THE AB INITIO STUDY OF IRON CYANIDE AND IRON ISOCYANIDE, AND ITS SURPRISING RESULTS

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The ground state and first three excited electronic states of FeCN and FeNC were studied using various levels of single- and multi-reference *ab initio theory. FeNC is the first spectroscopically observed monomeric transition metal isocyanide, discovered with laser fluourscence excitation spectroscopy. Studied seperately, both iron atom and cyanide ion pose great challenges to theorists, and the combination of the two has provided surprising results at very high levels of theory. By assuming that FeNC behaves like high-spin molecules such as FeCl and FeF, a high-spin* $^6\Delta$ *ground state was determined with a* $^6\Pi_{7/2} - ^6\Delta_{9/2}$ *electronic transition in the same wavelength region as FeCl. However, CCSDT-3 and MRCISD+q calculations with new correlation consistent basis sets for iron seem to favor an FeH-like low-spin* $^4\Delta$ *ground state. At CCSDT-3 with the Roos ANO basis set, the cyanide isomer is 3.21 kcal/mol lower in energy than the isocyanide with a* $^4\Delta$ *state 0.98 kcal/mol lower than the* $^6\Delta$ *state.*