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Ground-state geometry of small Ni-C clusters

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The ground-state geometry of the NiC_3 and NiC_4 clusters is investigated using accurate *ab initio* methods and compared with predictions using the tight-binding molecular-dynamics (TBMD) method as well as the density functional theory (DFT) based SIESTA method. The *ab initio* methods predict the ground-state geometry of the NiC_3 cluster to have a rhomboidal geometry, in agreement with the TBMD method. The SIESTA results, while predicting the ground-state geometry of NiC_4 cluster in agreement with *ab initio* methods, do not correctly predict the ground-state electronic configuration of this cluster.

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The studies of new compound materials consisting of transition metal atoms (TMA) and low dimension forms of carbon [i.e., graphite, fullerenes, single wall carbon nanotubes (SWCN) and benzene molecules] have been a subject of great current interest, mainly due to their potential applicability in the fast growing field of nanotechnology. Early studies of these materials have been focused on the investigation of the structural properties of small M_nC_m, $(C_{60})_mM_n$, SWCN-M_n and $(Bz)_mM_n$ clusters, where M indicates a $3d$-TMA and, Bz a benzene molecule.[1–4] It has become apparent from these studies that the ground-state properties (structural, electronic, and magnetic) of these clusters are sensitively dependent on the outcome of a very delicate interplay among various factors. Playing a dominant role among these are the extent of hybridization between the carbon-*p* and the metal-*d* orbitals as well as the occupancy of the *d*-shell of the TMA.[1–3] The sensitive dependence of many factors involved as well as the presence of the TMAs make the theoretical investigation of these materials a computationally challenging project putting it beyond the limits of the present day *ab initio* methods as the size of these clusters increases (i.e., for $n+m \geqslant 8$ and with $\min\{n,m\} \geqslant 2$).

As a result, approximate methods are usually employed for studying these materials. However, the degree of approximation employed by each method is a very crucial factor in obtaining a conclusive answer about the ground-state properties of these complex systems. A striking example of this problem appeared recently in association with the determination of the ground-state geometry of small Ni_mC_n ($n+m \leqslant 8$) clusters. In particular, Rey *et al.*[5] using the SIESTA code within the DFT and the nonlocal pseudopotential approach for the core electrons, have found the linear chain to be the most favorable (energetically) geometry for the NiC_3 and NiC_4 clusters. These geometries, in which the Ni atom is at one end of the chain, differ from the ground-state geometries predicted by the present authors for these clusters.

In particular, Andriotis *et al.*[1] have found a rhomboidal geometry for NiC_3 to be the most stable. Rey *et al.*[5] also find this geometry to be stable, but higher in energy than the linear structure. For the NiC_4 cluster, Andriotis *et al.*[1] find a distorted square pyramid (D_{4h} symmetry) to be the most stable, while Rey *et al.* find this structure to be higher in energy than three other structures they propose.[5] The disagreement found between our results[1] and those reported by Rey *et al.*[5] was attributed by the latter authors to the approximate nature inherent to the semi-empirical tight-binding molecular dynamics (TBMD) method that we have used. Based on this argument, Rey *et al.* claim that their prediction of the ground-state geometry of small Ni–C clusters should be more reliable than ours.

We would like to point out that the issue questionned by Rey *et al.* is not quite as simple as it may sound. This issue involves a number of crucial factors that must be taken into account very carefully before conclusive statements could be made. It is a well-known fact that the determination of the ground-state electronic configurations of monomers and dimers of the late $3d$-TMA is a very difficult problem and requires high-level configuration interaction (CI) schemes to be used for their determination. The case of the C_2 and NiC dimers is also similar. It should be noted that there are inherent approximations in the method employed by Rey *et al.*, as well (i.e., the level of the DFT used, the choice of the basis set, and the correlation functional employed, the approximations in constructing the core pseudopotentials, etc.) and these approximations may severely limit the accuracy of their claims. This is evident, for example, in their results for

C_2 and NiC (reported in Ref. 5) which fail to reproduce the corresponding exact results known.[6,7]

The purpose of the present Rapid Communication is to show that the determination of the ground-state geometry of small Ni–C clusters is very sensitive to the model approximations used and that the geometries reported by the present authors are in very good agreement with the most accurate *ab initio* results available.

It should be recalled that our TBMD scheme is based on a careful parametrization which exhibits excellent transferability. The adjustable parameters were fitted to ensure that the available experimental results for small Ni–C clusters were reproduced in very good agreement. In cases where experimental results were not available for fitting purposes, highly accurate *ab initio* results were used. Based on these facts, it is reasonable to expect our results for larger clusters to be quite reliable.

The case of the NiC_3 and NiC_4 clusters, for which no experimental information is available while accurate calculations can be performed, offers an excellent example for testing the reliability of our method justifying transferability resulting from the fitting procedure we employ. For studying these clusters we perform a series of calculations using three different *ab initio* theoretical methods with different levels of accuracy. They consist of, in the order of increasing accuracy: (i) Hartree-Fock self-consistent field calculations (HF-SCF), (ii) density functional theory (DFT), and (iii) the multireference configuration interaction method (MRD-CI).

The calculations using the HF-SCF were performed with the MOLCAS program using double zeta basis set with polarized functions (DZP),[8] and are included here only for comparison reasons.

The DFT calculations were carried out using the GAUSSIAN 98 program package.[9] The three-parameter hybrid functional of Becke using the Lee-Yang-Parr correlation functional (B3LYP) was employed for the geometry optimizations in this level of theory, while the atomic basis set that we use includes Gaussian functions of triple zeta quality augmented by *d*-polarization functions ($6\text{-}311G^\star$).

It should be recalled that both the HF-SCF and the DFT methods are single-reference methods. By contrast, MRD-CI is a multireference method. The use of a multireference method is essential to study the NiC_3 and NiC_4 clusters which constitute highly correlated systems and, therefore, require incorporation of correlation effects as accurately as possible. Our multireference computations (MRD-CI) were performed at the DFT-optimized equilibrium geometries with the multireference single and double excitation configuration interaction method MRD-CI as implemented in the DIESEL program.[10] The computations were performed in Abelian subgroups, i.e., C_{2v} for the linear isomer instead of $C_{\infty v}$. A set of reference configurations is automatically selected using a homogeneous selection scheme to ensure that both components of the π and δ configurations are treated equally. The automatic selection was carried out with a summation threshold of 0.85, which means that the sum of the squared coefficients of all reference configurations selected is above 0.85. An analysis of the molecular orbitals (MO) involved in this selected reference configurations justified the prior choice of treating active 28 electrons for the NiC_3 and 32 electrons for NiC_4, while keeping the remaining in doubly occupied molecular orbitals (frozen). From this set of reference configurations (mains) all single and double excitations in the form of configuration state functions (CSFs) are generated. From this set all configurations with an energy contribution $\delta E(T)$ above a threshold $T=10^{-7}$ Hartrees were selected, i.e., the contribution of a configuration larger than this value relative to the energy of the reference set is included in the final wave function, while the effect of those configurations which contribute less than $T=10^{-7}$ Hartree is accounted for in the energy computation (E_{MRD-CI}) by some perturbative technique. The contribution of higher excitations is estimated by applying a generalized Langhoff-Davidson correction formula (to be referred to as the MRD-CI+Q method):

$$E_{MRD-CI+Q}=E_{MRD-CI}+(1-c_0^2)[E_{ref}-E_{MRD-CI}]/c_0^2, \tag{1}$$

where c_0^2 is the sum of squared coefficients of the reference species in the total CI wave function and E_{ref} is the energy of the reference configurations. The set of reference configurations per irreducible representation was in the range between 16 (linear isomer) and 5 (rhombic isomer), the number of selected configurations in the MRD-CI space is in the size of 260.000 (rhombic) to 600.000 (linear) and about 1.1 to 2.58 million CSFs were directly included in the energy calculation.

For Ni we employed the Cowan-Griffin-relativistic-*ab-initio*-model-potential CG-AIMP of Barandiaran[11] implemented in the MOLCAS library.[12] For carbon we used a basis set of triple zeta quality augmented by an *f*-polarization function, that was used in prior MRD-CI calculations for the similar C_4 cluster.[12]

Our MRD-CI+Q calculations for both NiC_3 and NiC_4 were applied on the optimal geometries found at the $B3LYP/6\text{-}311G^\star$ level of the theory. No structural optimization was attempted at the MRD-CI+Q level of approximation as this was found to be computationally prohibitive, especially for the NiC_4 cluster. Nevertheless, from these calculations we expect to draw valuable conclusions regarding the effect of the accuracy of the method used in predicting the ground-state properties of NiC_n clusters.

Our results for the energetics of the two lowest lying NiC_3 isomers, the linear and the rhombic, are summarized in Table I. From this, it can be seen that the ordering of the two competing structures in the $B3LYP/6\text{-}311G^\star$ level of theory is in agreement with the DFT results of Rey *et al.*[5] obtained with the SIESTA program. Our calculated energy difference between the two structures, however, is less than 2 kcal/mol and, therefore, does not allow a conclusive answer to be extracted for the optimum ground-state geometry of the NiC_3 cluster. We note that Rey *et al.* report a very large energy difference of 17.5 kcal/mol in favor of the linear formation. The significance of the correlation energy is reflected in our HF-SCF results which resulted in a reversing of the energetic ordering of the two isomers, favoring the rhombic formation by 5 kcal/mol. There was a further increase to ≈8 kcal/mol

TABLE I. Energies (in kcal/mol) of the NiC_3 and NiC_4 clusters as obtained by different *ab initio* methods at various levels of approximation.

	Method						
Cluster and Geometry	HF-SCF/DZP Energy	B3LYP/6-311G* Energy	2S+1	MRD-CI+Q/cc-p-VTZ Energy	2S+1	Ref. 5 Energy	2S+1
NiC_3							
linear	0.0	0.0	3	0.0	1	0.0	1
rhombic	−5.2	+1.8	1	−7.9	1	17.5	3
NiC_4							
linear	66.8	0.0	1	0.0	1		
	0.0	−	3	18.4	3	0.0	3
planar		24.6	3	34.6	3	29.5	1
pyramid		38.0	1	41.5	1	59.9	3

in this energy difference (favoring the rhombic formation) when correlation effects are included in our calculations with the MRD-CI+Q method using the correlation-consistent polarized triple zeta (cc-p-VTZ) basis set for carbon. For both structures, the lowest states are singlets and exhibit the following charge states. In the linear geometry the Ni atom loses 0.56 electrons and the C atoms gain 0.29, 0.14, and 0.13 electrons, respectively. In the rhombic geometry, the Ni atom loses 0.81 electrons while the C atoms gain 0.35, 0.35, and 0.11 electrons, respectively.

Our results for the B3LYP/6-311G* geometric features of the two lowest lying NiC_3 isomers are presented in Fig. 1. It is worth noting that Rey *et al.*[5] find a much larger Ni-C bond length (1.71 Å) in their linear structure.

We also performed MRD-CI+Q computations for the NiC_4 cluster in the linear, planar and pyramidal geometry. In the linear geometry, we keep the Ni atom at the end of the chain. At the DFT(B3LYP) level of theory we find that the linear singlet state is energetically more favorable over the planar triplet (by 24.6 kcal/mol) and over the pyramidal singlet state (by 38.0 Kcal/mol)—in agreement with Rey *et al.*[5] At the DFT(B3LYP) level no convergence has been achieved for the linear triplet state. On the other hand, at the MRD-CI+Q level, we find the same energetic ordering as with the DFT(B3LYP) and in addition to that the singlet state is found more favorable than the triplet state by 18.4 kcal/mol. It is worth mentioning that at the less accurate MRD-CI level (without the +Q correction) the linear singlet is found to be more favorable than the triplet state by 2.3 kcal/mol. For comparison we also quote the result of the single-reference calculation obtained at the HF-SCF level: The triplet state is more favorable by 66.8 kcal/mol over the singlet state. This discrepancy is expected if one recalls that NiC_4 is a highly correlated system and that single-reference methods favor the triplet state in general. These are, in fact, the basic reasons why our multireference results do not agree with the SIESTA (DFT-based) results obtained by Rey *et al.*[5] which are closer to our HF-SCF results. The observed difference is crucial if one considers the magnetic properties of this cluster. At this point, it is worth pointing out that our TBMD results show the ground state of both NiC_3 and NiC_4 clusters to be a singlet,[1] in agreement with the present MRD-CI results. Furthermore, it should be noted that in the linear singlet state the Ni loses $0.76|e|$ to C atoms while the length of the Ni–C bond is found to be 1.699 Å. The value of the bond length is, just as in the case of NiC_3, smaller than the corresponding value (1.77 Å) found by Rey *et al.*[5]

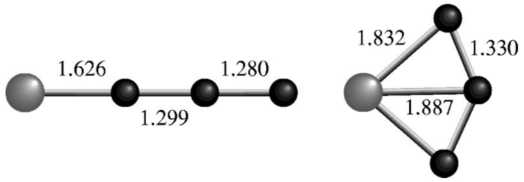

FIG. 1. Geometry and bond lengths (in Å) of the lowest energy states of the NiC_3 cluster obtained using the B3LYP/6-311G* method.

At the MRD-CI+Q level, the planar and pyramidal geometries were found higher in energy than the linear one by 34.6 and 41.5 kcal/mol, respectively, favoring the corresponding results of Rey *et al.* Thus, the treatment of the correlation effects at the MRD-CI+Q level does not change the energy-ordering of the various geometric configurations as found at the DFT(B3LYP) level of approximation. However, as indicated in Table I, there is disagreement with respect to the spin state predicted by our calculations as compared to those of Rey *et al.* In particular, as we found in the case of the linear NiC_4 geometry, the MRD-CI+Q results predict a planar triplet state compared to planar singlet of Rey *et al.* It is also worth noting that in the planar and pyramidal geometries the Ni-C bond lengths are found much larger (1.82 and 1.95 Å, respectively) than in the linear geometry (1.699 Å). Finally, the charge transfer from Ni to C is found to be much larger in the pyramidal ($0.86|e|$) than in the linear geometry ($0.76|e|$) and smaller ($0.58|e|$) in the planar than in the linear geometry. Thus, our MRD-CI results differ substantially from those of Rey *et al.*, indicating that their method consistently misses the exact ground-state electronic configuration of small NiC_n clusters.

Our results for the NiC_4 cluster indicate, as in the case of the NiC_3 cluster, that caution must be exercised in dealing with DFT-based results as they do not guarantee a reliably definitive answer for the ground-state properties of highly correlated systems. Additionally, one should consider the different chemistry exhibited by the free carbon chains consisting of even and odd number of atoms.[13] We attribute this effect to the different bonding features (geometry, spin state, and charge transfer) found between the NiC_3 and NiC_4. Based on this argument, we predict that NiC_5 may deviate from the linear geometry.

The conclusions reached from the present results can be summarized as follows: For the NiC_3 cluster two competing low energy structures exist, namely a rhombic and a linear one. Accurate *ab initio* calculations at the MRD-CI+Q level of approximation favor the rhombic structure, in agreement with our earlier predictions using the TBMD scheme.[1] At the level of the DFT within the B3LYP approximation, the linear structure appears energetically more favorable. While this is in qualitative agreement with the results of Ref. 5, the DFT as implemented by these authors, leads to much larger Ni–C bond lengths and practically zero charge transfer from the Ni atom. Furthermore, their prediction of linear ground state for the NiC_3 cluster is in qualitative disagreement with more accurate *ab initio* calculations which predict it to have a rhomboidal structure. For the NiC_4 cluster our *ab initio* results at the MRD-CI+Q level of approximation are not conclusive regarding the optimal ground-state geometry of this cluster as no geometry optimization was performed. However, they are in disagreement with the SIESTA (DFT-based) results regarding the spin state and the charge transfer in the various geometric configurations of the NiC_4 cluster (obtained using the DFT method). Our results for the spin state should not be surprising if one recalls that single-reference methods favor the triplet state over the singlet state, while multireference methods favor the singlet configuration in general. In view of all these results it is clear that the highly correlated nature of the NiC_3 and NiC_4 clusters requires an accurate incorporation of correlation effects in their study. This can be achieved with multireference methods such as the one we have used. Additionally, the present results clearly indicate that the results of Ref. 5 cannot be considered as conclusive and casts serious doubt on their claim that SIESTA is a ‘‘more accurate’’ method than TBMD method for treating Ni_mC_n clusters.

The predictions of our TBMD method, on the other hand, appear to be quite reliable as they reproduce the existing experimental and/or *ab initio* results (structural, electronic, and magnetic properties as well as the vibrational frequencies) for these clusters. We note that Rey *et al.* do not give vibrational frequencies for any of their clusters. We do not, however, claim that the predictions of our TBMD method are the best possible. On the contrary, we would like to point out that metallo-organic complexes involving TMA require highly accurate calculations for conclusive answers. It is worth pointing out, however, that semi-empirical methods (like our TBMD) which are parametrized by fittings to experimental and/or accurate *ab initio* results of small clusters are computationally efficient and offer consistently reliable predictions for the structural properties of larger clusters.

At the completion of this work, we became aware of another work by the same group[14] criticizing our results dealing with the interaction of Ni with the C_{60} molecule.[2] In view of the above discussion, the reported discrepancy can be easily understood.

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