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# Geometry and bonding in small $(C_{60})_n Ni_m$ clusters

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Small $Ni_m(C_{60})_n$ clusters with $n+m \leqslant 4$ are studied using the tight-binding molecular-dynamics method generalized to treat heteronuclear systems. Our results confirm recent experimental deduction of the bonding behavior of Ni towards $C_{60}$. The direction of the charge transfer is found to depend on the geometry of the $Ni_m(C_{60})_n$ cluster. Furthermore, the present results reveal a striking dissimilarity in the bonding behavior between Ni-$C_{60}$ and Ni-graphite systems. [S0163-1829(99)01531-3]

Recent experimental studies[1–10] have shown that the interaction of $C_{60}$ with the transition-metal atoms (TMA's) exhibits a wide variety of behavior. As in the case of the interaction between TMA's and graphite (see, for example, Ref. 11 and references therein), such a variety demonstrates a strong hybridization strength between the carbon *p*- and the TMA *d*-orbitals. However, the range of this variation appears to be more pronounced in the case of $C_{60}$-TMA interaction where it was found that $C_{60}$ possesses a great ability to adapt itself to various environments, being able to act either as an electron donor or as an electron acceptor.

Among the key issues related to the problem of the interaction of $C_{60}$ with TMA's, which are the subject of current investigations, are the strength of the $C_{60}$-TMA bond, the charge transfer between $C_{60}$ and TMA, the binding sites for the TMA adsorption on the $C_{60}$ (or vice versa) and the effects of all these factors on the ground-state geometry of the $C_{60}$-TMA's systems.

The broadening of the valence photoelectron spectra of $C_{60}$ adsorbed on Ni(110),[7] the observed electron transfer ($2 \pm 1$ electrons) from Ni(110) surface to the adsorbed $C_{60}$ molecules[8] and the observed decomposition of $C_{60}$ on Ni(111) and Ni(110) surfaces at relatively low temperatures,[6,9] reveal a strong $C_{60}$-Ni interaction. Rough estimates based on measured desorption lifetimes of $C_{60}$ from $Ni_m$ clusters give a bond strength of the order 2.06 eV for the $C_{60}$-$Ni_m$ bond.[10] However, the high-ionization potential energies of Co, measured in the Co-$C_{60}$ clusters,[5] were found to decline from the trend exhibited by other $M_m(C_{60})_n$, $M = $Sc, Ti, V, clusters indicating a system dependence of the $M$-$C_{60}$ bond strength. Other experimental information[10] obtained by comparing ionization efficiencies and ionization potentials of $Ni_m$ and $(C_{60})_n Ni_m$ clusters indicate a charge transfer consistent with that found in the case of adsorbed $C_{60}$ molecules on the Ni(110) surface.[8] However, the strong localization of the molecular orbitals in the $Ni_m$ clusters could lead to considerably smaller charge transfer in the case of $(C_{60})_n Ni_m$ clusters than that observed in the case of $C_{60}$ adsorbed on bulk transition-metal surfaces. As Parks *et al.*,[10] notice, the charge transfer in the $(C_{60})_n Ni_m$ clusters should, in general, decrease with decreasing cluster size due to charging of the $Ni_m$ core.

At present a knowledge of the binding sites of the TMA's on $C_{60}$ molecules or those of a $C_{60}$ molecule onto a cluster $M_m$ of TMA's of species $M$ is limited mainly to experimental results. These pertain either to the determination of saturation coverage of $C_{60}$ molecules onto $Ni_m$ clusters[10] or to the specification of the reactivity of the $(C_{60})_n M_m$ clusters towards $O_2$, CO, $NH_3$, $C_2H_4$, and $C_6H_6$.[3–5] The latter experimental approach applied to $(C_{60})_n V_m$ clusters additionally supported with ionization energy measurements[3] led to the conclusion that the clusters $V_m(C_{60})_n^+$, $(n,m) = (1,2)$, (2,3), (3,4), (4,4), and (5,5), have no external V atoms and that the $V_1(C_{60})_2$ cluster takes the structure of $V_1[\eta^6\text{-}(C_{60})_2]$, where $\eta^6$ indicates that six ligand (carbon-ring) atoms are bonded to the metal (V) atom. These results led to the conclusion that the $V(C_{60})_2$ cluster takes the form of a dumbbell and that the V atom is sandwiched between the six-membered rings of $C_{60}$ rather than the five-membered rings. Similar behavior has also been observed in the case of $Sc_m(C_{60})_n$ and the $Ti_m(C_{60})_n$ clusters. On the other hand, the nonreactivity of the $Co(C_{60})_3^+$ cluster toward all the probe gases implies that the Co-$C_{60}$ bond is different in nature from those of Sc-, Ti-, and V-$C_{60}$ bonds and that the $Co(C_{60})_3$ has the form of a tricapped planar structure. In the $Co_m(C_{60})_n$ clusters $C_{60}$ was found to react rather as an $\eta^3$ than as an $\eta^6$ or $\eta^5$ ligand. Behavior similar to the Co-$C_{60}$ system was also observed in the interaction of Fe and Ni with $C_{60}$. Finally, Cr was found to exhibit a behavior towards $C_{60}$ which is intermediate between the early and late $3d$ transition metals( i.e., can bind either as $\eta^3$ or as $\eta^6$ ligand). In the case of $Ni_2(C_{60})_2$, sideways or end on binding to the Ni dimer seems to be possible.[10] For larger $M_m(C_{60})_n$ clusters, however, the early transition metals ($M = $Sc, Ti, V, Cr) seem to prefer the form of a linear chain or a ring structure, whereas for the late $3d$ transition metals [$M = $(Cr), Fe, Co, Ni], a three-dimensional lump structure seems preferable with Cr being at the border between these two behaviors.[5] All these results indicate that $C_{60}$ interacting with TMA's can ligate either with its hexagon rings or with its pentagon rings depending on the TMA involved.

Additional information about the stability of the $C_{60}M_x$ (and $C_{70}M_x$) clusters is obtained by (a) cage-destruction ($x=0,\ldots,150$; $M=$Ti, V, Nb, Ta),[1] (b) cage-substitution ($x=0,\ldots,30$; $M=$Fe, Co, Ni, Rh),[2] and (c) cage-coating ($x=0,\ldots,150$; $M=$Ti, Zr, V, Y, Ta, Nb) (Ref. 1) experiments.

From a theoretical point of view, an understanding of these experimental results requires a series of systematic computations which, however, due to the size of the systems, their low symmetry, and the presence of the TMA's, are beyond the reach of the present day *ab initio* methods. Consequently, to the best of our knowledge, no theoretical study of Ni-$C_{60}$ clusters based on quantum-mechanical symmetry unconstrained optimization has been reported. With this in view, we have recently developed a tight-binding molecular dynamics (TBMD) method[12,13] which has been generalized to treat complex hetero-nuclear magnetic systems.[11,14] The scheme is orders of magnitude faster than *ab initio* methods while allowing one to perform spin and geometry unrestricted energy minimization realistically for the determination of lowest energy structures. The details of our TBMD formulation can be found elsewhere (see, for example, Refs. 11–14 and references therein). The method makes use of Harrison's universal scheme[15] incorporating realistic distance dependence of the Slater-Koster-type[16] parameters. A minimal parameters basis set is used to obtain a transferable TB parametrization of the Ni-Ni, C-C, and Ni-C interactions applicable to binary $Ni_mC_n$ clusters. The data base for fitting the parameters is obtained from experimental and/or *ab initio* results for small $Ni_m$, $C_m$, and $Ni_mC_n$, $n+m\leqslant 4$ clusters, the latter obtained using the density-functional method and the single, double- and triple-coupled clusters method.[11] This parametrization, incorporated into the TBMD scheme, has been used with success to study $Ni_mC_n$ clusters of arbitrary sizes and the interaction of Ni with graphite.[11]

In this paper, we present results from applications of our TBMD method to the $Ni_m(C_{60})_n$ clusters with $n+m\leqslant 4$. Our results are as follows:

For the $NiC_{60}$ cluster TBMD optimizations were carried out to determine energetically most favorable sites at which Ni can bind to $C_{60}$. In contrast to the case of the interaction of Ni with graphite,[11] the hole site (i.e., above the center of a hexagonal ring of carbon atoms) is found to be unstable for Ni on $C_{60}$. Instead, a Ni atom, initially placed at a hole site, moves and relaxes on a bridge site (i.e. over a C-C bond) either over a C-C double bond [shared by two adjacent hexagonal rings - see Fig. 1(a)] or over a single C-C bond [shared by a pentagonal and an hexagonal ring - see Fig. 1(b)]. The former site was found to be energetically more favorable than the latter by 0.65 eV. For a Ni atom at the bridge sites the $C_{60}$ acts as an $\eta^2$ ligand forming two Ni-C bonds (1.76 Å each). At these sites Ni has the tendency to gain some electronic charge ($\approx 0.05-0.08|e|$) from the $C_{60}$. The atop site [on top of a C atom of a pentagon ring - see Fig. 1(c)], however, is found to be the most stable site for the Ni atom bonding to a $C_{60}$ molecule. At this site the Ni atom can form three Ni-C bonds (1.73, 2.03, 2.03 Å) and has a tendency to loose electronic charge ($\approx 0.04|e|$) to $C_{60}$. Also, for this bonding configuration, the $C_{60}$ molecule acts as an $\eta^3$ ligand, in agreement with the bonding behavior found for the late $3d$ transition metals towards $C_{60}$.[4,5] Furthermore, at all of the three binding sites described, the Ni atom exhibits a small magnetic moment of the order of 0.12-0.18$\mu_B$, just as found in the case of Ni on graphite.[11]

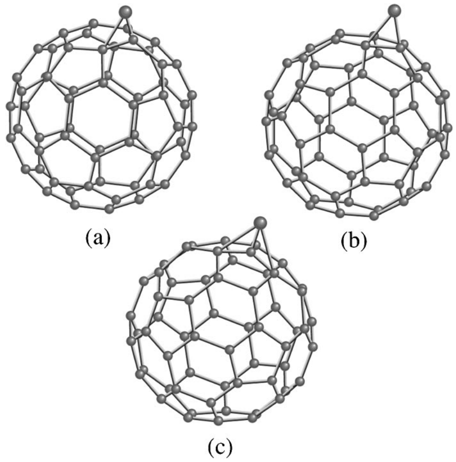

FIG. 1. The three binding sites of Ni on $C_{60}$; (a) bridge site between two hexagons, (b) bridge site between a hexagon and a pentagon, and (c) atop site on a C atom of a pentagonal ring.

Our simulations show that a $Ni_2$ dimer can also bind to the $C_{60}$ molecule in a stable configuration. Among the two geometries investigated, the most stable configuration had both Ni atoms of the $Ni_2$ dimer bonded to the $C_{60}$. The other stable geometry had linear $C_{60}$-Ni-Ni configuration with only one Ni atom binding to the $C_{60}$ molecule. In the most stable geometry the Ni atoms bind to the same pentagonal ring with one Ni binding at an atop site on $C_{60}$ ($C_{60}$ acting as an $\eta^3$ ligand) and with the other Ni binding at a bridge site on the $C_{60}$ (acting as an $\eta^2$ ligand). Also, in the most stable configuration the Ni atoms loose charge to $C_{60}$ (0.21 and 0.38$|e|$, respectively) while exhibiting magnetic moments of magnitudes 0.31 and 0.52$\mu_B$, respectively. The equilibrium Ni-Ni bond length is found to be 2.42 Å and the Ni-C bond lengths are found to correspond to those found for the single Ni atom adsorption at the atop and bridge sites, respectively. It is worth noting that the Ni-Ni bond length found is larger than that of a free $Ni_2$ dimer and smaller than that found for the $Ni_2$ dimer on graphite.[17]

For the $Ni(C_{60})_2$ cluster we examined the relative stabilities of the linear and bent $C_{60}$-Ni-$C_{60}$ geometries. A number of distinct stable structures were obtained on relaxation (see see Fig. 2). In the first case [Fig. 2(a)] the Ni atom binds at the bridge sites ($\eta^2$ ligand) of both $C_{60}$ molecules. The bridge site is over C-C bonds shared by two hexagons. In the second case also the Ni atom binds at the bridge sites on both $C_{60}$ molecules but the bridge sites are now over C-C bonds shared by a pentagon and an hexagon [Fig. 2(b)]. The former geometry is found to be more stable than the latter. A third geometry in which the Ni atom binds at the bridge site ($\eta^2$ ligand) of one of the $C_{60}$ molecule and at the atop site ($\eta^3$ ligand) of the other $C_{60}$ molecule was found to be almost isoenergetic with the first case. The binding obtained in all these cases is different from that proposed for $V(C_{60})_2$ (see

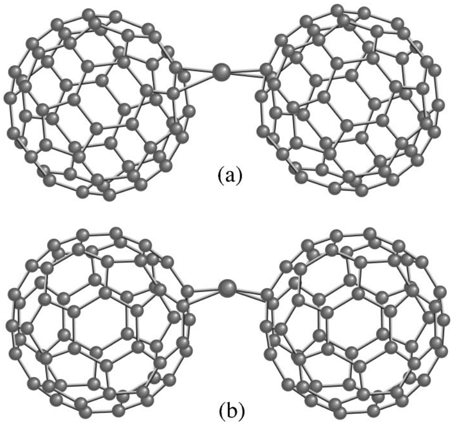

FIG. 2. Relaxed geometries for the $\mathrm{Ni(C_{60})_2}$ system.

discussion earlier) indicating the different nature of bonding between $\mathrm{C_{60}}$ and the late $3d$ transition metals.

For the $\mathrm{Ni_2(C_{60})_2}$ clusters, we studied the following three geometries. The linear geometries $\mathrm{C_{60}}$-Ni-$\mathrm{C_{60}}$-Ni (denoted by $D1$) and $\mathrm{C_{60}}$-Ni-Ni-$\mathrm{C_{60}}$ (denoted by $D2$); the geometry $\mathrm{C_{60}}$-$\mathrm{Ni_2}$-$\mathrm{C_{60}}$ (denoted by $D3$, see Fig. 3) in which the $\mathrm{Ni_2}$ dimer binds with its two atoms to both $\mathrm{C_{60}}$ molecules. Among these three geometries, $D3$ was found to be considerably more stable than the other two, followed by $D1$. In the $D3$ configuration, the Ni-Ni bond length is 2.47 Å and both Ni atoms exhibit identical behavior described as follows; (i) they gain $0.31|e|$ from the $\mathrm{C_{60}}$ molecules, (ii) they exhibit a small magnetic moment of the order of $0.10\mu_B$, (iii) they bind at one pentagon bridge site on one $\mathrm{C_{60}}$ ($\eta^2$ ligand) and at one pentagon atop site on the other $\mathrm{C_{60}}$ ($\eta^3$ ligand) as shown in Fig. 3. The Ni-C bond lengths at the atop site are 2.16, 2.19, and 1.85 Å , while at the bridge site are 1.91 and 1.91 Å . For the sake of comparison it should be noted that in the $D2$ configuration the Ni atoms loose some charge to the $\mathrm{C_{60}}$'s. Also, the Ni-Ni bond is 2.66 Å and each Ni atom binds to an atop position on one $\mathrm{C_{60}}$ molecule.

Finally, we performed two more series of simulations. In the first, we considered one Ni atom inside the $\mathrm{C_{60}}$ molecule. This was found to be a stable configuration showing that a Ni atom can be stably encapsulated within the $\mathrm{C_{60}}$. In the second case, we considered a substitutional Ni impurity on $\mathrm{C_{60}}$. This configuration was found unstable with the Ni atom protruding outward and the $\mathrm{C_{59}}$ cage closing underneath, resulting in a $\mathrm{C_{59}Ni}$ cluster. This process leads to an increase in the number of Ni-C bonds. This result is in disagreement with the conclusions arrived at by Branz *et al.*,[2] following their fragmentation mass spectra of metal-fullerene clusters. Our calculations indicate that in the $\mathrm{C_{59}Ni}$ cluster the presence of the Ni atom outside the $\mathrm{C_{59}}$ cage stabilizes it. The simple accommodation of the substitutional Ni atom (with a corresponding increase in the Ni-C bond lengths) without any cage disruption would have resulted in threefold coordination for the Ni atom. This is inconsistent with the tendency of Ni to bond to larger number of neighbors. Further experimental results are needed to verify our prediction that this configuration is the ground-state geometry of the $\mathrm{C_{59}Ni}$ cluster.

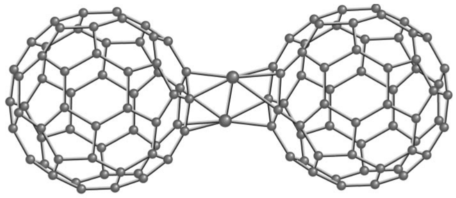

FIG. 3. The most stable geometry and the bonding of the $\mathrm{Ni_2(C_{60})_2}$ cluster.

In conclusion, we have studied small $\mathrm{Ni}_m(\mathrm{C_{60}})_n$, $n+m \leqslant 4$, clusters using our TBMD method generalized to treat heteronuclear systems.[11] Our main conclusions are that $\mathrm{C_{60}}$ acts as an $\eta^3$ or $\eta^2$ ligand towards Ni, which in turn, exhibits a small magnetic moment and undergoes a small charge transfer. The direction of the charge transfer was found to depend on the geometry of the $\mathrm{Ni}_m(\mathrm{C_{60}})_n$ cluster. Furthermore, the present results revealed a behavior of the Ni bonding towards the $\mathrm{C_{60}}$ which, while showing some similarities with that of Ni on graphite (i.e. atop binding position, small charge transfer, small magnetic moment, comparable Ni-C bond lengths, and weakening of the Ni-Ni bond), also exhibits some striking differences. Among the latter, the most conspicuous being the preference of the Ni atoms to bind on bridge sites on $\mathrm{C_{60}}$; such sites were found unstable on graphite.[11] The very good agreement with the existing experimental results confirm the validity of our approach in its applicability to the complex heteroatomic systems discussed in the present paper.

Very recently, we became aware of a review article on metal-fullerene systems.[18] The main assertion there is that most of the transition elements form organometallic fullerenes in which the $\mathrm{C_{60}}$ acts as an $\eta^2$ ligand, supporting our results in the present paper.

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