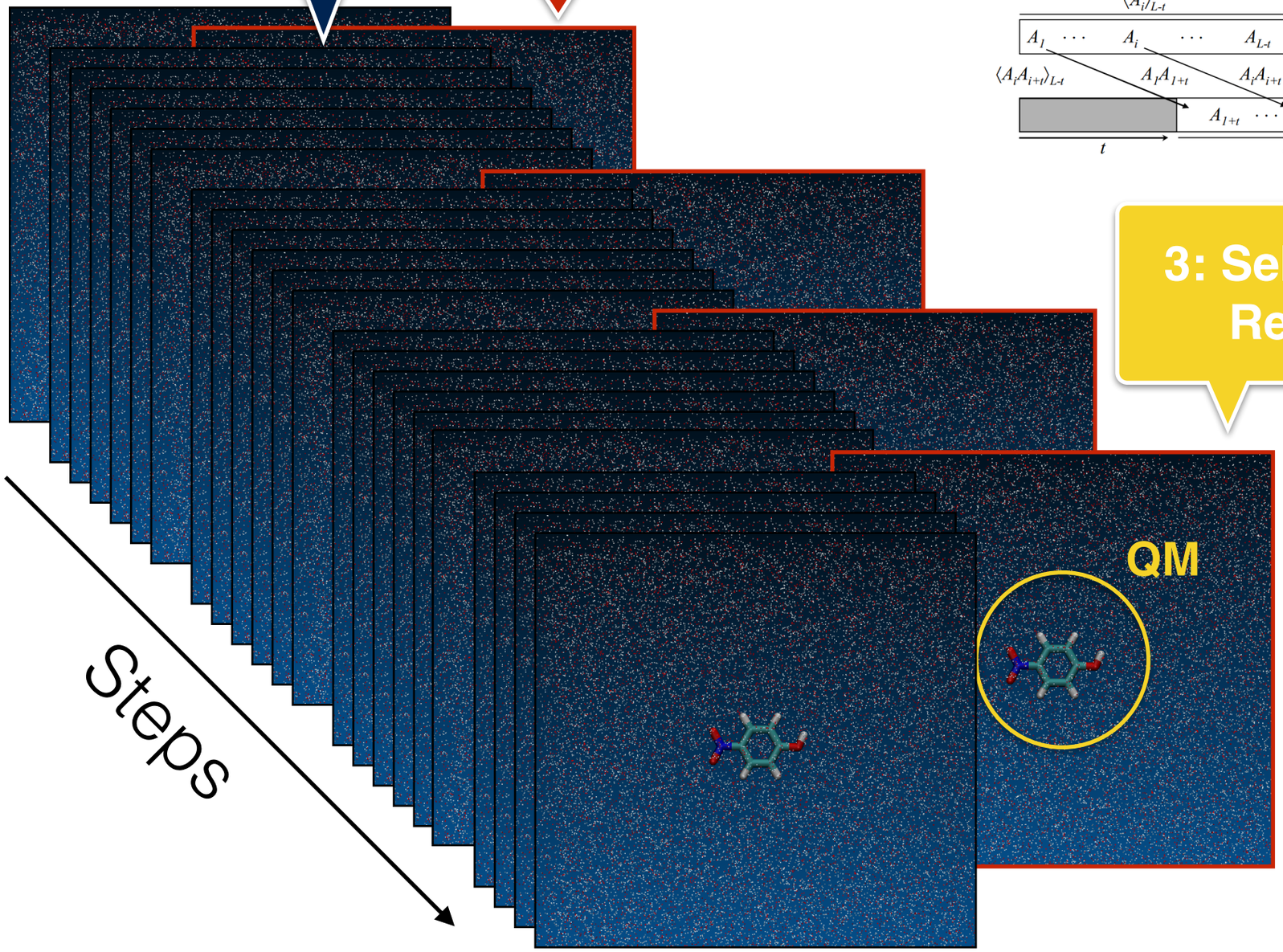


FIG. 1.—*p*-nitrophenol in water ; $3{\cdot}6 \times 10^{-5}$ mole/l.

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

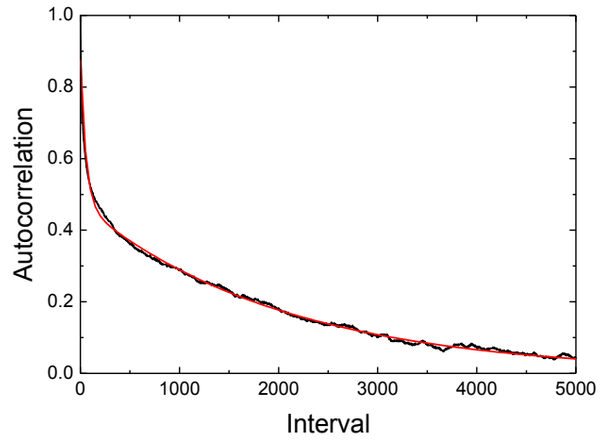
1: Classical Simulation

2: Select Relevant Confs



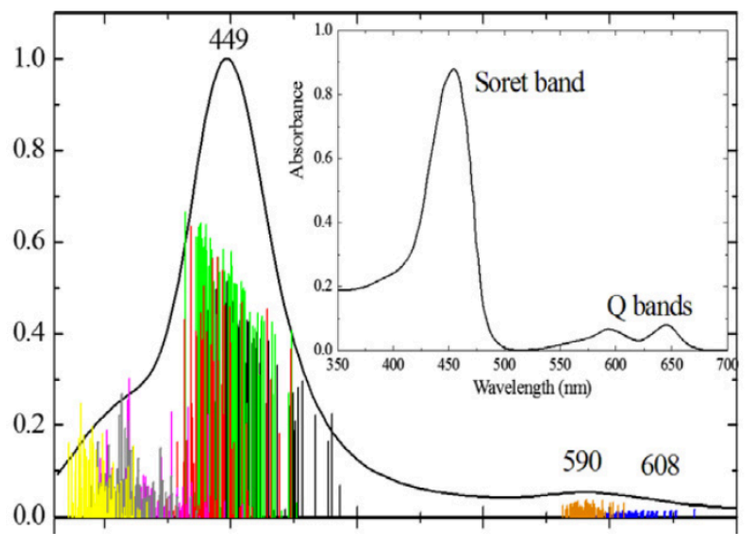
$$C(t) = \frac{\langle \partial A_i \partial A_{i+t} \rangle}{\langle \partial A^2 \rangle} = \frac{\langle A_i A_{i+t} \rangle_{L-t} - \langle A_i \rangle_{L-t} \langle A_{i+t} \rangle_{L-t}}{\langle A^2 \rangle_L - \langle A \rangle_L^2}$$

Previous CREST-WS



3: Select QM Region

4: Obtain QM Properties



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

S. Canuto & K. Coutinho, *IJQC* **77** (2000)192

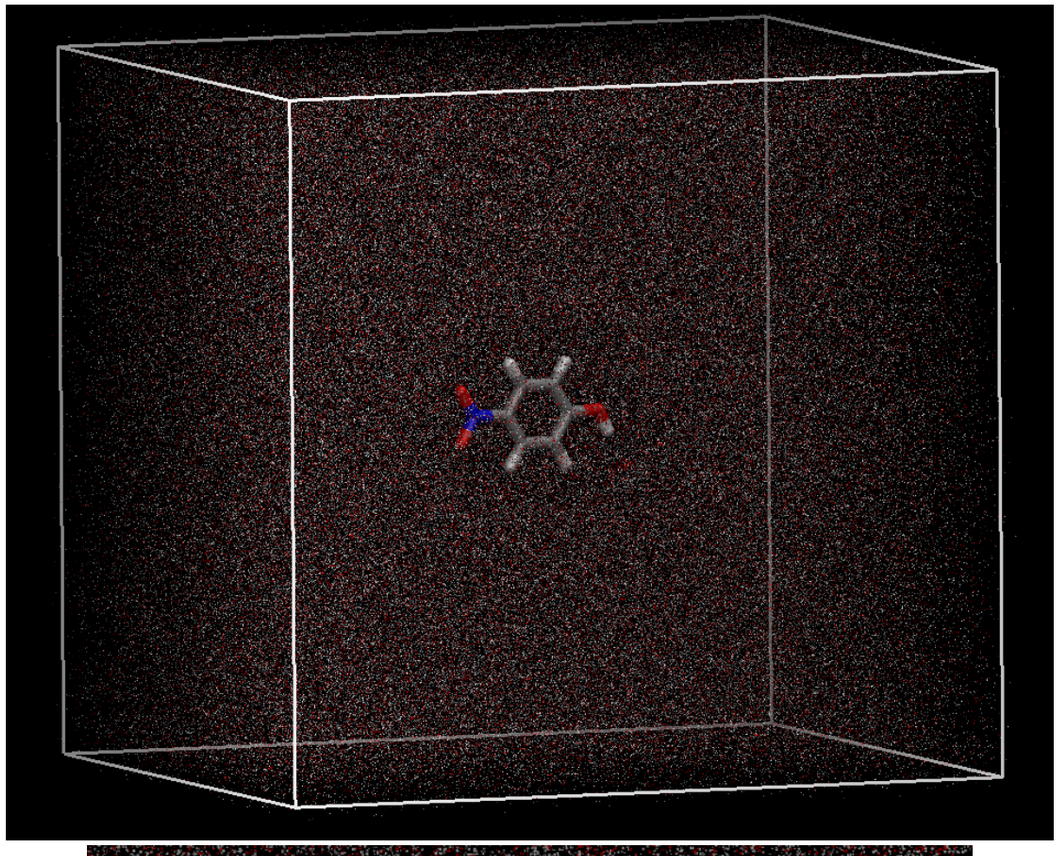
Solvent Effects on Molecules and Biomolecules, S. Canuto (ed.), Springer 2008 (chap. 6)

ASEC: Average Solvent Electrostatic Configuration

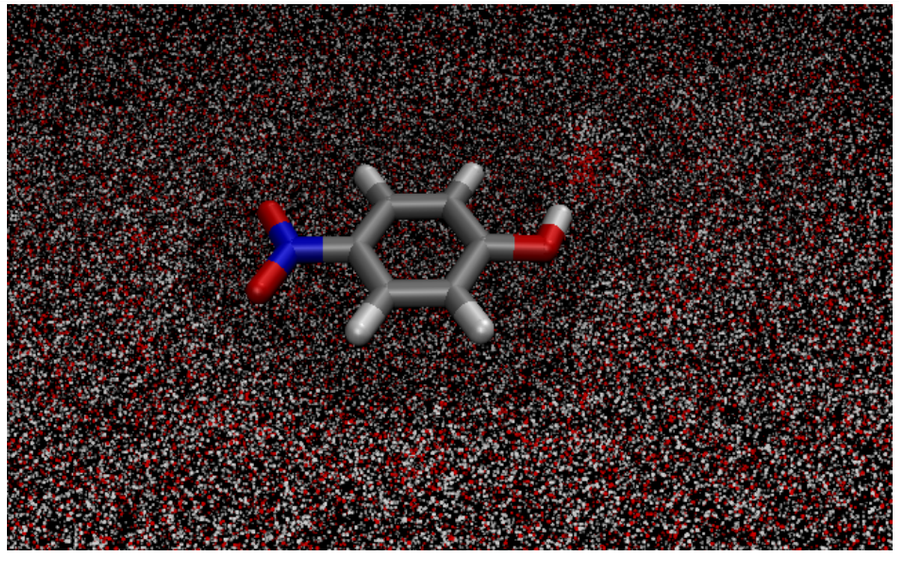
Previous CREST-WS

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:

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



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

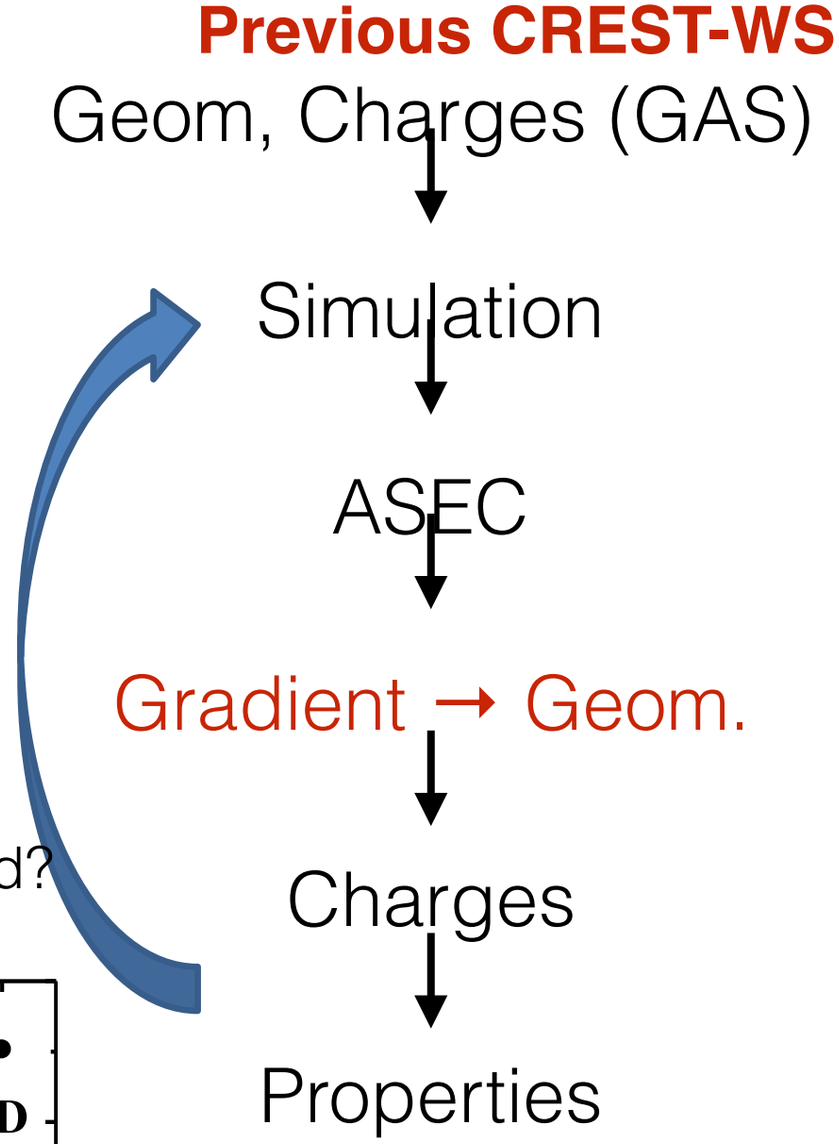
M. Nagaoka & co-wks.,
IJQC 70 (1998) 95:

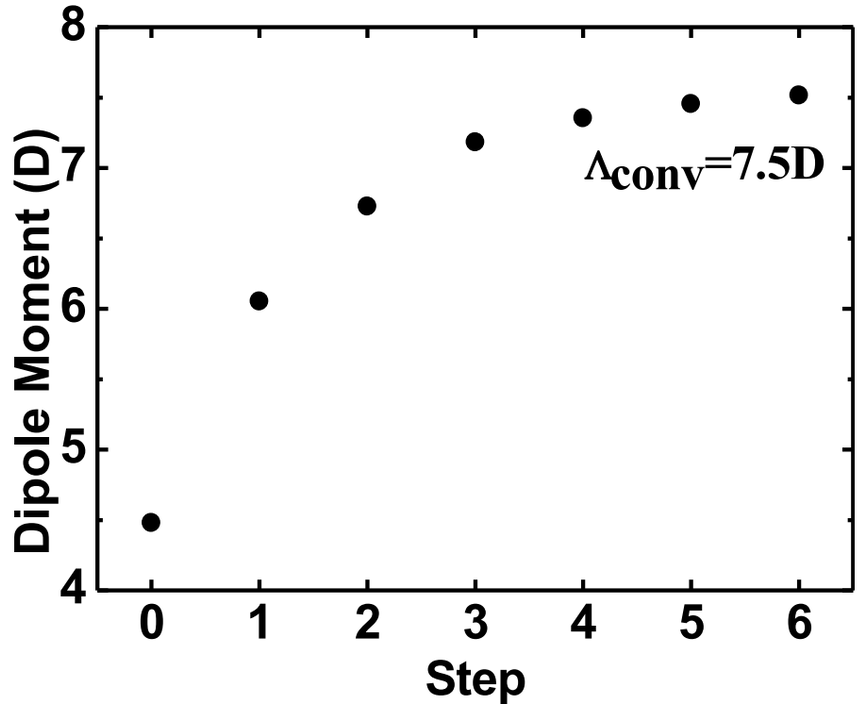
$$F(q) = -\frac{\partial G(q)}{\partial q} = -\left\langle \frac{\partial V(q)}{\partial q} \right\rangle$$

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

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

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





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

The first 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.

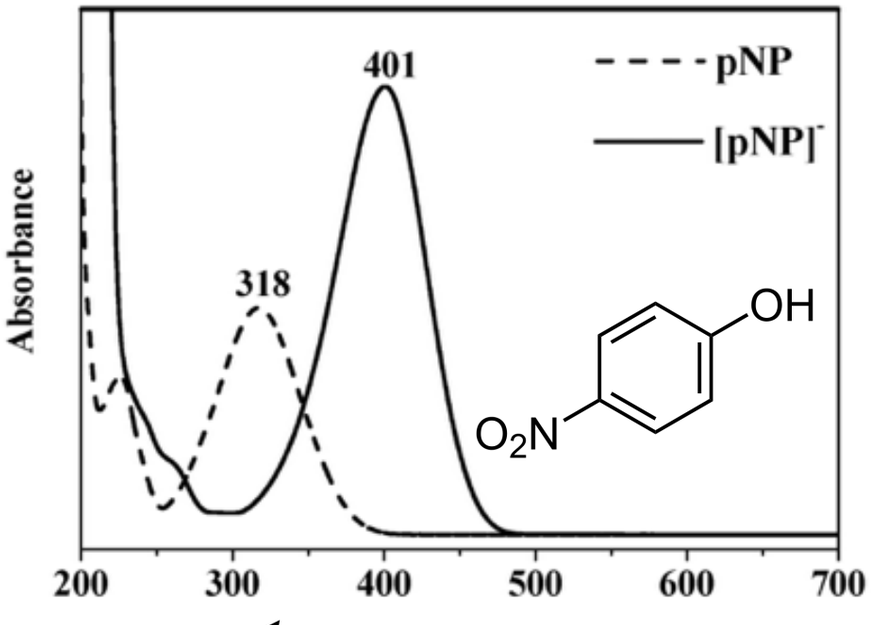
Geometry	pNP	pNP^-	Shift
GAS	4.51	-- [a]	
PCM	4.22	3.37	0.85
FEG	3.99	3.38	0.61/0.71[d]
EXP	3.90[b]	3.09[b,c]	0.81

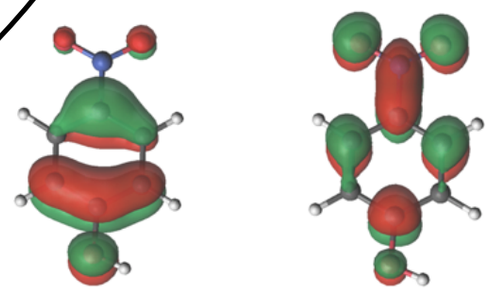
a) In gas phase, the geometry of pNP^- has C2v symmetry, whereas the interaction with the solvent breaks this symmetry (C1 group);

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.

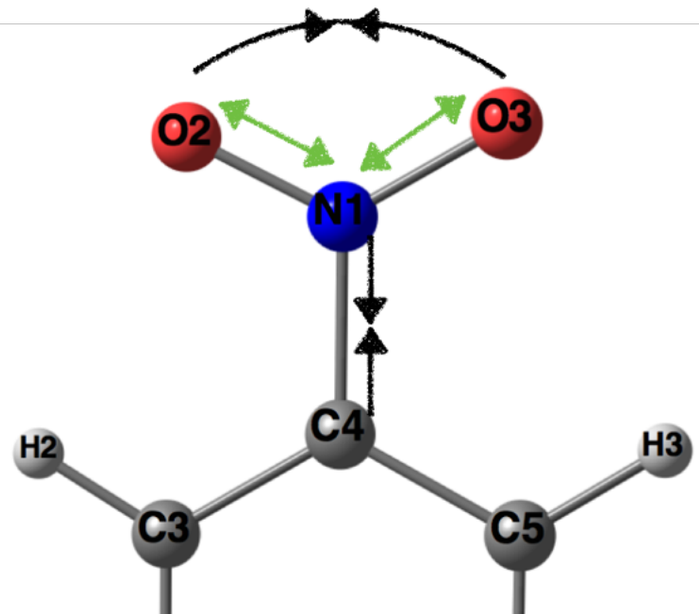




HOMO LUMO

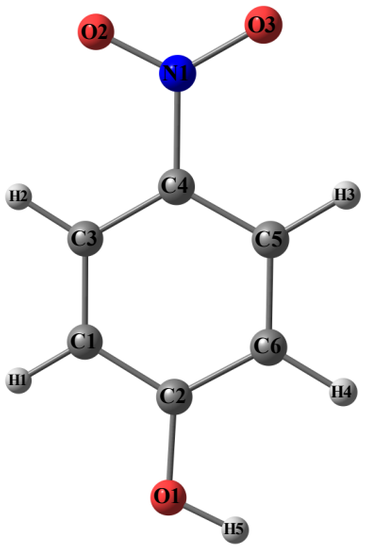
Table 2: Geometrical changes in the nitro group. Bond distances in Å and bond angle in degree.

	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



Our Goal

Previous CREST-WS



Acid pH

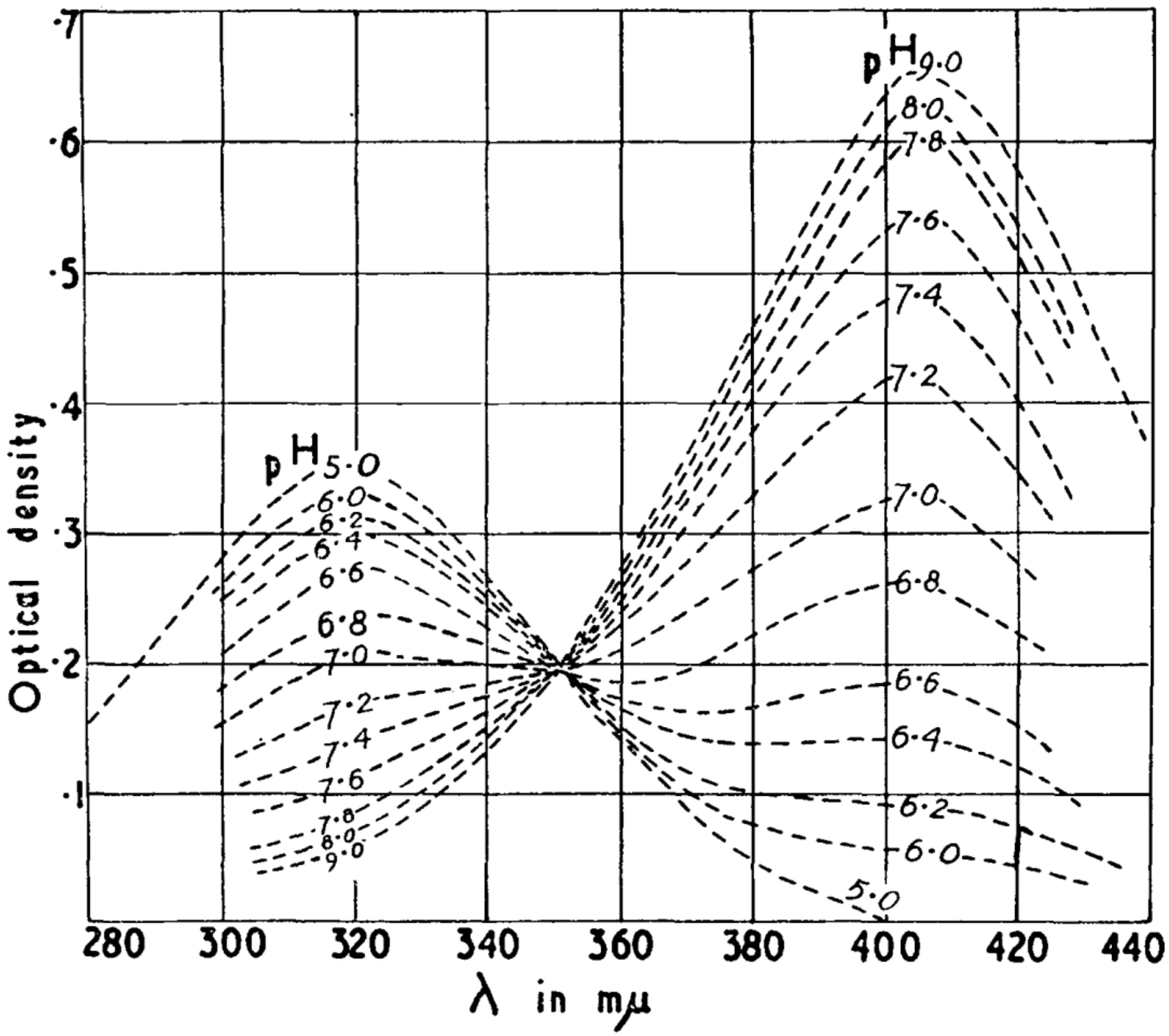
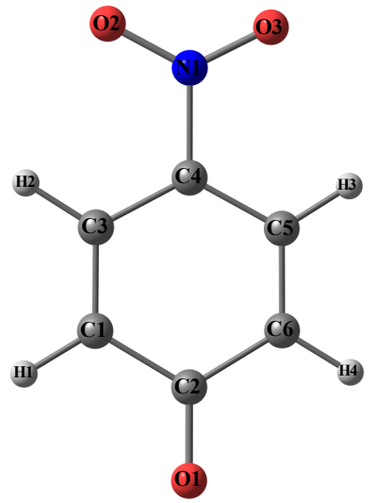


FIG. 1.—*p*-nitrophenol in water ; $3{\cdot}6 \times 10^{-5}$ mole/l.

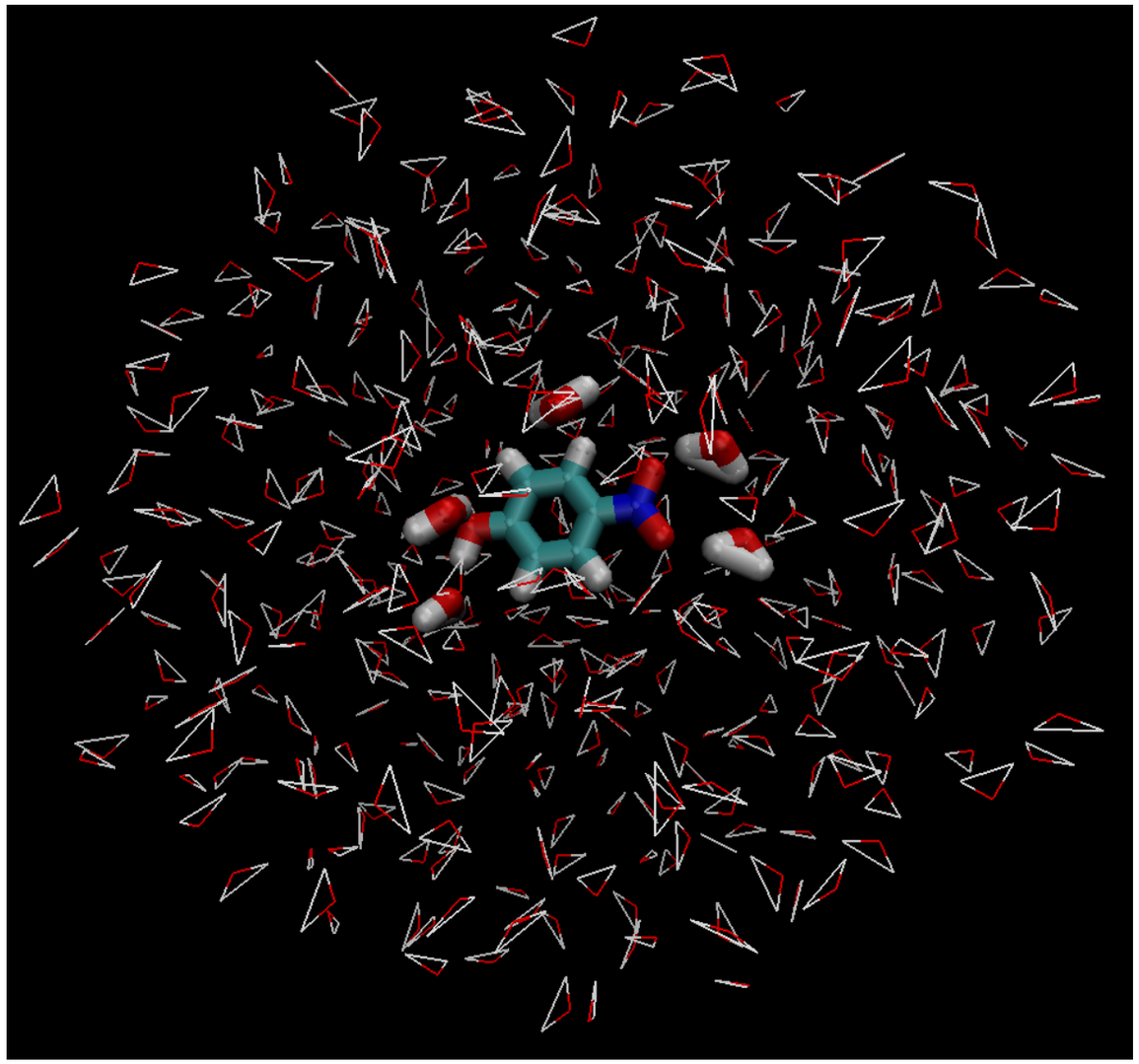


Basic pH

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

Configuration

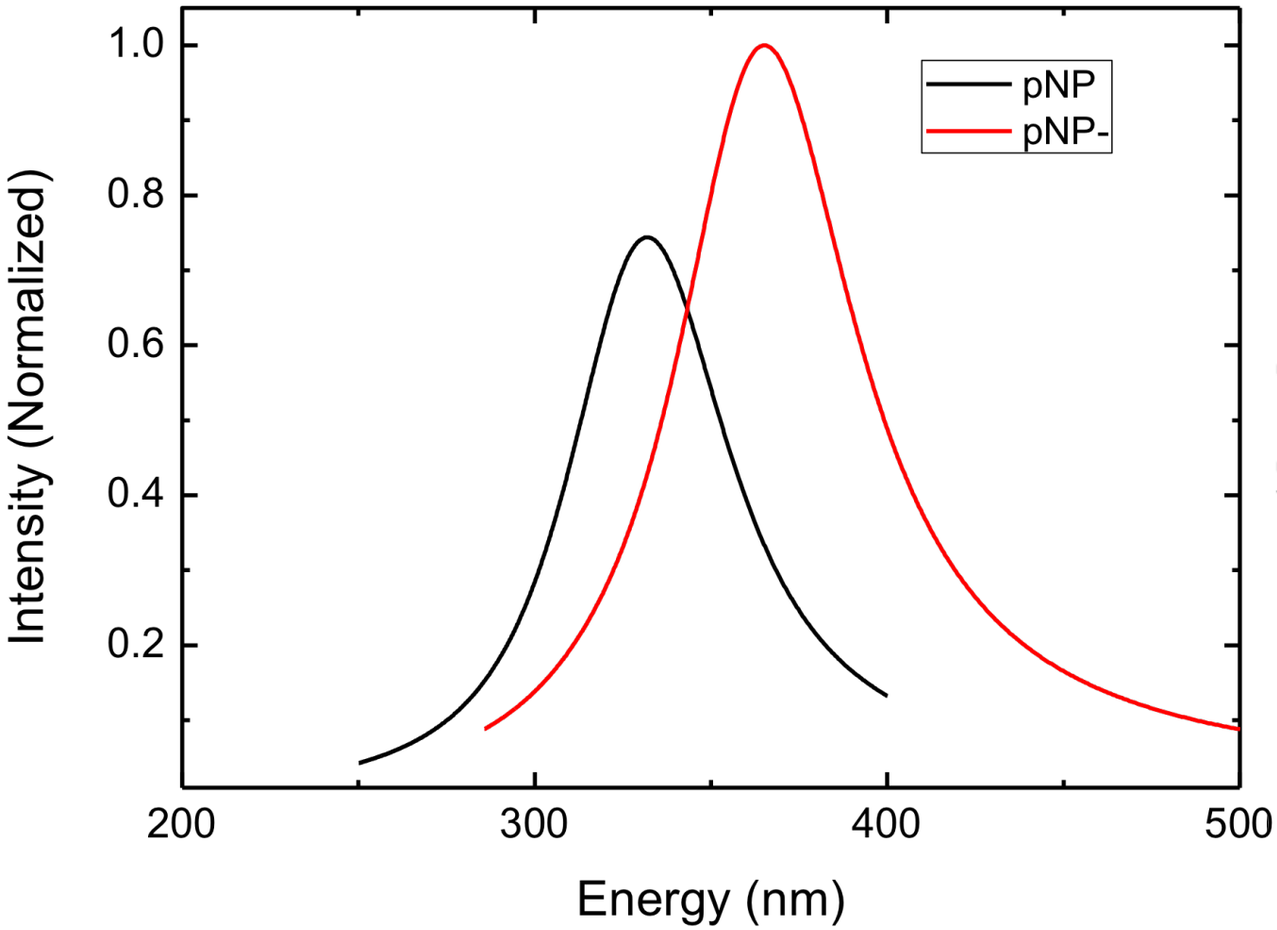
Previous CREST-WS

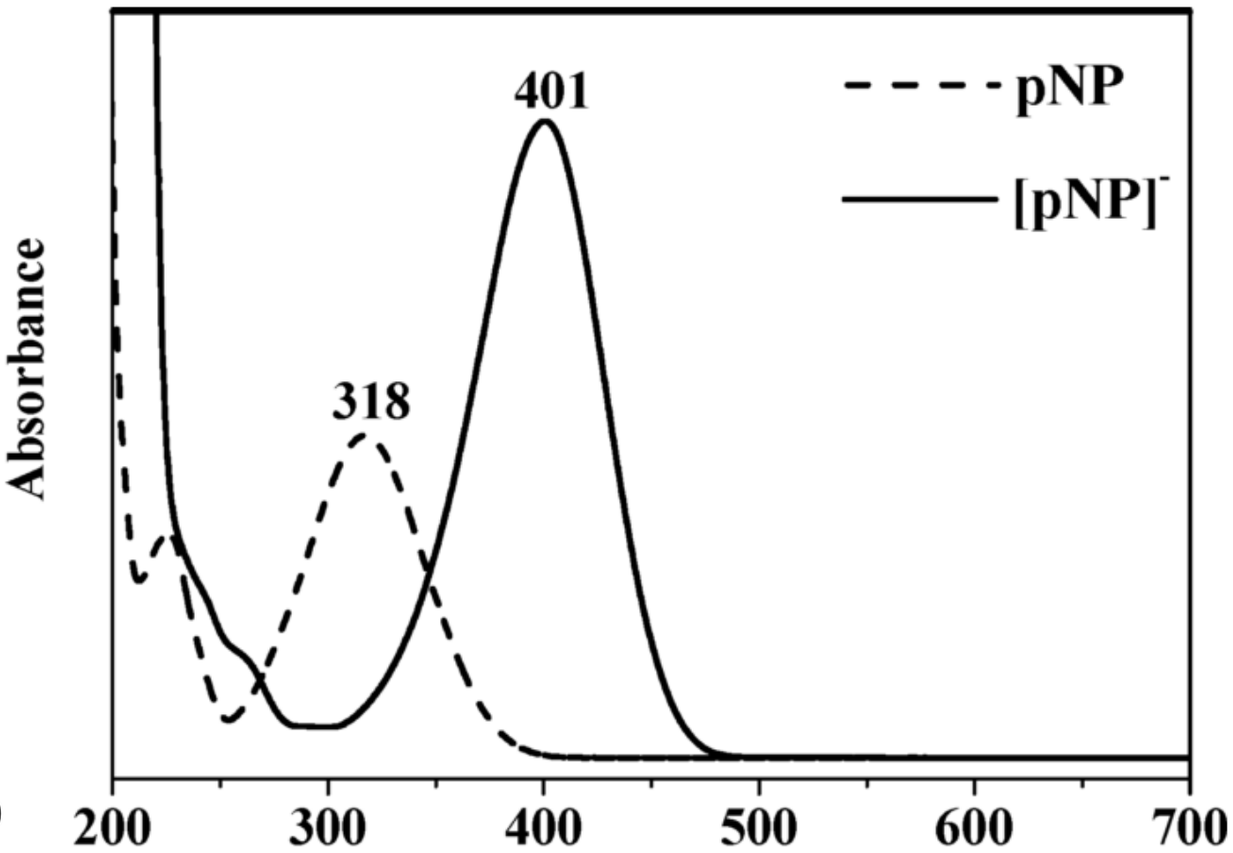


x 100

One of the configurations used in the TD-B3LYP/aug-cc-pVDZ 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. The electronic transitions used in the convolution are also shown. Level of calculation: TD-B3LYP/aug-cc-PDVZ; Right) the experimental spectrum [Ando et al., *JPCA* **111** (2007) 7194].

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

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

$x_0 =$ center of the distribution

Convergence of the Values

Previous CREST-WS

Table: TD-B3LYP/aug-cc-pVDZ calculation for configurations randomly chosen of pNP and pNP- in water. For each configuration, an increasing number of QM water molecules was considered. Only the brightest transition is shown. Note that, the energy value of the transitions is converged, while the dimensionless oscillator strenght seem to be fluctuating around an average value, with a mild trend to decrease.

Configuration 1

	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.67	0.434	3.38	0.527
10	3.66	0.412	3.34	0.511
15	3.65	0.414	3.33	0.503
20	3.62	0.384	3.34	0.478
25	3.62	0.372	3.34	0.477
30	3.60	0.371	3.33	0.464
35	3.60	0.363	3.31	0.463

Configuration 26

	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.74	0.412	3.43	0.488
10	3.72	0.420	3.40	0.516
15	3.70	0.403	3.39	0.508
20	3.68	0.390	3.39	0.469
25	3.67	0.380	3.37	0.459
30	3.67	0.365	3.37	0.440
35	3.67	0.382	3.35	0.438

Configuration 52

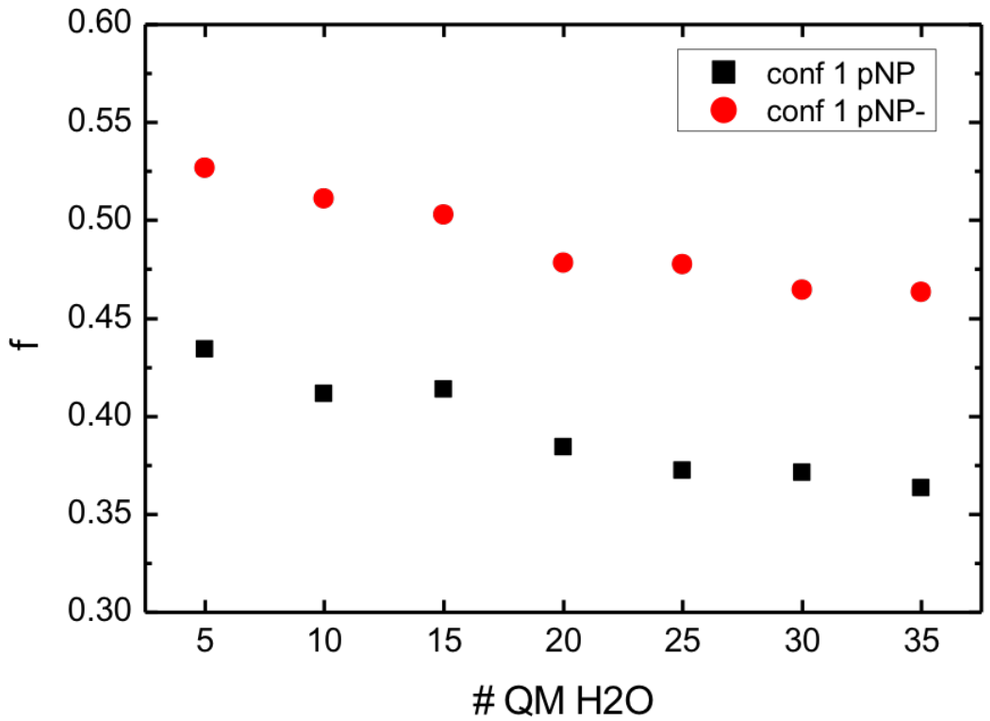
	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.67	0.442	3.46	0.523
10	3.66	0.454	3.37	0.540
15	3.66	0.390	3.37	0.509
20	3.65	0.317	3.36	0.487
25	3.65	0.411	3.36	0.475
30	3.65	*0.418*	3.36	0.466
35	3.64	0.407	3.35	0.471

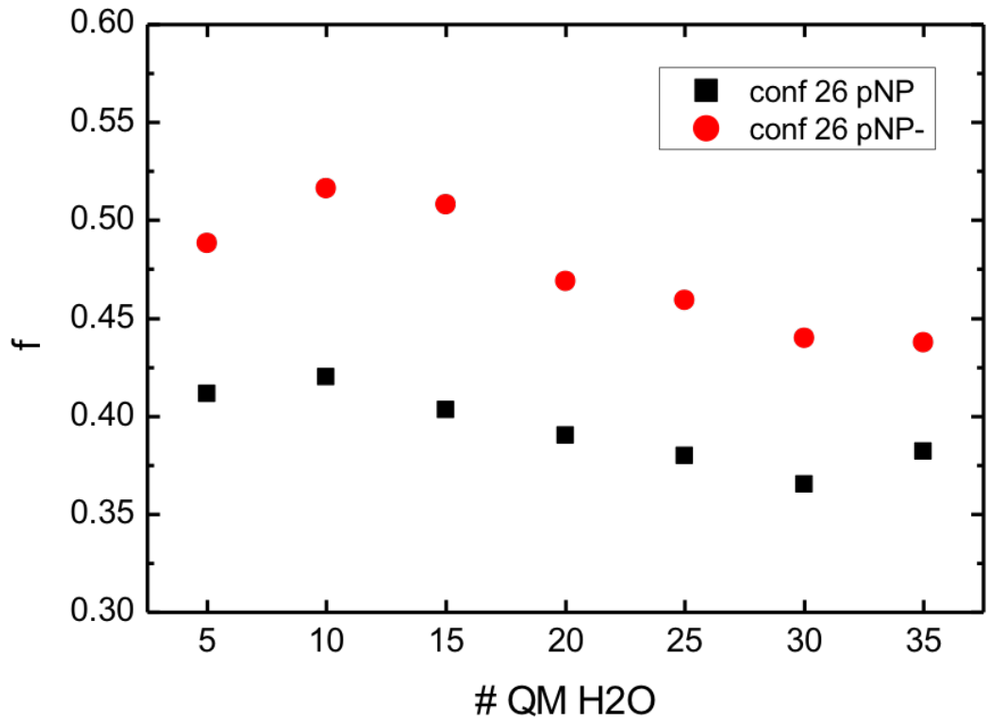
Configuration 99

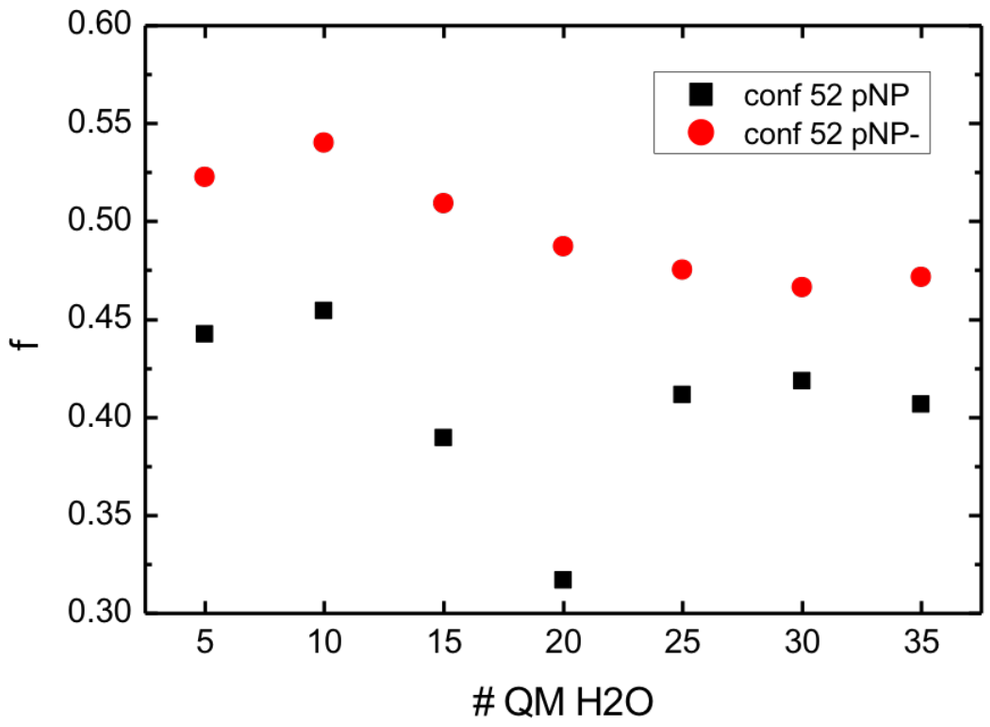
	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.83	0.422	3.41	0.546
10	3.82	0.416	3.38	0.561
15	3.75	0.374	3.37	0.528
20	3.75	0.353	3.36	0.509
25	3.72	0.354	3.35	0.480
30	3.71	0.334	3.34	0.459
35	3.70	0.334	3.33	0.471

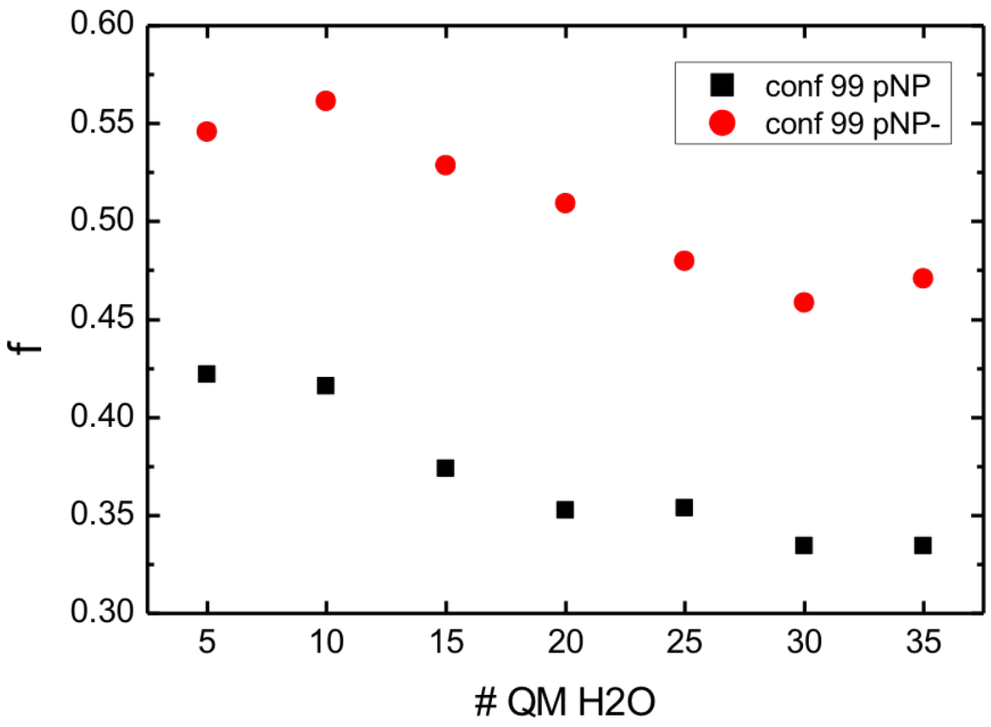
Oscillator Strength

Previous CREST-WS









Today's Talk

- CpH-MD results;
- (Tentative) construction of the spectrum depending on the pH.

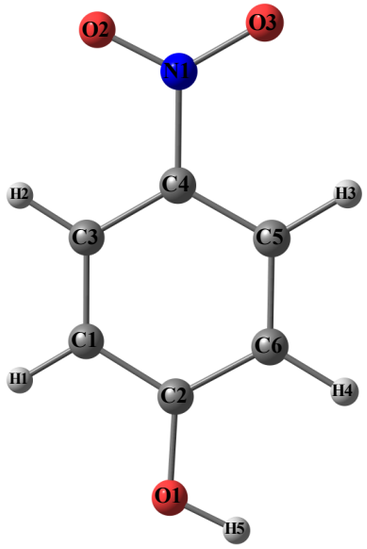
CpH-MD Simulations

Simulation details:

- Amber simulation: NPT ensemble, 1 atm, 298.15K;
- 1 solute molecule + counter-ion + 854 water molecules;
- Every 50ps, 1 trial to change the protonation state is done (10 trials were done);
- 3 pH conditions were considered: 5, 7 and 9.

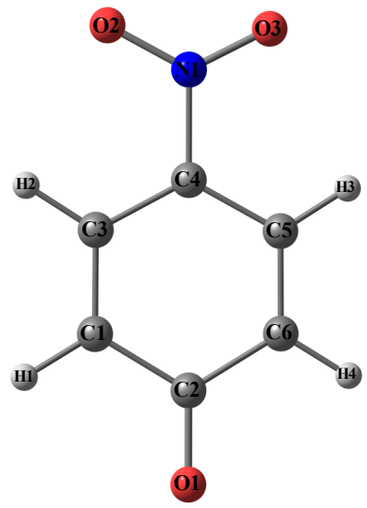
Results

- Population ratio of pNP and pNP- depending on the pH:



Acid pH

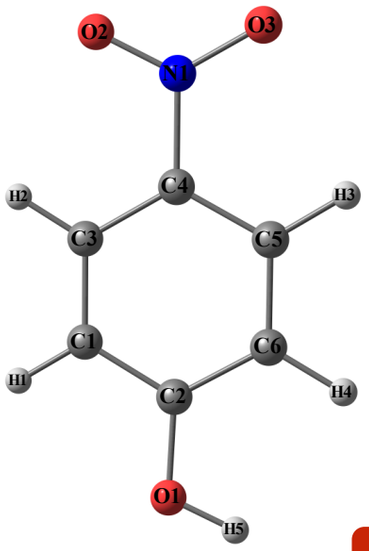
pH	pNP	pNP-
5	100%	0%
7	70%	30%
9	10%	90%



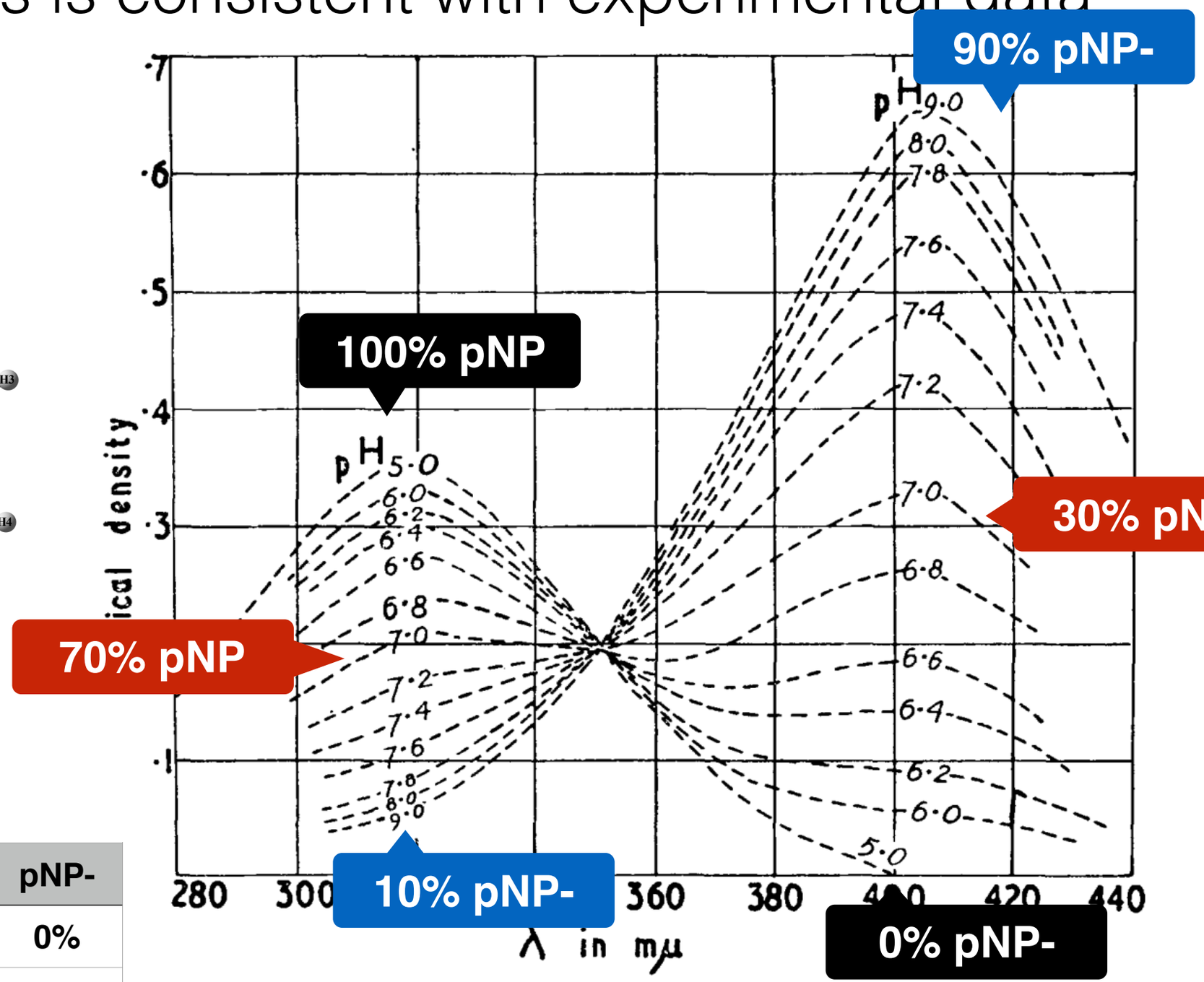
Basic pH

Results

- This is consistent with experimental data



Acid pH



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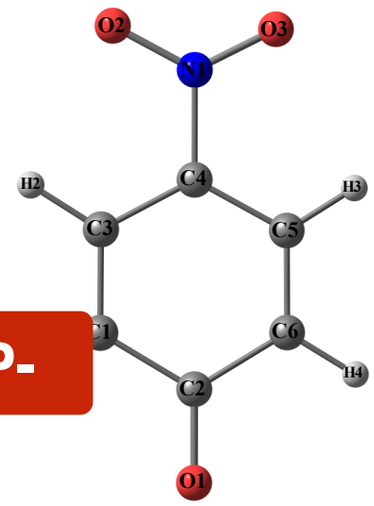


Basic pH

pH	pNP	pNP-
5	100%	0%
7	70%	30%
9	10%	90%

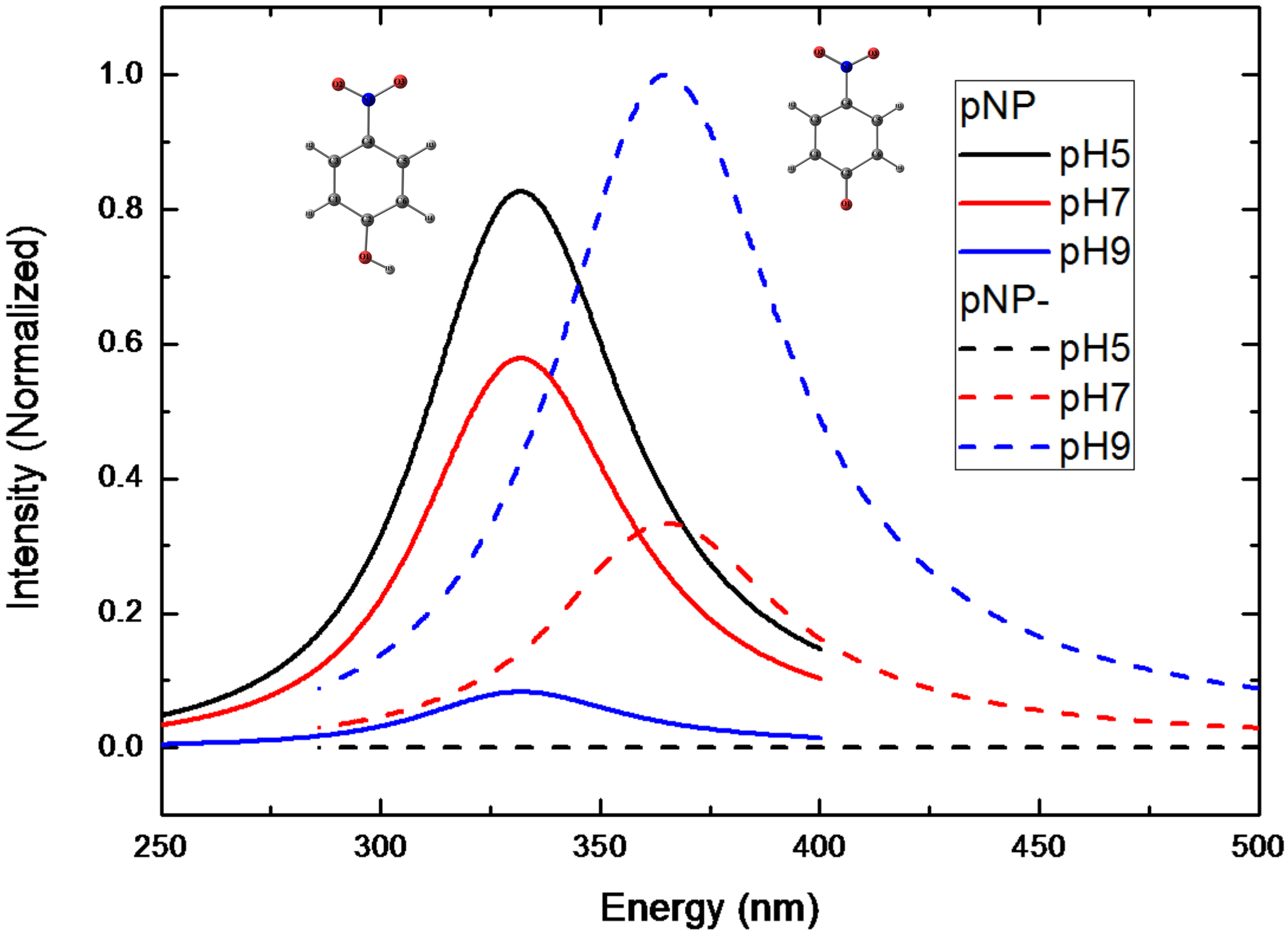
Biggs, *Trans. Faraday Soc.* **50** (1954) 800

Spectrum

Simple tentative:

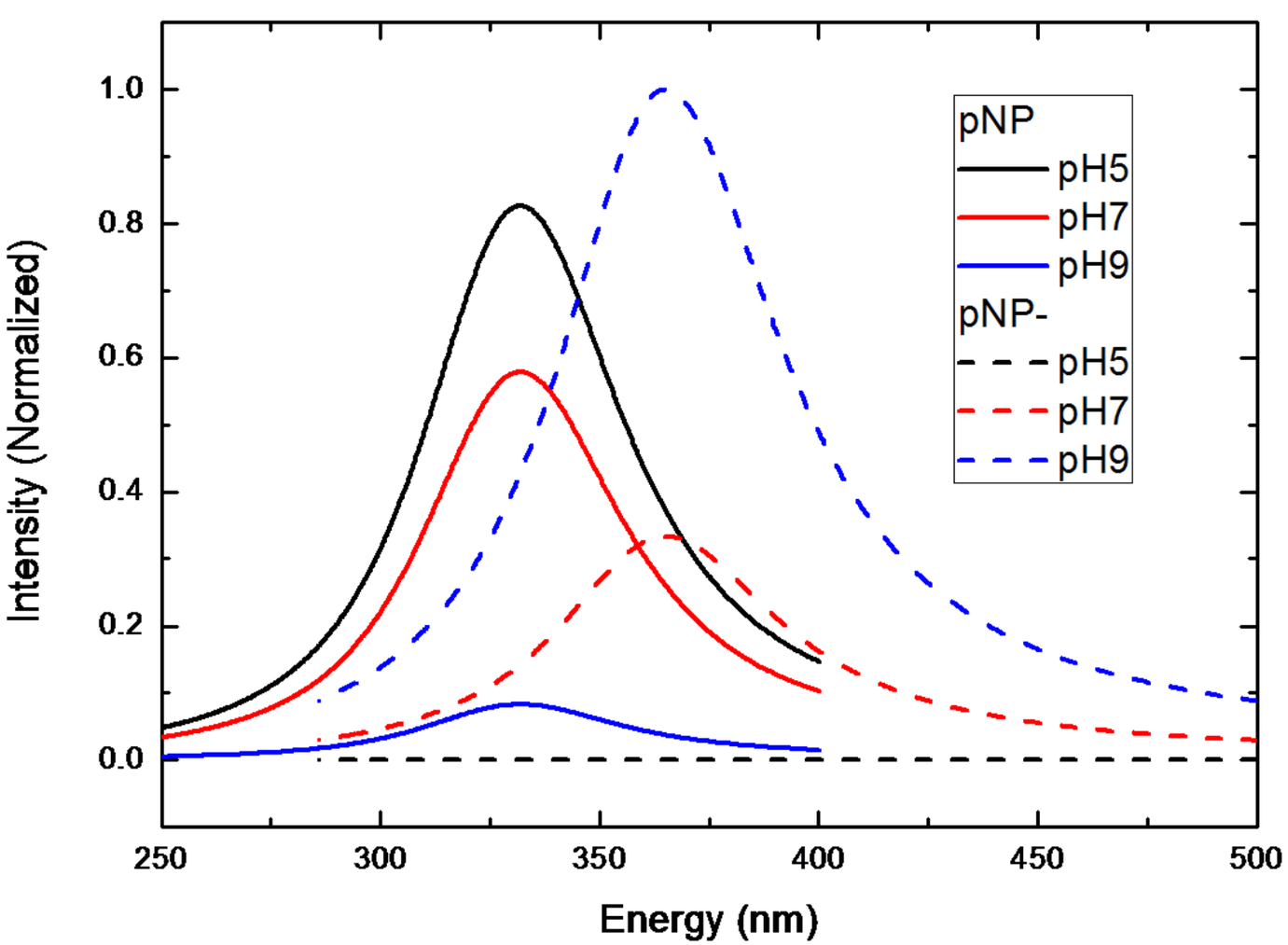
1. Assume that the intensity is proportional to the population ratio;
2. Multiply the intensity previously obtained by the population ratio (and normalize considering all the pH conditions.

Spectrum


Intensity (Normalized)
1.0
0.8
0.6
0.4
0.2
0.0
250
300
350
400
450
500
Energy (nm)
pNP
pH5
pH7
pH9
pNP-
pH5
pH7
pH9

Spectrum

The most acid (pH = 5) and most basic cases (pH = 9) are in good agreement with the experimental spectrum. This is not true for the intermediate case (pH =7).



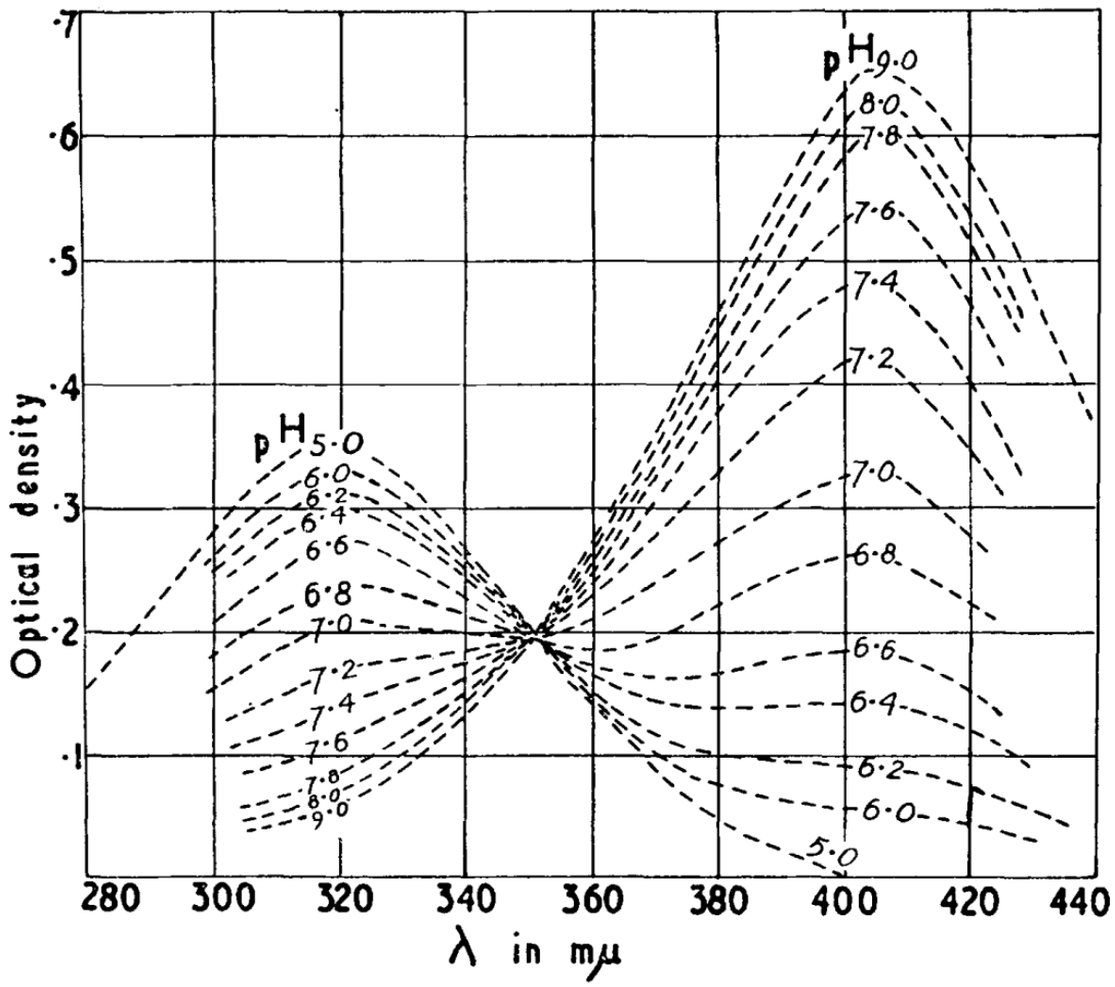


FIG. 1.—*p*-nitrophenol in water ; $3{\cdot}6 \times 10^{-5}$ mole/l.

Some points to be investigated

- Accuracy of the CpH-MD;
- Relation between electronic transition intensity and population ratio

Conclusions

- The results of the CpH-MD simulation seem to be consistent with the observed electronic spectrum;

- We could successfully reproduce the main aspects of the pNP electronic spectrum pH dependence for the most acid (pH = 5) and most basic (pH = 9) cases.

- However, the intermediate case (pH = 7) presented just a qualitative agreement, i.e., showed a correct change in the intensity, but the values are not in agreement with the experimental results.

Next Steps

- Search in the literature results about the population ratio of pNP in different pHs in order to validate our CpH-MD results;

- Try to establish a more accurate relation between intensity and population ration in order to construct a more realistic spectrum;

- Perform calculations in other intermediate pH cases (e.g., 6.6 and 7.4).