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Softening of C−H Symmetric Stretching Vibrational Modes for CH_2 and CH_3 Radicals Adsorbed on Cu_n (n=1−6) Clusters

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The properties of C−H vibration softening for CH_2 and CH_3 radicals absorbed on Cu_n (n=1−6) clusters have been investigated, using the density functional theory with hybrid functional. The results indicate that the absorption of CH_2 on Cu clusters is stronger than the case of CH_3. The vibrational frequencies of C−H bonding agree with the experimental results obtained for CH_2 and CH_3 absorbed on Cu(111). With the increase of cluster size, the softening (Einstein shift) of C−H vibrational modes become stronger.

Key words: Radical CH_2, Radical CH_3, Cu cluster, C−H vibrational mode softening (Einstein shift)

I. INTRODUCTION

The adsorption is used more and more widely with in-depth understanding the nature and mechanism of adsorption phenomena, and the adsorption maybe lead to a hot study on hydrogen storage [1, 2]. The adsorption behavior of small molecules and radicals in transition metal clusters gains the attention of researchers, the studies that CH_n (n=1, 2, 3, 4) small groups, CO molecule, NO molecule, O_2 molecules, and some large organic molecules adsorbed on the metal have also been reported [3−5]. Poveda et al. studied the adsorption energy of CH_n (n=1, 2, 3) on Ni_{14} cluster by MINDO/SR methods, the results shows that the order of adsorption energy is CH_3<CH_2<CH, and the electron transferred from metal to radicals [6]. Chan et al. investigated the vibrational spectrum of CH_2 and CH_3 radicals absorbed on Cu(111) using the High-resolution electron energy loss spectroscopy, and determined the vibrational band of CH_2 and CH_3 radicals absorbed on Cu(111) through the analysis of vibrational spectrum [7]. Michaelides et al. studied the softening of the C−H vibrational frequency and dehydrogenation of CH_3 adsorbed on Cu(111), Ni(111), and Pt(111) using cluster simulation metal solids and density functional theory (DFT) methods [8]. Robinson et al. calculated the absorption energy of CH_3 adsorbed on Cu(111) using DFT, the results showed that Cu−C atom distance was very close to experimental results, but the distance of Cu−C layer was more than the experimental results [9]. All of these studies limited the structure of metal ma-

terial and simulated the metal surface 110 and 111 by clusters. It is found that there is red shift (the Einstein shift or vibration softening) of C−H bond stretching vibration modes for hydrocarbon absorbed on metal surface, that is, the frequency of C−H vibrational frequency is less than 2900 cm^{-1} [8, 10−14]. The red shift is closely related to adsorption substrate, and increases from left to right, top to bottom in elements periodic table.

In this work, DFT was used to study the adsorption properties of CH_2 and CH_3 on Cu_n (n=1−6) clusters, that is, optimizing the geometries of adsorbed clusters, calculating the C−H average bond lengths with increasing cluster size. The change trend of C−H symmetric stretching vibration frequencies was observed and compared with the results of metal surface. Whether there is softening for C−H bond symmetric stretching vibration frequencies or not, and the relationship of softening on C−H bond were estimated. The information and results are not enough to reveal the essence and the mechanism of softening, but at least provide a powerful data evidence for the future research work.

II. CALCULATION METHODS

The calculation were carried out by DFT of Becke three parameters exchange function and Lee-Yang-Parr of correlation function hybrid density functional B3LYP [15]. Heavy atoms Cu used double ζ covalence basis set and Los Alamos relativity effective core potential (RECP), namely LANL2DZ [16]. The basis sets are corrected by the scalar relativistic through the effective nuclear potential, and they are suitable for the heavy elements. Due to the relativistic effect, there is a hybrid interaction between the inner d electron and the outer

TABLE I The bond lengths of CH_2 and CH_3 radicals adsorbed on Cu_n (n=1−6) obtained by B3LYP.

	CH_2-Cu_n		CH_3-Cu_n		$(CH_3)_2$-Cu_n	
	$R_{\text{Cu−C}}$/Å	$R_{\text{C−H}}$/Å	$R_{\text{Cu−C}}$/Å	$R_{\text{C−H}}$/Å	$R_{\text{Cu−C}}$/Å	$R_{\text{C−H}}$/Å
n=1	1.867	1.088	1.923	1.091	1.983	1.090
					1.983	
n=2	1.898	1.091	1.960	1.091	1.940	1.096
	1.898				1.992	
n=3	1.928	1.092	1.960	1.094	2.046	1.099
	1.929				2.046	
n=4	1.982	1.100	2.114	1.097	2.059	1.100
	2.113		2.171		2.059	
n=5	2.014	1.094	2.114	1.098	2.032	1.099
	2.014		2.133		2.046	
n=6	1.972	1.099	2.111	1.098	2.047	1.099
	2.040		2.138		2.047	
Cu(111)-CH_3	2.22±0.02 [18]	1.100[a]				
	1.99[a]					
	1.98[a]					

[a] C−Cu bond length is layer spacing [9].

s electron of Cu atom, resulting in some dispersion in orbits. The dispersion will induce that the inner electronic nuclear shield effect becomes weaker, so the outer s electron closes to the nuclear area and the energy becomes lower. The combined result of these two effects decreased Cu atomic radius, and reduced the total energy of the system. 6-311++G(3d,f) full electronic base set, which contain polarization and dispersion function, can be a better description C and H. The calculation of spin contamination is neglected. The structures are optimized and the frequencies are analyzed, there is no imaginary frequency, which indicate that the optimized geometries are obtained at the minima of the energy cure, not the transition state or higher order saddle points. The calculation are processed by the Gaussian 03 package [17].

III. RESULTS AND DISCUSSION

When CH_2 and CH_3 radicals are adsorbed on Cu_n (n=1−6) clusters, the C−H bond length is increased for those clusters compared to CH_2 and CH_3 radicals itself, as shown in Table I. With the increasing of the Cu atoms, C−H bond length is increasingly close to the value of CH_3 adsorbed onto Cu(111) surface [9]. When the adsorption occurs, the distances of C to two Cu atoms are equal for CH_2-Cu_2 and CH_2-Cu_5, but the distances are irregular in others cases. With the increasing of clusters size, C−Cu bond length increases except CH_2-Cu_5, CH_2-Cu_6, CH_3-Cu_5, and $(CH_3)_2$-Cu_5. Ni−C bond length is 1.904 Å for CH_2 and CH_3 radicals adsorbed on Ni_{14}(100) faces [6], Cu−C bond length is smaller than this value only for CH_2-Cu and CH_2-Cu_2

clusters, while the other bands are greater than the value. The height of CO molecules adsorbed on Cu cluster is between 2.42 and 3.75 Bohr (1 Bohr=0.53 Å) [5], while our calculation revealed that the distance from Cu to C is larger than this value, indicating that the interaction of CH_2 and CH_3 radicals with Cu is weaker than the CO molecule.

Figure 1 shows the dependence of C−H average bond length and C−H symmetric stretching vibration frequency on the clusters size for CH_2-Cu_n, CH_3-Cu_n, and $(CH_3)_2$-Cu_n (n=1−6) clusters. It can be seen that the trends of C−H average bond length and stretching vibration frequency are just opposite, the longer the bond length, the smaller the stretching vibration frequency; and the larger the clusters the smaller the C−H symmetric stretching vibration frequency. C−H average bond length is reduced for n=5 compared to the two neighboring clusters in CH_2-Cu_n and $(CH_3)_2$-Cu_n (n=1−6) system, and C−H symmetric stretching vibration frequency is higher than the neighboring clusters. In CH_3-Cu_n (n=1−6) system, C−H average bond length increases, the corresponding C−H symmetric stretching vibrational frequencies decrease. For two CH_3 radicals absorbed on Cu_n (n=1−6) clusters, there are two sets C−H symmetric stretching vibrational frequencies, one is less than 1200 cm^{-1}, and the other is more than 2800 cm^{-1}. In this work, the red shift (the Einstein shift or vibration softening) is compared to CH_4, therefore the second set frequencies are considered. The trends of C−H bond length and C−H symmetric stretching vobrational frequency are similar to CH_2-Cu_n (n=1−6) and CH_3-Cu_n (n=1−6) systems, the average C−H bond length increases with the in-

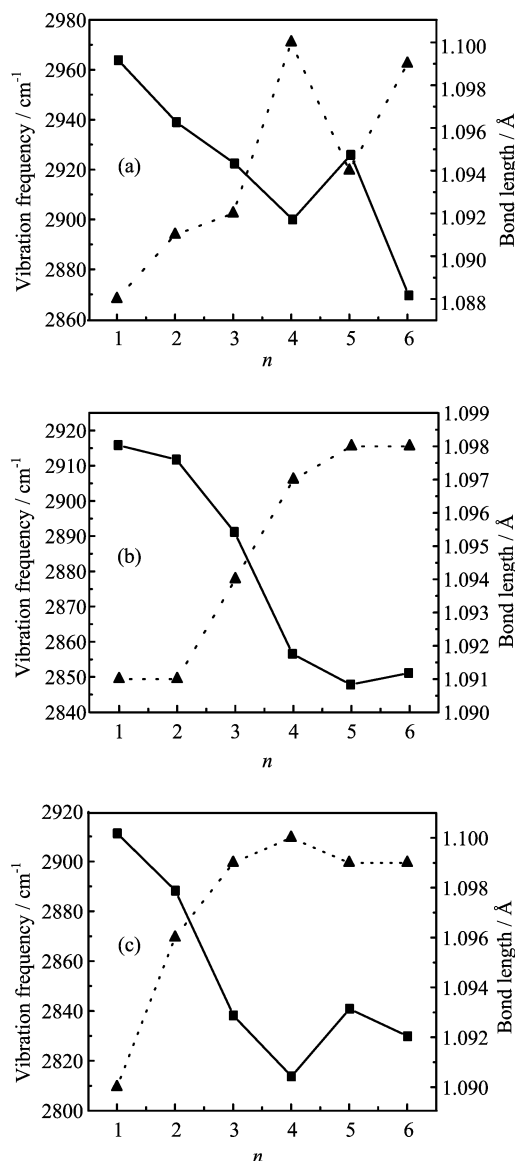FIG. 1 The dependence of C−H average bond length and C−H symmetric stretching vibration frequency on the clusters size for (a) CH_2-Cu_n, (b) CH_3-Cu_n, and (c) $(CH_3)_2$-Cu_n ($n=1-6$) systems. Triangles are bond lengths, squares are frequencies.

TABLE II The red shift for C−H symmetrical stretching vibration frequency in CH_2-Cu_n, CH_3-Cu_n, and $(CH_3)_2$-Cu_n ($n=1-6$) and hydrocarbons on metals surface.

	Frequency red shift/cm^{-1}	
	Theory	Experiment
CH_2-Cu	33	−47
CH_2-Cu_2	58	−22
CH_2-Cu_3	75	−5
CH_2-Cu_4	97	17
CH_2-Cu_5	72	−8
CH_2-Cu_6	128	48
CH_3-Cu	81	1
CH_3-Cu_2	85	5
CH_3-Cu_3	106	25
CH_3-Cu_4	140	60
CH_3-Cu_5	149	69
CH_3-Cu_6	146	6
$(CH_3)_2$-Cu	86	6
$(CH_3)_2$-Cu_2	109	29
$(CH_3)_2$-Cu_3	159	79
$(CH_3)_2$-Cu_4	183	103
$(CH_3)_2$-Cu_5	156	76
$(CH_3)_2$-Cu_6	167	87
CH_3/Cu(111) [8]	137 (fcc)	127
	50 (top)	
CH_3/Ni(111) [8]	267 (fcc)	262
CH_3/Pt(111) [8]	293 (fcc)	
	42 (top)	32
Alkyl/Ag(111) [19]		13 (CH_3CH_2)
		11 (CH_2CH_3)
		82 (CH_2CF_3)
CH_3O/Cu(100) [20]	172	112
Ethyl/Pt(111) [21]		1 (CH_2)
		68 (CH_3)
CH_3/Ni(111) [21, 22]	31 (3-fold)	
	96 (Titled)	
	62 (3-fold)	
1,4-dioxane/Cu(100) [23]		∼60 (CH_2)

creasing of clusters size, and C−H symmetric stretching vobrational frequency decreases with the increasing of clusters size.

For hydrocarbons adsorbed on metal surface, the criterion of C−H bond softening is considered as CH_4 molecules with the theoretical results of 2997 cm^{-1} and experimental results of 2917 cm^{-1}. Table II lists the comparison between theoretical results and experimental results for C−H symmetric stretching vibrational frequency red shift when CH_2 and CH_3 are adsorbed on Cu_n ($n=1-6$) clusters and other metal surfaces. The results of comparison can just interpret the deviation between our calculation and experimental measurement,

and whether the theoretical data obtained is valid or not. Whether the theoretical value can be compared with experimental data and explain the problem, it is an effective way of data processing between the experimental and theoretical calculations.

In this work, only comparatively simple discussion for the theoretical calculations is considered. In general, it can be considered that the softening did not occur in metal surfaces when the red shift of C−H stretching vibration frequency is smaller than 50 cm^{-1} [12]. The intensity of the red shift for C−H stretching vibration frequency depended on sites and type of adsorption. The red shift of the position, which is most prone to

lead to the chemical adsorption is greater than the other location or physical adsorption position. Although the system which we studied is not a surface, the red shift of C−H stretching vibration frequency obtained in our calculation increases with the size of cluster, only a red shift in the CH_2-Cu is less than 50 cm^{-1}. The red shift in CH_2 adsorption system increased from 33 cm^{-1} to 128 cm^{-1}, from 80 cm^{-1} to 149 cm^{-1} in CH_3 adsorption system and from 109 cm^{-1} to 183 cm^{-1} in two CH_3 radicals adsorbed on Cu clusters. It is less than the red shift values of hydrocarbons adsorbed on Cu(111) and Cu(100) surface of 137 cm^{-1} [8] and 172 cm^{-1} [20], and also less than the values of CH_3 adsorbed to Ni(111) 267 cm^{-1} and Pt(111) 293 cm^{-1} [8], which indicates that the softening degree of C−H for CH_2 and CH_3 adsorbed on Cu cluster relaxes on the Ni(111) and Pt(111) surface. Our calculated results of the red shift is greater than that of Schule *et al.* [22] and Yang *et al.* [24] who calculated CH_3 adsorbed on Ni(111). This deviation may be attributed to the different density functional methods and distinction between small cluster and metal surface. The red shift of the C−H stretching vibration for alkyl adsorption on Ag(111) should be smaller than our results, which indicate that the softening degree of CH_2 and CH_3 adsorbed on Cu cluster is stronger than alkyl adsorbed on Ag(111).

The dependence of C−H symmetric stretching softening of the theoretical and C−H average bond length on the clusters size is given in Fig.2. When CH_2 and CH_3 adsorbed on the Cu_n ($n=1-6$) clusters, the trend of redshift on C−H symmetric stretching is the same as C−H average bond length: the longer the C−H average bond length, the greater the red shift of the C−H stretching vibration frequency. Adsorption always occurs first in the location with higher energy and greater activity, and then turns to the low-energy and low activity position. Moreover, the red shift of the position which is most prone to occur the chemical adsorption is bigger than others. It is found that the red shift of C−H symmetric stretching vibration frequency increases with the increasing of cluster size expect CH_2-Cu_5 and $(CH_3)_2$-Cu_5. It can be concluded that the absorption of CH_2 and $(CH_3)_2$ on Cu_5 clusters is physical adsorption, and chemisorptions in the other clusters. Combined with the previous study of stability structure [25], it can be found that in the CH_2-Cu_n ($n=1-6$), the chemical absorption in Cu_4 and Cu_6 clusters makes the original clusters structure change, and this change leads to C−H symmetric stretching vibrational frequency red shift and C−H bond length decreasing for $n=5$. The trends of red shift for the C−H symmetric stretching vibration frequency and the C−H average bond length are exactly same in CH_3 adsorbed on Cu_n ($n=1-6$) clusters, so the adsorption type of CH_3 on Cu clusters is single chemical adsorption. When hydrocarbons adsorbed on metal surfaces, the quantum state analysis reveals that there is an interaction between C−H bond and metal atoms, this interaction is essentially a
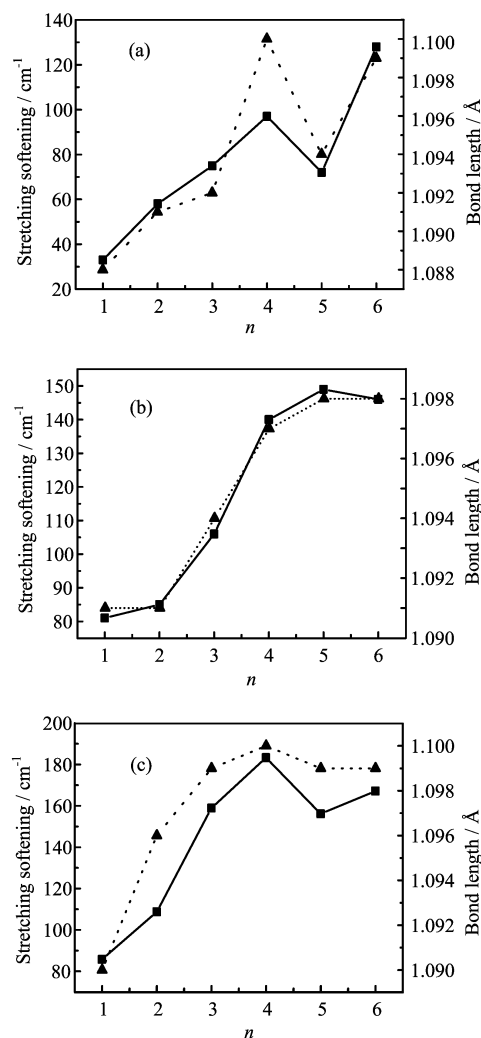

FIG. 2 The dependence of C−H average bond length and C−H symmetric stretching softening on the clusters size for (a) CH_2-Cu_n, (b) CH_3-Cu_n, and (c) $(CH_3)_2$-Cu_n ($n=1-6$) systems. Triangles are bond lengths, squares are redshifts.

mixture of bonding orbital e^1 of C−H bond with the metal atom d orbital. And it is the physical source of softening for C−H symmetric stretching vibrational frequency, the longer the C−H bond length, the weaker the C−H bonding. So it can be concluded that the interaction of the bonding orbital e^1 of C−H bond with the metal atom d orbital in CH_2-Cu_n ($n=1-6$) is stronger than CH_3 absorbed on Cu clusters, which coincides with previous studies of NPA analysis for CH_2 and CH_3 adsorbed on Cu clusters [25]. In other words, the charge transfers from the metal Cu cluster to CH_2 and CH_3 radicals, and the number of charge transferring to CH_2 is greater than to CH_3 from metal atoms.

IV. CONCLUSION

The softening nature of the symmetric stretching frequency of C−H bonds in CH_2 and CH_3 radicals ad-

sorbed on Cu_n ($n=1-6$) clusters has been calculated, using the hybrid density functional theory method. Adsorption of CH_2 radical on Cu cluster is easier to be found than that of CH_3 radical, and the red shift of C−H symmetric stretching vibrational frequency in CH_2-Cu_n is smaller than in CH_3-Cu_n and $(CH_3)_2$-Cu_n ($n=1-6$). With the increasing of the cluster size, the red shift of the C−H symmetric stretching vibrational frequency is more and more obviously, and the trends are similar to the trend of charge transfer from metal atoms to radicals.

V. ACKNOWLEDGMENTS

[1] B. K. Rao, P. Jena, S. Burkart, G. Gantefőr and G. Seifert, Phys. Rev. Lett. **86**, 692 (2001)

[2] J. Jaehoon and Y. K. Hana, J. Chem. Phys. **125**, 064306 (2006).

[3] M. Moskovits and J. E. Hulse, J. Chem. Phys. **81**, 2004 (1977).

[4] Q. Y. Yang, K. J. Maynard, A. D. Johnson, and S. T. Ceyer, J. Chem. Phys. **102**, 7734 (1995).

[5] D. Post and E. J. Baerends, J. Chem. Phys. **78**, 5663 (1983).

[6] F. M. Povedal, M. Sáchez, and F. Ruette, J. Phys.: Condens. Matter **5**, A237 (1993).

[7] Y. L. Chan, P. Chuang, and T. J. Chuang, J. Vac. Sci. Technol. A **16**, 1023 (1998).

[8] A. Michaelides and P. Hu, J. Chem. Phys. **114**, 2523 (2001).

[9] J. Robinson and D. P. Woodruff, Surf. Sci. **498**, 203 (2002).

[10] J. E. Demuth, H. Ibach, and S. Lehwald, Phys. Rev. Lett. **40**, 1044 (1978).

[11] R. Raval and M. A. Chesters, Surf. Sci. **219**, L505 (1989).

[12] N. Sheppard and C. De La Cruz, Adv. Catal. **42**, 181 (1998).

[13] J. L. Lin and B. E. Bent, Chem. Phys. Lett. **194**, 208 (1992).

[14] C. M. Chiang, T. H. Wentzlaff, and B. E. Bent, J. Phys. Chem. **96**, 1836 (1992).

[15] (a) A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
(b) C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
(c) S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
(d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).

[16] (a) P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).
(b) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, and P. D. W. Boyd, J. Chem. Phys. **91**, 1762 (1989).
(c) T. V. Russo, R. L. Martin, and P. J. Hay, J. Chem. Phys. **99**, 17085 (1995).
(d) W. C. Eemler, R. B. Ross, and P. A. Christiansen, Int. J. Quantun Chem. **40**, 829 (1991).

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci,M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, Ö. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision D.01*, Pittsburgh, PA: Gaussian, Inc., (2004).

[18] M. Pascal, C. L. A. Lamont, M. Kittel, J. T. Hoeft, L. Constantb, M. Polcik, A. M. Bradshaw, R. L. Toomes, and D. P. Woodruff, Surf. Sci. **512**, 173 (2002).

[19] W. X. Huang, Z. Q. Jiang, and J. M. White, Chem. Phys. Lett. **428**, 293 (2006).

[20] R. Ásmundsson and P. Uvdal, J. Chem. Phys. **112**, 366 (2000).

[21] H. E. Newell, M. R. S. McCoustra, M. A. Chesters, and C. De La Cruz, J. Chem. Soc. Faraday Trans. **94**, 3695 (1998).

[22] J. Schule, P. Siegbahn, and U. Wahlgren, J. Chem. Phys. **89**, 6982 (1988).

[23] P. T. Chang, C. Y. Chen, and J. L. Lin, Surf. Sci. Lett. **524**, L96 (2003).

[24] H. Yang and J. L. Whitten, J. Am. Chem. Soc. **113**, 6442 (1991).

[25] X. H. Cheng, M. X. Jin, Z. Hu, F. F. Hu, and D. J. Ding, Chin. J. Chem. Phys. **21**, 445 (2008).