

Abstract

Presented thesis is focused on the investigation of the lowest electronic states and some of their properties in the molecules lacking in closed-shell configuration. Thesis is divided into two parts - first part deals with biradicals, second with transition-metal compounds.

In the first part, we show that the so far rarely observed inverse heavy-atom effect could be in methylcarbenes achieved by changing the substituent. While bromo substitution of methylcarbene strengthens the spin-orbit coupling between S_0 and T_1 states, the presence of germyl group decreases SOC. According to our results, a decrease in SOC caused by the germyl group should reduce the probability of both radiationless and radiative S_0/T_1 transitions. We ascribe the qualitatively different effect of the substituents to absence of the lone pairs of GeH₃ group and we show that the contributions of heavy atoms are mainly caused by interactions of their p orbitals. Moreover, inverse heavy-atom effect seems to be additive and multiple substitutions may lead to its strong enhancement. We further suggest new approach to possible measurement of the parity-violation effects in chiral molecules based on the electronic-energy shifts of the components of the lowest triplet of a biradical. It seems that the best candidates among systems studied for measurement are molecules with the $-\text{GaH}-\ddot{\text{Bi}}^{\oplus}-\text{Bi}<$ fragment. There is high probability that these molecules would have triplet ground state and splitting of the parameter D of their lowest triplet due to parity violation is of the order of 10^4 Hz. Results support our presumption that the parity-violation effect on splitting of the triplet T_1 should be dominated by its interactions with the close-lying singlet S_0 .

In the second part of the thesis, we come with MS-CASPT2 results for the lowest electronic states of model systems representing various arrangements of the active site of multicopper oxidases. This methodology predicts multiplicity of the ground state in agreement with experimental data for all studied structures and points out the necessity of use of multiconfigurational methods. Our results suggest that NI_C is better candidate for real structure of the native intermediate and correct QM/MM prediction of the ground-state multiplicity of PI_C structural motive. We further show how spin-orbit coupling affects reduction potentials of the octahedral ruthenium and osmium complexes. Strong spin-orbit coupling between three close-lying doublets leads to relative stabilization of their oxidized forms, thus to a systematic negative shift of their reduction potential. This negative shift is for ruthenium complexes usually smaller than 100 mV, but in the case of heavier osmium reaches the value of 400 mV. Our results suggest that the influence of higher states is for oxidized and reduced forms very well compensated. Last but not least, our calculations predict that $[\text{RuCl}_6]^{4-}$ complex could have solvatochromic and solvatomagnetic properties.