TOO SHORT CN BOND LENGTHS FOUND IN Fe, Co, AND Ni ISOCYANIDE AND CYANIDES

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We were surprised, thinking it might be a misprint, with such a short C-N bond length, 1.03(8) Å, of $\hat{X}\,^6\Delta$ FeNC when the Lie and Dagdigian paper (2001) on FeNC by LIF[a] came out. Ziurys and Sheridan aslo found a short CN bond length for the $\hat{X}$ CoCN, 1.13133 Å, by MW, last year.[b] For $\hat{X}\,^2\Delta_i$ NiCN, Kingston and Merer[c] has reported a little short CN bond length of 1.1591(29) Å, determined by LIF, and Sheridan and Ziurys[d] 1.1580(8) Å by MW. Our *ab initio* calculated r_e values, though some of them are preliminary at the moment, are 1.172 (FeNC), 1.171 (CoCN), and 1.166 Å (NiCN). The discrepancy between experimental and theoretical values is in the order FeNC $>$ CoCN $>$ NiCN, in parallel with the expected ionic character of the metal-ligand bond and accordingly with the floppy character of the bending motion. The observed too-short CN bond lengths in these radicals probably come from the inadequate model used for the analysis of observed spectra.

A new model will be proposed, and calculations of the three dimensional potential energy surfaces for $\hat{X}\,^6\Delta$ FeNC/FeCN , which are necessary for the theoretical analysis based on the new model, are in progress at the level of MR-SDCI+Q with Roos-ANO (Fe) and aug-cc-pVQZ (C and N) basis sets.

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[a] J. Lie and P. J. Dagdigian, *J. Chem. Phys.* **114**, 2137 (2001).

[b] P.M. Sheridan and L.M. Ziurys, University of Arizona, Private communication (2003).

[c] C.T. Kingston, A.J. Merer, and T.D. Varberg, *J. Molc. Spectrosc.*, **215**, 106 (2002).

[d] P.M. Sheridan and L.M. Ziurys, *J. Chem. Phys*., **118**, 6370 (2003).