Understanding and characterization of the electronic excited states (ESs) of molecules is crucial for their industrial applications in doping 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 possible 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 wavelengths, as well as radiative lifetimes of ESs [3-5].

The radiative lifetime \( \tau_{\text{r}} \) and experimental lifetime or quantum efficiency can be obtained according to the following protocol: The spontaneous emission decay rate \( k_{\text{sp}} \), excited to ground state (\( N_{\text{GS}} \)), can be expressed as:

\[
k_{\text{sp}} = \frac{4 \pi f^2}{3} \mu^2 \tau_{\text{r}}
\]

where \( f \) - the (4S-1E) transition energy \( \lambda \), \( i \) - light speed \( c \) \( \lambda \), transition dipole strength in atomic units

The radiative lifetime \( \tau_{\text{r}} \) can be obtained as:

\[
\tau_{\text{r}} = \frac{1}{k_{\text{sp}}}
\]

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

\[
\Phi = \frac{k_{\text{exp}}}{k_{\text{sp}}} = \frac{\tau_{\text{exp}}}{\tau_{\text{r}}}
\]

Experimental lifetime affected by the nonradiative decay rate \( k_{\text{n}} \),

\[
\tau_{\text{exp}} = \tau_{\text{r}} \Phi
\]

Computational Details

Radiative lifetime and experimental lifetime or quantum efficiency can be obtained according to the following protocol: The spontaneous emission decay rate \( k_{\text{sp}} \), excited to ground state (\( N_{\text{GS}} \)), can be expressed as:

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Experimental lifetime affected by the nonradiative decay rate \( k_{\text{n}} \),

\[
\tau_{\text{exp}} = \tau_{\text{r}} \Phi
\]

Results and Discussion

![Fig. 1. Representation of the computed energies for ground and excited states.](image)

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

<table>
<thead>
<tr>
<th>Method/ molecule</th>
<th>trans-stilbene</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(GS) (eV)</td>
<td>4.02</td>
<td>4.67</td>
</tr>
<tr>
<td>( \lambda_{\text{GS}} ) (nm)</td>
<td>354</td>
<td>326</td>
</tr>
<tr>
<td>E(ES) (eV)</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>( \lambda_{\text{ES}} ) (nm)</td>
<td>482</td>
<td>462</td>
</tr>
<tr>
<td>( \Phi_{\text{exp}} ) (ns)</td>
<td>17.40</td>
<td>15.50</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Method/ molecule</th>
<th>biphenyl</th>
<th>trans-stilbene</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(GS) (eV)</td>
<td>4.02</td>
<td>4.02</td>
<td>4.67</td>
</tr>
<tr>
<td>( \lambda_{\text{GS}} ) (nm)</td>
<td>354</td>
<td>354</td>
<td>326</td>
</tr>
<tr>
<td>E(ES) (eV)</td>
<td>0.41</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>( \lambda_{\text{ES}} ) (nm)</td>
<td>482</td>
<td>482</td>
<td>462</td>
</tr>
<tr>
<td>( \Phi_{\text{exp}} ) (ns)</td>
<td>17.40</td>
<td>17.40</td>
<td>15.50</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Method/ molecule</th>
<th>pyrene</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(GS) (eV)</td>
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<td>5.04</td>
</tr>
<tr>
<td>( \lambda_{\text{GS}} ) (nm)</td>
<td>404</td>
<td>404</td>
</tr>
<tr>
<td>E(ES) (eV)</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>( \lambda_{\text{ES}} ) (nm)</td>
<td>390</td>
<td>390</td>
</tr>
<tr>
<td>( \Phi_{\text{exp}} ) (ns)</td>
<td>13.66</td>
<td>13.66</td>
</tr>
</tbody>
</table>

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 B3PY offers the best results for the first excited state, while B3PY is better in case of the second allowed excited state.
- Explicit solvent inclusion for describing the dispersion interactions seems to be a beneficial tool for calculating absorption energies. The improvement is observed even for pyrene.
- 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


Acknowledgments

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