

Open-shell fullerene derivatives: low temperature ESR spectroscopy and quantum chemical (DFT) calculations

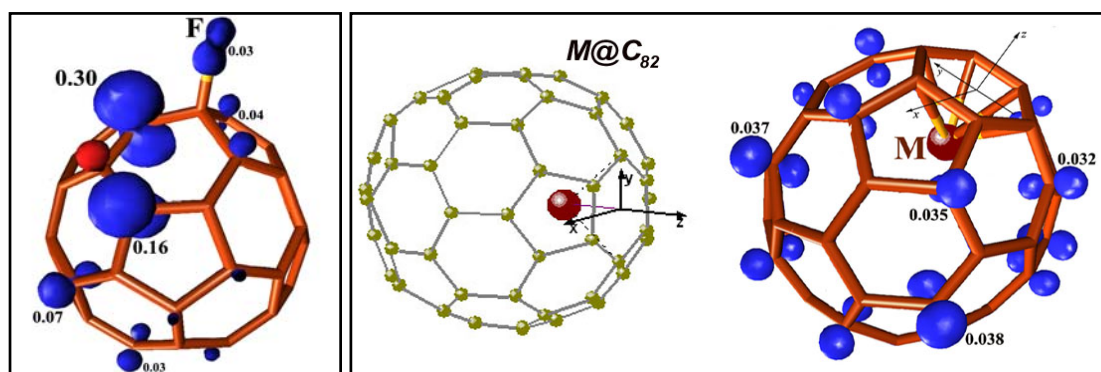
Misochko E.Ya.¹, Akimov A.V.¹, Tyurin D.A.²

¹*Institute of Problems of Chemical Physics of the Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia*

²*Lomonosov Moscow State University, Department of Chemistry, 119899, Moscow, Russia*
*e-mail: misochko@icp.ac.ru

Here we report how ESR and matrix-isolation techniques supported by quantum-chemical computations can be used for molecular modeling of novel open-shell species, such as paramagnetic fullerene derivatives. In this study, free radicals $\cdot\text{C}_{60}\text{F}$ and $\cdot\text{C}_{70}\text{F}$ and paramagnetic endometallofullerene $\text{Y}@\text{C}_{82}$ molecules were isolated in solid argon matrices at cryogenic temperatures. High resolution anisotropic EPR spectra of the isolated molecules at temperature 5 K have been obtained for the first time. [1]

Both of hyperfine coupling constants characterizing Fermi contact interaction and electron-nuclear-magnetic-dipole interaction have been derived from the ESR spectra recorded. We have used these parameters for testing the validity of various computational methods (PBE, PBE1, and B3LYP) to predict an electronic structure of such type species. Based on the comparison of the measured hyperfine constants with those estimated by the quantum chemical calculation, the electron spin distribution and reactivity of the radical $\cdot\text{C}_{60}\text{F}$, various regioisomers of $\cdot\text{C}_{70}\text{F}$, and endometallofullerenes $\text{M}@\text{C}_{82}$ ($\text{M} = \text{Sc}, \text{Y}, \text{La}$) are discussed.



Calculated electron spin populations on fullerene sphere in the radical C_{60}F (left) and the endometallofullerene $\text{Y}@\text{C}_{82}$ (right).

Relativistic and solvation effects in a series of engaged 3B group metal atoms in the molecules $\text{M}@\text{C}_{82}$ are discussed based on the results of these calculations and available experimental data.

[1] Misochko E.Ya., Akimov A.V. et al., *Phys. Chem. Chem. Phys.* **12**, 8863, (2010).