FROM THE GROUND STATE TO THE EXCITED STATES OF POLYCYCLIC AROMATIC HYDROCARBONS WITH DFT & TD-DFT

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Polycyclic Aromatic Hydrocarbons, also known as PAHs are organic compounds constituting solely of carbon and hydrogen atoms and forming multiple aromatic rings, with a network of electrons delocalizing over the whole molecule. Those molecules are very dangerous to the environment and are known to be carcinogens, making them very interesting cases to be studied [1]. While a lot of research work has already been carried out on their physical properties, not much is known about the fluorescence of these compounds. Some of them are known to emit a dual fluorescence, a property of PAHs which has not been studied for a long time [2].

In order to understand the mechanism, we decided to study several PAHs, namely, pyrene, perylene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*g,h,i*]perylene and coronene [3]. Experimentally, those molecules were dissolved in toluene and their absorbance spectra and fluorescence spectra were recorded. Theoretically, we proceeded through several steps. The DFT and TD-DFT calculations were performed with Gaussian16. First of all, a benchmark with different functionals and bases was done to see which model corresponds best to the experimental results.

Different parameters of the optimized molecules at the fundamental state and the excited states were closely studied. To go deeper in the analysis, it was interesting to choose parameters which can be used as reactional coordinates to enable us to see how the optimized geometry at the first and second excited states vary with respect to the optimized geometry at the ground state. A form factor, generated from the surface and the perimeter, was calculated. In addition, an ellipse was fitted around the various PAHs chosen and the surface of this ellipse was evaluated. These two parameters were plotted separately with respect to the energy of the molecules to witness any dissimilarities. In parallel, the bond lengths of all the molecules at the three states were computed and compared to examine the geometric changes in the molecules when they change state and if this change is similar in all the cases.

The association of the spectroscopic techniques, the DFT calculations as well as all the parameters specific to the molecules can help us to understand better the processes occurring in the excited states and from there, the dual fluorescence of some PAHs can be explained.

[1] K. Ravindra, R. Sokhi, et R. Vangrieken, Atmospheric Environment, avr. **2008** vol. 42, no 13, p. 2895-2921.
[2] R. Waris et al., Applied Spectroscopy, **1988** vol. 42, no 8, p. 1525-1531.
[3] S. A. Tucker, J. William E. Acree, J. Kenneth W. Street, et J. C. Fetzer, Applied Spectroscopy, **1989** vol. 43, no 1, p. 162-164.