

The electronic structure of homoleptic $\text{Fe}(\text{NO})_4^-$ anion

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The dinitrosyliron complexes (DNIC) in the fashion of $\text{Fe}(\text{NO})_2\text{L}_2$ (L=carbonyl, nitrosyl or imino- complexing ligands) is one of the functional species responsible for transportation and storage of nitric oxide (NO) that occurs in various physiological processes in biological systems. In a recent study the structure of homoleptic $\text{Fe}(\text{NO})_4^-$ anion has been experimentally characterized and its spectroscopic information has been reported.[1] Quantum mechanical calculation at the level of symmetry-adapted cluster configuration interaction (SAC-CI) theory confirms the structural motif of $\text{Fe}(\text{NO})_4^-$ as a tetrahedrally coordinated iron center supported by two associated $\bullet\text{NO}$ radicals with almost linear Fe–N–O bond angles as well as two NO^- ligands with bent Fe–N–O bond angles of approximately 110° . Extensive wavefunction and orbital analysis also demonstrate that its electronic structure is best described as an electron-attached state to the neutral molecule in the singlet state, while it is difficult to converge the unrestricted wavefunctions for the anionic state. Due to strong static correlation effect the singly-occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) are nearly degenerate though different symmetry, and hence density functional theories failed to describe this complex properly. In addition, multiconfiguration computations using complete active-space (CAS) orbitals suggest that dynamical correlation is also of considerable importance. Nevertheless, comparative studies carried out for similar DNIC species including $[\text{I}_2\text{Fe}(\text{NO})_2]^-$, $[(\text{N}_3)_2\text{Fe}(\text{NO})_2]^-$, and $[(\text{SCN})_2\text{Fe}(\text{NO})_2]^-$ show that both of density functional and wavefunction approaches yield consistent results in the optimized geometries and spectral assignments.

[1] Lin, Z.-S., Chiou, T.-W., Liu K.-Y., Hsieh C.-C., Yu, J.-S.K., Liaw, W.F. *Inorg. Chem.*, 51:10094-10094, 2012.

[2] Author, Q. *Theor. Phys. Chem.*, 333:11-1, 2012.