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Chemical Physics 346 (2008) 13–22
Chemical Physics
www.elsevier.com/locate/chemphys

Ab initio molecular orbital study of ground and low-lying electronic states of NiCN

Tsuneo Hirano [a,1], Rei Okuda [b], Umpei Nagashima [b], Kiyoshi Tanaka [c,2], Per Jensen [d,*]

[a] *Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan*
[b] *Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*
[c] *Division of Chemistry, Graduate School of Science, Hokkaido University, Kita 10, Nishi 8, Kita-ku, Sapporo 060-0810, Japan*
[d] *Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany*

Received 30 November 2007; accepted 15 January 2008
Available online 19 January 2008

Abstract

The electronic ground state and some low-lying excited states of NiCN have been studied by *ab initio* multi-reference single and double excitation configuration interaction calculations (MR-SDCI) with Davidson's correction Q and Cowan–Griffin's relativistic corrections E_{rel}. The electronic ground state of NiCN is $^2\Delta_i$ and the equilibrium geometry is linear with bond lengths of $r_e(\text{Ni–C}) = 1.8141$ Å and $r_e(\text{C–N}) = 1.1665$ Å. According to multi-reference averaged quadratic coupled-cluster theory (MR-AQCC) with E_{rel}, the first excited state is $^2\Sigma^+$, separated from the ground state by 446 cm^{-1}, the second and third excited states are $^2\Pi_i$ (at 1594 cm^{-1}) and $^4\Delta_i$ (at 8930 cm^{-1}), respectively, and other quartet states follow. The relative stabilities and the molecular properties of the low- and high-spin states having the same electronic total angular momentum are shown to be determined by dynamical electron correlation effects. A spin–orbit interaction scheme for the lowest doublet manifold is proposed. The predicted term values (in cm^{-1}) are 0 ($\tilde{X}\,^2\Delta_{5/2}$), 793 ($^2\Sigma^+_{1/2}$), 891 ($^2\Delta_{3/2}$), 2321 ($^2\Pi_{3/2}$), and 2773 ($^2\Pi_{1/2}$). Thus, an unassigned state reported by Kingston et al. [C.T. Kingston, A.J. Merer, T.D. Varberg, J. Mol. Spectrosc. 215 (2002) 106] at 755 cm^{-1} could be the $1\,^2\Sigma^+_{1/2}$ state.

Keywords: *Ab initio* molecular orbital study; NiCN; Ground and low-lying excited states; Electronic structure; Properties; Low-spin/high-spin issue; Spin–orbit coupling scheme; MR-SDCI; MR-AQCC; Relativistic correction

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1. Introduction

We have studied *ab initio* the first-row transition-metal-containing isocyanide FeNC [1] and the cyanides FeCN [2] and CoCN [3,4] with a view to investigate the effects of the large-amplitude bending motion and the low-spin/high-spin issues [3]. These molecules are basically ionic and can be written as $\text{M}^{\delta+}(\text{CN or NC})^{\delta-}$. They have no, or a very limited, covalent character. The degenerate nature of the electronic structure of M^+ is not fully lifted and brought into the ionic cyanides and isocyanides as a quasi-degeneracy. Hence, care must be taken to treat correctly the resulting multi-reference character of the electronic structure. In addition, we use an *ab initio* program [5] that forces us to calculate the electronic wavefunctions for linear configurations under C_{2v} symmetry and not under the correct symmetry of $C_{\infty v}$. Consequently, wavefunctions obtained in a single reference framework, such as in Hartree–Fock (HF) theory or in Pople-type density functional theory (DFT), become symmetry-broken for

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[*] Corresponding authors. Tel.: +49 202 439 2468; fax: +49 202 439 2509.
E-mail addresses: hirano@nccsk.com (T. Hirano), jensen@uni-wuppertal.de (P. Jensen).

[1] Present address: Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan.

[2] Present address: Institute of Industrial Science, The University of Tokyo, and Advancesoft, Center for Collaborative Research, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.

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doi:10.1016/j.chemphys.2008.01.022

doubly degenerate states of $\Pi, \Delta, \Phi, \ldots$ symmetry. In most cases, such symmetry-broken wavefunctions give rise to incorrect energies lower than those associated with correct symmetry-adapted wavefunctions. Therefore, a multi-reference treatment is necessary, even for the case where the weight of the leading configuration is dominant. To treat the quasi-degeneracy expected for the basically ionic radicals studied here, we construct the initial-guess orbitals by merging multi-configuration self-consistent field (MCSCF) molecular orbitals (MOs) of the constituents, here the metal cation M^+ and the ligand anion, corresponding to the electronic states at the adiabatic dissociation limit. Based on the MCSCF orbitals thus prepared, we carry out internally-contracted multi-reference single and double excitation configuration interaction (MR-SDCI) [6,7] calculations with Davidson correction [8] Q or multi-reference averaged quadratic coupled-cluster (MR-AQCC) theory [9] to include dynamical electron correlation. Relativistic energy corrections [10] are necessary to obtain theoretical results in satisfactory agreement with the existing experimental data.

For the triatomic molecules FeNC [1], FeCN [2], CoCN [3,4], and for the diatomic CoH [11], we have studied the electronic structure of the ground electronic states. In addition, for CoCN [3] we have also described the low-lying excited states. For each of the molecules treated, full-dimensional potential energy surfaces (PESs) have been calculated at the theory level of internally-contracted MR-SDCI [6,7] with Davidson's correction Q [8] for quadruple excitations (to recover partly the size-extensivity) and the Cowan–Griffin relativistic energy correction E_{rel} [10]. The computed PESs have been used for generating theoretical values of the standard spectroscopic parameters (i.e., vibrational term values, rotational constants,...) by perturbation methods and, in the case of the triatomic molecules, by means of the MORBID [12–15] and RENNER [16–19] variational approaches. The effects of large-amplitude bending motion have been analyzed for each of the triatomic molecules [1,2,4], and these analyses have demonstrated that several published, experimentally derived r_0 bond lengths for these molecules are of limited physical meaning since they were determined with the effects of large-amplitude bending motion being neglected. We suggest that theoretical, rovibrationally averaged bond lengths, obtained from MORBID or RENNER rovibrational wavefunctions, provide a sounder description of the molecular geometry. In addition we have studied, at the MR-SDCI + Q with second-order Douglas–Kroll relativistic Hamiltonian [20,21] level of theory, the $\widetilde{X}^2\Pi$ BrCN^+ radical [22] in order to investigate the effects of large-amplitude bending motion in the case of a non-metal-containing molecule. The conclusions drawn were essentially identical to those obtained for the metal-containing molecules.

NiCN is fifth in the series of isocyanide/cyanide molecules that we have studied *ab initio*. It has already been investigated extensively in laser-induced-fluorescence (LIF) experiments by Kingston et al. [23], in pure rotational-spectroscopy experiments by Sheridan and Ziurys [24] and theoretically, in *ab initio* calculations, by Paul et al. [25]. In addition, there are two earlier *ab initio* studies by Bauschlicher [26] and by Zhou et al. [27] on NiCN as a model for CN adsorbed on nickel metal surface. The authors of Refs. [23–25] are unanimous in concluding that in the electronic ground state $\widetilde{X}^2\Delta_{5/2}$, NiCN is linear at equilibrium. Experimentally for the $\widetilde{X}^2\Delta$ state, Kingston et al. [23] obtained the geometrical parameter values (quantities in parentheses are quoted uncertainties in units of the last digit given) $r_{0,\Omega=5/2}(\text{Ni–C}) = 1.8292(28)$ Å, $r_{0,\Omega=5/2}(\text{C–N}) = 1.1591(29)$ Å, and $B_{0,5/2} = 0.1444334(30)\ \mathrm{cm}^{-1}$, while Sheridan and Ziurys [24] determined $r_{0,\Omega=5/2}(\text{Ni–C}) = 1.8293(1)$ Å ($r_0(\text{Ni–C}) = 1.8281(6)$ Å), $r_{0,\Omega=5/2}(\text{C–N}) = 1.1590(2)$ Å ($r_0(\text{C–N}) = 1.1580(8)$ Å), and $B_{0,5/2} = 0.144435153(53)\ \mathrm{cm}^{-1}$. The reader should note the excellent agreement between these two sets of experimental results. Theoretically, $r_e(\text{Ni–C}) = 1.822$ Å and $r_e(\text{C–N}) = 1.167$ Å were predicted for the $\widetilde{X}^2\Delta$ state by Paul et al. [25] in single-reference DK-R/UCCSD(T)/cc-pVQZ_DK calculations. These authors claimed an excellent agreement with the experimentally determined value of $r_0(\text{Ni–C})$, but less satisfactory agreement for $r_0(\text{C–N})$.

We report here electronic structures and other molecular properties for the ground electronic state and the low-lying excited states of NiCN, computed *ab initio* at the MR-SDCI + Q + E_{rel} and MR-AQCC + E_{rel} levels of theory. In these calculations, we have taken into account the quasi-degeneracy effect described above. Owing to the symmetry restrictions of the *ab initio* program codes [5] utilized, C_{2v} symmetry was adopted for linear-structure calculations in place of the true $C_{\infty v}$ symmetry. The state-averaged (SA) complete active space self-consistent field (CASSCF) method was employed to maintain the correct symmetry in the C_{2v} calculations. We further report comparisons of the properties for the low-spin and high-spin states that we characterize, and we discuss the spin–orbit interaction scheme for NiCN. A detailed discussion, in terms of rovibrationally averaged molecular parameters, of the effects of large-amplitude bending motion in NiCN will be reported elsewhere [28].

2. Calculation method

All molecular orbital calculations have been carried out with the MOLPRO 2002.6 [5] suite of quantum chemistry programs. Roos' ANO basis set, (21s,15p,10d,6f,4g)/[8s,7p,5d,3f,2g], [29] was employed for Ni, and Dunning's aug-cc-pVQZ basis sets, (13s,7p,4d,3f,2g)/[6s,5p,4d,3f,2g], [30,31] for C and N. This set of basis sets will be denoted as [Roos ANO (Ni), aug-cc-pVQZ (C, N)]. For the calculation of the spin–orbit coupling constant A_{SO} and the Mulliken population, Wachters + f basis set, (14s,11p,6d,3f)/[8s,6p,4d,1f], [32–34] was used for Ni, and Dunning's aug-cc-pVTZ basis sets, (11s,6p,3d,2f)/[5s,4p,3d,2f], [30,31] for C and N. This combination will be denoted as [Wachters + f (Ni), aug-cc-pVTZ (C, N)].