

## COMPUTATIONAL MOLECULAR SPECTROSCOPY OF FeCN IN THE ${}^6\Delta$ ELECTRONIC GROUND STATE

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We have previously reported a computational molecular spectroscopic study of  ${}^6\Delta_i$  FeNC,<sup>a</sup> where we showed that the experimentally derived, too-short C-N bond length ( $r_e(\text{C-N}) = 1.03(8) \text{ \AA}$ )<sup>b</sup> can be ascribed to an inadequate treatment of the large amplitude bending motion in the experimental determination of  $r_0$ . Here, we report analogous calculations for  ${}^6\Delta_i$  FeCN.<sup>c</sup>

Based on the three-dimensional potential energy surface calculated at the MR-SDCI+Q+ $E_{\text{rel}}$ /[Roos ANO (Fe), aug-cc-pVQZ (C, N)] level of theory, the standard spectroscopic parameters of Fe<sup>12</sup>CN and Fe<sup>13</sup>CN are derived by perturbation methods, and ro-vibrationally averaged bond lengths  $\langle r \rangle$  have been predicted as expectation values obtained with ro-vibrational wavefunctions from the MORBID program. Some of the spectroscopic constants thus determined are:  $r_e(\text{Fe-C}) = 2.048 \text{ \AA}$  and  $r_e(\text{C-N}) = 1.168 \text{ \AA}$ ,  $\omega_1 = 2179 \text{ cm}^{-1}$ ,  $\omega_2 = 173 \text{ cm}^{-1}$ ,  $\omega_3 = 420 \text{ cm}^{-1}$ , dipole moment = 4.59 D, spin-orbit coupling constant  $A_{\text{SO}} = -83 \text{ cm}^{-1}$ ,  $\langle r(\text{Fe-C}) \rangle_0 = 2.082 \text{ \AA}$ , and  $\langle r(\text{C-N}) \rangle_0 = 1.172 \text{ \AA}$ . In variational MORBID calculations, rovibronic energy levels are determined, and some vibrational bands are simulated. The bending potential is shallow, and the MORBID calculations show that the zero-point averaged structure is bent with the expectation value  $\langle \angle(\text{Fe-C-N}) \rangle_0 = 170(5)^\circ$  (where the number in parentheses is the quantum-mechanical uncertainty). We compare the  ${}^6\Delta_i$  FeCN results with those obtained for  ${}^6\Delta_i$  FeNC. Since there are no experimental spectroscopic data available for FeCN, we hope that the predictions made here may be useful in the experimental investigation of this molecule.

<sup>a</sup>T. Hirano, R. Okuda, U. Nagashima, V. Špirko, and P. Jensen, *J. Mol. Spectrosc.*, **236**, 234-247 (2006).

<sup>b</sup>J. Lie and P. J. Dagdigian, *J. Chem. Phys.*, **114**, 2137-2143 (2001).

<sup>c</sup>T. Hirano, M. Amano, Y. Mitsui, S.S. Itono, R. Okuda, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.*, *in press* (2007).