Theoretical and computational modeling of chemical reactions: from gas to solution phase

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In this seminar, I will show how it is possible to model and understand ground-state chemical reactivity by molecular simulations in different physical conditions. A common and unified approach is the use of molecular dynamics in conjunction with electronic structure calculations within the Born-Oppenheimer approximation.

First, we were able to describe and predicts mechanisms relevant to unimolecular fragmentation with applications in mass spectrometry: the use of an ensemble of reactive trajectories was at the basis to obtain qualitative information (nature of reaction products and corresponding mechanisms) but also quantitative kinetic data (rate constants and activation energies). This was done by coupling molecular simulations with kinetic theories and graph-theory base methods for data analysis.

We will then discuss how nowadays chemical reactions in solution can be understood using molecular simulations including explicit solvation: as an example we studied how pressure effects in Diels-Alder reactions can be modeled via QM/MM simulations. The explicit solute-solvent interaction can provide a microscopic understanding of the *endo:exo* diastereoselectivity under high-pressure conditions.

References:

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