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,[a] where we showed that the experimentally derived, too-short C-N bond length (r_e(C-N) = 1.03(8) Å)[b] 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.[c]
Based on the three-dimensional potential energy surface calculated at the MR-SDCI+Q+$E_{\rm rel}$/[Roos ANO (Fe), aug-cc-pVQZ (C, N)] level of theory, the standard spectroscopic parameters of $Fe^{12}CN$ and $Fe^{13}CN$ 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(Fe-C) = 2.048 Å and r_e(C-N) = 1.168 Å, $\omega_1 = 2179$ cm^{-1}, $\omega_2 = 173$ cm^{-1}, $\omega_3 = 420$ cm^{-1}, dipole moment = 4.59 D, spin-orbit coupling constant $A_{\rm SO} = -83$ cm^{-1}, $\langle r$(Fe-C)$\rangle_0$ = 2.082 Å, and $\langle r$(C-N)$\rangle_0$ = 1.172 Å. 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 $\langle \angle$(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.

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[b] J. Lie and P. J. Dagdigian, *J. Chem. Phys.*, **114**, 2137-2143 (2001).
[c] T. Hirano, M. Amano, Y. Mitsui, S.S. Itono, R. Okuda, U. Nagashima, and P. Jensen, *J. Mol. Spectrosc.*, *in press* (2007).