

# EXCITED STATES PROPERTIES OF A SET OF POLYCYCLIC AROMATIC HYDROCARBONS: A TD-DFT ANALYSIS

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## Introduction

Understanding and characterization of the electronic excited states (ESs) of molecules is crucial for their industrial applications in dyeing and chemical colors, energy conversion, but also in biological and medical processes and organic molecular electronics [1,2]. Being short-lived, highly reactive and often coupled together, the electronically excited-states are computationally much more demanding than their ground state counterparts.

During the last decade, Time-Dependent Density Functional Theory (TD-DFT) has become an extremely popular method for modeling ESs, yet remaining much more affordable than the electron-correlated wave function approaches. It is now able to provide not only the vertical transition energies, but also geometries and other properties of the excited states, like: electronic densities, polarizabilities, vibronic structures of optical spectra, dipole moments, emission wavelengths, as well as radiative lifetimes of ESs [3-5].

The key objective of the present work is to address the performance of TD-DFT in the linear response regime for describing the electronically ESs of a set of four polycyclic aromatic hydrocarbon molecules. We were particularly interested in the vertical absorption and emission energies, geometries of the emitting structures, adiabatic energies, 0-0 transition energies and the radiative lifetimes.

For this purposes, extensive TD-DFT calculations have been carried out using two hybrid exchange-correlation (xc) functionals, B3LYP and PBE0, coupled to 6-31+G(2d,2p) and 6-311G(d,p) basis sets. Both, monomers and dimers have been considered in order to assess the influence of the molecular aggregation on the ES properties. To account for solvent effects we used both, the discrete and continuum models, as well as the solute-solvent complexes embedded in a continuum. Dispersion-correcting potentials [6] have been used for tackling the dispersion interactions responsible for the stability of the dimers of these molecules.

Calculated data are compared to reference experimental results where available or to previously reported computational data. Even though the ES are environmentally sensitive and the results depend significantly on the selected xc functional, however, using appropriate models and computational methods we were able to reproduce the existing experimental data within the experimental errors.

## Computational Details

Radiative lifetime and experimental lifetime or quantum efficiency can be obtained according to the following protocol. The spontaneous emission decay rate  $k_r$  from excited to ground state ( $S_0 \leftarrow S_1$ ) can be expressed as:

$$k_r = \frac{4 \Delta E^2}{3 c^3} \mu_{10}^2 \quad \text{where: } \Delta E \text{ - the } (S_0 \leftarrow S_1) \text{ transition energy}$$

$c$  - light speed  
 $\mu_{10}^2$  - transition dipole strength in atomic units

The radiative lifetime  $\tau_r$  can be obtained as:

$$\tau_r = \frac{1}{k_r}$$

Quantum yield as the radiative fraction of the total decay rate can be expressed as:

$$\Phi = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{exp}}{\tau_r}$$

Experimental lifetime affected by the nonradiative decay rate  $k_{nr}$  is:

$$\tau_{exp} = \tau_r * \Phi$$

## Results and Discussion

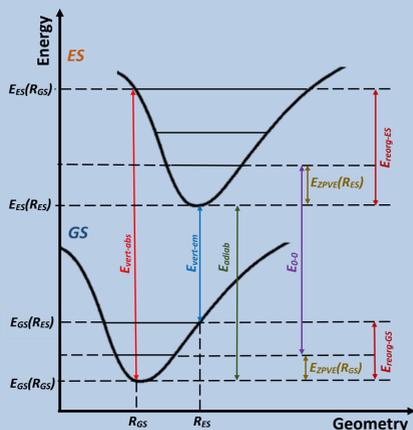


Fig. 1. Representation of the computed energies for ground and excited states.

Table 1. UV-Vis calculated energies (eV), wavelengths (nm), radiative and experimental lifetimes estimates (ns) at B3LYP/6-31+G(2d,2p)/PCM level of theory

	biphenyl	naphthalene	pyrene	trans-stilbene
(ZPVE)(GS) (eV)	5.04	4.09	5.76	5.96
(ZPVE)(ES) (eV)	4.92	3.97	5.65	5.88
$E_{reorg}$ (GS) (eV)	0.29	0.28	0.15	0.28
$E_{reorg}$ (ES) (eV)	0.31	0.28	0.15	0.29
$E_{ext}$ (eV)	4.58	4.44	3.69	3.80
$E_{adiabatic}$ (eV)	4.28	4.15	3.54	3.51
$E_{o-0}$ (eV)	4.16	4.03	3.42	3.44
$\lambda_{abs exp}$ (nm)	247	220, 266, 275	305, 319, 335	228, 293, 307
$\lambda_{abs calc}$ (nm)	208, 242, 270	200, 214, 279	230, 266, 336	242, 270, 326
$\lambda_{ems exp}$ (nm)	303, 313, 326	334, 322	390, 348, 381	345
$\lambda_{ems cal}$ (nm)	311	320	366	383
$\tau_r$ (ns)	13.66	99.02	32.82	17.40
$\tau_{exp}$ (ns)	2.46	22.77	10.50	0.87

Table 2. UV-Vis calculated and experimental wavelengths, orbitals and oscillator strength of biphenyl and trans-stilbene at different levels of theory

Method/molecule	biphenyl					
$\lambda_{exp}$	$\lambda$					248
	$\lambda$	189	206			247
PBE0	f	0.8176	0.1826			0.5744
mixed	orbital	H L+1	H-1 L+2	H-2 L	H L+2	H L
	%	36%	28%	26%	46%	98%
	$\lambda$			242	246	
PBE0	f			0.660	0.078	
dimer	orbital	H-1 L	H L+1	H-1 L	H L+1	
	%	52%	41%	41%	54%	
	$\lambda$	248	251	259	274	
B3LYP	f	0.387	0.122	0.045	0.015	
pseudo	orbital	H-1 L	H L+1	H-2 L	H L+2	H-1 L
dimer	%	19%	41%	18%	18%	64%
	$\lambda$	247	250	255	274	
PBE0	f	0.951	0.089	0.018		
dimer	orbital	H-1 L	H L+1	H-1 L	H L+1	H L
PCM	%	61%	36%	33%	58%	93%
	$\lambda$	244	249			
PBE0	f	0.553	0.085			
dimer	orbital	H-1 L+2	H-1 L	H L+1		
explicit	%	69%	20%	73%		
	$\lambda$	248	251	255		
PBE0	f	0.828	0.102	0.033		
dimer	orbital	H-1 L	H L+2	H L		
mixed	%	77%	69%	85%		

Method/molecule

Method/molecule	trans-stilbene					
$\lambda_{exp}$	$\lambda$					294
	$\lambda$	191	231			307
PBE0	f	0.174	0.208			0.973
orbital	H-3 L+2	H-1 L+1	H-1 L	H L+1		H L
	%	23%	34%	46%	50%	99%
	$\lambda$	240	270	315	315	
B3LYP	f	0.24	0.03	0.93		
pseudo	orbital	H-1 L	H L+1	H-1 L	H L+1	H L
dimer	%	53%	42%	43%	54%	99%
	$\lambda$	232	308	317	317	
PBE0	f	0.176		0.838		
explicit	orbital	H-1 L	H L+1			H L
	%	46%	50%	99%		99%
	$\lambda$	234	317	317	317	
PBE0	f	0.222		0.994		
mixed	orbital	H-1 L	H L+1			H L
	%	47%	50%	99%		99%
	$\lambda$			305	306	327
PBE0	f			0.672	0.704	0.036
dimer	orbital	H-1 L+1	H-1 L	H L+1	H L	
	%	74%	63%	56%	67%	
	$\lambda$	243	312	315	328	331
PBE0	f	0.015	0.755	0.849	0.075	0.114
dimer	orbital	H-2 L	H L+2	H-1 L+1	H-1 L	H L+1
PCM	%	22%	28%	85%	70%	67%

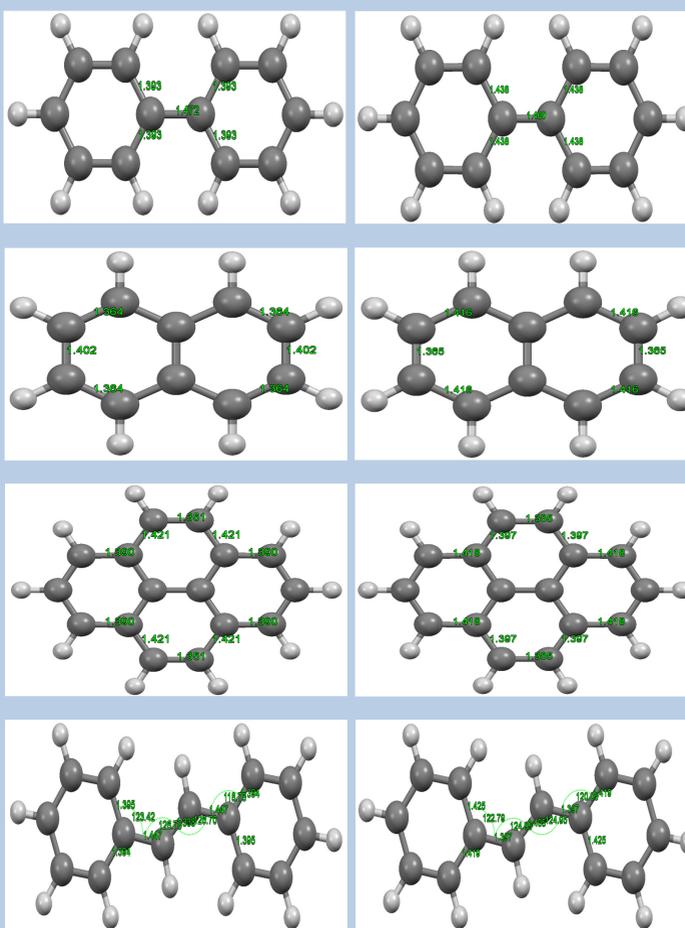


Fig. 2. Ground state (left column) and excited state (right column) structures of the investigated molecules (from top to bottom): biphenyl, naphthalene, pyrene and trans-stilbene at B3LYP/6-31+G(2d,2p) level of theory (solvent included)

Table 3. UV-Vis calculated and experimental wavelengths, orbitals and oscillator strength of naphthalene and pyrene at different levels of theory

Method/molecule	naphthalene					
$\lambda_{exp}$	$\lambda$					220
	$\lambda$	198	222	266	275	286
B3LYP	f	0.022	1.492			0.083
PCM	orbital	H-1 L+3	H-1 L	H L+1		H L
	%	96%	49%	48%		95%
	$\lambda$	205	213	218		286
B3LYP	f	0.178	1.110	0.014		0.053
explicit	orbital	H-1 L+1	H-1 L	H L+1	H L+5	H L
	%	90.08%	47.04%	46.06%	94.95%	94.15%
	$\lambda$			266	277	
PBE0	f			0.012	0.107	
dimer	orbital			H-1 L+1	H L	
	%			86%	89%	
	$\lambda$			275	300	
B3LYP	f			0.059	0.038	
pseudo	orbital			H-1 L+1	H L	
dimer	%			72%	85%	
	$\lambda$				286	
B3LYP	f				0.071	
dimer	orbital				H-1 L	
	%				96%	
	$\lambda$			276		
PBE0	f			0.074		
dimer	orbital			H L		
explicit	%			74%		
	$\lambda$				286	
B3LYP	f				0.053	
dimer	orbital				H-1 L	
explicit	%				94%	

Method/molecule

Method/molecule	pyrene					
$\lambda_{exp}$	$\lambda$					232
	$\lambda$	230	266	273	306	320
B3LYP	f	1.120	0.394			0.336
PCM	orbital	H L+1	H-1 L	H L+1		H L
pseudo	%	90%	56%	39%		93%
	$\lambda$			273		340
B3LYP	f			0.242		0.251
explicit	orbital			H-1 L	H L+1	H L
	%			52%	41%	90%
	$\lambda$	229	266			333
PBE0	f	0.980	0.364			0.381
mixed	orbital	H L+1	H-1 L	H L+1		H L
	%	90%	54%	42%		93%
	$\lambda$			268		336
B3LYP	f			0.337		0.383
pseudo	orbital			H-1 L	H L+1	H L
mixed	%			57%	38%	93%
	$\lambda$			275	286	325
PBE0	f			0.054	0.033	0.240
dimer	orbital	H-3 L	H-2 L	H L+2	H L+3	H-1 L
explicit	%	36%	19%	48%	19%	19%
	$\lambda$	288	300	323	334	334
B3LYP	f	0.101	0.015	0.044	0.247	
pseudo	orbital	H-3 L	H L+1	H L+2	H L+3	H L+1
dimer	%	35%	34%	47%	27%	28%
explicit	%			24%	29%	44%

## Conclusions

- The methods providing the best agreement between the experiment and theory depend on the system investigated and also on the excited state of interest. Thus, for naphthalene PBE0 offers the best results for the first excited state, while B3LYP is better in case of the second allowed excited state.
- Explicit solvation method is mandatory for reaching the chemical accuracy for the excitation energies.
- Pseudopotential inclusion for treating the dispersion interactions seems to be a benefit for calculating absorption energies. The improvement is observed even for monomers.
- Dimer models provide results similar to those obtained on monomers.
- The excited state geometries of the investigated compounds points to an elongation of the molecules along the long axis as a results of excitation. Their planarity is preserved.

## References

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