The quartet-quartet crossing in Ir...benzene half-sandwich complex

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The adsorption of aromatic molecules on metal surfaces is an important process in surface science, catalysis, molecular electronics, and spintronics. Theoretical calculations can provide essential understanding of the nature of binding between various aromatic adsorbates and metals.

In our previous study[1] we found out, that the resulting MS-CASPT2-SO/ANO-RCC-VQTZP curve showed the double minimum. While the first minimum corresponds to the interaction of singlet closed-shell $^1S_0$ state of Pt atom, the second minimum which appears after inclusion of spin-orbit coupling corresponds to the interaction of $^3F_4$ state of Pt atom with benzene molecule.

The Ir...benzene was studied at the single- and multi-reference WFT level. The two different single-reference WFT approaches used include the MP2 and more accurate spin-adapted CCSD(T) method with restricted open-shell Hartree–Fock (HF) reference functions. The multireference CASPT2 with RASSI-SO and MRCI with Breit-Pauli-SO operator were also utilized.

The nature of bonding and stability of Ir...benzene is similar to the interaction between Pt metal atom with benzene molecule. The double-minimum potential curve for Ir...benzene complex corresponds to the quartet-quartet spin-crossing and it is not neccessary to include the SOC effects.

[1] Granatier, J., Dubecký, M., Lazar, P., Otyepka, M., Hobza, P., *J. Chem. Theory Comput.*, **9**, 1461-1468, 2013.