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Structural properties of Rh_n ($n = 2 \sim 100$) clusters by using Gupta potential with the simulation of quenching method

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Abstract. The ground-state geometries and energies of $Rh_n (n = 2 \sim 100)$ clusters are investigated by using Gupta potential combined with the molecular dynamics simulated quenching method and the genetic algorithm. Our results show that: As comparing the lowest energy structure obtained from the simulated quenching method which can be regarded as the ground-state structure, almost all these ground-state geometries can be found (except Rh_{50}) by using the genetic algorithm for clusters containing 60 or less atoms, but the efficiency of capturing the ground-state geometry decreases obviously with increasing the cluster size. The effective temperature range for obtaining the ground-state energy (geometry) is obtained by systematically analyzing the energy distributions of the simulated quenching structures, and the correlation between the quenching method of finding the ground-state and the cluster size is also investigated further.

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Key words: Gupta potential, cluster, ground-state, molecular dynamics, simulated quenching

1 Introduction

Clusters are aggregates composed of several to thousands of atoms (molecules) bonding in certain physical or chemical forces, that exist stably in microscopic state [1]. It has been aroused a great interest, just because of its unique physical and chemical properties and applications in nano-electronics, nano-catalyst and new material physics [2-8]. It has already become a new and significantly important field to study the formation, structures, evolution behavior and other properties of clusters. As the first step, determination of the ground-state geometry of a cluster plays a significant role in studying many other

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properties of the cluster. For free clusters containing three or more atoms, their geometrical structures can not be measured directly from experiments so far, and it becomes very important to ascertain the ground-state of clusters combining with theoretical calculations. Nowadays theoretical computations are mainly based on either the first-principles (ab-initio) calculations in quantum mechanics level or the empirical (semi-empirical) calculations based on interatomic potentials. The former has a very accurate result, but large amount of calculation time needed, and it is very difficult to handle a cluster with relatively large size (especially more than 20 atoms). The latter, according to the different ways of simulation, can be classified into several methods such as the molecular dynamic method [9,10] the Monte Carlo simulation method [11,12] the genetic algorithm [13-15], the simulated annealing method [16,17] and the simulated quenching method, etc.

As a transition metal and constituent of many catalysts, rhodium plays important role in catalytic field, and particular attention has been paid to studying rhodium clusters. Chien and co-workers[18] studied the paramagnetic and ferromagnetic properties of Rh_n(n=2∼58) clusters based on the generalized gradient approximation (GAA) within the density functional theory (DFT); Aguilera-Granja and co-workers [19], by using the genetic algorithm combined with self-consistent spd tight binding method, systematically studied the structural and magnetic properties of Rh_n (n=4∼26) clusters; Zhang and co-workers [20] profoundly studied the ground state structures of Rh_n and Pt_n (n=2∼20) clusters by applying the genetic algorithm. Many researchers use the traditional genetic algorithm and Monte Carlo simulation method to solve the ground-state structures (energies) of clusters containing less than 60 atoms, but the solving methods are still so complex as increasing the cluster size.

In this paper, not only we systematically studied, by using the molecular dynamic method based on the semi-empirical Gupta interatomic potential combined with the molecular dynamic simulation of quenching technique, the ground-state structures (energies) of Rh_n (n=2∼100) clusters, but also analyzed the contrast of the genetic algorithm results.

2 Computational methods

The interaction between atoms, which is depicted by the potential function, is the fundamental to determine the dynamic behaviors of clusters. In this letter, the interaction between atoms of Rh clusters are described by using the semi-empirical many body Gupta potential [21] based on the embedded-atom potential and tight-binding model of the second moment approximation, in which the potential parameters are obtained from fitting the relevant physical parameters of crystal (cohesive energy, lattice constant and elastic moduli, etc). Moreover, this kind of many body potential has been extensively used to study the geometries [22] and dynamic behaviors [23] of the metal and alloy clusters. Gupta potential can be written as the sum of a Born-Mayer type repulsive part and a

Table 1: The parameters of Gupta potential of Rh clusters.

	p	q	A (eV)	B (eV)	r_0(Å)
Rh	18.450	1.867	0.0629	1.660	2.69

many-body attractive part, as is shown below

$$V=\sum_i\Big(\sum_{j(\neq i)}A\exp[-p(\frac{r_{ij}}{r_0}-1)]-\sqrt{\sum_{j(\neq i)}B^2\exp[-2q(\frac{r_{ij}}{r_0}-1)]}\Big) \tag{1}$$

where r_0 is the nearest-neighbor distance of crystal, and r_{ij} is the distance between the ith and jth atoms. A is the index to measure the interatomic repulsive strength, and B is a effective jump integral only related to the category of atoms. In this paper, the parameters of Gupta potential of Rh clusters were given by Table 1 [24].

2.1 Genetic algorithm (GA)

The genetic algorithm (GA) is an optimization strategy inspired by the Darwinian evolution. In this letter, we applied genetic algorithm to optimize structures of Rh_n cluster with concrete steps as follows: Firstly, for a given size of Rh cluster, the initial group is consist of ten different structures. And then, by acting the selection operator on the initial group, two parental clusters are chosen from the group based on the principle that an individual will be chosen with higher probability if its energy is lower. The choosing probability satisfies the Boltzman distribution:

$$p(G)\sim\exp[-E(G)/T] \tag{2}$$

where $E(G)$ is the energy of the candidate parent (G), and T is the mating temperature chosen as a constant here. By working the mating operator on the parental generation one can obtain the offspring cluster with concrete steps as follows:

Firstly, the centers of the two parental clusters are shifted to zero (the origin of coordinate), and it might confirms a plane (cross the zero) through randomly choosing a direction as normal line, and the offspring cluster can be obtained by joining part of the male parent on the one side of the plane and part of the female parent cluster on the other side of the plane (for assuring the offspring cluster must be inherited the structural information of parental generation, offspring cluster must has same number of atoms with parental cluster, otherwise moves the plane until meet the need).

Secondly, the offspring cluster is relaxed to the near minimum point on the energy surface by applying the steepest descent method. According to the "eliminating rule" either the offspring cluster or one individual of the group will be eliminated in order to maintain the conservation of the total number of individuals in the group with steps as follows:

1. If the energy of the offspring cluster is higher than the highest energy of individual cluster in the group, then the offspring will be eliminated.

2. If the absolute value of the energy difference between the offspring cluster and any individual cluster in the group (except the lowest energy one) is smaller than δE (δE=0.001eV here), then the offspring cluster will be eliminated.

3. If the absolute value of the energy difference between the offspring cluster and the lowest-energy individual of the group is smaller than δE, then the one with little higher energy will be eliminated (avoiding from the close breeding).

4. The highest energy one in the group will be eliminated.

One circle step is achieved with producing a new generation from the previous group through completing the above steps, and 5000 steps are performed for each cluster size in the practical optimization process, and finally the lowest energy structure (and its energy value) will be marked, which might be the candidate of the ground-state cluster.

2.2 Simulated quenching method (SQ)

We applied the constant temperature molecular dynamic method combined with quenching technique. The Berendsen thermostat is used to control the temperature, velocity Verlet algorithm is used to integrate Newtonian equation of motion. The ground-state geometries and energies of Rh_n(n=2$\sim$100) clusters are investigated. The specific procedures are as follows:

(1) The initial stable structure of a Rh cluster is obtained by applying the molecular dynamic simulated annealing method with specific steps as follows: Firstly, for any chosen initial stable structure (for example, this can be achieved by using the stochastic method combined with the steepest descent method), it is heated directly to 2300K (ensure the cluster is in liquid-state). Secondly, the temperature of the cluster is decreased slowly through applying molecular dynamic simulated annealing method, and the final temperature is 150K (ensure the cluster is in the solid-state). The temperature interval is taken to be 10K in the cooling process. The time step of integration is 1fs, and total of 1×10^6 MD steps are propagated at each temperature point. For the final structure at 150K, it is relaxed to a stable structure by using the steepest descent method.

(2) Started from the (above) initial stable structure obtained by simulated annealing method, the cluster is heated from 150K to 2300K by carrying out the MD simulation with the temperature interval of 10K, and 5×10^6 MD steps are propagated at each temperature point.

(3) With accompanying the MD warming process the MD simulated quenching process is carried out with concrete steps as follows: One Rh cluster geometry is preserved

every 5×10^4 MD steps at each temperature (so 100 cluster structures obtained at each temperature point), and then quenching all structures obtained at each temperature to the stable states (that means each original structure will be relaxed to its near stable state on the potential energy surface). Finally, keep all simulated quenching structures and their energies (Thus, the potential energy distributions of all simulated quenching structures can be obtained) and mark the lowest energy one of them, which might be one candidate of the ground-state cluster.

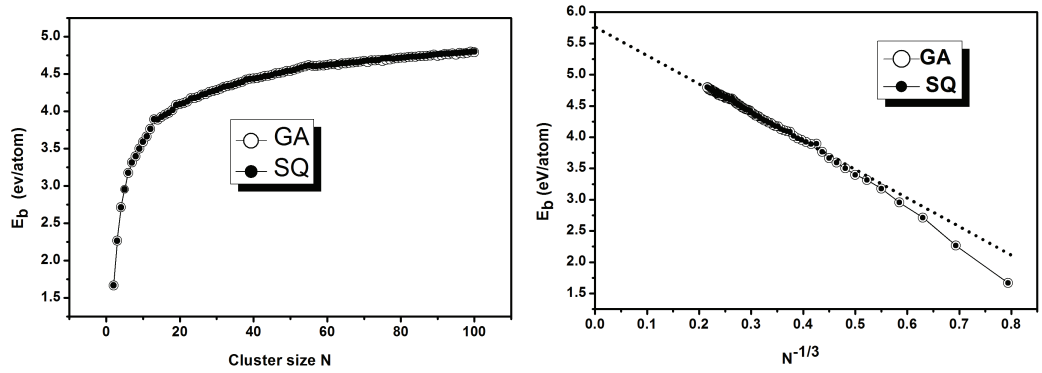
3 Results and discussion

To investigate the structural stabilities of Rh_n ($n=2\sim100$) clusters, the average binding-energy (E_b) of a Rh cluster is defined as

$$E_b=-\frac{E(n)}{n} \tag{3}$$

where $E(n)$ is the total binding energy of the cluster containing n rhodium atoms.

Variation of the average binding-energies of the lowest-energy structures of Rh_n ($n=2\sim100$) clusters with cluster size is given in Fig. 1 (a), and the results from both the MD quenching method (SQ) and genetic algorithm (GA) are all shown in this figure. From Fig. 1 one can see that the average binding energies increase overall but with little fluctuation around few cluster sizes (which are relevant to the magic-number clusters). The calculated average binding energy of the cluster with the largest-size (Rh_{100}) is about 4.80 eV, and it is still apparently smaller than the cohesive energy of Rh crystal (5.75 eV), which indicates that there is still a discrepancy between properties of the Rh clusters investigated and that of the bulk materialsFig. 1 (b) shows the variation of the average binding energies as a function of $N^{-1/3}$ (N is the cluster size), and one can see that values



(a) (b)

Figure 1: The average binding energy E_b as a function of cluster size.

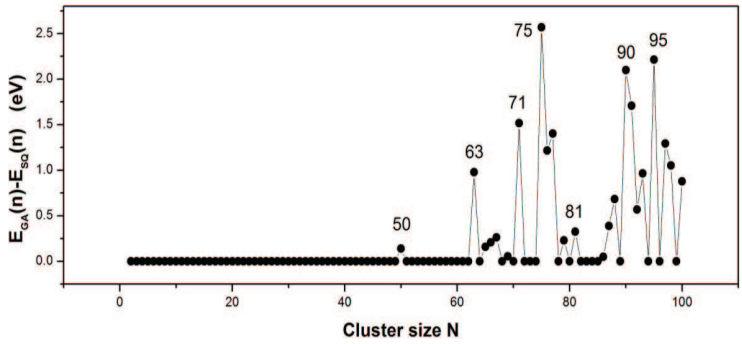


Figure 2: The energy difference between the lowest energy structures obtained from the simulated quenching method and the genetic algorithm as a function of cluster size.

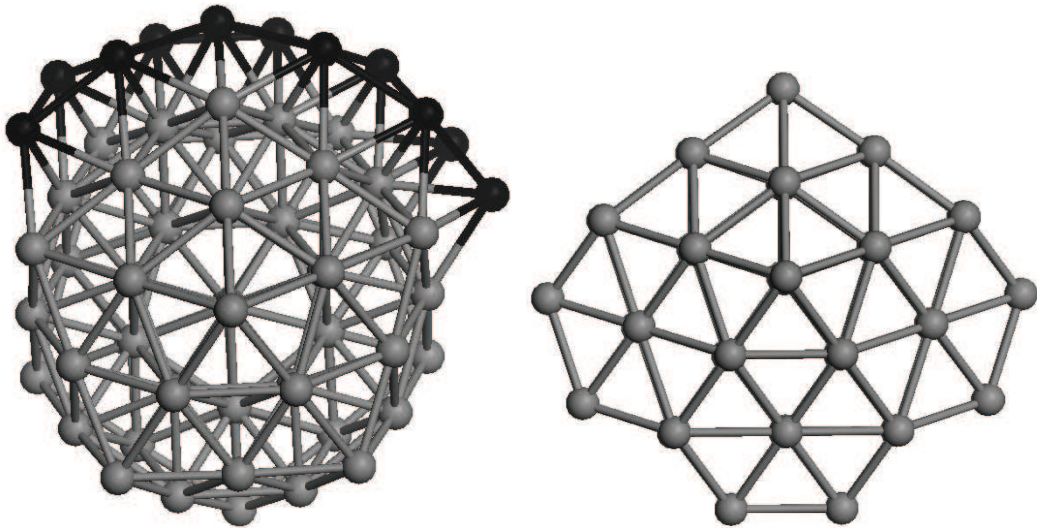
of the average binding energies tend to a straight line with increasing the cluster size, and the extrapolated limit to the vertical axis falls in around 5.75 eV (cohesive energy of Rh crystal), that is unanimous for the potential parameters used here are obtained from fitting the bulk's properties.

As seen directly from Fig. 1, nearly no differences can be found in the variation trend of those average binding energies as a function of cluster sizes obtained from both the GA and the SQ methods, but actually there exits large differences between the two results (the lowest-energy structures and energies) for large-size clusters.

For all the Rh_n ($n = 2 \sim 100$) clusters investigated here, by comparison with the values of the lowest energies from both methods we find that values obtained from the SQ method are always equal to or less than that obtained from the GA method, and the lowest-energy structures and energies obtained from the SQ method can be regarded as the corresponding ground-state structures and energies.

Fig. 2 gives the variation of energy differences of the lowest-energy Rh_n ($n = 2 \sim 100$) clusters obtained from both the GA and the SQ methods as a function of cluster size, and one can find that for clusters containing 60 or less atoms (except Rh_{50}) same results (the lowest-energy structures and energies) can be obtained from both methods. As seen from Fig. 2, for clusters containing more than 60 atoms ($n = 61 \sim 100$), the GA method cannot find the ground-state in 22 cluster sizes (Rh_{63}, $Rh_{65} \sim Rh_{67}$, Rh_{69}, Rh_{71}, $Rh_{75} \sim Rh_{77}$, Rh_{79}, Rh_{81}, $Rh_{86} \sim Rh_{88}$, $Rh_{90} \sim Rh_{93}$, Rh_{95}, Rh_{97}, Rh_{98}, and Rh_{100}). One may conclude that for the large-size Rh clusters (for example, containing more than 60 atoms) in order to obtain the ground-state energy, as comparing genetic algorithm, the simulated quenching method can achieve better efficiency.

For a further study of the origin of the differences between the results (the lowest-energy structures and energies) obtained from the two different simulation methods for the large-size Rh clusters, the lowest-energy geometrical structures obtained from both methods are analyzed comparatively. As an illustration, the lowest-energy geometries of Rh_{66} cluster obtained from the genetic algorithm and the simulated quenching method



(a) (b)

Figure 3: The lowest energy structures of Rh_{66} cluster obtained from the genetic algorithm (a) and the simulated quenching method (b).

are shown in Fig. 3 (a) and (b), respectively. The energy difference between the two structures is not large enough (about 0.33eV, as shows in Fig. 2), but the two structure themselves are fundamentally different: The lowest-energy geometry of Rh_{66} obtained from the genetic algorithm is derived from adding 11 atoms (as shown in black atoms in Fig. 3 (a)) on the surface of the ground-state Rh_{55} cluster (an icosahedral cluster with the I_h high symmetry, as shown in grey atoms in Fig. 3 (a)); but the lowest-energy geometry obtained from the simulated quenching method prefers a structure with a complete pentagonal prism as its basic unit, which is the ground-state structure of Rh_{66} cluster.

For the relatively large-size Rh_n (n=60∼100) clusters, one may deduce the differences between the lowest-energy structures from the two different methods as follows: In most cases the lowest-energy structures obtained from the genetic algorithm have icosahedral core units, but both the icosahedral-core structures and the pentagonal-prism-core structures can be found by the simulated quenching method. For example, for those rhodium clusters (Rh_{64}, Rh_{70}, Rh_{73}, Rh_{74}, Rh_{78}, Rh_{80}, Rh_{82} ∼ Rh_{85}, Rh_{89} and Rh_{94}), their ground-states all prefer icosahedral core structures, and same ground-state geometries are obtained from both methods.

To further investigate the correlation between cluster size (temperature) and the efficiency of searching cluster's ground-state, the potential energy distributions (100 quenching structures and energies at each temperature, as shown in hollow circles) and ratio (percentage of the ground-state structures in the 100 quenching structures, as shown in solid circles) of capturing the ground-state of the quenching structures of Rh_{66} and Rh_{69} clusters at different temperatures are shown in Figs. 4 and 5, respectively. T_1 and T_2 in

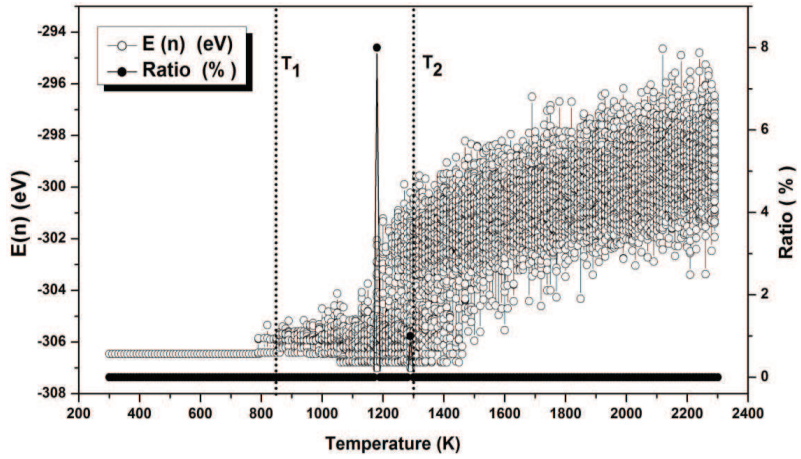


Figure 4: The potential energy distributions and ratio of capturing the ground-state of the quenching structures of Rh_{66} cluster at different temperatures.

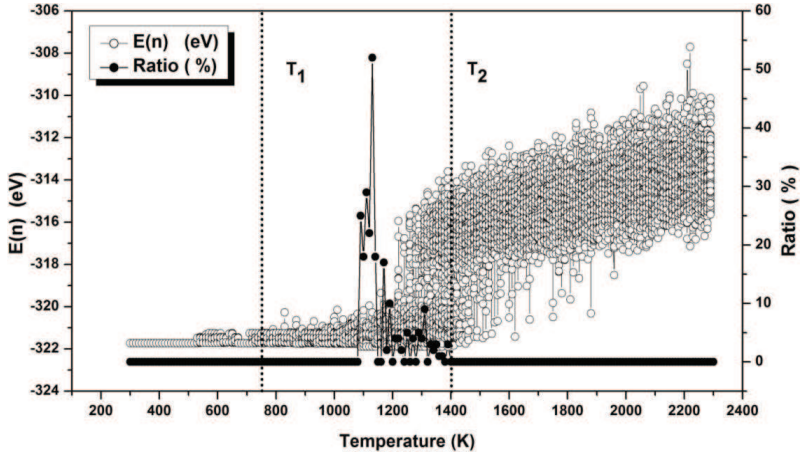


Figure 5: The potential energy distributions and ratio of capturing the ground-state of the quenching structures of Rh_{69} cluster at different temperatures..

Figs. 4 and 5 denote the pre-melting temperature regions (the solid-liquid coexistence states) of relevant clusters (T_1 is the initial temperature of pre-melting stage and T_2 is the melting point of the cluster). One can see that it's hard in general to find the ground-state of rhodium clusters in solid-like ($T < T_1$) or liquid-like states ($T > T_2$), but it becomes possible to find the ground-state at pre-melting stage ($T_1 < T < T_2$). As shown in Fig. 4, the pre-melting temperature stage of Rh_{66} cluster ranges from 850 K to 1300 K, and the ratio of capturing the ground-state is respectively 8% (eight times) and 1%(one time) among the 100 simulated quenching structures when cluster temperatures is 1180 K and 1290 K, respectively.

It is generally believed that it becomes much more difficult to find the ground-states

of clusters with increasing the cluster size, but from Figs. 4 and 5 one gets the opposite for the two rhodium clusters with different sizes: As mentioned above and as shown in Fig. 4, only at two temperature points (1180 K and 1290 K) where the ground-state of Rh_{66} cluster can be found from the quenching structures; But for Rh_{69} cluster, as shown in Fig. 5, it's pre-melting region ranges from 750 K to 1400 K, and the ground-state of Rh_{69} can be ascertained at many temperature points and at several points the efficiency of capturing the ground-state becomes quite large. For example, at 1130 K the ratio of finding the ground-state is bigger than half (52%). Thus for the two different clusters Rh_{66} and Rh_{69}, by applying the simulated quenching method to search the ground-state geometries (energies), the possibility of finding the ground-state of the Rh_{69} cluster is larger than that of the Rh_{66} cluster. It indicates that the efficiency of capturing the ground-state using the simulated quenching method is irrelevant directly to the cluster size, and the potential energy surface and the cluster geometry are highly correlated.

4 Conclusions

The ground-state geometries and energies of $Rh_n (n=2\sim100)$ clusters are investigated by using Gupta many-body interatomic potential combined with the molecular dynamics simulated quenching method and the genetic algorithm. Our results show that: The average binding energies obtained from both methods increase in general with increasing the cluster size and same energies are obtained for clusters containing 60 or less atoms (except Rh_{50}), and that means both methods can achieve high efficiency at this size range ($n \leq 60$). But the efficiency of capturing the ground-state geometry using genetic algorithm method, as compared to the simulated quenching method, decreases obviously with increasing the cluster size (Generally, the genetic algorithm will sink into some local minimum closed-packed structures on potential energy surface, such as the icosahedral structures). Nevertheless, the simulated quenching method can still achieve high efficiency and can find all ground-states of Rh clusters. By analyzing the energy distributions of the simulated quenching structures of Rh clusters at different temperatures, the effective temperature range for obtaining the ground-state energy (geometry) is obtained, and that lies in the pre-melting region. Furthermore, we emphasized that no simple and direct correlation can be found between the quenching method of finding the ground-state and the cluster size.

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References

[1] G. H. Wang, Cluster Physics (Shanghai Scientific and Technology Press, Shanghai, 2003). (in Chinese)
[2] J. T. Liu and H. M. Duan, Acta Phys. Sin. 58 (2009) 4826. (in Chinese)
[3] X. J. Kuang, X. Q. Wang, and G. B. Liu, J. At. Mol. Phys. 27 (2010) 254. (in Chinese)
[4] L. Liu, X. L. E, and H. M. Duan, J. At. Mol. Phys. 28 (2011) 14. (in Chinese)
[5] A. W. Castleman and S. N. Khanna, J. Phys. Chem. C. 113 (2009) 2664.
[6] Y. C. Bae, V. Kumar, H. Qsnanai, *et al*., Phys. Rev. B. 72 (2005) 125427.
[7] Y. C. Bae, H. Qsnanai, V. Kumar, *et al*., Phys. Rev. B 70 (2004) 195413.
[8] J. L. Rodríguez-López, K. Michaelian, F. Aguilera-Granja, *et al*., Phys. Rev. B. 67 (2003) 174413.
[9] J. L. Wang, J. J. Zhao, F. Ding, *et al*., Solid State Commun. 117 (2001) 598.
[10] Y. Xu, L. Wang, and X. F. Bian, J. At. Mol. Phys. 19 (2002) 65. (in Chinese)
[11] A. Sebetci and Z. B. Güvengc, Surf. Sci. 525 (2003) 66.
[12] M. L. Zhang, G. P. Li, X. Y. Guo, *et al*., J. At. Mol. Phys. 22 (2005) 515. (in Chinese)
[13] B. Hartke, J. Phys. Chem. 97 (1993) 9973.
[14] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. 75 (1995) 288.
[15] A. X. Liu and H. M. Duan, J. At. Mol. Phys. 25 (2008) 702. (in Chinese)
[16] S. Maruyama and Y. Yamaguchi, Chem. Phys. Lett. 286 (1998) 343.
[17] F. Ruette and C. González, Chem. Phys. Lett. 359 (2002) 428.
[18] C. H. Chien, E. Blaisten-Barojas, and M. K. Pederson, J. Chem. Phys. 112 (2010) 2301.
[19] F. Aguilera-Granja, J. L. Rodríguez-López, K. Michaelian, *et al*., Phys. Rev. B 66 (2002) 224410.
[20] C. R. Zhang, H. S. Chen, and G. H. Wang, J. At. Mol. Phys. 21 (2004) 235. (in Chinese)
[21] R. P. Gupta, Phys. Rev. B 23 (1981) 6265.
[22] C. Mottet, G. Rossi, F. Baletto, *et al*., Phys. Rev. Lett. 95 (2005) 035501.
[23] W. Zhang, F. S. Zhang, and Z. Y. Zhu, Phys. Rev. B 74 (2006) 33412.
[24] F. Cleri and V. Rosato, Phys. Rev. B 48 (1998) 22.