

Theoretical & Computational Chemistry

Matthias Lein

Nina Leeb, Kevin Tsuno and Zhikang Weng

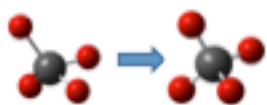
The Computational Chemistry Group at SCPS uses computer simulations of molecular materials to predict structure, reactivity and spectroscopic parameters of known and currently unknown compounds. These simulations stretch all the way from empirical classical models to highly accurate quantum mechanical descriptions of the electronic structure

$$\hat{H} = - \sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^n \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_{i=1}^n \sum_A \frac{Z_A}{r_{iA}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} + \sum_A \sum_{B>A}^N \frac{Z_A Z_B}{r_{AB}}$$

Structural Determination

In chemistry it is often important to know the physical structure and shape of the molecule or system of interest.

Computational chemistry allows us to determine this by finding minima in the potential energy surface associated with your system. This shifts the atomic positions to that of the lowest energy.

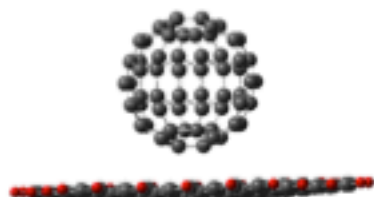


This lets us get a lot of useful structural information about a molecule such as bond lengths and angles.

This method can also be used for a system of interacting molecules to determine the geometry of how these interactions occur.

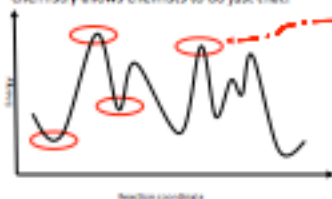
For example:

This C_{60} molecule coordinated with a circumcircumcoronene molecule through Van der Waals interactions in a pseudo C_{6v} arrangement.



Reactivity

Reaction mechanism, a wonderful scheme that depicts the chemistry occurring in a reaction at molecular level. But how does one identify the mechanism of a reaction? Well, computational chemistry allows chemists to do just that!

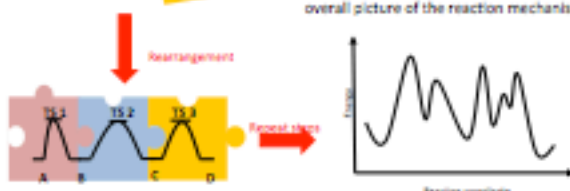


Identification of **stationary points** along the reaction coordinate; intermediates and transition states (TS). There is no way of isolating TS in an experimental work and it becomes important to utilise computational chemistry to extract more information on the mechanism from the TS structures.

The fun doesn't end there! The TS would have an imaginary vibrational mode which shows how the structure changes from reactant to product. By going energetically downhill to either side of the TS's potential energy surface (PES), we are able to locate the two minima, which are the reactant and product.



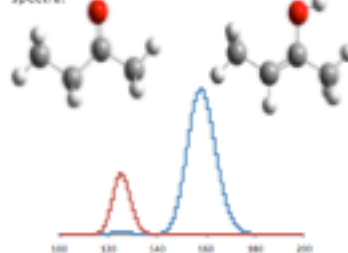
After locating TS structures and tracing the intrinsic reaction coordinate to the corresponding reactants and products, we put together the pieces of puzzles to get the overall picture of the reaction mechanism!



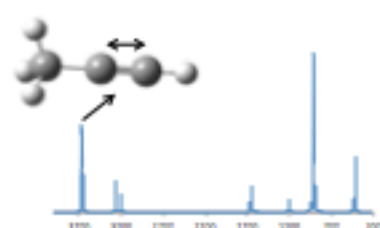
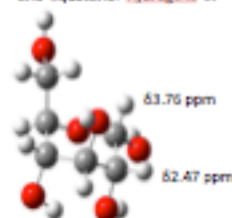
Spectroscopic Characterization

Spectroscopic techniques are widely used to determine structure and aid in characterization of compounds. Computational chemistry can help here too!

Calculators on tautomers can give an indication of how each affects your experimentally obtained UV spectra.



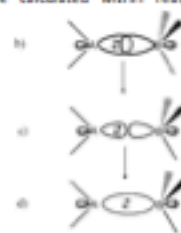
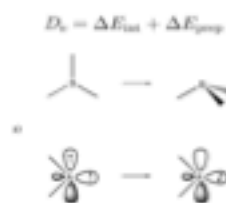
NMR calculations can be used to aid in assigning shifts in difficult cases, for example distinguishing between axial and equatorial hydrogens in



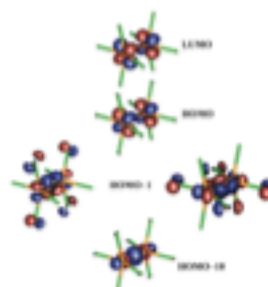
Frequency calculations can be performed to determine vibrational energies and assign IR spectra.

Analysis of the chemical bonding

It is often important to make a connection between the exact electron density and model quantities of a system such as bond orders or oxidation states. These model quantities are not strictly defined, but can be calculated within reasonable approximations.



$$\Delta E_{\text{tot}} = \Delta E_{\text{kin}} + \Delta E_{\text{pot}} + \Delta E_{\text{nuc}}$$



Term	$\text{Hf}_2\text{Cl}_6^{2-}$ $\sigma^2 \pi^4 \delta^2 \delta^0$
ΔE_{tot}	-54.1
ΔE_{pot}	405.2
ΔE_{kin}^*	-244.3 (53.2%)
ΔE_{pot}^*	-215.0 (46.8%)
$\sigma_1^2(\sigma)$	-84.4 (39.3%)
σ_2	-0.1 (<0.1%)
δ_1^2	-1.5 (0.7%)
$\delta_2^2(\delta)$	-0.5 (0.2%)
$\pi^2(\pi)$	-128.5 (59.8%)
ΔE_{prop}	27.2