Electronic transitions of paranitrophenol in different pH conditions II

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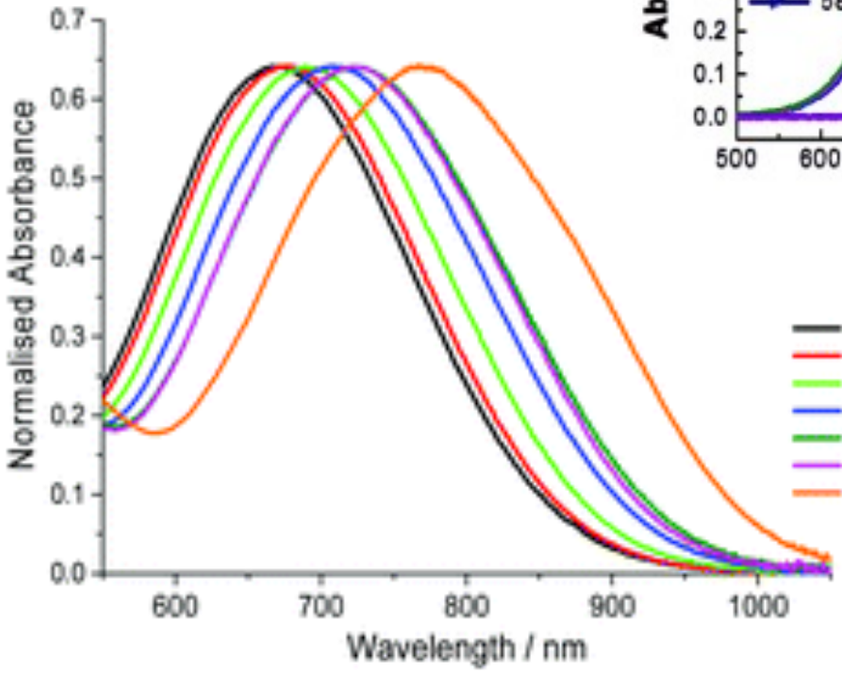
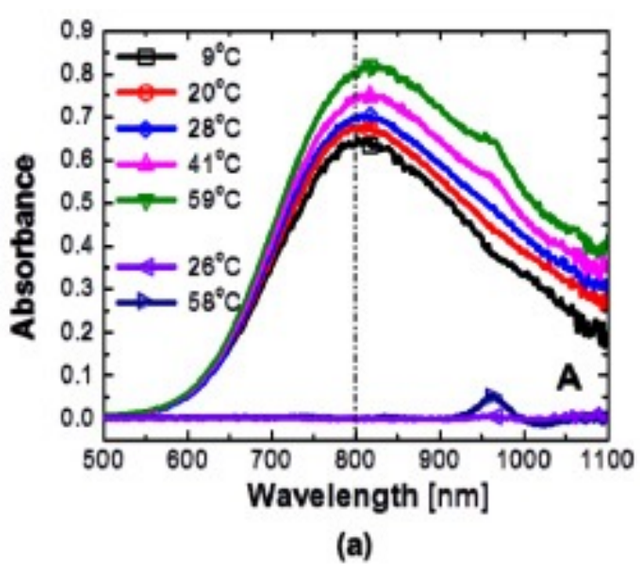
5th CREST-WS, Sep. 29th 2016

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.





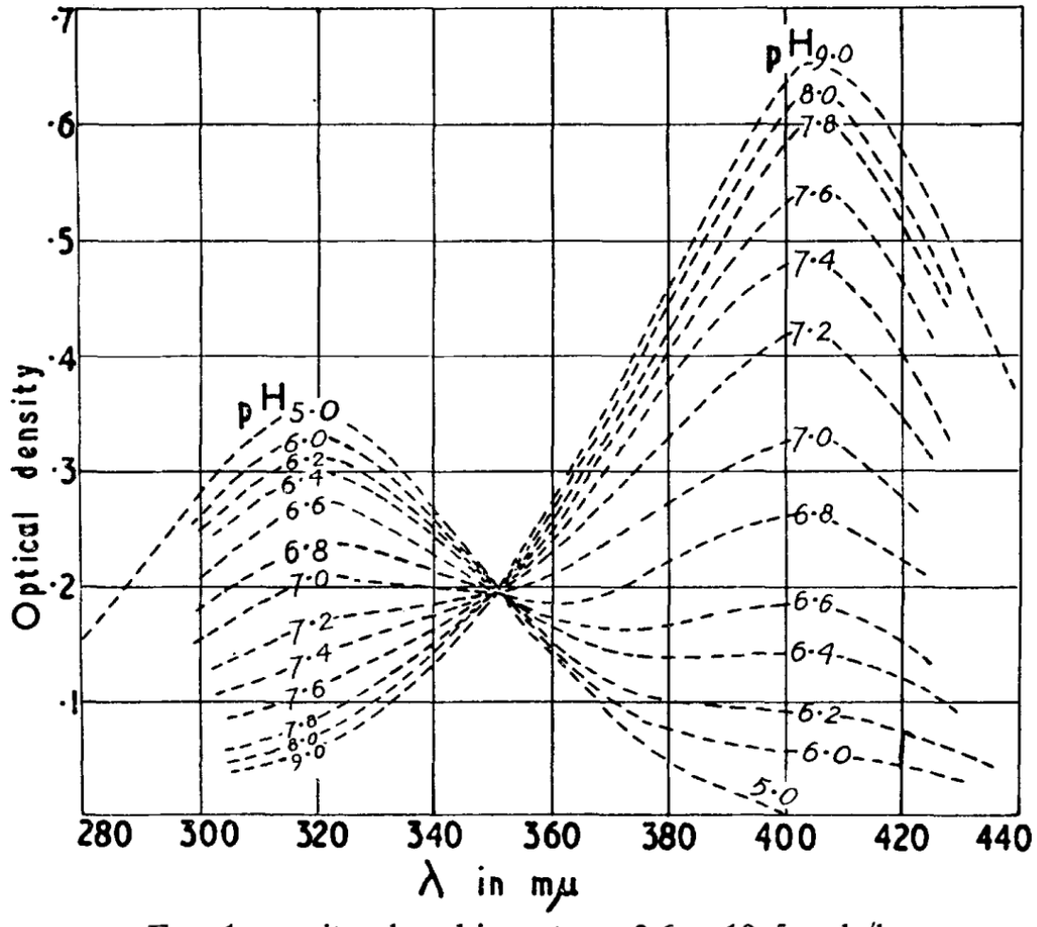
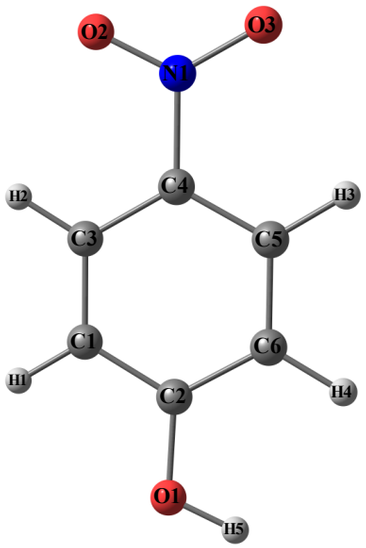


FIG. 1.—*p*-nitrophenol in water ; $3{\cdot}6 \times 10^{-5}$ mole/l.

Our Goal

3rd CREST-WS



Acid pH

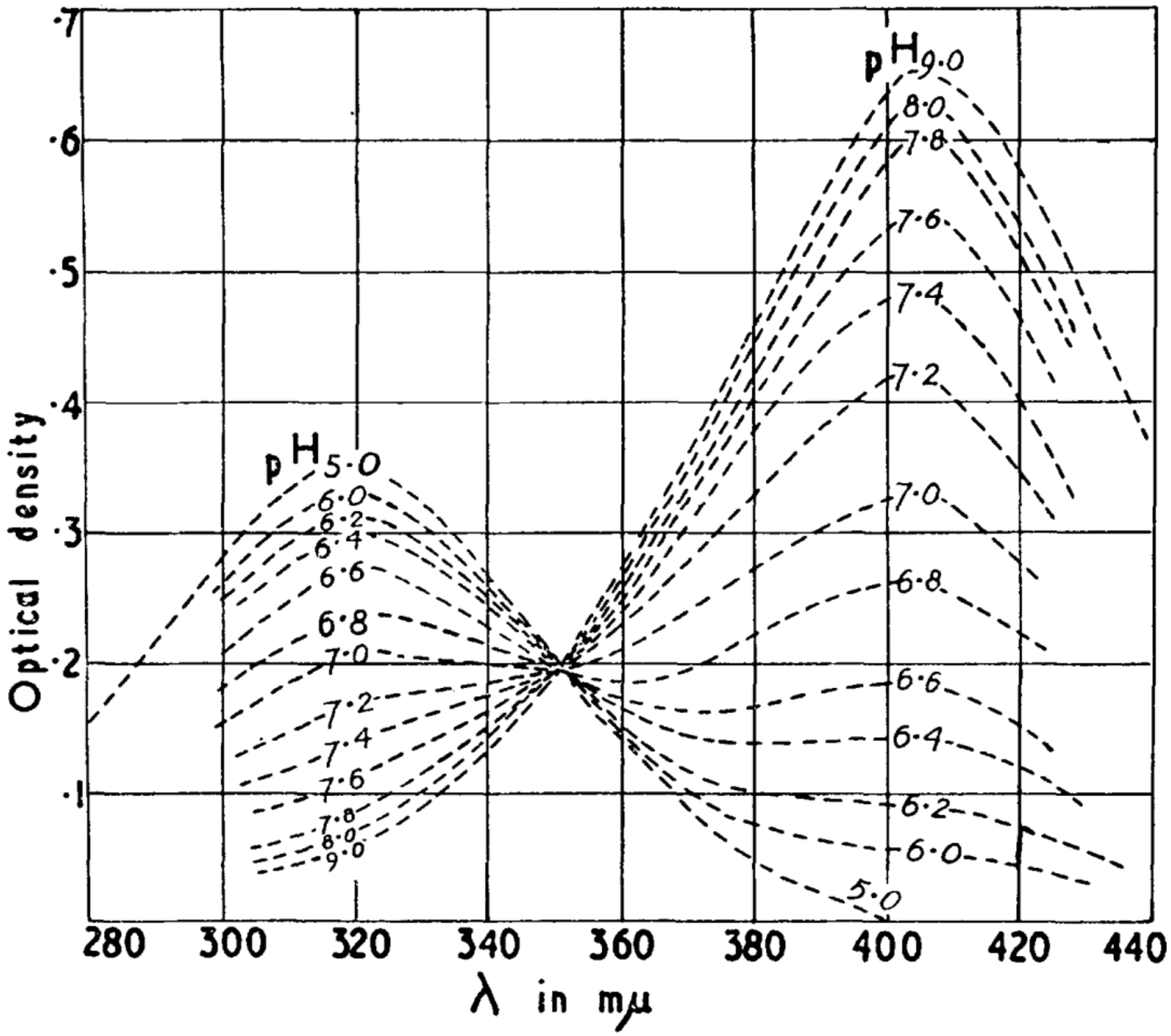
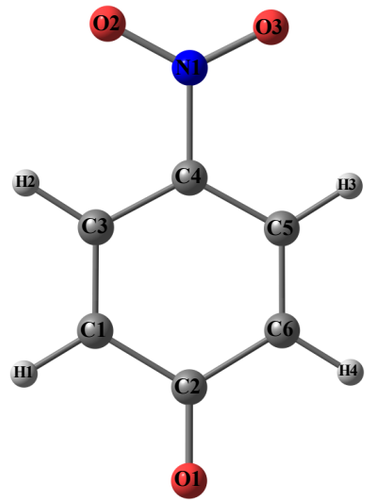


FIG. 1.—*p*-nitrophenol in water ; $3{\cdot}6 \times 10^{-5}$ mole/l.

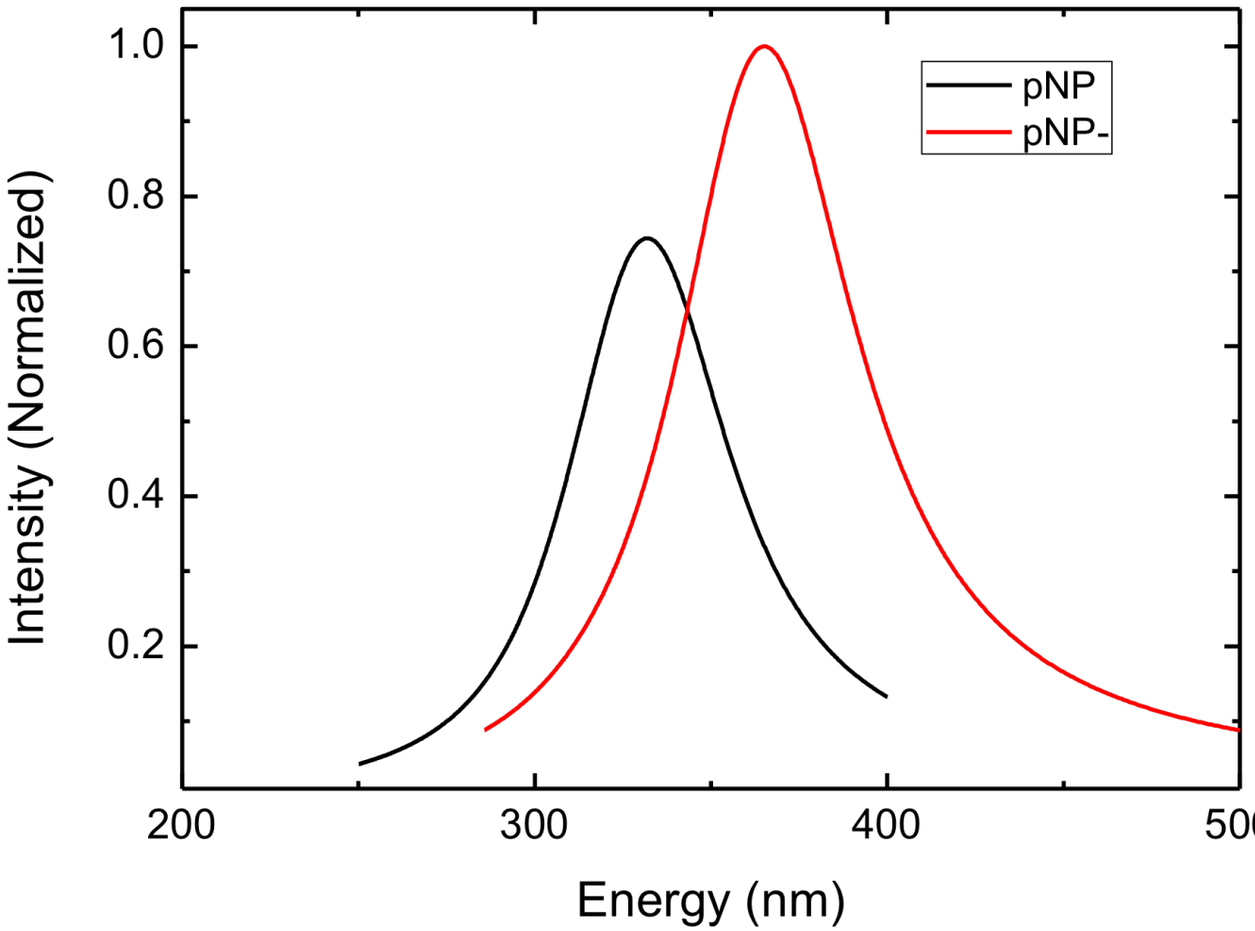


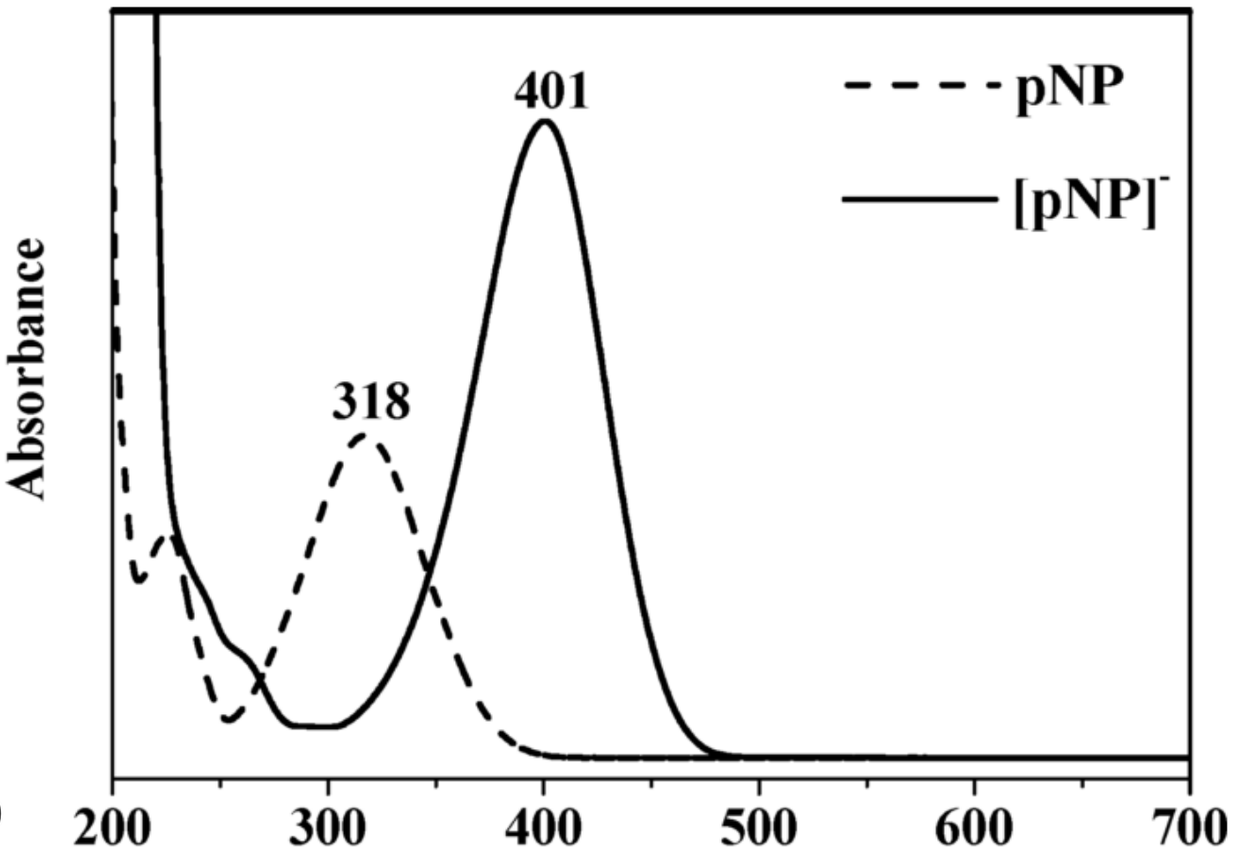
Basic pH

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

Theoretical Spectrum

3rd CREST-WS





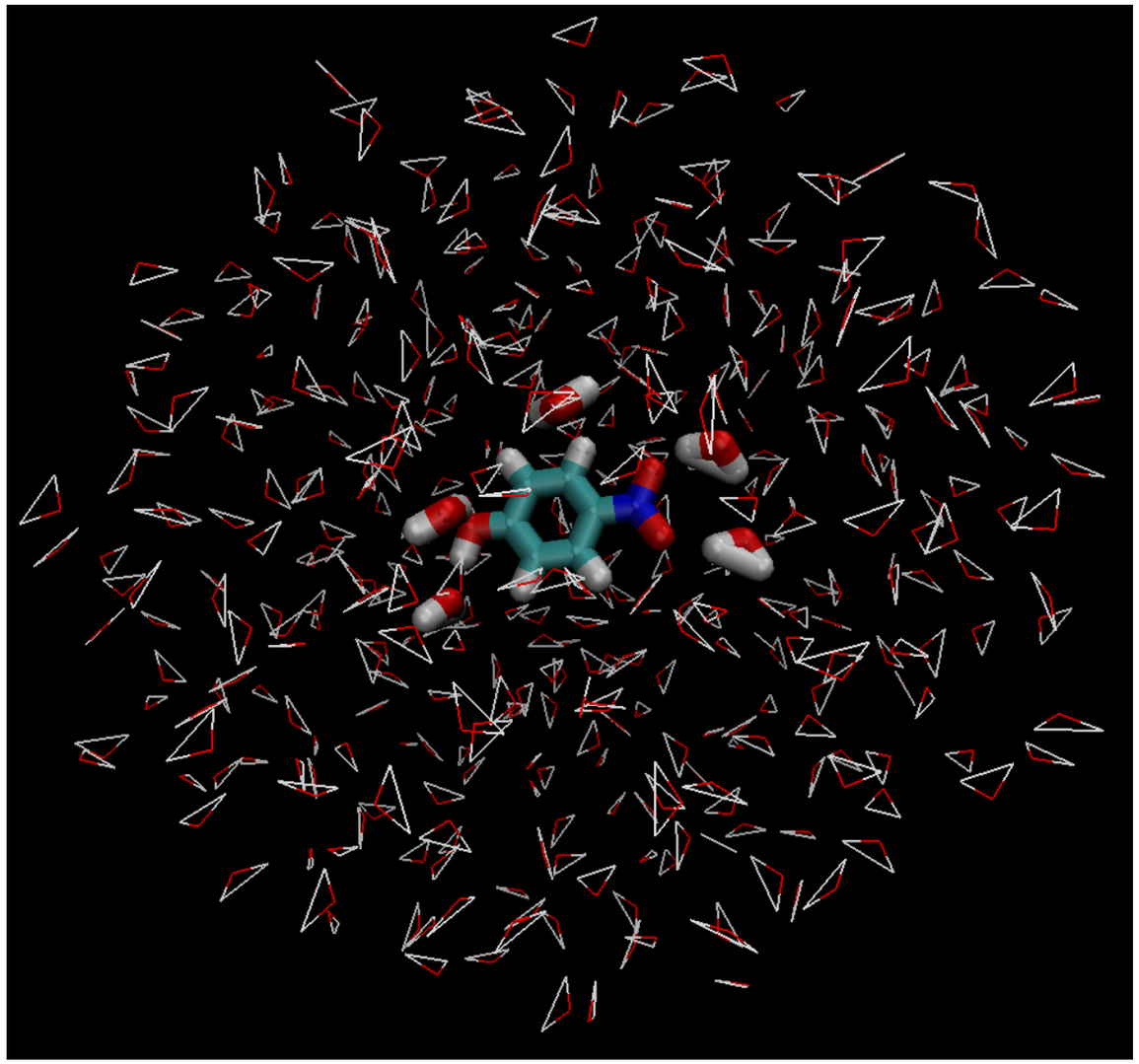
Left) The theoretical spectrum obtained from the electronic transitions convoluted by a Lorentzian function. The electronic transitions used in the convolution are also shown. Level of calculation: TD-B3LYP/aug-cc-PDVZ; Right) the experimental spectrum [Ando et al., *JPCA* **111** (2007) 7194].

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

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

$x_0 =$ center of the distribution

Configuration



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.

Today's Talk:

- Dependence of the results with the number of explicit water molecules;
- Convergence of the results obtained for transition energy values and oscillator strength;
- Currently status of CpH calculations.

of QM water molecules

Table: TD-B3LYP/aug-cc-pVDZ calculation for configurations randomly chosen. For each configuration, an increasing number of QM water molecule was considered. Red Color is used to indicate the same electronic transition in different calculations. Note that, despite the large increasing of water molecules, the change in the energy values is around 0.1 eV.

Configuration 1

pNP	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.61	0.000	3.59	0.000	3.59	0.027
2	3.67	0.434	3.66	0.412	3.60	0.363
3	3.85	0.015	3.85	0.021	3.82	0.026
4	4.44	0.000	4.41	0.000	4.35	0.000
5	4.66	0.001	4.53	0.003	4.37	0.001

pNP-	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.38	0.527	3.34	0.511	3.31	0.463
2	3.45	0.017	3.47	0.005	3.50	0.001
3	3.77	0.000	3.70	0.006	3.66	0.000
4	3.82	0.004	3.80	0.000	3.71	0.008
5	4.48	0.001	4.48	0.000	3.79	0.000

Configuration 26

pNP	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.54	0.000	3.54	0.001	3.56	0.001
2	3.74	0.412	3.72	0.420	3.67	0.382
3	3.87	0.016	3.88	0.015	3.81	0.012
4	4.33	0.001	4.19	0.007	3.92	0.002
5	4.44	0.001	4.34	0.001	4.00	0.001

pNP-	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.43	0.488	3.40	0.516	3.35	0.438
2	3.48	0.070	3.46	0.038	3.45	0.010
3	3.71	0.000	3.69	0.001	3.53	0.035
4	4.02	0.001	3.97	0.001	3.67	0.002
5	4.04	0.003	3.99	0.005	3.89	0.002

Configuration 52

pNP	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.57	0.005	3.57	0.006	3.30	0.000
2	3.67	0.442	3.66	0.454	3.42	0.000
3	3.80	0.007	3.81	0.008	3.54	0.007
4	4.20	0.002	4.19	0.002	3.64	0.407
5	4.53	0.004	4.51	0.003	3.78	0.011

pNP-	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.20	0.024	3.11	0.014	2.87	0.007
2	3.46	0.523	3.37	0.540	3.35	0.471
3	3.58	0.005	3.58	0.000	3.55	0.002
4	3.81	0.001	3.70	0.004	3.64	0.001
5	3.83	0.010	3.77	0.003	3.67	0.000

Configuration 99

pNP	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.51	0.000	3.51	0.000	3.52	0.000
2	3.83	0.422	3.82	0.416	3.70	0.334
3	3.94	0.022	3.94	0.024	3.86	0.014
4	4.38	0.000	4.29	0.001	4.30	0.001
5	4.78	0.002	4.71	0.002	4.36	0.002

pNP-	5 H2O		10 H2O		35 H2O	
Transition	eV	f	eV	f	eV	f
1	3.41	0.546	3.38	0.561	3.33	0.471
2	3.47	0.001	3.48	0.000	3.47	0.001
3	3.80	0.001	3.76	0.002	3.62	0.000
4	3.84	0.006	3.78	0.010	3.70	0.008
5	4.50	0.001	4.15	0.000	3.76	0.000

Convergence of the Values

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

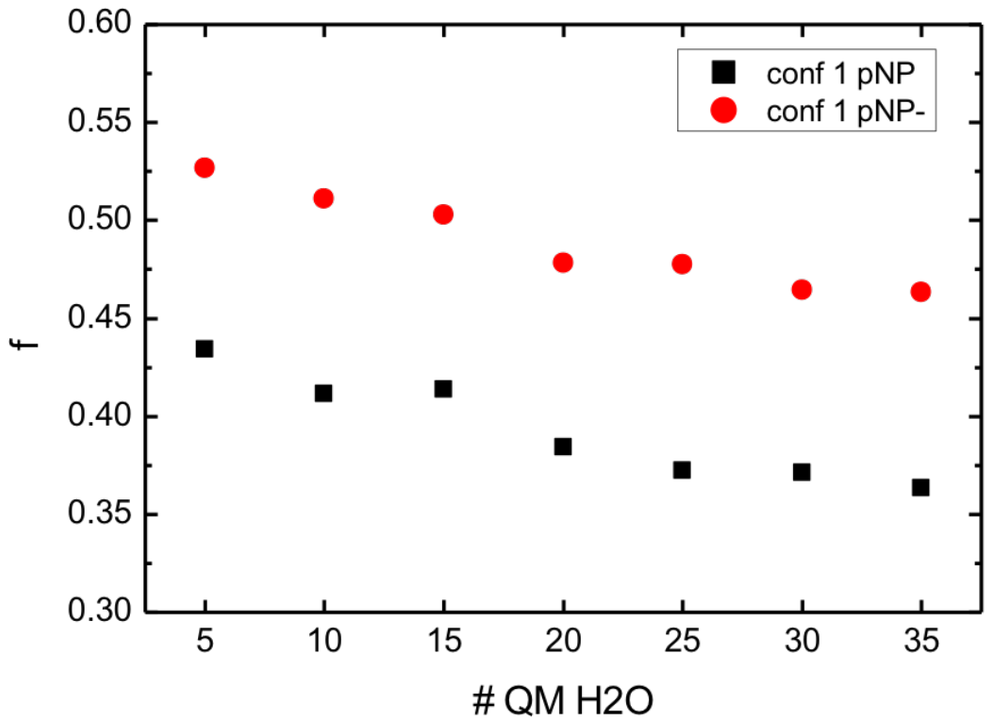
Configuration 52

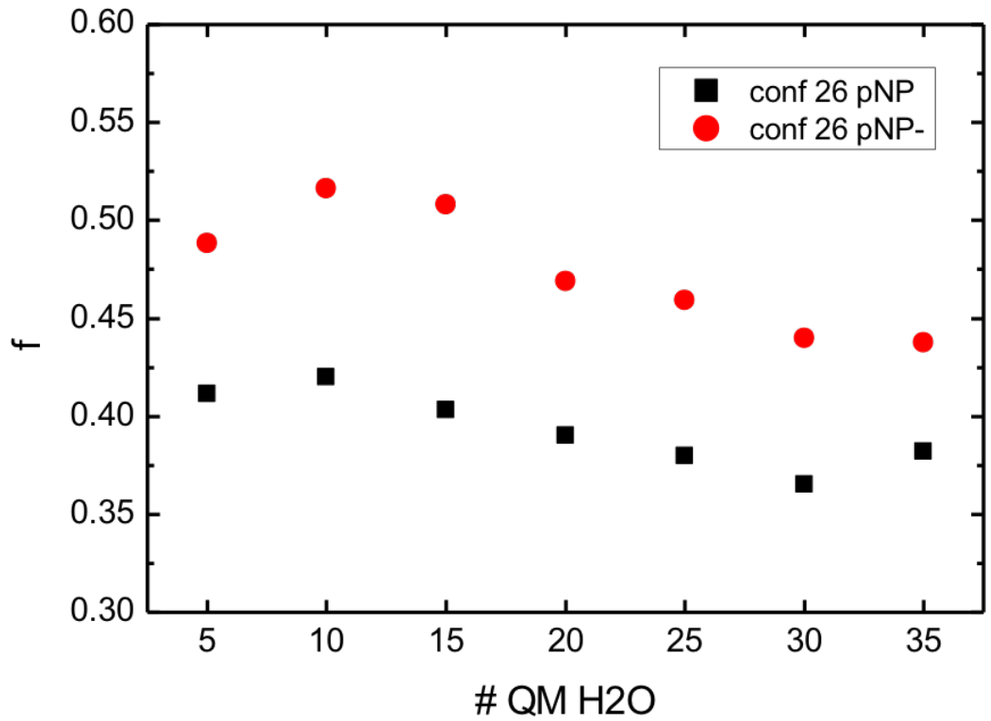
	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.67	0.442	3.46	0.523
10	3.66	0.454	3.37	0.540
15	3.66	0.390	3.37	0.509
20	3.65	0.317	3.36	0.487
25	3.65	0.411	3.36	0.475
30	3.65	*0.418*	3.36	0.466
35	3.64	0.407	3.35	0.471

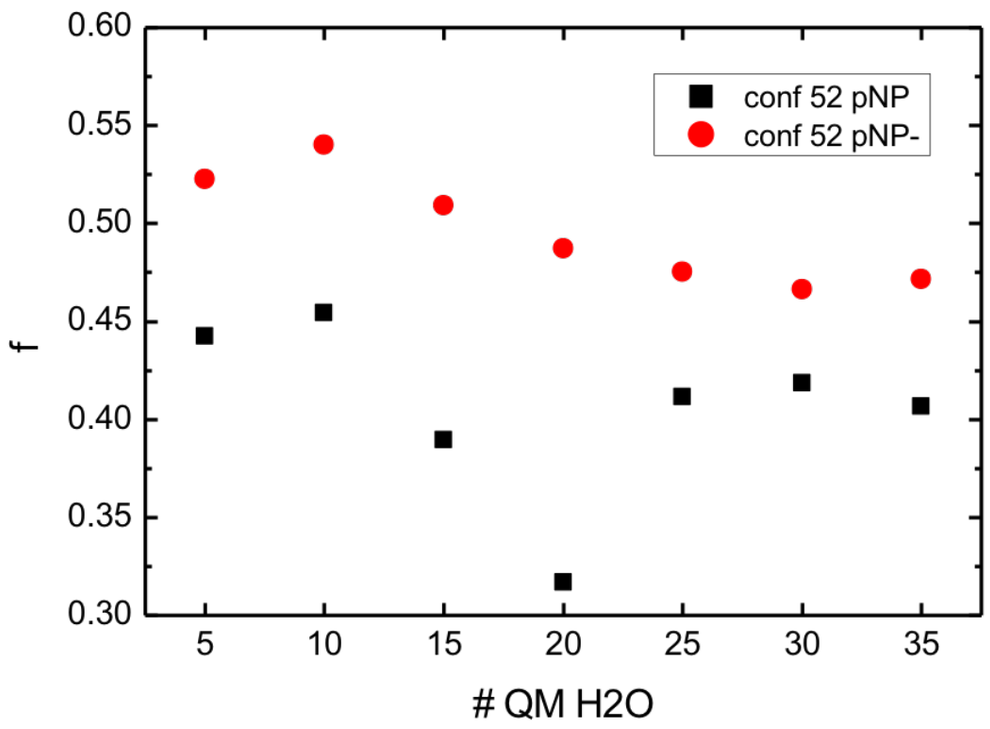
Configuration 99

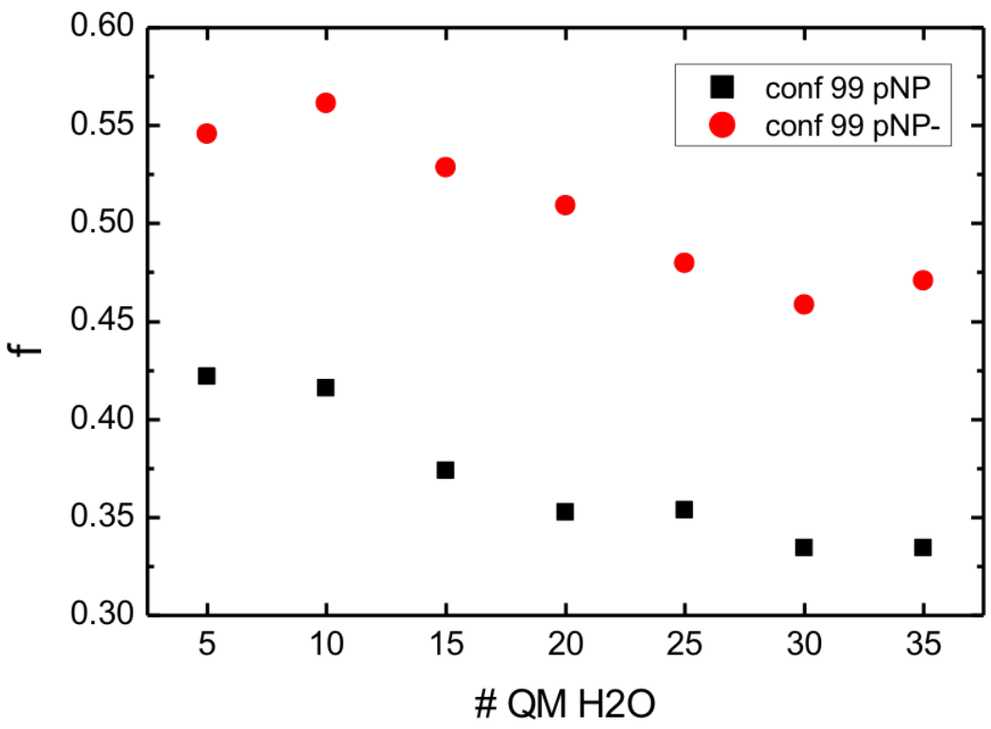
	pNP		pNP-	
# QM H2O	E(eV)	f	E(eV)	f
5	3.83	0.422	3.41	0.546
10	3.82	0.416	3.38	0.561
15	3.75	0.374	3.37	0.528
20	3.75	0.353	3.36	0.509
25	3.72	0.354	3.35	0.480
30	3.71	0.334	3.34	0.459
35	3.70	0.334	3.33	0.471

Oscillator Strength









Oscillator Strength

The oscillator strength f_{ij} of a transition from a lower state $|im_i>$ and an upper state $|jm_j>$ may be defined as:

$$f_{ij} = \frac{2}{3}\frac{m_e}{\hbar^2}\left(E_j - E_i\right)\sum_{\alpha=x,y,z}\left|\left\langle im_i \mid R_\alpha \mid jm_j \right\rangle\right|^2$$

where:

$$R_\alpha = \sum_{i=1}^{N} r_{i,\alpha}$$

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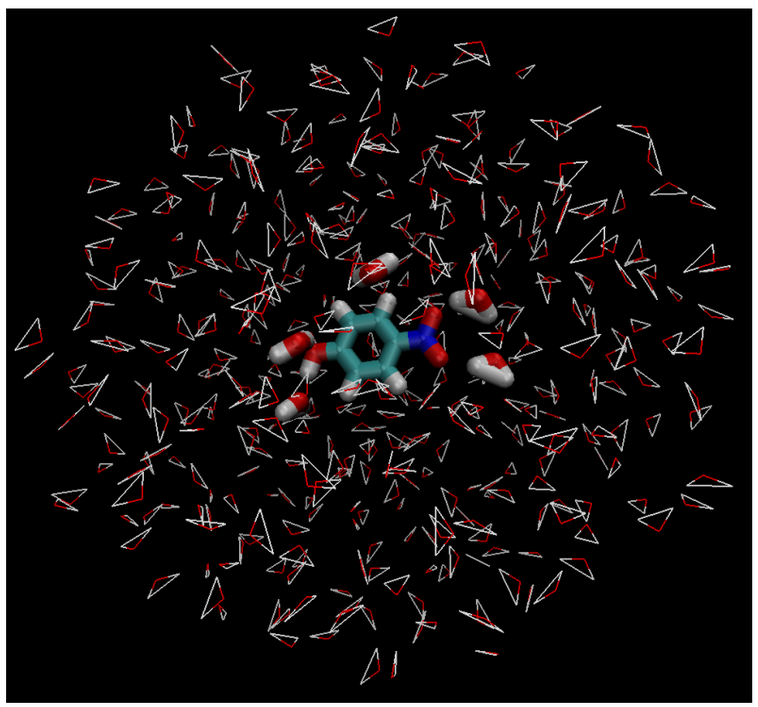
$$f_{ij} = \frac{2}{3}\frac{m_e}{\hbar^2 e^2}\left(E_j - E_i\right)\sum_{\alpha=x,y,z}\left|\left\langle im_i \left| eR_\alpha \right| jm_j \right\rangle\right|^2$$

μ_{ij} Transition Dipole Moment

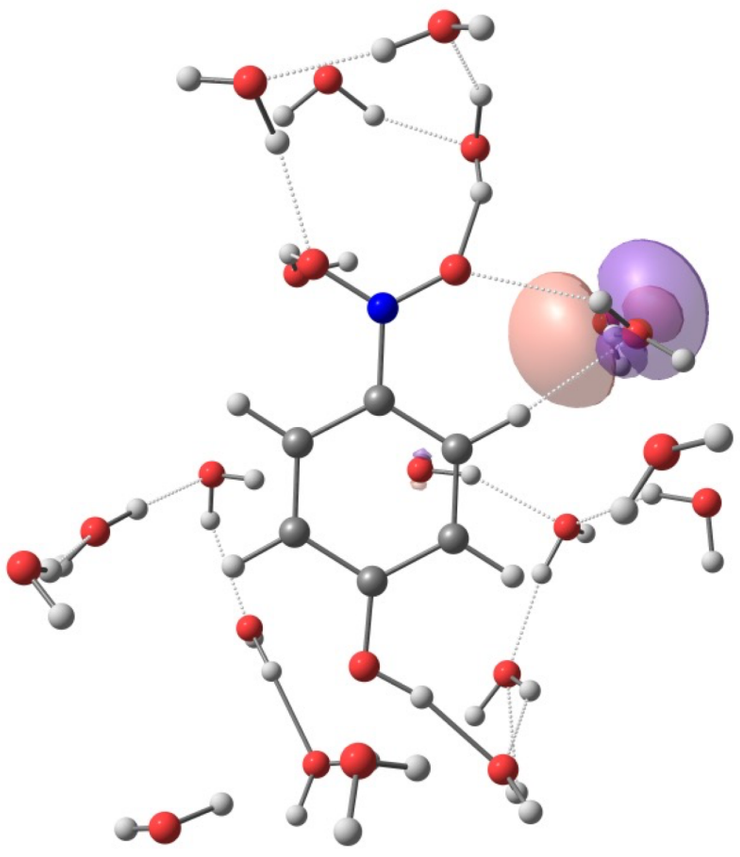
where:

$$R_\alpha = \sum_{i=1}^{N} r_{i,\alpha}$$

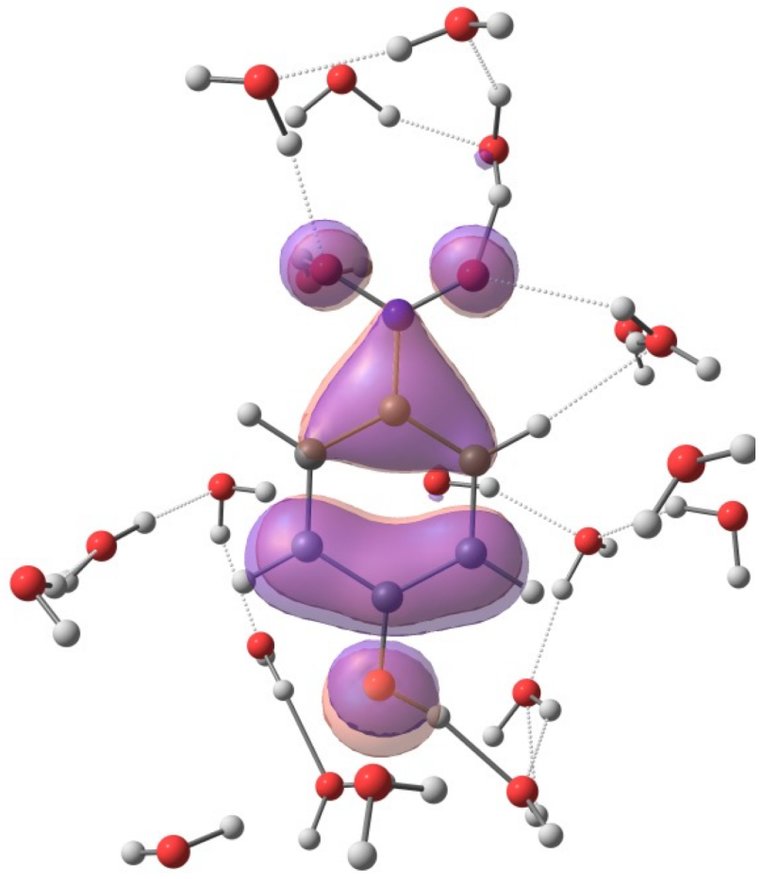


Oscillator Strength

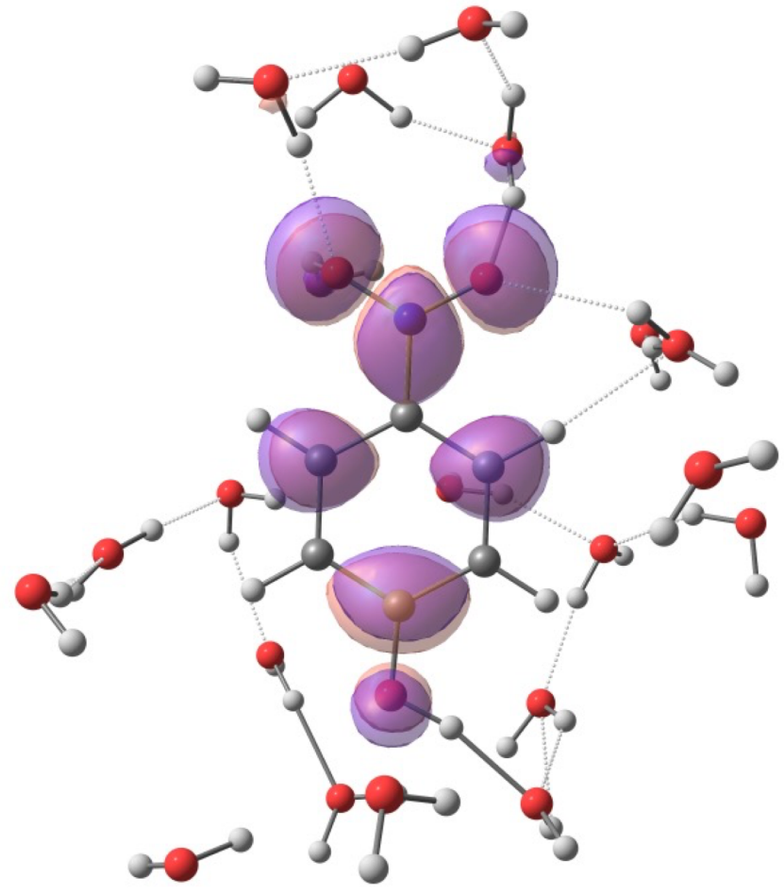
MO 135



MO 136 (HOMO)



MO 137 (LUMO)



```
Excited State   2:      Singlet-?Sym    3.6487 eV  339.80 nm  f=0.3169
    135 -> 137         -0.36544
    136 -> 137          0.59482

Excited State   3:      Singlet-?Sym    3.6742 eV  337.44 nm  f=0.1145
    135 -> 137          0.60398
    136 -> 137          0.35681
```

CpH Calculations

I have prepared files and executed a test calculation that resulted in a fail. The problem seems to be related to the description of a torsion angle. This is in some sense connected to the calculation artifacts that have to be used to prepare the topology file for the CpH-MD method. I am working with Kitamura-san to solve the problem and then resume the calculations.

Conclusions

- The inclusion of 5 QM water molecules seems to be enough to describe the electronic transitions;

- The energy values are converged;

- Oscillator Strength values are fluctuating with a little trend to decrease, as expected.

Next Steps

- I will try to solve the problem with the CpH input files and resume the calculations CpH-MD simulations;

- If we get consistent results, it will be possible to convolute the spectrum in different pH conditions.