Accurate Structures of PAHs and Aza-derivatives Using Anharmonic DFT Calculations

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Aromaticity is known as one of the most important concept in physical chemistry, and some methods to determine the aromatic character of the compounds are based on molecular structures. As the rotational constants of a molecule are directly linked to its equilibrium geometry, we used high resolution spectroscopic data to calibrate density functional theory (DFT) calculations at the anharmonic level. In particular, the rotational parameters, rather than the vibrational frequencies, are used as reference data to validate the theoretical approach.

In a first step, the dependence of the theoretical results on the functional and basis set has been tested in the case of naphthalene [1]. Then, results from the optimal method have been compared to the available data of 39 vibrational states of 18 Polycyclic Aromatic Hydrocarbons (PAHs) and aza-derivatives. It resulted in a mean absolute error (MAE) of the experimental minus calculated values (e-c) of less than 2 MHz. When correcting the rotational constants of the excited vibrational states from the relative error on the ground vibrational state values, the MAE of the (e-c) decreased to about 200 kHz. To quantify the influence of the rotational constants' deviations on the molecular equilibrium structures, the geometry of azulene corresponding to corrected rotational constants has been determined. Its comparison to the uncorrected structure led to an estimated uncertainty of 0.22 pm on bonds lengths and 0.11° on angles.

Therefore, this method appears to be able to calculate excellent equilibrium geometries for the PAHs family of compounds and should permit to accurately simulate the rotational structure of their infrared bands.

[1] O. Pirali, M. Goubet, T. R. Huet, R. Georges, P. Soulard, P. Asselin, J. Courbe, P. Roy and M. Vervloet, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10141.