NMR parametrs of $Hg\cdots H_2O$ complex: relativistic four-component calculations.

Katarzyna Jakubowska[a] and Magdalena Pecul[a]

[a] *Faculty of Chemistry, University of Warsaw*
kjakubowska@chem.uw.edu.pl

Main objective of the project was to calculate dependencies of nuclear shielding constants of ^{199}Hg, ^{17}O and ^{1}H and indirect spin-spin coupling constants on geometric parameters of $Hg\cdots H_2O$ complex. In case of systems that include a heavy atom, mercury in particular, it is essential to perform all the calculations with a method that takes relativistic effects into account. That is why, NMR parameters studied in this project were computed with relativistic four-component DFT method.
Before calculating NMR parameters we studied potential energy surface of the dimer by means of CCSD(T) and DFT methods. CC theory is one of the most mathematically elegant techniques for estimating electron correlation energy and, thus, it is also one of the most popular methods of computations in cases, where correlation energy plays a key role in obtaining results in agreement with experiment. That is why, the CC results were considered benchmark for further density functional theory (DFT) calculations with the use of a wide variety of exchange-correlation functionals, for example, B3LYP, BLYP and PBE0. Moreover, some interesting results with regard to equilibrum geometry of the system were obtained. DFT calculations gave a global minimum with mecury atom on C_{2v} axis of water molecule, whereas in case of CCSD(T) the complex in eguilibrium dis not have C_{2v} symmetry.
After that NMR parameters were calculated at the DFT level with four-component relativistic Dirac-Coulomb Hamiltonian since there is currently no implementation of four-component coupled-cluster theory for calculating NMR parameters. In addition to this, some of the calculations were also performed with nonrelativistic Hamiltonian or a relativistic Hamiltonian that did not take spin-orbit effects into account. This enabled us to study the importance of relativistic effects, the effects of spin-orbit splitting and also the HALA (heavy-atom-on-light-atom) effect. It turned out that mercury atom in the neighbourhood of water molecule has significant impact on the values of the proton and oxygen shieldin constants and on the spin-spin coupling constants between oxygen and hydrogen atoms. All of the calculated shielding constants increase with the increase in the distance between mercury and oxygen atoms. σ_O at assumed equilibrium geometry is about 2 ppm smaller than in single water molecule and σ_{Hg} at equilibrium geometry is 12 ppm smaller than in single mercury atom.