Theoretical studies of large molecular systems of astrophysical interest: static and dynamic properties

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Exploring the potential energy surface (PES) of large molecular aggregates and unraveling their dynamic evolution under energy input have long been major challenges in theoretical chemistry. To address these issues, efficient algorithms based on Monte Carlo (MC) and molecular dynamics (MD) have been developed and are now routinely combined with electronic structure methods that provide a favorable balance between computational cost and accuracy. Among these, the Density Functional Tight Binding (DFTB) method has emerged as a particularly attractive approach [1].

Using examples from recent studies of astrophysical relevance, we will illustrate:

(i) The structural, energetic, and spectral information accessible for complex systems such as neutral and charged polycyclic aromatic hydrocarbon (PAH)-water aggregates, as well as PAHs complexed with metal atoms. These results are obtained using a multistep approach that combines parallel tempering Monte Carlo (PTMC) with DFTB, followed by local optimization at the density functional theory (DFT) level [2,3].

(ii) How MD/DFTB simulations complement experimental investigations in elucidating unimolecular dissociation mechanisms of large carbon-based molecules such as PAHs [4,5], collision-induced dissociation of protonated PAH-water aggregates, and formation of silver-hydrocarbon complexes in a plasma reactor.

The advantages and limitations of the adopted methodologies will also be discussed.

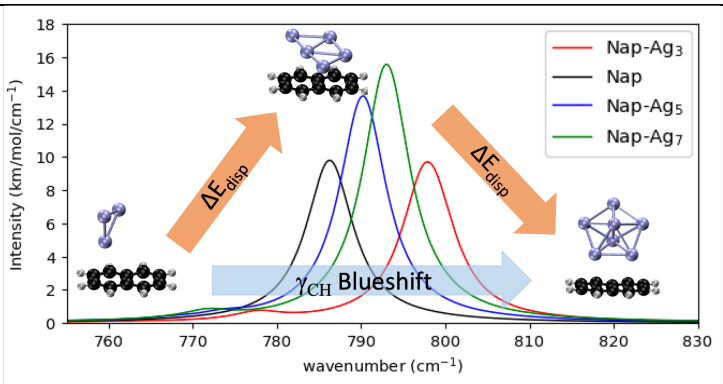

Figure 1 : adapted from [3]. Influence of the coordination of Ag_n (n=3,5,7) on the out-of-plane CH mode of naphthalene.

[1] F. Spiegelman et al., *Adv. Phys. X*, **5 :1**, 1710252 (2021)
[2] H. Leboucher et al., *J. Chem. Phys.*, **158**, 114308 (2023), *ACS Earth Space Chem.*, in revision
[3] R. Dahmani et al., *J. Phys. Chem. A,* **129**, 3829 (2025)
[4] D. Kumar-Singh et al., *Astron. Astrophys.,* **704**, A345 (2025)
[5] A. I. Lozano et al., *ACS Earth Space Chem.*, **9,** 2017 (2025)