Modifying the Fullerene Surface Using Endohedral light guests. From Ab Initio Molecular Dynamics and Metadynamics to Quantum Chemical Topology.

Andrzej Bil[1]

[1] Institute of Physical Chemistry, University of Zürich, Switzerland

Unlike the C_{60} molecule, C_{70} has five non-equivalent carbon atom types (commonly labelled with letters from *a* to *e*), which leads to eight non-equivalent C-C bonds. It has been shown that the *a,b*- and *c,c*- isomers are the two most stable structures on the $C_{70}O_3$ potential energy surface, which suggests that the reaction pathway toward oxide formation must proceed via the corresponding ozonide structure. We offer a mechanism for the thermally-induced dissociation of $C_{70}O_3$ that share the first two steps with the general mechanism for ozonolysis of alkenes proposed by Criegee. The calculations also reveal the likely time scale of the reaction (ab initio Molecular Dynamics), and indicate that it is the breaking of the C-C bond that triggers the whole process. [1]

Although MD study gave us a clue as for the initial steps of the ozonolysis, further steps were not accessible due to the energy barrier larger than the thermal boost. Advanced technics of the free energy surface exploration, such as a metadynamics or thermodynamical integration, allowed us to find structures relevant for the further steps of the reaction. The free energy surface has turned out to have complicated topology. [3]

New achievements in the endohedral modification of fullerenes triggered questions about influence of endohedral guests on carbon atoms reactivity and properties of fullerene derivatives. We analyzed how light endohedral guests such as noble gas atoms or small molecules (H_2, $2H_2$, CO_2, H_2O, HCl, CH_4, NH_3, BH_3) influence the thermodynamics of ozone ring-opening. The effect is isomer dependent, with the enthalpy of the reaction increasing for *a,b*-$C_{70}O_3$ and decreasing for *e,e*-$C_{70}O_3$ when doped with the heavy noble gas atoms Xe and Rn. [2] In case of light molecules we observe that at room temperature the impact of the guest is more prominent that it can be expected on the basis of the static (NEB) calculations at 0K. [3]

Quantum chemical topology provides a tool linking the concept of a chemical bond based on the Lewis theory and the quantum mechanical description of many-electron systems. We analyzed a bond evolution during the ozone ring opening on the basis of the topological features of the electron density and the electron localization function. [3]

[1] Bil, A., Latajka, Z., Morrison, C. A. *J. Phys. Chem. A*, 113:9891-9898, 2009.
[2] Bil, A., Morrison, C. A. J. Phys. Chem. A, 116: 3413-3419, 2012
[3] unpublished