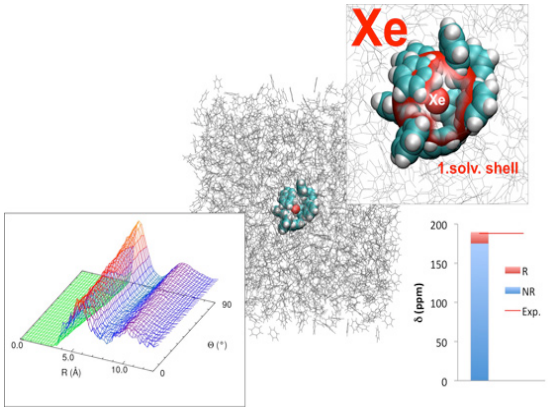
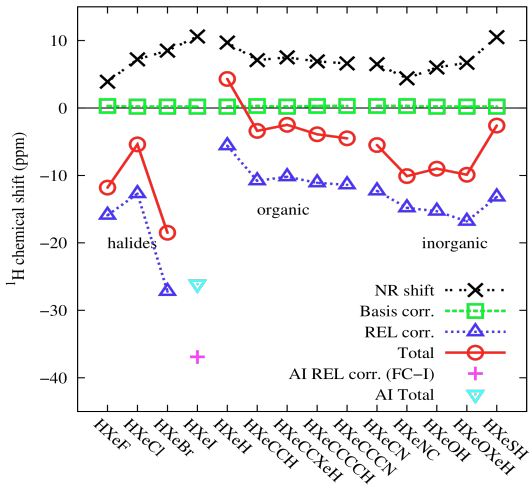
Effects of temperature, dynamics, and media on magnetic resonance parameters in endohedral fullerenes and confined Xe atom systems.

Summary of the ERG project No. 230955

Most important scientific results

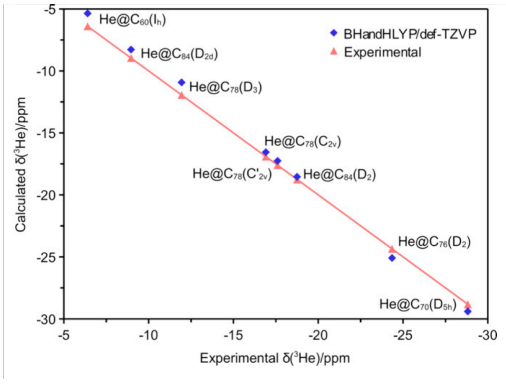
^{129}Xe NMR parameters simulated at experimental conditions.[1] We have shown that ^{129}Xe NMR chemical shift of atomic Xe dissolved in liquid benzene can be accurately simulated by combining classical molecular dynamics and quantum-chemical calculations of ^{129}Xe nuclear magnetic shielding. Our study **opened the way for simulations of ^{129}Xe NMR parameters** of Xe atom enclosed in different guest-host systems such as liquids, clathrates, or molecular cages. The simulations provide understanding of experimental results on the microscopic structure.





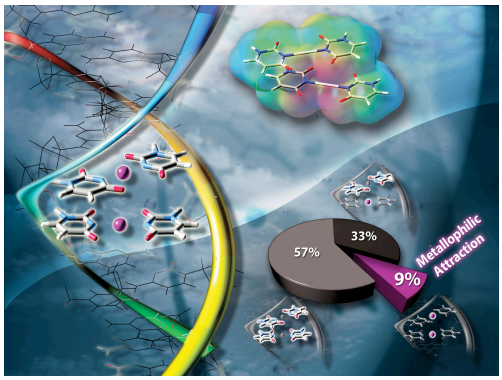
Hydrogen was found more relativistic than xenon.[2] Challenging state-of-the-art theoretical predictions of NMR parameters for novel HXeY compounds were done to guide the future experimental efforts in their identification. It turned out that in novel HXeY species, the **^{129}Xe chemical shift lies in a range so far unexplored (~500-1500 ppm vs. Xe atom)**. This ranges falls between usual Xe compounds and weakly-bonded Xe guest-host systems. Contrary to the chemical intuition, the ^{1}H chemical shifts were found strongly affected by the Xe-induced relativistic effects while only moderate relativistic effects are observed for ^{129}Xe chemical shift.

Calculations help to identify endohedral helium fullerenes.[3] Our calculations have revealed that the density functional theory (DFT) can describe NMR parameters of noble gas atoms in weakly-bonded endohedral systems, despite the well-known fact that DFT does not provide correct description of structure and energetics of weakly-bonding systems. Our study have shown that **computationally-aided assignment of endohedral ^{3}He fullerenes via ^{3}He signal** is possible.

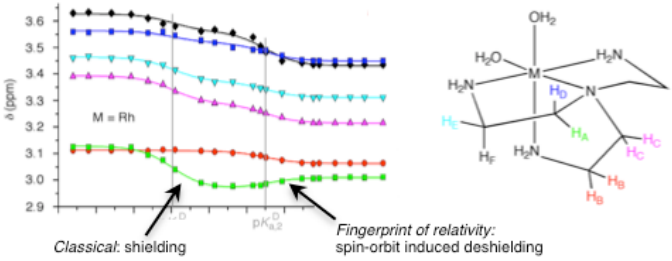


Simple and fast calculations of energetics in endohedral systems.[4] We have participated in the development of simple formulae for evaluations of energetics of weak-bonding interactions in endohedral systems. Suggested formulas are extendable to cavities and novel materials based on nanotubes.

Mercurophilic attraction stabilizes nucleic acids with metals.[5] We highlighted unprecedented metallophilic interactions in Hg-mediated T-T (T=thymine) paired nucleic acids. In the presence of metal-mediated T-Hg-T base pairs the base-pair interactions are enriched by metallophilic interactions between the neighboring Hg^{II} atoms. The metallophilic attraction is a concept so far not fully explored in the world of nucleic acids and opens new possibilities in nucleic acids synthesis.



When light Co atoms induce large relativistic effects and heavy Rh and Ir atoms induce small relativistic effects.[6] Unprecedented large relativistic spin-orbit (SO) induced ligand ^{1}H chemical shifts were detected theoretically and experimentally in a series of cobalt amine aqua complexes. Analysis via perturbation theory formulas have shown that relatively small relativistic effect induced by the cobalt atom center is amplified by the small ligand field splitting in the complexes. Contrary to intuition, for heavier Rh and Ir centers the relativistic SO contribution to ^{1}H chemical shifts does not grow with Z^2 (Z=atomic number). This is due to considerably larger ligand field splitting in Rh and Ir complexes, which is present in the denominators of perturbation theory formulas and cancels out the, in fact larger, relativistic SO integrals present in the nominators of perturbation theory formula.



Literature

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