A THEORETICAL STUDY OF FeNC IN THE $^6\Delta$ ELECTRONIC GROUND STATE

TSUNEO HIRANO, REI OKUDA, and UMPEI NAGASHIMA, *Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*; VLADIMÍR SPIRKO, *Center for Biomolecules and Complex Molecular Systems, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, CZ-166 10 Praha 6, Czech Republic*; PER JENSEN, *Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany*.

We report an *ab initio* calculation, at the MR-SDCI+Q+$E_{\rm rel}$/[Roos ANO (Fe), aug-cc-pVQZ (C, N)] level of theory, of the potential energy surface for $^6\Delta_i$ FeNC. From the *ab initio* results, we have computed values for the standard spectroscopic parameters of $FeN^{12}C$ and $FeN^{13}C$. Analytical representations of the potential energy surfaces have been fitted through the *ab initio* points, and the resulting functions have been used for directly solving the rotation-vibration Schrödinger equation by means of the MORBID program and by means of an adiabatic-separation method. For $^6\Delta_i$ FeNC, our *ab initio* calculations show that the equilibrium structure is linear with $r_{\rm e}$(Fe-N) = 1.9354 Å and $r_{\rm e}$(N-C) = 1.1823 Å. We find that the bending potential is very shallow, and the MORBID calculations show that the zero-point averaged structure is bent with the expectation values $\langle r$(Fe-N)$\rangle$ = 1.9672 Å, $\langle r$(N-C)$\rangle$ = 1.1866 Å, and $\langle\bar{\rho}\rangle$ = $180^\circ - \langle\angle$(Fe-N-C)$\rangle = 13^\circ$. The experimentally derived bond length r_0(N-C) = 1.03(8) Å reported for $^6\Delta_i$ FeNC by J. Lie and P. J. Dagdigian [*J. Chem. Phys.* **114**, 2137-2143 (2001)] is much shorter than the corresponding *ab initio* $r_{\rm e}$-value and the averaged value from MORBID. Our calculations suggest that this discrepancy is caused by the inadequate treatment of the large-amplitude bending motion of $^6\Delta_i$ FeNC. It would appear that for floppy triatomic molecules such as FeNC, r_0-values have little physical meaning, at least when they are determined with the effects of the large-amplitude motion being ignored, i.e., under the assumption that the r_0 structure is linear.