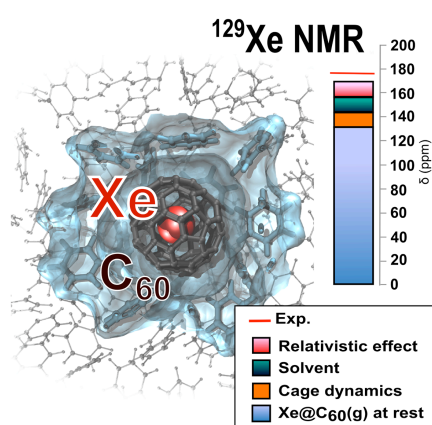


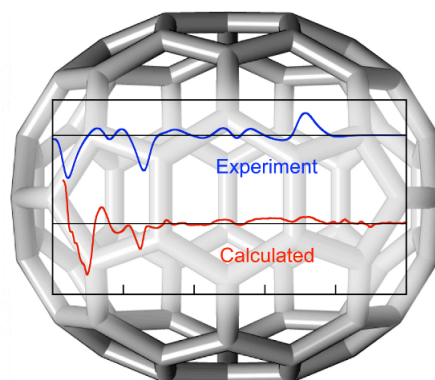
Highlights of our research in 2013



^{129}Xe NMR Chemical Shift in $\text{Xe}@C_{60}$ Calculated at Experimental Conditions: Essential Role of the Relativity, Dynamics, and Explicit Solvent: We have developed a **piecewise approximation** that includes relativistic effects via Breit-Pauli perturbation theory while simulating effects of dynamics and explicit dynamical solvent, including the relativistic corrections. Both studies **opened the way to quantum-chemical studies ^{129}Xe NMR parameters simulated including experimental conditions** 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. Published in *J. Comput. Chem.* 2013, *online*.

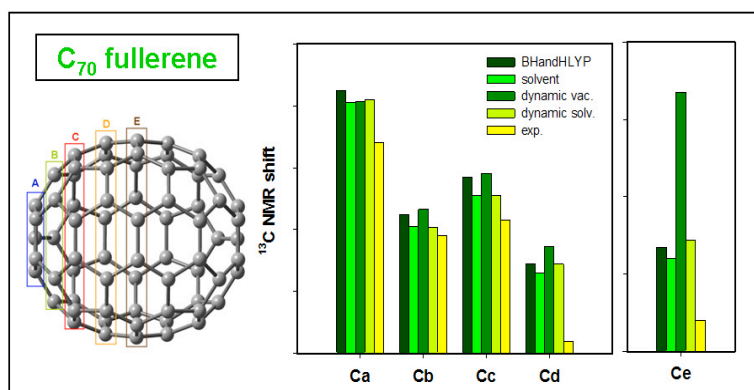
Fullerene resolution by the magnetic circular

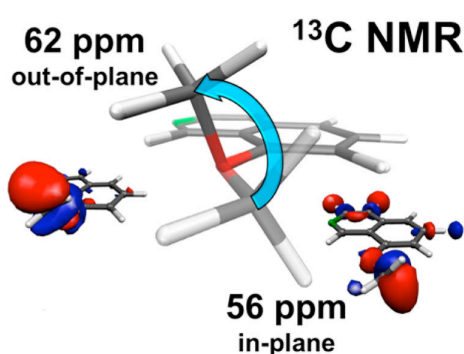
dichroism. The separation and identification of fullerenes is difficult. The magnetic circular dichroism (MCD) spectroscopy is presented as a useful tool for this purpose. Experimental C_{60} and C_{70} spectra were obtained and reproduced with the aid of density functional computations and the complex polarization propagator method. **Theoretical spectra of fullerenes revealed distinctive patterns extremely sensitive to molecular structure.** Requiring tiny amounts of the sample, the MCD technique thus appears as a useful for detailed fullerene studies. Published in *J. Chem. Phys.* 2013, **138**, 151103.



Fullerene C_{70} characterization by ^{13}C NMR and the importance of the solvent and dynamics in spectral simulations.

Different computational aspects needed to simulate realistically **chemical shifts in the C_{70} molecule** were investigated. The importance of the functional choice, basis set, solvent, and molecular motions was assessed. The molecular motions were included via anharmonic corrections and averaging of snapshots obtained from classical and first-principles molecular dynamics (MD) simulations. Comparison to experiment revealed that density functional calculations typically overestimate the ^{13}C NMR chemical shifts. Hybrid functionals, such as BHandH and BHandHLYP, and long-range corrected functionals, such as wB97xd and CAM-B3LYP, give the best results. The vibrational and dynamical effects are surprisingly large, causing changes up to 9 ppm. Consideration of the latter was also necessary to explain the observed temperature dependence. While the dynamical corrections for MD performed in vacuum were overestimated, inclusion of the solvent in simulations provided more realistic results. Published in *Phys. Chem. Chem. Phys.* 2013, **15**, 9223.





Origin of the Conformational Modulation of the ^{13}C NMR Chemical Shift of Methoxy Groups in Aromatic Natural Compounds:

In many aromatic natural compounds, unusual ^{13}C NMR chemical shifts have been reported for out-of-plane methoxy groups bonded to the aromatic ring (~ 62 ppm as compared to the typical value of ~ 56 ppm for an aromatic methoxy group). The conformational effects of the methoxy group on the ^{13}C NMR chemical shift then were interpreted by the Natural Bond Orbital (NBO) and Natural Chemical Shift (NCS) approaches, and by excitation analysis of the chemical

shifts. We discovered that the atypical ^{13}C NMR chemical shifts observed are not directly related to a different conjugation of the lone pair of electrons of the methoxy oxygen with the aromatic ring, as has been suggested. Our analysis indicates that rotation of the methoxy group induces changes in the virtual molecular orbital space, which, in turn, correlate with the predominant part of the contribution of the paramagnetic deshielding connected with the magnetic interactions of the bonding $\text{C}_{\text{Met}}\text{-H}$ \rightarrow antibonding $\text{C}_{\text{Met}}\text{-O}$ orbitals, resulting in the experimentally observed deshielding of the ^{13}C NMR resonance of the out-of-plane methoxy group. Published in *J. Phys. Chem. A* 2013, **117**, 661–669.

Exploring new ^{129}Xe chemical shift ranges in HXeY compounds: Hydrogen more relativistic than xenon:

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 ($\sim 500\text{-}1500$ ppm vs. Xe atom). This range falls between usual Xe compounds and weakly-bonded Xe guest-host systems. Contrary to the chemical intuition, the ^1H chemical shifts were found strongly affected by the Xe-induced relativistic effects while only moderate relativistic effects are observed for ^{129}Xe chemical shift. Published in *Physical Chemistry Chemical Physics*, **14**, 10944-10952 (2012).

