

# A quantum chemist's view of fragmentation

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In this presentation, we will make an introductory review on the theoretical description of the dissociation of large molecules of astrophysical interest. We will present the astrophysical context, the computational approaches, and the information that can be retrieved from the simulations.

The use of wavefunction approaches to explicitly describe the electronic structure of large molecules is most of the time ruled out for question of computational cost. As interesting alternatives, methods based on Density Functional Theory (DFT) are now widely used to describe the electronic structure of large carbonaceous molecules. For instance, in the astrophysical context, many studies were achieved to obtain structural, energetic and spectroscopic properties of PAH-derived species at thermodynamic equilibrium [1]. On the opposite, the description of out-of-equilibrium dissociation processes of large molecules using quantum approaches remains a theoretical challenge [2].

We will focus in this review on the statistical modeling of dissociation *ie* at long timescale, after fast internal conversion and intramolecular vibrational redistribution. Modeling dissociation assuming that reaction intermediates and products are in their ground electronic state can be achieved using DFT calculations followed by RRKM modeling [3]. Alternatively, extensive on-the-fly molecular dynamics using the efficient Density Functional based Tight Binding (DFTB) scheme to describe the electronic structure, allow to probe the dissociation dynamics within the one nanosecond timescale without a pre-knowledge of the dissociation paths [4]. These two approaches are complementary and allow to gain insights into dissociation mechanisms, branching ratios, thermodynamics and kinetics. Given the assumptions and approximations of the approaches, comparison with experimental data is mandatory for benchmarking. Examples of results obtained for polycyclic aromatic hydrocarbons (PAHs) will be presented [5-7]. The advantages and drawbacks of the approaches will be emphasized.

Among the challenges for the future that we will present, we may mention the description of electronic excited states in the dissociation paths and kinetics.

## References

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