Periodic Trends of Spin-Orbit Heavy Atom on the Light Atom Effect to NMR Chemical Shifts Rationalized

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The importance of relativistic effects on the NMR parameters in heavy-atom (HA) compounds, particularly the SO-HALA (Spin-Orbit Heavy Atom on the Light Atom) effect on NMR chemical shifts, has been known for about 40 years. However, generally valid correlation between the electronic-structure of heavy element complexes and SO-HALA effect have been missing. By analyzing ^{1}H NMR chemical shifts of the 6th-period hydrides (Cs-At) we uncovered the basic electronic-structure principles and mechanisms that dictate the size and sign of the SO-HALA NMR chemical shifts.[1] In brief, partially occupied HA valence shells induce relativistic shielding at the light atom (LA) nuclei, while empty HA valence shells induce relativistic deshielding. The LA nucleus thus became relativistically shielded in $5d^2$-$5d^8$ and $6p^4$ HA hydrides and deshielded in $4f^0$, $5d^0$, $6s^0$, $6p^0$ HA hydrides. The introduced principles have a general validity across the periodic table and can be extended to non-hydride LAs as well. Moreover, the connection between the SO-HALA NMR chemical shifts and Spin-Orbit-induced Electron Deformation Density (SO-EDD) is derived. SO-EDD provides an intuitive understanding of the SO-HALA effect in terms of the depletion/concentration of the electron density at LA nuclei caused by spin-orbit coupling due to HA in the presence of magnetic field. Using an analogy between SO-EDD concept and arguments from classic NMR theory, the complex question of the SO-HALA NMR chemical shifts becomes easily understandable for a wide chemical audience.

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References:

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