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The electronic structure and magnetic properties of the nickel tetramer and its partially carbonylated forms

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Abstract. Density functional calculations using nonlocal functionals for exchange and correlation have been carried out on Ni_4 and $Ni_4(CO)_x$ $(x = 1, 2)$ species. In the case of the nonligated cluster, all the forms originated by Jahn–Teller distortion of the tetrahedron have been investigated. The lowest-energy states are all characterized by a spin multiplicity corresponding to the total spin $S = 2$; the four unpaired electrons are strongly localized in the atomic 3*d* shells. The Ni–Ni bond is dominated by the *s*–*s* interaction, as is proved by changes in electron distribution caused by the ionization. The interaction of the nickel tetramer with one CO ligand has no substantial effect on magnetic properties. On the contrary, two CO groups are already sufficient, when coordinated in a μ_2 mode, to quench completely the magnetism of the cluster. The μ_2 coordination is found to be more effective in reducing the paramagnetism than the μ_3 coordination.

PACS. 31.15.Ew Density-functional theory – 31.25.Qm Electron-correlation calculation for polyatomic molecules – 36.40.Cg Electronic and magnetic properties of clusters

1 Introduction

The electronic and geometrical structure of transition metal (TM) clusters is still a largely unexplored area of the cluster chemistry, due to the well-known methodological and computational difficulties connected with the *d*-electron elements. In order to elucidate the electronic mechanisms underlying the cluster stability, the following basic questions should be answered: (i) which role do the *d* electrons play in the metal–metal bond formation; (ii) to which extent are the *d* states localized on atoms; and (iii) which is the mechanism governing the appearance of magnetism in TM clusters?

In this paper, we will consider in detail the Ni_4 cluster which is a very interesting prototype of magnetic clusters. In addition, we will discuss the electronic structure of the derivatives $Ni_4(CO)_x$ $(x = 1, 2)$ in order to show how the presence of a few ligands is sufficient to quench partially or totally the cluster magnetism.

The stability of Ni_4 depends only on the strength of the metal–metal bond, which may be qualitatively described as follows. The Ni atoms, being at the end of the first transition series, are characterized by a large effective nuclear charge and, therefore, by localized 3*d* states and relatively diffuse 4*s* orbitals. In fact, maxima in the radial functions for 3*d* and 4*s* orbitals occur at 0.33 Å and 1.2 Å, respectively [1]. Therefore, in small clusters, the two-center overlap between 3*d* orbitals is expected to be small, while the 4*s*–4*s* interaction may play a dominant role in the metal–metal bond formation. The d^9s^1 electronic configuration is the most suitable one for promoting *s*–*s* interaction. This means that on each nickel atom taking part into the formation of a Ni_n cluster do exist a localized *d*-electron hole, responsible for the appearance of the magnetic moment which is expected to be close to $S = n/2$.

The theoretical studies on nickel clusters so far reported in the literature [2] do not give unambiguous answers to the above questions. In particular the lack of a complete characterization of Ni_4 is mainly due to the fact that no systematic analysis has been carried out on possible spin states and isomeric forms.

The aim of the present paper is to contribute to a better understanding of the electronic structure of the nickel tetramer on the basis of results of density functional theory (DFT) calculations on Ni_4 and on its partially carbonylated forms. In the following section, a brief outline of the adopted computational method is presented, while results and discussion are presented in Sect. 3.

2 Computational methods

The electronic and geometrical structures of Ni_4 and $Ni_4(CO)_x$ $(x = 1, 2)$ have been investigated by means of DFT calculations, based on the nonlocal exchange and correlation energy functionals proposed by Becke [3] and Lee, Yang and Parr [4] (BLYP). For Ni atoms the effective core

Table 1. Atomic properties of Ni atom.

Config.	Term symbol	Exp.	HF	DFT-BLYP
d^9s^1	^{3}D	0.00	1.41	0.00
d^8s^2	^{3}F	0.03	0.00	0.11
d^{10}	^{1}S	1.73	4.79	2.65
IP(a)		7.62	9.00	7.98
EA(b)		1.16		0.88

(a) The IP values are computed for the process Ni (d^9s^1,^{3}D) → Ni$^+$ (d^9,^{2}D).

(b) The EA values are computed for the process Ni (d^9s^1,^{3}D) → Ni$^-$ (d^9s^2,^{2}D).

potential (ECP, 18 valence electrons) proposed by Hay and Wadt [5] has been adopted, together with the associated basis set, used with the contraction scheme (2111/41/311) (basis A). On C and O atoms, the ECP and the (31/31) basis sets of [6] have been adopted. The electronic structure of Ni_4 has been first studied using the basis A, while the contraction (2111/41/41) has been used (basis B) for nickel atoms so that the computational effort in the study of the carbonylated forms may be reduced. It has been carefully checked that the two basis sets A and B for Ni atoms give substantially the same energy ordering of the Ni_4 forms and the same cluster stability and equilibrium geometry.

As is well known, the ECP operators of [5] for Ni atoms have been derived in the context of the Hartree–Fock (HF) model. The same ECP has been validated in the framework of DFT, carrying out BLYP calculations on low-lying states of the nickel atom (see Table 1). When compared with the experimental data [7], the DFT results appear to be much better than the corresponding HF results. In particular, the energy sequence $E(^3\mathrm{D}) < E(^3\mathrm{F}) < E(^1\mathrm{S})$ is correctly described at the BLYP level, while the HF method gives a completely wrong ordering of the states, predicting the d^8s^2 ^{3}F state to be 1.4 eV lower in energy than the state ^{3}D. In fact, ^{3}D is the true ground state, correctly predicted by the DFT. The d^{10} ^{1}S state lies too high in energy both at the HF and BLYP levels, although the latter yields considerably smaller error (about 0.9 eV) than the former (3.0 eV). The correct ordering of the low-lying configurations is an important requisite, especially for the study of the metal–metal bond formation. In this respect, the HF method seems to be largely inadequate, because the coupling of the s electrons of the d^9s^1 configuration leading to the Ni–Ni bond is a process possible only after promotion to an excited state. Such an energy demand is, on the other hand, absent in the DFT description.

The ground-state geometries of Ni_4 isomers have been determined by gradient-based energy minimization in the framework of spin-polarized DFT. Care has been exercised in order that self-consistent solutions may be obtained that belong exactly to an irreducible representation of the cluster point group. This an obvious requirement, since we aim also at discussing electronic and geometrical relaxations caused by the occurrence of static Jahn–Teller instabilities.

The stability of the Ni_4 clusters will be discussed in terms of binding energy per atom, defined as

$$\frac{\mathrm{BE}}{n} = -\frac{E(\mathrm{Ni}_4) - nE(\mathrm{Ni})}{n} ,$$

while the stability of the carbonylated derivates is defined according to

$$\frac{\mathrm{BE}}{x} = -\frac{E(\mathrm{Ni}_4(\mathrm{CO})_x) - E(\mathrm{Ni}_4) - xE(\mathrm{CO})}{x} ,$$

where $E(\mathrm{Ni}_4)$ and $E(\mathrm{CO})$ are the energies of the most stable nickel tetramer and of the free CO ligand, respectively.

3 Results and discussion

3.1 The Ni_4 cluster

A systematic DFT–BLYP investigation has been carried out on Ni_4 clusters in order to identify its electronic ground state and the associated cluster geometry. Our calculations show that all the spin states with multiplicity smaller than 5 lie high in energy [8]. Therefore, the low-energy forms of the nickel tetramer are characterized by the presence of four unpaired electrons, all strongly localized in the atomic 3*d* shells. In other words, evidence has been obtained that the spin coupling among the unpaired *d* electrons on different Ni atoms is an energy-demanding process, independent from the cluster symmetry.

The most compact form of Ni_4 is the tetrahedron. The DFT geometry optimization, carried out by the imposition of the T_d symmetry constraint, gives a form characterized by $\mathrm{BE}/n = 1.543$ eV and by equilibrium distance $r^{\mathrm{e}}_{\mathrm{Ni-Ni}} = 2.39$ Å. The associated electronic state $^5\mathrm{T}_2$ $(t_2^3t_2^1)$ is Jahn–Teller-unstable. As well known, distortions along not totally symmetric normal modes can produce different cluster isomers. A distortion along the C_3 axis of the tetrahedron lowers the symmetry to C_{3v} and, after the geometry optimization, a stable isomer is found with the ground state $^5\mathrm{A}_1$ (e^2e^2). The computed symmetry-independent $r^{\mathrm{e}}_{\mathrm{Ni-Ni}}$ distances are equal to 2.44 and 2.34 Å (average value 2.39 Å), while the value of BE/n is equal to 1.552 eV. When the distortion of the tetrahedron is applied along a C_2 axis, a cluster of D_{2d} symmetry is generated. Its optimized geometry corresponds to a Jahn–Teller-stable configuration of type $a_2^1e^2b_2^1$. The two independent $r^{\mathrm{e}}_{\mathrm{Ni-Ni}}$ distances are equal to 2.30 and 2.45 Å (average value 2.38 Å) and the cluster's stability ($\mathrm{BE}/n = 1.574$ eV) is 0.07 eV higher than that of the tetrahedron (see Table 2). As expected, the geometrical rearrangement (measured in terms of variation of the mean Ni–Ni distances) and the energy stabilization caused by Jahn–Teller distortions are very small. Another Ni_4 isomer has been identified which is characterized by a lower symmetry (C_{2v}), and which can be obtained by the allowance of a double distortion along two orthogonal twofold axes of the tetrahedron. The C_{2v} form has stability similar to all other forms ($\mathrm{BE}/n = 1.566$ eV; see Table 2 and Fig. 1) but lies slightly higher in energy with respect to

Table 2. Ground state properties of Ni_4 and Ni_4^+ clusters.

Cluster	State			BE/$n^{(a)}$	IP$_v$/VDE$^{(b)}$	IP$_a$/EA$^{(b)}$
Ni_4	D_{2d}	$a_2e^2b_2$	$^5A_2$	1.574	5.66	5.57
Ni_4	C_{2v}	$a_2b_2b_1b_2$	$^5B_2$	1.566	5.67	5.54
Ni_4	C_{3v}	e^2e^2	$^5A_1$	1.552	5.53	5.49
Ni_4	T_d	$t_2^3t_2$	$^5T_2$	1.543	5.45	5.45
Ni_4	D_{4h}	$e_u^2e_u^2b_{1g}b_{1u}$	$^7A_{1u}$	1.527		
Ni_4^+	T_d	t_2^3	$^4A_1$	2.177		

(a) BE/n is the binding energy per atom (eV), see text.
(b) Vertical (IP$_v$) and adiabatic (IP$_a$) ionization potential (eV) for Ni_4.

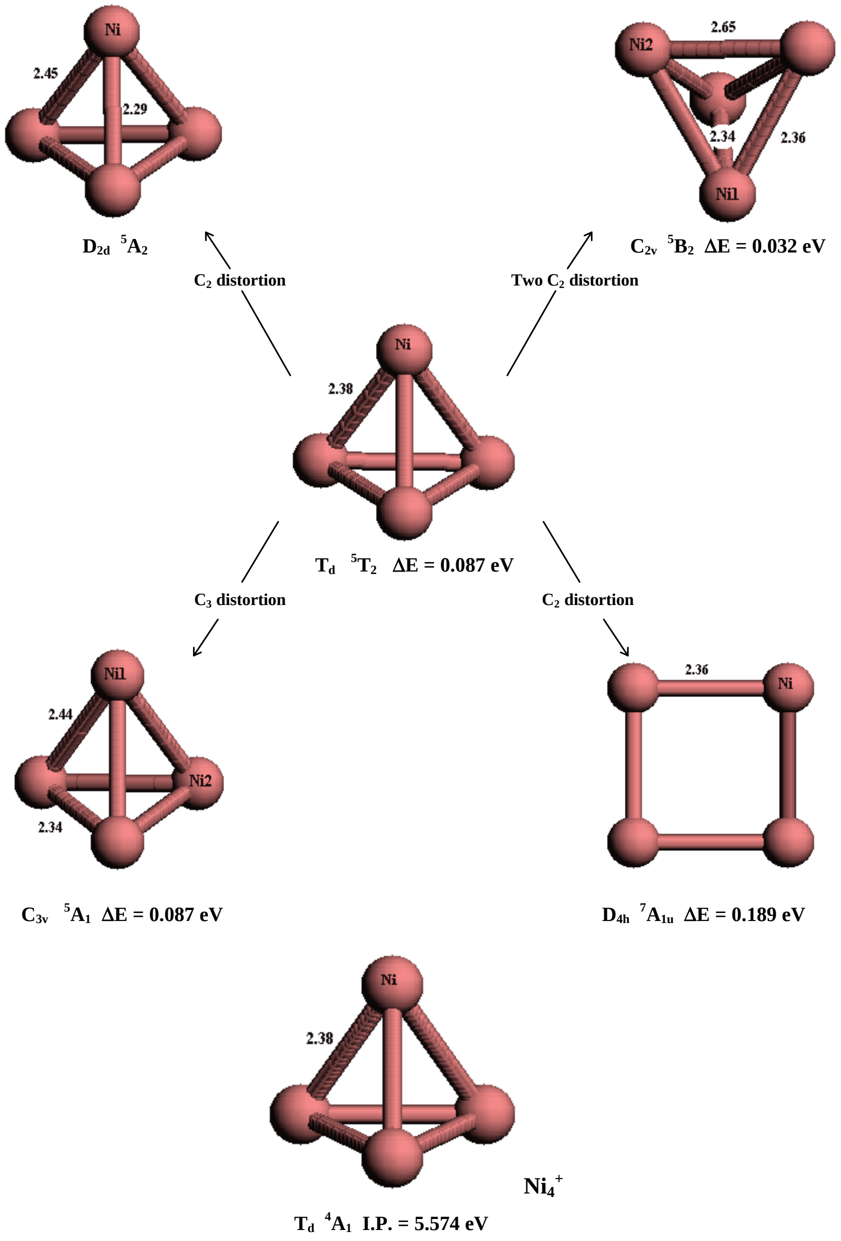


Fig. 1. Schematical structure of isomers of the neutral Ni_4 clusters, as derived by the distortion of the Jahn–Teller-unstable T_d form. Data for the cationic Ni_4^+ are also reported.

Table 3. Electron and spin distribution in Ni_4 isomers and in Ni_4^+ cation$^{(a)}$.

Cluster	State	Atom	*s*	*p*	*d*
Ni_4	D_{2d}, $^5A_2$	Ni	3.006	6.019	8.975
			0.097	0.010	0.893
Ni_4	C_{2v}, $^5B_2$	Ni_1	2.822	6.047	9.037
			−0.146	0.034	0.841
		Ni_2	3.188	5.995	8.909
			0.329	−0.012	0.953
Ni_4	C_{3v}, $^5A_1$	Ni_1	3.378	5.965	8.837
			0.612	−0.048	1.015
		Ni_2	2.882	6.040	9.020
			−0.079	0.034	0.852
Ni_4	T_d, $^5T_2$	Ni	3.006	6.017	8.976
			0.104	0.010	0.886
Ni_4	D_{4h}, $^7B_{1g}$	Ni	3.162	6.055	8.783
			0.324	0.004	1.172
Ni_4^+	T_d, $^1A_1$	Ni	2.730	6.007	9.012
			−0.092	0.004	0.837

$^{(a)}$ The atoms are labelled as in the figures. For each atom, the total electron population and the spin density are reported in first and second entry respectively.

the D_{2d} form, which therefore appears to be the most stable Ni_4 isomer. Note that the transformation $T_d \rightarrow C_{2v}$ is not a spontaneous Jahn–Teller distortion. Finally, we have considered also the square arrangement D_{4h} which can be generated from the stable structures D_{2d} (or the unstable T_d) by the allowance of the shift of a pair of Ni atoms along a C_2 axis. In the case of the Ni_4 (D_{4h}) cluster, we found that the quintuplet state lies higher in energy than the $S = 3$ state: The ground state is in fact $^7A_1$ ($e_u^2 e_u^2 b_{1g}^1 b_{1u}^1$) and the stability of Ni_4 (D_{4h}) (BE/$n = 1.53$ eV) is significantly lower than of all other forms, even lower than that of the Jahn–Teller unstable T_d form. Although the energy differences among the isomeric forms are relatively small, the details of the gradient-corrected functionals do not influence their energy sequence.

The removal of an electron occupying the highest t_2 orbital in Ni_4 (T_d) leads to a cation of T_d symmetry in which the Jahn–Teller instability is completely removed (see Fig. 1). An optimum $r^e_{Ni–Ni}$ value equal to 2.38 Å has been computed for the Ni_4^+ species (t_2^3 $^4A_1$), which is used as reference structure to compute the values for adiabatic ionization potential (IP_a). The IP_a values, together with the corresponding values for the vertical ionization (IP_v), are reported in Table 2. It is interesting to note that the maximum difference between IP_v and IP_a values is as small as 0.13 eV, a fact proving that the geometry relaxation caused by the ionization occurs on a flat potential energy surface, whatever is the symmetry of the ionized Ni_4 cluster.

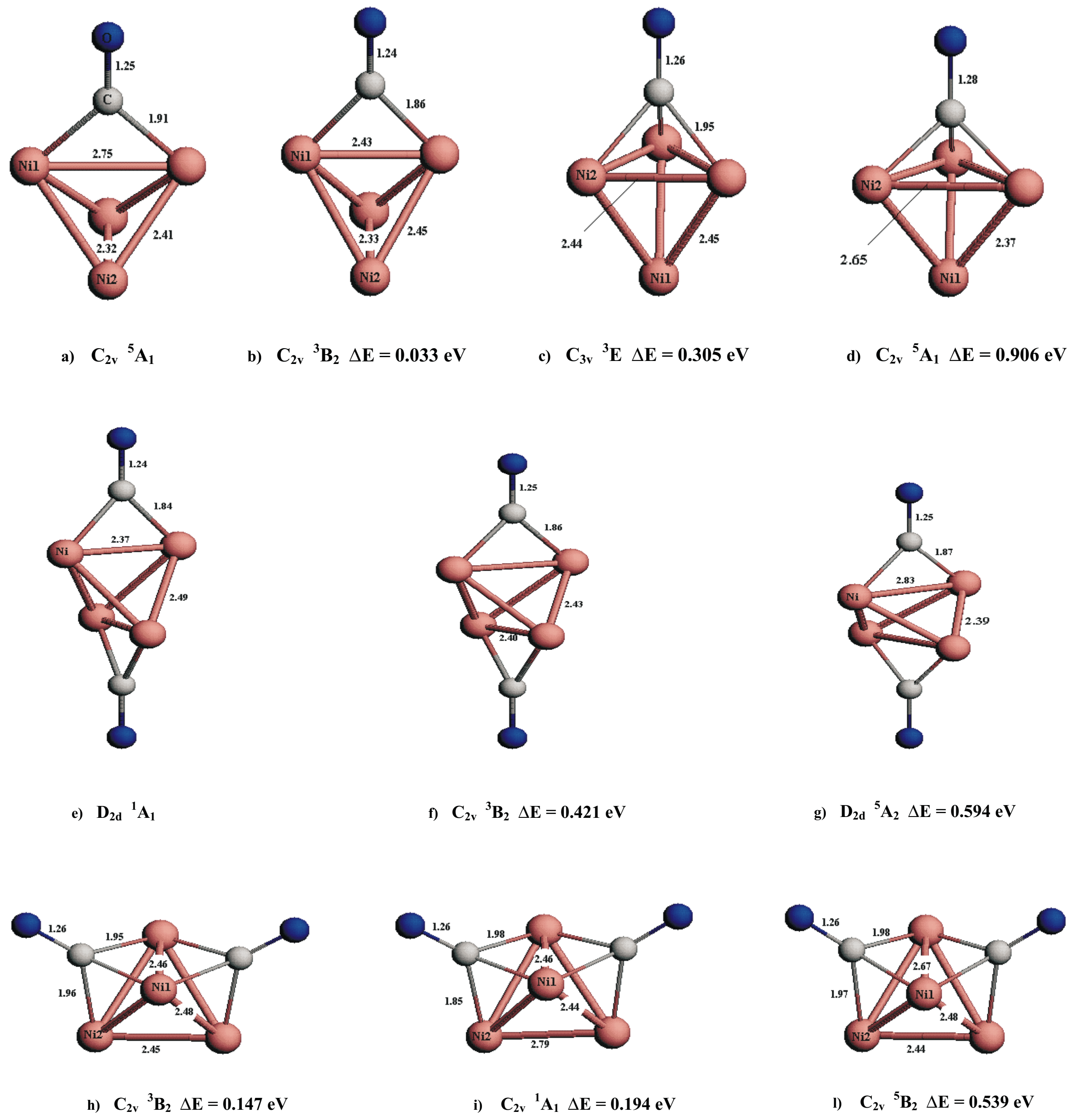
The analysis of the electron distribution has been carried out according to the standard Mulliken's scheme (see Table 3). Such a procedure is known to be based on a quite arbitrary partitioning of the electronic charge, and it is used here just to show in a qualitative way that the metal–metal bond in the nickel tetramer actually occurs according to the simple scheme already commented on in the introduction. In fact, all the nickel atoms have a valence electron configuration very close to the $3d^9 4s^1$, with a very small occupancy of the $4p$ orbitals. In the case of the C_{3v} and C_{2v} forms, the symmetry-independent pairs of nickel atoms have occupancy of the $4s$ orbitals slightly higher and lower than 1, respectively, but the average configuration is again very close to $3d^9 4s^1$. Is is also important to note that in Ni_4^+ the occupancy of the $3d$ orbitals remains almost unchanged, and that the ionized electron is fully of *s* character. This suggests that the nine *d* electrons behave almost as core electrons and play the major role in determining the magnetism of the nickel tetramer. This is further confirmed by the analysis of the electron spin distribution (see Table 3) which shows that the largest part (about 90%) of the unpaired electrons is associated with the $3d$ orbitals. Only in the case of the C_{3v} and C_{2v} forms can one note a small spin transfer between symmetry-nonequivalent atoms, which is accompanied by a spin polarization process [8].

3.2 The $Ni_4(CO)_x$ ($x = 1, 2$) carbonylated species

3.2.1 Ni_4CO

The first carbonylation reaction of the nickel tetramer leads to the species Ni_4CO, in which the CO group can occupy a terminal (μ_1), side-bridge (μ_2), or face-bridge position (μ_3). The coordination of a μ_1CO ligand has been found to be quite unfavorable from an energetic point of view, and it will not be discussed further.

When the carbonyl group occupies a μ_2 position, the symmetry of the cluster cannot be higher than C_{2v} (see



a) C_{2v} $^5A_1$

b) C_{2v} $^3B_2$ $\Delta E = 0.033$ eV

c) C_{3v} ^3E $\Delta E = 0.305$ eV

d) C_{2v} $^5A_1$ $\Delta E = 0.906$ eV

e) D_{2d} $^1A_1$

f) C_{2v} $^3B_2$ $\Delta E = 0.421$ eV

g) D_{2d} $^5A_2$ $\Delta E = 0.594$ eV

h) C_{2v} $^3B_2$ $\Delta E = 0.147$ eV

i) C_{2v} $^1A_1$ $\Delta E = 0.194$ eV

l) C_{2v} $^5B_2$ $\Delta E = 0.539$ eV

Fig. 2. Schematic structures of $Ni_4(CO)$ and $Ni_4(CO)_2$ clusters. The monocarbonyl forms are characterized by a μ_2 (a,b) and μ_3 (c,d) coordination. The dicarbonyl derivatives have either a (μ_2–μ_2) (e–g) or a (μ_3–μ_3) (h–l) coordination.

Fig. 2). The two more stable electronic states have high ($^5A_1$) and low ($^3B_2$) spin character, and their BE/x energy is equal to 2.098 and 2.064 eV, respectively (see Table 4). Therefore, the quintet state is more stable than the triplet by about 0.033 eV; this proves that the perturbation of the electronic structure of the bare Ni_4 cluster caused by the μ_2 coordination of a single CO group is not sufficiently large to modify the ground-state magnetism. Note, however, that the triplet state (with a reduced paramagnetism) already lies quite low in energy.

The $Ni_4(\mu_3CO)$ species has C_{3v} symmetry (see Fig. 2). In this case, the stability order of quintet and triplet states is reversed with respect to the μ_2 coordination (see Table 4). The quintet state seems to be quite unfavorable, while the triplet state lies well (about 0.3 eV) above the (μ_2CO) $^5A_1$ state.

The wave functions of the $Ni_4(CO)$ systems have been projected along the σ and π local components of the carbonyl group, in order that the amount of σ CO → cluster donation and the π cluster → CO back-donation may be computed. This leads to the Mulliken type analysis, reported in Table 4. In the case of the μ_2 coordination of the CO ligand, no appreciable differences can be found between the cluster–CO bonding mode in the quintet or

Table 4. Reaction energy and charge rearrangements due to the coordination of CO groups to the Ni_4 clusters[(a)].

	BE/x	State	Q_{Ni_4}	Q_{CO_σ}	Q_{CO_π}
$Ni_4(CO)$	2.10	C_{2v}, ${}^5A_1, \mu_2$	0.492	0.215	0.707
$Ni_4(CO)$	2.06	C_{2v}, ${}^3B_2, \mu_2$	0.506	0.214	0.720
$Ni_4(CO)$	1.79	C_{3v}, ${}^3E, \mu_3$	0.693	0.215	0.908
$Ni_4(CO)$	1.19	C_{3v}, ${}^5A_1, \mu_3$	0.746	0.321	1.068
$Ni_4(CO)_2$	2.12	D_{2d}, ${}^1A_1, \mu_2$	0.928	0.261	0.725
$Ni_4(CO)_2$	1.91	C_{2v}, ${}^3B_2, \mu_2$	0.965	0.230 0.224	0.706[(b)] 0.713
$Ni_4(CO)_2$	1.83	D_{2d}, ${}^5A_2, \mu_2$	1.091	0.241	0.786
$Ni_4(CO)_2$	2.05	C_{2v}, ${}^3B_2, \mu_3$	1.378	0.196	0.885
$Ni_4(CO)_2$	2.03	C_{2v}, ${}^1A_1, \mu_3$	1.355	0.194	0.856
$Ni_4(CO)_2$	1.85	C_{2v}, ${}^5A_1, \mu_3$	1.302	0.256	0.906

(a) The reaction energy is the BE/x quantity, see text. $Q_{Ni_4} = q^0_{Ni_4} - q_{Ni_4}$ where $q^0_{Ni_4}$ is the total electron population on the lowest energy Ni_4 form and q_{Ni_4} is the total electron population on the Ni_4 framework in the $Ni_4(CO)_x$ system. $Q_{CO_{\sigma,\pi}} = q^0_{CO_{\sigma,\pi}} - q_{CO_{\sigma,\pi}}$ where $q^0_{CO_{\sigma,\pi}}$ and $q_{CO_{\sigma,\pi}}$ are the populations on free and coordinated CO, respectively.

(b) The population on two symmetry independent CO groups (see Fig. 2) are reported in first and second entry, respectively.

triplet state. In both cases, as expected, the CO ligand acts better as a π acceptor (about 0.7 electrons) than as a σ donor (about 0.2 electrons). In the case of the μ_3 coordination, the triplet and quintet states slightly differ concerning the σ, π contributions. The π back-bonding is always larger for the μ_3 than for the μ_2 coordination. This is consistent with the expectations based on qualitative arguments [9]. However, our present calculations show that an enhanced π back donation does not necessarily leads to a stronger cluster–CO bond.

3.2.2 $Ni_4(CO)_2$

The different geometrical arrangements of the two carbonyl ligands here considered are reported schematically in Fig. 2: only the forms with both CO groups in a μ_2 or in a μ_3 coordination will be discussed. Table 4 shows that in the case of CO (μ_2, μ_2) coordination the three states ${}^1A_1$ (D_{2d}), ${}^3B_2$ (C_{2v}), and ${}^5A_2$ (D_{2d}) are characterized by BE/x values equal to 2.123, 1.912, and 1.826 eV, respectively. The strength of the cluster–CO bond is therefore very similar for the first and the second ligand but the perturbation of the electronic cluster structure is now so pronounced that the paramagnetism is quenched. The triplet state, the lowest-energy paramagnetic form, lies about 0.4 eV higher in energy than the diamagnetic form. The efficiency of the second CO ligand in quenching the paramagnetism is very evident also in the case of the (μ_3, μ_3) coordination. In fact, the three states ${}^3B_2$ (C_{2v}), ${}^1A_1$ (C_{2v}), and ${}^5A_1$ (C_{2v}) are characterized by BE/x values equal to 2.049, 2.026 and 1.853 eV, respectively. These results show that (i) the μ_3 coordination is slightly less favorable than the μ_2 one in the case of two coordinated carbonyls also, (ii) the triplet state is the most stable one but is virtually degenerate with the singlet one, and (iii) the quintet state lies much higher in energy (about 0.4 eV). This confirms that the coordination of a second CO ligand is really effective in quenching completely the paramagnetism of the nickel tetramer. The data of Table 4 show that the extent of σ donation and π back-donation present in the cluster–CO bond in the $Ni_4(CO)_2$ species is very similar to that already discussed for the monocarbonyl derivative.

4 Conclusions

On the basis of the present DFT–BLYP calculations on Ni_4 and $Ni_4(CO)_x$ ($x = 1, 2$) species, the following conclusions can be drawn: (i) The Ni–Ni bond is largely dominated by s–s interaction. Indeed, the first ionization removes only s electrons, while the d electrons remain almost unmodified, strongly localized in a core-like shell where all the unpaired spins are present. (ii) The coordination of a single CO ligand to the nickel tetramer does not induce an appreciable change in the global electron distribution, and in particular, does not promote any spin coupling: the spin multiplicity of the monocarbonyl derivative remains equal to 2, with the four unpaired electrons again localized in the $3d$ atom shells. (iii) A completely different picture arises when a second CO group is bound. The $Ni_4(CO)_2$ species are characterized by a completely quenched magnetism in the case of the (μ_2, μ_2) coordination. In the case of (μ_3, μ_3) coordination, an almost complete quenching of the magnetism can be claimed, because the singlet state is nearly degenerate with the triplet one.

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