Modeling the DABCO molecule in various environments (Ar, H_2O, CO_2, NH_3) with extended Density Functional Tight Binding schemes

P. Guibourg[1], F. Spiegelman[1] and M. Rapacioli[1]

[1] Laboratoire de Chimie et Physique Quantiques - Université Paul Sabatier, Toulouse

It is often challenging to model the evolution of properties of molecular compounds when they interact with an environment. One may cite the trapping of species in rare gas matrices or the deposition of molecules at the surface or in the volume of finite size clusters. We will present the combination of the Density Functional Tight Binding (DFTB) scheme [1], to describe molecules, with a Force-Field (FF) approach, to describe Rare gas (Rg) atoms. We have extended a former model [2] by introducing an atomic-population-dependent correction to a repulsion term between the DFTB atoms and Rg atoms. In this new model, the dispersion contribution also depends on the atomic populations. This model allows, in particular, to describe neutral and ionic systems and has been applied to simulate clusters of argon atoms and a 1,4-diazabicyclo[2.2.2]octan (DABCO) molecule. New reference calculations (MP2, CCSD(T)-F12) on small $DABCO^{0/+}$-Ar_n clusters will be presented. We show that the new DFTB-FF model performances are significantly improved with respect the former model for small aggregates, in particular with regard to cohesive energies. Finally, by coupling the new DFTB-FF model with a minima global search algorithm, namely a combination of Parallel Tempering Monte Carlo (PTMC) explorations and quenches [3], we provide a set of stable structures for $DABCO^{0/+}$-Ar_n clusters in the range n=1-50 atoms pointing out the size-evolution of geometric features and energetic properties. Ionization potentials are shown to decrease with size, consistently with new experimental measurements. Similar global research was performed to obtain structural and energetic properties of DABCO surrounded by other solvents like H_2O, CO_2 and NH_3.

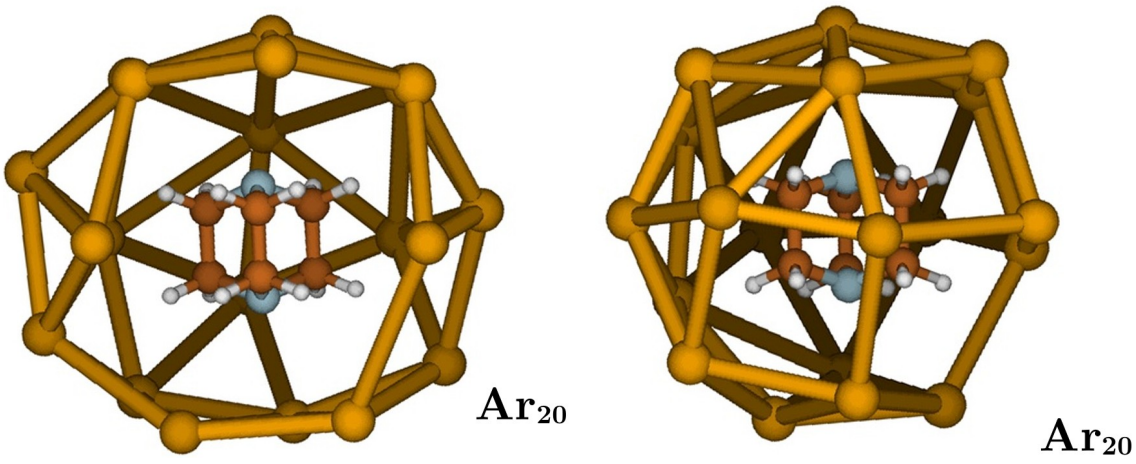

Figure 1 : Relaxed structures for DABCO-$Ar^{o/+}$ 20. Structure on the left are quenched with neutral DABCO and with ionic DABCO on the right.

[1] Phys. Rev. B 58, 7260 (1998)

[2] *J. Chem. Phys.* 140, 034301 (2014)

[3] *J. Phys. Chem. A* 2019, 123, 44, 9531–9543