A THEORETICAL STUDY OF NiCN IN THE $^2\Delta$ ELECTRONIC GROUND STATE

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The three-dimensional potential energy surface of $\tilde{X}\ ^2\Delta_i$ NiCN has been calculated *ab initio* at the MR-SDCI+Q+$E_{\rm rel}$/[Roos ANO (Ni), aug-cc-pVQZ (C, N)] level of theory. The equilibrium geometry derived from this surface is linear with $r_{\rm e}$(Ni-C) = 1.814 [1.8292(28), 1.8293(1)] Å and $r_{\rm e}$(C-N) = 1.167 [1.1591(29), 1.1590(2)] Å, where the values in brackets are r_0 values for the ground $\Omega = 5/2$ spin-substate determined experimentally by Kingston *et al.*[a] and Sheridan *et al.*,[b] respectively. From the electronic structure given in terms of natural orbitals, and the Mulliken population[c] of +0.83 on Ni, we conclude that the Ni-C bond is basically ionic but less ionic than those of FeNC and CoCN. The electron from Ni goes into the Ni-mediated CN σ* orbital, giving the electron distribution Ni$^{+0.8}$(CN)$^{-0.8}$. The $3d$-π* backbonding is not observed. Molecular constants determined from the *ab initio* potential energy surface by perturbation methods and in variational calculations will be reported: For example, ω_1 = 2198 $\rm cm^{-1}$, $\omega_2 = 254\ \rm cm^{-1}$, and $\omega_3 = 511\ \rm cm^{-1}$. A severe Fermi resonance between $2\nu_2$ and ν_3 is expected. A spin-orbit interaction scheme including the *ab initio* predicted spin-orbit coupling constant $A_{\rm SO} = -613\ \rm cm^{-1}$[d] will be presented.

[a] C. T. Kingston, A. J. Merer, and T. D. Varberg, *J. Mol. Spectrosc.*, **215**, 106 (2002).
[b] P. M. Sheridan and L. M. Ziurys, *J. Chem. Phys.*, **118**, 6370 (2003).
[c] Computed at the MR-SDCI/[Wachters+f (Ni), aug-cc-pVTZ (C, N)] level of theory
[d] *cf.* the unperturbed $A_{\rm SO}$-value of $-594.2(5)\ \rm cm^{-1}$ for $X\ ^2\Delta$ NiH; J. A. Gray, M. Li, T. Nelis, and R. W. Field, *J. Chem. Phys.*, **95**, 7164 (1991).