

O–H·· π interactions between aromatic hydrocarbons and small water aggregates

Authors: Murillo H. Queiroz, Tiago V. Alves, Roberto Rivelino

Address: Departamento de Físico-Química, Instituto de Química, UFBA. Instituto de Física, UFBA

Abstract: Studies of weakly bound complexes have been of great interest from the fundamental point of view as well as from applications in the fields of materials [1] and astrochemistry [2]. Usually, complexes formed between polycyclic aromatic hydrocarbons (PAH's) and water aggregates have been proposed as agents in the mechanism of ice formation in interstellar environments [2]. However, in theoretical studies of complexes formed between PAH's and water aggregates, sophisticated electronic structure calculations can be computationally demanding. Thus, the use of low computational cost methods is required, but considering the compromise in the calculation accuracy for the description of the system. In this communication, we present a theoretical study within this context. Firstly, we carried a screening of the O–H·· π interaction between benzene water system with different density functionals [3]. For that, we employ hybrid meta-DFT (HMDFT) methods and functionals containing empirical dispersion corrections (DFT-D), combined with a proper basis set (containing diffuse and polarization functions) and we compared our results to second order Møller-Plesset perturbation theory and quadratic configuration interaction, restricted to single and double substitutions in order to obtain a reliable methodology for systems beyond the 1:1 complex. In this sense, we studied the intermolecular interactions formed between an acenaphthylene molecule and the water trimer. This system works as an interesting model for PAH's interacting with water clusters. From our calculations, we evaluated the more energetically favorable configuration of the water trimer with respect to the aromatic ring. Hence, we have obtained that the ddd configuration of the water trimer appears to be the possible structure in this case. After the vibrational analysis, we identify the modes of the aromatic molecule also present in the complex to evaluate the impact of this type of microhydration on the infrared spectrum. We also identify relevant vibrational modes with higher Raman activity and determine their depolarization rates. Our results suggest that the water trimer can anchor to the acenaphthylene molecule in a configuration different from the conventional (udd or ddu) and that the stability of the complex can be interpreted as a balance between the O–H··O and O–H·· π interactions

Key-words: Hydrogen Bond, van der Waals interactions, density-functionals.

Support: CNPq, CAPES and INCT-FCx

References:

- [1] C. Calero, G. Franzese, *J. Mol. Liq* 317, 114027 (2020).
- [2] A. K. Lemmens, S. Gruet, A. L. Steber, J. Antony, S. Grimme, M. Schnell, A. M. Rijs, *Phys. Chem. Chem. Phys* 21, 3414 (2019)
- [3] M. H. Queiroz, T. V. Alves, R. Rivelino, *Comput. Theor. Chem* 1206, 113464 (2021).