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Ab initio density-functional calculations of the geometries, electronic structures, and magnetic moments of Ni-C clusters

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We have performed *ab initio* molecular dynamics simulations of the clusters Ni_2, C_2, C_3, NiC_n ($n=1-6$), and $\mathrm{Ni}_2\mathrm{C}_n$ ($n=4-6$) using a fully self-consistent density-functional method that employs linear combinations of atomic orbitals as basis sets, standard norm-conserving pseudopotentials and the generalized gradient approximation to exchange and correlation. Our results for the pure clusters, which are compared with those obtained by other *ab initio* calculations, are in good agreement with available experimental data. Linear forms are energetically preferred for all the mixed clusters except NiC_2, NiC_6, and $\mathrm{Ni}_2\mathrm{C}_6$, which have cyclic structures. These latter findings differ markedly from results obtained recently using a tight-binding molecular dynamics method, which predict rhombic geometry for NiC_3 and three-dimensional structures for NiC_4, $\mathrm{Ni}_2\mathrm{C}_4$, $\mathrm{Ni}_2\mathrm{C}_5$, and $\mathrm{Ni}_2\mathrm{C}_6$.

In the last few years there has been great interest in producing new materials composed of transition metals and carbon due to their potential for use as catalysts, semiconductors, and superconductors, and in quantum well and quantum dot devices (see Ref. 1 and references cited therein). The interactions of transition metal (TM) atoms with graphite and with C_{60} and other fullerene molecules have been the subject of intense research (see, e.g., Refs. 2–5). Also, a new class of molecular clusters of remarkable stability has been discovered, namely the metallocarbohedrenes (''met-cars''), in which TM and C atoms constitute cagelike structures (for a review, see Ref. 1); the extraordinary stability of these mixed clusters has been attributed to a presumptive pentagonal dodecahedral structure. Due to the presence of TM atoms, the experimental information on TM-C materials is far from easy to interpret. The difficulties are particularly great for prediction of the ground state structures of TM-C clusters of moderate and large size, because of the large number of local minima of their potential energy surfaces (PES's). However, determination of geometry is one of the fundamental problems in cluster research, since it may affect optical, magnetic, and chemical properties. It is therefore highly desirable to get accurate information on the structures of the smaller TM-C species, in the hope that it will provide insight into TM-C growth mechanisms. Similarly, an understanding of the behavior of small TM-C systems may throw light on the TM-catalyzed growth of novel all-C structures such as C nanotubes.[6]

To our knowledge, the only previous systematic theoretical study of the structures and magnetic moments of small TM-C clusters is the work recently reported by Andriotis *et al.*,[3] who performed spin- and geometry-unrestricted calculations for some $\mathrm{Ni}_n\mathrm{C}_m$ clusters ($n+m\leqslant 8$) using a tight-binding molecular dynamics (TBMD) method. Due to the status of these pioneering results as a probable basis for further studies on TM-C structures, we decided to test them by performing theoretically more exact *ab initio* MD simulations of the same kind of cluster. In this paper we report the results we obtained using SIESTA,[7–9] a method based on density-functional theory (DFT), which has recently been applied to several systems, including C nanotubes, Au nanostructures, adsorbates on Si surfaces, nucleic acids, and Ni-Al clusters (see Refs. 9–11). Our findings turned out to differ markedly from those of Andriotis *et al.*[3] Unfortunately, experimental data for small Ni-C clusters are not available to decide between the two sets of theoretical results, but the reliability of our calculations is supported by the results we report here for Ni_2, C_2 and C_3, which are in good agreement with available experimental data.[9]

SIESTA has been described in detail elsewhere.[7–9] It performs *ab initio* DFT calculations using numerical atomic orbitals as basis sets. In these calculations we used triple-ζ bases with polarization functions. For Ni, the basis contains three orbitals with different radial forms to describe the $4s$ shell and three orbitals for each of the angular functions of the $3d$ shell, and the $4s$ shell is polarized by the inclusion of a double set of p orbitals. For C, we have three orbitals for the $2s$ and each of the $2p$ functions, and the latter are polarized with a single set of d functions. The triple-ζ orbitals are defined in the split-valence spirit, and the polarization functions are obtained perturbatively by applying a small electric field to the free atom.[9] In order to achieve linear scaling in the calculation of the matrix elements, orbitals have a finite spacial range defined by limiting the orbital confinement energy (the difference between the atomic eigenvalues of the confined and free orbitals) to 0.001 Ry.[9]

The core electrons were represented by non-local, norm-conserving Troullier-Martins pseudopotentials[12] generated by nonrelativistic spin-polarized atomic calculations. The reference valence configurations were $4s^1(\uparrow)3d^5(\uparrow)3d^4(\downarrow)$ for Ni, and $2s^1(\uparrow)2s^1(\downarrow)2p^2(\uparrow)$ for C (arrows indicate up or down spins), and the pseudopotential radii were 2.05 bohr for Ni and 1.49, 1.52, and 2.19 bohr for the s, p, and d orbitals of C. Due to the significant overlap of the core charge with the $3d$ orbitals of Ni, it was found necessary to include nonlinear core corrections (NLCC) in the description of these atoms. A radius of $r_c=0.8$ bohr was used to define

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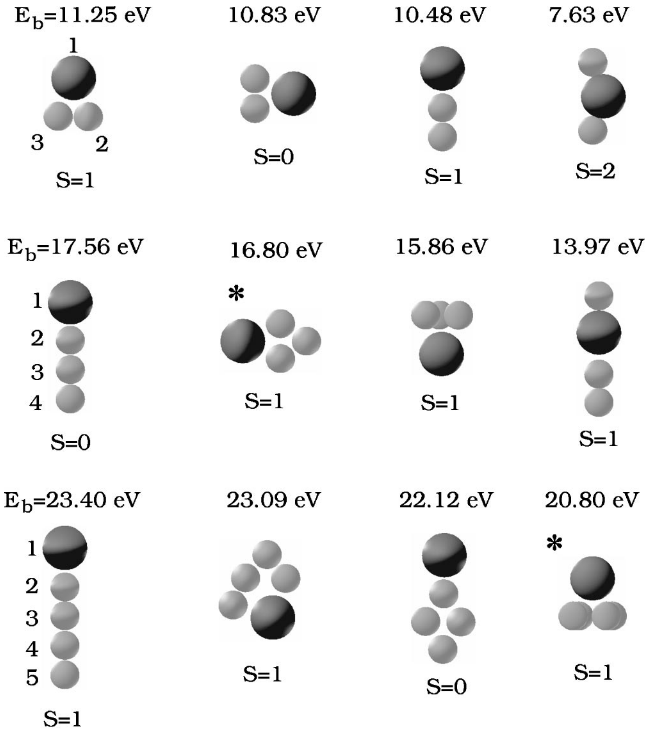

FIG. 1. Structures, binding energies, and total spins of the four lowest-energy isomers found for each NiC_2, NiC_3, and NiC_4 clusters. Large spheres represent Ni atoms, smaller spheres C atoms. The bond lengths and bond angles of the ground state structures are as follows. NiC_2, $R_{12}=R_{13}=1.87$ Å, $R_{23}=1.36$ Å, $\alpha_1=42.7°$, $\alpha_2=\alpha_3=68.6°$; NiC_3, $R_{12}=1.71$ Å, $R_{23}=R_{34}=1.33$ Å; NiC_4, $R_{12}=1.77$ Å, $R_{23}=1.31$ Å, $R_{34}=1.34$ Å, $R_{45}=1.33$ Å. The geometries identified by Andriotis *et al.* (Ref. 3) as the minimum energy structures for NiC_3 and NiC_4 are marked by an asterisk.

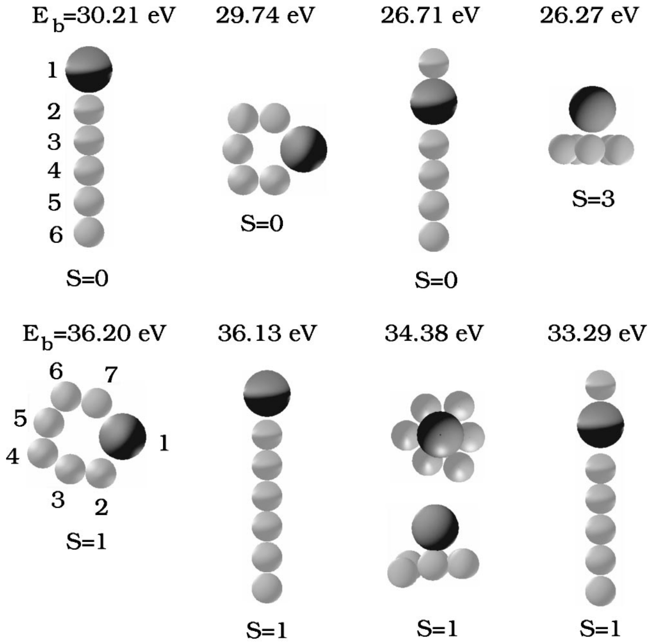

FIG. 2. Structures, binding energies and total spins of the four lowest-energy isomers found for NiC_5 and NiC_6 (the third isomer of NiC_6, with two different views). Large spheres represent Ni atoms, smaller spheres C atoms. The bond lengths and bond angles of the ground state structures are as follows. NiC_5, $R_{12}=1.72$ Å, $R_{23}=R_{45}=R_{56}=1.32$ Å, $R_{34}=1.30$ Å; NiC_6, $R_{12}=1.83$ Å, $R_{17}=1.81$ Å, $R_{23}=R_{45}=1.33$ Å, $R_{34}=1.36$ Å, $R_{56}=R_{67}=1.34$ Å, $\alpha_1=111.7°$, $\alpha_2=112.8°$, $\alpha_3=157.3°$, $\alpha_4=109°$, $\alpha_5=158.2°$, $\alpha_6=111°$, $\alpha_7=139.9°$.

the NLCC charge density.[13] For a given configuration of the ion cores, the valence electrons were treated self-consistently within the DFT using the Perdew-Burke-Ernzerhof form of the generalized gradient approximation (GGA) for the exchange correlation potential.[14]

In all cluster calculations we considered a supercell geometry with an $18\times18\times24$ Å unit cell (large enough for interaction between the clusters in neighboring cells to be negligible) and used a 100 Ry energy cutoff to define the finite real space grid for the numerical integrals.[7–9] To obtain the cluster structures we carried out quenching MD simulations[15] using the velocity Verlet algorithm. For each cluster, the set of starting geometries (40 for the largest clusters) was extensive enough to ensure thorough exploration of the PES and hence allow identification of the computed minimum energy structure with the ground state of the cluster. The forces on ions were computed using a variant of the Hellman-Feynman theorem, which includes Pulay-like corrections to account for the fact that the basis sets are not complete and move with the atoms.[7–9] The clusters were allowed to relax until the interatomic forces were smaller than 0.001 eV/Å. A Mulliken population analysis was carried out to obtain both the charge and spin of each atom.

As a test of the computational method, we performed calculations for Ni_2, C_2 and C_3, for which experimental data are available for comparison. The computed binding energies E_b and bond lengths R of Ni_2 and C_2 are, respectively, $E_b=2.54$ eV, $R=2.17$ Å and $E_b=6.26$ eV, $R=1.35$ Å, in good agreement with the corresponding experimental data, $E_b=2.08$ eV, $R=2.20$ Å and $E_b=6.21$ eV, $R=1.24$ Å.[16–18] The calculated total spin of both Ni_2 and C_2 is $S=1$. For Ni_2 this result agrees with matrix isolation measurements;[19] for C_2, however, it differs from the experimental finding $S=0$,[18] a result which is not unexpected in view of the difficulty of accurate theoretical determination of the spin state of C_2.[20] C_3 is predicted to be a bent structure in a singlet state, in keeping with the experimental data.[21] The experimental binding energy, bond length and bond angle are $E_b=13.7$ eV, $R=1.2897$ Å, and $\alpha=162.5°$ (see Refs. 21 and 22), in good agreement with our computed values, $E_b=13.78$ eV, $R=1.33$ Å, and $\alpha=141°$.

Several *ab initio* studies of pure Ni and C clusters have been carried out, particularly in the case of C. Here we mention same of those that are most relevant to our work. Reuse and Khanna[23] used DFT to investigate the geometries of Ni_n clusters ($n=2-6$, 8, 13). For the ground state of Ni_2, they found $E_b=3.22$ eV and $R=2.0$ Å. *Ab initio* calculations for C_n clusters have been performed by Raghavachari and Binkley[22] (for $n=2-10$) using the Hartree-Fock method, and by Hutter *et al.*[21] (for $n=2-18$) using DFT. For C_2, Raghavachari and Binkley found the values $E_b=5.8$ eV and $R=1.245$ Å, and Hutter *et al.* the value $R=1.259$ Å (the binding energy of C_2 was not reported by the latter authors). These previously computed binding energies for Ni_2 and C_2 agree with the experimental data less well than our results. For C_3, a bent singlet ground state structure with $R=1.305$ Å and $\alpha=153.3°$ has been found by Hutter *et al.*[21]

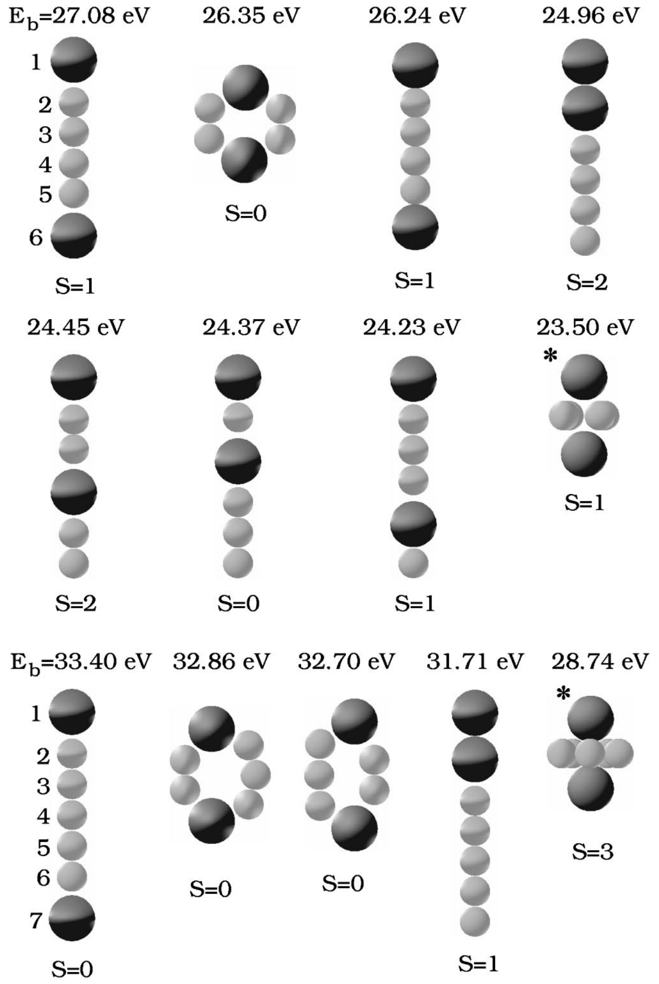

FIG. 3. Structures, binding energies and total spins of the eight lowest-energy isomers found for Ni_2C_4 and the five lowest-energy isomers found for Ni_2C_5. Large spheres represent Ni atoms, smaller spheres C atoms. The bond lengths of the ground state structures are as follows. Ni_2C_4, $R_{12}=R_{56}=1.85$ Å, $R_{23}=R_{45}=1.29$ Å, $R_{34}=1.38$ Å; Ni_2C_5, $R_{12}=R_{67}=1.81$ Å, $R_{23}=R_{34}=R_{45}=R_{56}=1.34$ Å. Geometries identified by Andriotis *et al.*[3] as the minimum energy structures for NiC_3 and NiC_4 are marked by an asterisk.

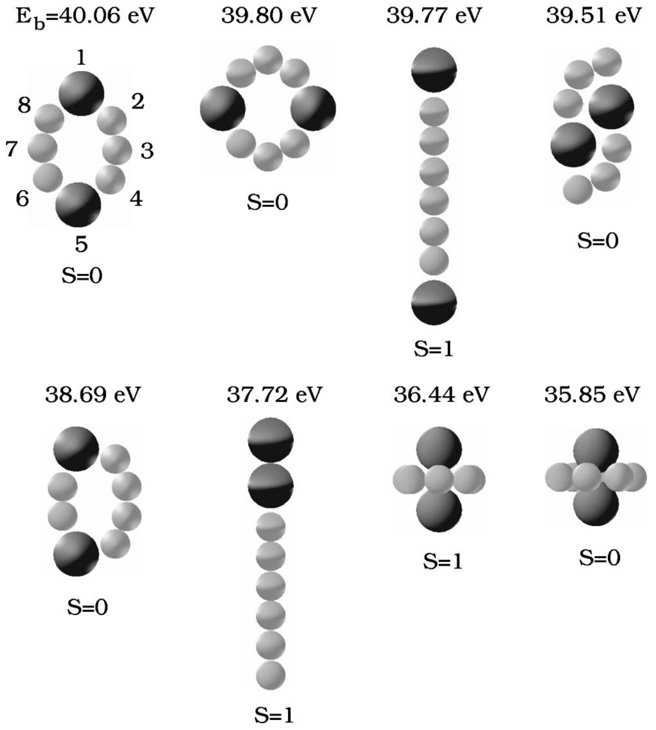

FIG. 4. Structures, binding energies and total spins of the eight lowest-energy isomers found for Ni_2C_6. Large spheres represent Ni atoms, smaller spheres C atoms. The bond lengths and bond angles of the ground state structure are as follows. $R_{12}=R_{18}=R_{45}=R_{56}=1.81$ Å, $R_{23}=R_{34}=R_{67}=R_{78}=1.33$ Å, $\alpha_1=\alpha_5=99.9°$, $\alpha_2=\alpha_4=\alpha_6=\alpha_8=141.9°$, $\alpha_3=\alpha_7=157°$.

using DFT, but the Hartree-Fock calculations of Raghavachari and Binkley[22] predicted that the minimum energy structure of C_3 is a linear chain with C-C distances of 1.278 Å and a binding energy of 12.7 eV. Our calculations show that the bent and the linear forms of C_3 are, in fact, almost isoenergetic (their energy difference is only 0.01 eV).

Having tested the method, we performed calculations for the mixed clusters NiC_n $(n=1-6)$ and Ni_2C_n $(n=4-6)$. The structures, binding energies, and total spins of the lowest-energy isomers of NiC_n $(n=2-6)$ and Ni_2C_n $(n=4-6)$ are shown in Figs. 1–4; bond lengths and bond angles are only given for the ground state structures. Except for NiC_2, NiC_5, and NiC_6, all these clusters were studied by Andriotis *et al.*[3] using the TBMD method; and except in the case of Ni_2C_6, which is discussed below, the geometries identified by Andriotis *et al.* as minimum energy structures have been marked by an asterisk, although it should be pointed out that all the Ni_nC_m clusters studied by these authors were predicted to have ground state structures of zero total magnetic moment. The main conclusions drawn from the results obtained for the mixed clusters are as follows.

The computed binding energy and bond length of NiC are $E_b=4.13$ eV and $R=1.67$ Å. This cluster is predicted to have antiferromagnetic spin ordering. The same result was obtained by Andriotis *et al.*[3] using the TBMD method, but their predicted absolute value for the magnetic moments of the C and Ni atoms, $0.334\mu_B$, where μ_B is the Bohr magneton, is much larger that the value obtained in our calculations, $0.011\mu_B$.

For NiC_2, our calculations predict that a triplet triangular form is the ground state. There is a charge transfer of 0.17*e* from the Ni atom to the C atoms, where *e* is the charge of the electron, and the magnetic moments of the Ni and C atoms are $\mu(\mathrm{Ni})=0.94\mu_B$ and $\mu(\mathrm{C})=0.53\mu_B$, respectively. Hence the magnetic moment of the Ni atom in NiC_2 is not far from its free-atom value, $1\mu_B$. The minimum-energy structure of NiC_3 was found to be a singlet linear chain in which there is no significant charge transfer and the magnetic moment of every atom is zero.

In the case of NiC_4, we found a triplet linear form to be the ground state. The magnetic moment of the Ni atom is $0.79\mu_B$ and those of the C atoms are $\mu(2)=0.28\mu_B$, $\mu(3)=0.20\mu_B$, $\mu(4)=0.14\mu_B$, and $\mu(5)=0.58\mu_B$ (see Fig. 1 for atom numbering). The C atom farthest from the Ni atom has an excess charge of 0.21*e*, which is taken from the C atoms at intermediate positions. The C atom closest to the Ni atom takes only 0.08*e* from it.

For NiC_5 we found the ground state to be a singlet linear chain with the Ni atom at one end. All the atoms have zero magnetic moment, and the C atom farthest from the Ni atom has an excess charge of $0.21e$. For NiC_6, however, we found a triplet cyclic ground state, with $\mu(1)=0.78\mu_B$, $\mu(2)=0.46\mu_B$, $\mu(3)=0.13\mu_B$, $\mu(4)=0.25\mu_B$, $\mu(5)=0.08\mu_B$, $\mu(6)=-0.02\mu_B$, $\mu(7)=0.31\mu_B$, and a small excess charge on C atoms 2, 4, and 6.

For Ni_2C_4 we found the ground state to be a triplet linear chain with $\mu(1)=\mu(6)=0.80\mu_B$, $\mu(2)=\mu(5)=0.14\mu_B$, and $\mu(3)=\mu(4)=0.07\mu_B$. The two C atoms closest to the Ni atoms bear an excess charge of $0.18e$, of which $0.06e$ is taken from the Ni atom and $0.12e$ from the neighboring C atom.

For Ni_2C_5 our predicted ground state structure is a singlet linear chain. All the atoms have zero magnetic moment and the Ni atoms and neighboring C atoms bear a slight excess charge.

For Ni_2C_6, Andriotis *et al.*[3] found that a starting hexagonal bipyramid with apical Ni atoms was unstable and relaxed to a distorted cubic structure. According to our calculations several hexagonal bipyramids are metastable and the ground state is a singlet cyclic structure in which all the atoms have zero magnetic moment (Fig. 4).

To sum up, in this work we performed *ab initio* MD simulations of Ni_2, C_2, C_3 and Ni-C clusters [NiC_n $(n=1-6)$ and Ni_2C_n $(n=4-6)$] using a DFT-based method, standard norm-conserving pseudopotentials and the GGA to the exchange and correlation. Our results for the pure clusters are in good agreement with available experimental data,[16–19,21,22] which they generally approximate better than those obtained in previous *ab initio* studies of these clusters.[21–23] For the mixed NiC_n and Ni_2C_n clusters our results differ markedly from those obtained by Andriotis *et al.*[3] using the TBM method: we found no three-dimensional ground state structures, and total spin is not always zero. Our results do agree qualitatively with Andriotis *et al.*'s findings in that the magnetic moment of each Ni atom in the Ni-C clusters is predicted to be smaller than its free-atom value, being in some cases zero. These results show that larger sizes than those studied here are necessary for these complex Ni-C clusters to adopt three-dimensional structures. The size at which this occurs for these and other TM-C clusters is an open question.

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[1] B.C. Guo and A.W. Castleman, Jr., in *Advances in Metal and Semiconductor Clusters*, edited by M. A. Duncan (Jai Press, London, 1994), Vol. 2, p. 137.

[2] D.M. Duffy and J.A. Blackman, Phys. Rev. B **58**, 7443 (1998).

[3] A.N. Andriotis, M. Menon, G.E. Froudakis, and J.E. Lowther, Chem. Phys. Lett. **301**, 503 (1999).

[4] A.N. Andriotis and M. Menon, Phys. Rev. B **60**, 4521 (1999).

[5] E.K. Parks, K.P. Kerns, S.J. Riley, and B.J. Winter, Phys. Rev. B **59**, 13 431 (1999).

[6] Y.H. Lee, S.G. Kim, and D. Tománek, Phys. Rev. Lett. **78**, 2393 (1997).

[7] P. Ordejón, E. Artacho, and J.M. Soler, Phys. Rev. B **53**, R10 441 (1996).

[8] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).

[9] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J.M. Soler, Phys. Status Solidi B **215**, 809 (1999).

[10] M. Calleja, C. Rey, M.M.G. Alemany, L.J. Gallego, P. Ordejón, D. Sánchez-Portal, E. Artacho, and J.M. Soler, Phys. Rev. B **60**, 2020 (1999).

[11] P. Ordejón, Phys. Status Solidi B **217**, 335 (2000).

[12] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[13] J. Zhu, X.W. Wang, and S.G. Louie, Phys. Rev. B **45**, 8887 (1992).

[14] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] G.J. Ackland and R. Thetford, Philos. Mag. A **56**, 15 (1987).

[16] H. Basch, M.D. Newton, and J.W. Moskowitz, J. Chem. Phys. **73**, 4492 (1980).

[17] E.M. Nour, C. Alfaro-Franco, K.A. Gingerich, and J. Laane, J. Chem. Phys. **86**, 4779 (1987).

[18] K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[19] M. Moskovits and J.E. Hulse, J. Chem. Phys. **66**, 3988 (1977).

[20] F.W. Kutzler and G.S. Painter, Phys. Rev. B **45**, 3236 (1992).

[21] J. Hutter, H.P. Lüthi, and F. Diederich, J. Am. Chem. Soc. **116**, 750 (1994).

[22] K. Raghavachari and J.S. Binkley, J. Chem. Phys. **87**, 2191 (1987).

[23] F.A. Reuse and S.N. Khanna, Chem. Phys. Lett. **234**, 77 (1995).