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

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The three-dimensional potential energy surface of $X^2\Delta$ NiCN has been calculated ab initio at the MR-SDCI+Q+E_{c+r}/[Roos ANO (Ni), aug-cc-pVQZ (C, N)] level of theory. The equilibrium geometry derived from this surface is linear with $r_e$(Ni-C) = 1.814 [1.8292(28), 1.8293(1)] Å and $r_e$(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.\textsuperscript{a} and Sheridan et al.\textsuperscript{b} respectively. From the electronic structure given in terms of natural orbitals, and the Mulliken population\textsuperscript{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 $\sigma^*$ orbital, giving the electron distribution Ni$^+$[(CN)$^-$]. The $3d-\pi^*$ 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, $\omega_1 = 2198$ cm\textsuperscript{-1}, $\omega_2 = 254$ cm\textsuperscript{-1}, and $\omega_3 = 511$ cm\textsuperscript{-1}. A severe Fermi resonance between $2\nu_3$ and $\nu_2$ is expected. A spin-orbit interaction scheme including the ab initio predicted spin-orbit coupling constant $A_{\Delta \Omega} = -613$ cm\textsuperscript{-1} will be presented.

\textsuperscript{c}Computed at the MR-SDCI/[Wachters+f (Ni), aug-cc-pVTZ (C, N)] level of theory
\textsuperscript{d}cf. the unperturbed $A_{\Omega \Omega}$-value of $-594.2(5)$ cm\textsuperscript{-1} for $X^2\Delta$ NiH; J. A. Gray, M. Li, T. Nelis, and R. W. Field, J. Chem. Phys., 95, 7164 (1991).