Spin exchange in biradicals as a model to study long-range interactions

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Around 60 years ago, V.V. Voevodsky announced his idea concerning importance of energetically weak long-range interactions on the pathway and mechanism of chemical reactions. Among the first scientists who have started experimental studies in this area were his PhD studerts Yury Molin and Kirill Zamaraev. Among other tested physical and chemical processes, the electron spin exchange (eSE), specially intramolecular spin exchange (IMSE) in stable biradicals was chosen as a promising object of studies. Indeed, IMSE in biradicals is rather weak, EPR technique allows quantitative measurements of the exchange integral value $|J|$ from 2 to *ca*. 300 G (6 – 900 MGz), and a numerous number of the synthesized nitroxyde biradicals of different types and structures permit vary all necessary parameters and features.

Practically all investigated biradicals exist in liquid solutions in two or several "effective" conformations *k* which are characterized by the value of J_k and a life-time τ_k of this conformation [1]. Between these conformers, there are transitions which are well described by the theory developed by V.N. Parmon and G.M. Zhidomirov [1,2]. EPR study of biradicals allows quantitative characterize intramolecular dynamics of the system and efficiency of interaction between long-range linked unpaired electrons in nitroxide biradicals. One example of experimental correlations is shown in the Figure.

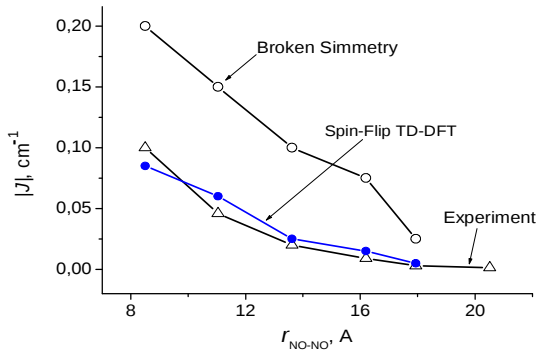

Figure: Electron spin exchange integral value $|J|$ as a function of the distance $r_{NO\text{-}NO}$ between the ubpaired electrons in biradicals X-Y: experimental and DFT calculated.

Some actual properties of nitroxide biradicals were published in [3,4] and will be discussed in the report.

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G.I. Likhtenstein (Springer, New York, **2020**), Ch. 5, pp. 93-118.