Interaction of Cu cluster anions (Cu$_n^-$, n = 8–11) with oxygen

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Abstract. The reaction of oxygen with Cu cluster anions consisting of 6–11 atoms was studied by means of Time-of-Flight mass (TOF) spectroscopy and Ultraviolet Photoelectron Spectroscopy (UPS). Using molecular oxygen, we found that a Cu$_n^-$ cluster ($n = 6-11$) can react only with one single oxygen molecule, which adsorbs molecularly, implying that the clusters studied here are less reactive towards oxygen chemisorption compared to the smaller clusters ($n < 5$). This result indicates that chemical properties can alter significantly with increasing cluster size. Depending on the cluster source conditions, different cluster structures and reactivity patterns were found. These results are used to qualitatively describe the chemisorption energetics of oxygen on Cu cluster anions.

PACS. 33.60.Cv Ultraviolet and vacuum ultraviolet photoelectron spectra – 36.40.Jn Reactivity of clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters – 36.40.Wa Charged clusters

1 Introduction

Metal clusters are highly correlated electron systems. The increase of the electron-electron interaction in nanoclusters can be directly observed by measuring the energy difference of the singlet and triplet state of a metal cluster, which decreases dramatically with increasing cluster size from about 1 eV for Cu and Ag clusters down to zero for the bulk [1,2]. Another effect of the confinement is the quantisation of the continuous bulk conduction bands into discrete electronic levels. For spherical particles, electronic levels order in shells with a defined angular momentum, and shell closings occur at 8, 18 and 20... electrons, yielding stable "magic" clusters. This difference in electronic properties of the nanoclusters from those of the respective bulk materials can have influence on chemical properties.

Among various metal clusters, the chemical properties of coinage metal clusters have recently drawn particular attention due to their interesting cluster size effects and high activities towards catalytic reactions such as low temperature CO-oxidation and partial oxidation of hydrocarbons [3–9]. The oxygen chemisorption reactivity is of particular interest, since O$_2$ chemisorption is one of the most important elementary steps in various heterogeneously catalyzed reactions [10–16]. Moreover, O$_2$ chemisorption is related to the corrosion process as well as the development of oxide-based electronic devices [17].

Recent studies on oxygen chemisorption on Au and Ag cluster anions have shown that the chemisorption reactivities of these metal clusters are closely related to the electronic structures of the metal clusters, whereas the geometric structures play a minor role for the chemisorption [7,11–16]. Generally, even-numbered Au and Ag cluster anions react with O$_2$, whereas the odd-numbered ones are inert. This correlates with the even-odd behaviour of the electron affinities of the coinage metal cluster neutrals [11–16,18,19]. It was also shown that O$_2$ mostly chemisorbs molecularly on these metal cluster anions. It turned out that the charge state of a cluster plays a crucial role for the chemical reactivity: positively charged Au clusters are not reactive towards O$_2$ chemisorption, whereas negatively charged ones may well react with O$_2$ [20].

The origin of the molecular chemisorption of oxygen is generally thought to be a high kinetic barrier towards dissociative chemisorption, which is energetically more stable than molecular chemisorption. However, it may be also the case that molecular chemisorption of O$_2$ is energetically more stable than dissociative chemisorption. To shed light to this issue, we have recently developed a new technique for the preparation of reacted metal clusters in order to compare structures of M$_n$O$_2^-$ (M: metal, n: number of metal atoms) prepared using molecular and atomic oxygen. This technique is a widely used one in surface science; however, this method has been utilized for the mass-selected free clusters for the first time in our group [21–24]. Using atomic oxygen, the energetic ground states of chemisorption can easily be obtained, in contrast to molecular oxygen due to its high activation barriers. One can get a better understanding of the chemisorption energetics of diatomic molecules on clusters by comparing results of the chemisorption of atomic and molecular species. Interestingly, we found that on some metal

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clusters, molecular chemisorption of diatomic molecules is more stable than dissociative chemisorption [21–24].

In the present work, our results on O_2 chemisorption on Cu cluster anions are reported. Previous studies of Lee and Ervin have shown that the even-odd relationship of the O_2 chemisorption reactivity, which was found for Au and Ag cluster anions, is much less pronounced for the Cu cluster anions, i.e. not only even-numbered but also odd-numbered Cu cluster anions show significantly high reactivities towards O_2 chemisorption [18]. Cu is known to be able to efficiently dissociate O_2, forming Cu oxide [25,26]. However, our results using mass spectrometry and Ultraviolet Photoelectron Spectroscopy (UPS) show that on $Cu_8^- $–$Cu_{11}^-$, O_2 chemisorption includes high activation barriers, i.e. it is most likely that the O_2 dissociation is thermodynamically feasible, but kinetically strongly hindered [27]. The chemisorption energetics of oxygen on the Cu cluster anions is discussed qualitatively.

2 Technical details

To synthesize $Cu_nO_2^-$ (n = number of Cu atoms), Cu clusters were produced in the Pulsed Arc Cluster Ion Source (PACIS) with He as buffer gas (purity better than 99.9999%) [28]. The mass spectrum of the pure Cu cluster anions shows no Cu-oxide clusters. After the Cu clusters were cooled down to room temperature in the extender, they were exposed to O_2 at 0.1 mbar or less (molecular oxygen method). Alternatively, O_2 was dissociated in the electric arc, and then reacted with metal atoms evaporated from the Cu electrode (atomic oxygen method). In this case, Cu and oxygen atoms pass the extender together, in which the clusters form. Using the molecular oxygen method, dissociative chemisorption may not take place, since the dissociation is thermodynamically more favourable, but kinetically hindered. In the atomic oxygen method, kinetic barriers for breaking the O=O bond do not play a role, and thus most likely the ultimate thermodynamic ground state in the chemisorption is reached. As it is shown in Figure 1, the molecular oxygen method yields only $Cu_nO_2^-$, whereas the atomic oxygen method allows the formation of $Cu_nO_1^-$ and $Cu_nO_2^-$, indicative of an efficient dissociation of O_2 in the gas phase before reacting with Cu. In principle, we cannot rule out the possibility of the existence of small amounts of molecular oxygen in the atomic oxygen environment. However, it has been previously shown that UPS spectra of $Cu_6O_2^-$ synthesized using two different methods are completely dissimilar, indicating that the concentration of molecular oxygen in the gas phase is negligibly small, or even if significant amounts of molecular oxygen should exist in this case, clusters react preferentially with atomic oxygen due to its much higher reactivity [29]. The temperature of the clusters at the UPS measurement stage is estimated to be room temperature. The mass of the clusters was selected using a Time-of-Flight (TOF) mass spectrometer, and the UPS spectra of the mass-selected clusters were taken using UV Laser pulse (photon energy = 4.66 eV). As it is shown in Figure 1, the mass-resolution is high
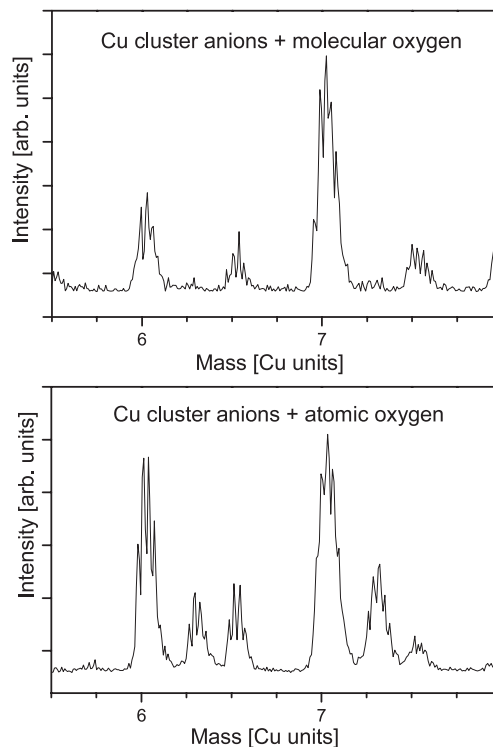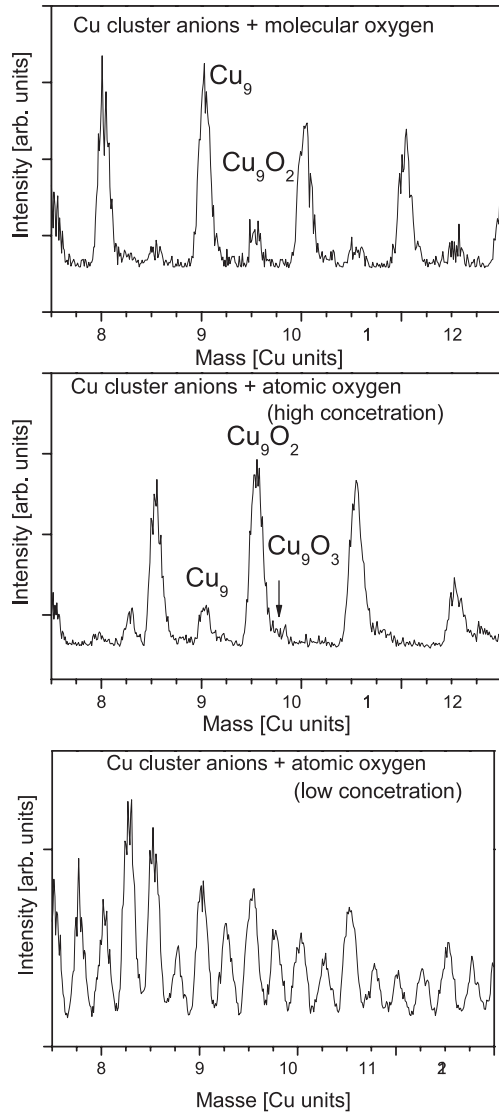

Fig. 1. Mass spectra of $Cu_mO_n^-$ with n = 6, 7 synthesized using molecular (top) and atomic (bottom) oxygen methods.

enough to resolve different isotopes of Cu. More detailed information on our experimental set-up can be found in references [21–24]. The masses of the $Cu_{n-1}O_6$ and Cu_nO_2 clusters are separated by 1 atomic unit, and therefore, discrimination between these two different clusters using our mass spectrometer is difficult for larger clusters. However, it is important to note that Cu_n^- with n = 6–12 exhibited the addition of only one O_2 molecule in the previous studies of Ervin et al. and therefore, we rule out the possibility of the formation of $Cu_nO_6^-$ at the cluster size range of $n > 5$ [18]. Our UPS spectra of CuO_2^- and $Cu_2O_2^-$ are consistent with previous ones from Wang et al. [30,31].

3 Results and discussions

Figures 1 and 2 display the mass spectra obtained for the Cu cluster anions reacted with oxygen. As mentioned above, two different methods were used to create oxygen environments in the cluster source, namely the atomic oxygen and the molecular oxygen method. First, we focus on the reaction of oxygen with Cu_6^- and Cu_7^- clusters (Fig. 1). One can observe the existence of the $Cu_6O_m^-$ and $Cu_7O_m^-$ clusters with m = 0, 1, 2 in the atomic oxygen method, implying that atomic oxygen is indeed formed in the cluster source. Using the molecular oxygen method, only $Cu_6O_m^-$ and $Cu_7O_m^-$ with m = 0, 2 can be detected. Using atomic oxygen, almost no changes in the intensities of the $Cu_nO_2^-$ (n = 6, 7) peaks can be found compared to the case of the molecular oxygen method. It is remarkable that the Cu_6^- peak intensity decreases in the molecular

Fig. 2. Mass spectra of $Cu_mO_n^-$ ($n = 8$–11) synthesized using molecular (top) and atomic (middle, bottom) oxygen methods.

oxygen preparation mode compared to the result of the atomic oxygen method. The origin of this phenomenon cannot be clearly understood, even though several different explanations can be provided: there are reaction channels like $Cu_6O_2^- \rightarrow Cu_{6-n}^- + Cu_nO_2$ in the molecular oxygen mode, which is absent in the atomic oxygen preparation. This could be also partially related to the low electron affinity of $Cu_6O_2^-$ prepared using molecular oxygen compared to the ones prepared using atomic oxygen, which does not have a high probability for the attachment of an electron. One may also argue that the abundance of the Cu_6 clusters is very sensitive to the cluster source conditions, most likely due to the different stabilities and electron affinities of various isomers.

Using molecular oxygen, only small amounts of Cu clusters react with oxygen for Cu_n^- with $n = 8$–11 (Fig. 2), and most of the Cu cluster anions remain unreacted. In the atomic oxygen mode, in contrast, one can observe that

almost all Cu clusters are reacted with oxygen at a high oxygen concentration. At the lower atomic oxygen concentration, $Cu_nO_m^-$ with $m = 1$–4 can be seen, and it can be observed that the formation of $Cu_nO_2^-$ for $n = 9$–11 is slightly favored than one or three oxygen atoms attached to the Cu clusters. At the high atomic oxygen concentration, it is interesting to note that $Cu_nO_m^-$ ($n = 9$–11, $m = 1,3$) can hardly be found, whereas only the peaks corresponding to $Cu_nO_2^-$ are pronounced, i.e. a Cu_n^- cluster with $n = 9$–11 preferentially reacts with two oxygen atoms. This indicates that the $Cu_nO_2^-$ formation is favored to $Cu_nO_3^-$ or Cu_nO^-, or monoxide and trioxide clusters can be more easily fragmented. Regarding these two possibilities, it can be suggested that the attachment of two oxygen atoms is energetically favored [18]. The concentration of $Cu_nO_3^-$ decreases in intensity with increasing atomic oxygen concentration. One possible explanation of this phenomenon is that $Cu_nO_3^-$ is not very stable, and therefore one oxygen atom of this cluster can readily react with a small amount of impurities such as hydrogen existing in the chamber, thus forming of $Cu_nO_2^-$, which is very stable. The amount of impurities can increase with increasing oxygen pressure, due to the impurities in the O_2 gas as well as exchange reactions between the water or hydrogen on the chamber wall and oxygen in the gas phase.

Our observation in Figure 2 that Cu clusters react with atomic oxygen more efficiently than molecular oxygen suggests that the chemisorption of molecular oxygen on Cu_n^- clusters with $n = 8$–11 is kinetically hindered. Only by using the atomic oxygen method, one may obtain the ground state structures of $Cu_nO_2^-$. It can be suggested that the metastable state of a $Cu_nO_2^-$ cluster corresponds to the molecular chemisorption of oxygen, whereas oxygen exists in the atomic form in the ground state structure. This scenario is quite likely considering that a dissociative chemisorption is often hindered due to a high kinetic barrier, even though it is energetically more favored than the molecular chemisorption. An alternative explanation of the results in Figure 2 is that in the ground states of $Cu_nO_2^-$, the Cu_n^- frameworks significantly differ from those in the respective metastable states, i.e. strong reconstructions are required for the Cu_n^- frameworks to reach the thermodynamic ground states of $Cu_nO_2^-$ at the cost of high activation energies. In the molecular oxygen mode, Cu clusters are synthesized and cooled down to room temperature, and then react with O_2. If a Cu isomer with a different Cu framework from that of $Cu_nO_2^-$ synthesized by atomic oxygen is formed, it can have a different structure than the same cluster prepared using atomic oxygen.

UPS was used to shed light onto the structures of the $Cu_nO_2^-$ clusters studied here (Figs. 3–5). UPS spectra of the $Cu_nO_2^-$ clusters prepared using two different methods are dissimilar: using molecular oxygen, one can find various distinct features in the binding energy range of 2–3.5 eV. In the atomic oxygen mode, the intensities of the features at the lower binding energy regime are significantly reduced, and features in higher binding energies become pronounced. It seems that a new isomer with a
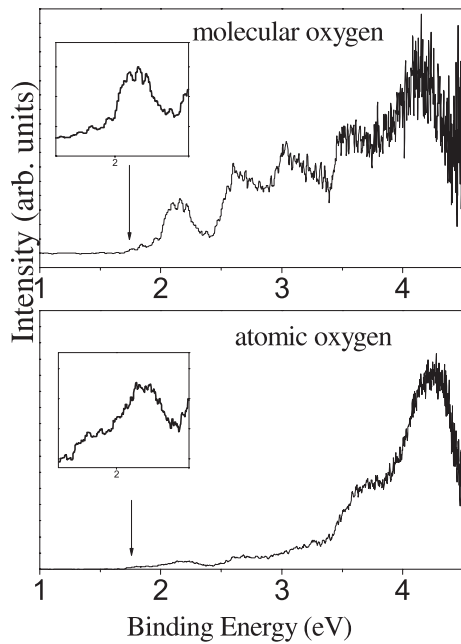
Fig. 3. UPS spectra of $Cu_8O_2^-$ prepared using atomic and molecular oxygen methods. Magnified views of the low energy part can be seen in the insets.
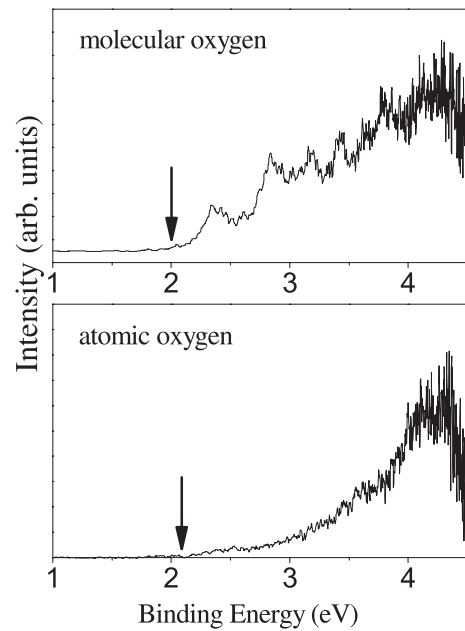
Fig. 5. UPS spectra of $Cu_{10}O_2^-$ prepared using atomic and molecular oxygen methods.
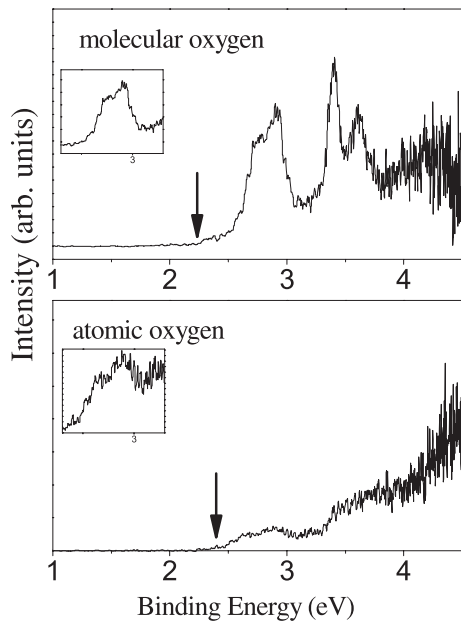
Fig. 4. UPS spectra of $Cu_9O_2^-$ prepared using atomic and molecular oxygen methods. Magnified views of the low energy part can be seen in the insets.

higher electron affinity appears when atomic oxygen is used instead of molecular oxygen, and at the same time, the isomer prepared using molecular oxygen decreases in concentration in the atomic oxygen preparation mode. The features visible in the molecular oxygen preparation mode can still be seen in the atomic oxygen mode, implying that there is still some molecular oxygen present in the atomic oxygen preparation mode, which can react

with Cu. The onsets of the electron signals in the low binding energy side are denoted with arrows, corresponding to the electron affinities of the neutral clusters. For $Cu_8O_2^-$ prepared using molecular oxygen, some periodic structures of 100 meV and 60 meV can faintly be discriminated, which can be related to the vibrational frequency of oxygen species. However, due to a low reproducibility of these periodic signals, this issue is not going to be discussed further. The first features from the lowest binding energy of the photoelectron spectra can become slightly broader, when atomic oxygen was used for the preparation (Fig. 4). This might be related to the fact that hot Cu clusters react in this case with hot, non-dissociated oxygen molecules, which can yield higher cluster temperatures than those in the case of the molecular oxygen mode (reaction of cooled cluster and cool molecular oxygen). The $Cu_nO_2^-$ species with dissociatively chemisorbed oxygen should have much higher electron affinities of the respective neutral clusters compared to the isomers with molecularly bound oxygen, since a dissociative chemisorption should yield a much larger metal to oxygen charge transfer, and thus a higher electron affinity. These results imply that most likely oxygen dissociatively chemisorbs only in the atomic oxygen preparation, whereas di-oxygen species are formed when the molecular oxygen method is used for the cluster synthesis [13].

Previous studies of Ervin et al. as well as ours show that the Cu cluster anions consisting of 5–12 atoms can allow the attachment of only one O_2 molecule per a cluster, whereas smaller Cu cluster anions can react with more than 2 O_2 molecules, i.e. the large Cu clusters with $n = 5$–12 are less reactive towards O_2 chemisorption [18]. As mentioned in the introduction, the chemical reactivities

for the coinage metal clusters consisting of less than 30–40 atoms are often dominated by their electronic structures, whereas the site-specific chemistry plays a minor role [32,33]. Our results on larger clusters showing lower reactivities towards oxygen chemisorption than smaller clusters are in a disagreement with the site-specific chemistry, since with increasing cluster size, the number of specific chemisorption sites should increase, resulting in an increased uptake of oxygen. One may therefore assume that the chemisorption reactivities of the Cu cluster anions in this size regime are governed by the electronic structure. Actually, the smaller Cu clusters (with $n = 1$–4) generally have lower electron affinities than those of the larger Cu clusters ($n = 5$–11), and a lower electron affinity of a neutral cluster can facilitate the metal to oxygen charge transfer of the respective anionic cluster, resulting in a higher oxygen chemisorption reactivity of the anionic cluster [19]. However, details of our experimental observations cannot be easily understood taking into account both geometric and electronic factors. For example, our experimental observation that the formation of $Cu_nO_2^-$ ($n = 9$–11) is strongly preferred to the $Cu_nO_m^-$ clusters with $m = 1, 3$ at the high oxygen concentration cannot be explained by simple electronic models. In contrast, Cu_6^-, Cu_7^- and Cu_8^- can form Cu_6O^-, Cu_7O^- and Cu_8O^- under the same conditions. Further theoretical studies may shed light on this issue.

4 Conclusion

In summary, $Cu_nO_2^-$ clusters were prepared using atomic oxygen as well as molecular oxygen. Much higher reactivities of Cu_n^- ($n = 8$–11) towards the $Cu_nO_2^-$ formation were observed using atomic oxygen preparation instead of molecular oxygen method. We found that the clusters studied here are even less reactive towards oxygen chemisorption compared to the smaller clusters. This result indicates that chemical properties can alter significantly with increasing cluster size atom by atom.

References

1. C.-Y. Cha, G. Ganteför, W. Eberhardt, J. Chem. Phys. **99**, 6308 (1993)
2. H. Handschuh, C.-Y. Cha, P.S. Bechthold, G. Ganteför, W. Eberhardt, J. Chem. Phys. **102**, 6406 (1995)
3. M. Valden, X. Lai, D.W. Goodman, Science **281**, 1647 (1998)
4. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. **144**, 175 (1993)
5. A. Cho, Science **299**, 1684 (2003)
6. A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Häkkinen, R.N. Barnett, U. Landman, J. Phys. Chem. A **103**, 9573 (1999)
7. W.T. Wallace, R.L. Whetten, J. Am. Chem. Soc. **124**, 7499 (2002)
8. L.D. Socaciu, J. Hagen, T.M. Bernhardt, L. Wöste, U. Heiz, H. Hakkinen, U. Landman, J. Am. Chem. Soc. **125**, 10437 (2003)
9. T.S. Kim, J.D. Stiehl, C.T. Reeves, R.J. Meyer, C.B. Mullins, J. Am. Chem. Soc. **125**, 2018 (2003)
10. N. Lopez, J.K. Norskov, J. Am. Chem. Soc. **124**, 11262 (2002)
11. J. Hagen, L.D. Socaciu, J. Le Roux, D. Popolan, T.M. Bernhardt, L. Wöste, R. Mitrić, H. Noack, V. Bonačić-Koutecký, J. Am. Chem. Soc. **126**, 3442 (2004)
12. D. Stolcic, M. Fischer, G. Ganteför, Y.D. Kim, Q. Sun, P. Jena, J. Am. Chem. Soc. **125**, 2848 (2003)
13. Y.D. Kim, M. Fischer, G. Ganteför, Chem. Phys. Lett. **377**, 170 (2003)
14. Q. Sun, P. Jena, Y.D. Kim, M. Fischer, G. Ganteför, J. Chem. Phys. **120**, 6510 (2004)
15. Y.D. Kim, G. Ganteför, Chem. Phys. Lett. **383**, 80 (2004)
16. B. Yoon, H. Häkkinen, U. Landman, J. Phys. Chem. **107**, 4066 (2003)
17. V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxide* (Cambridge University press, Cambridge, 1996)
18. T.H. Lee, K.M. Ervin, J. Phys. Chem. **98**, 10023 (1994)
19. K.J. Taylor, C.L. Pettiette-Hall, O. Cheshnovsky, R.E. Smalley, J. Chem. Phys. **96**, 3319 (1992)
20. K. Koszinowski, D. Schröder, H. Schwarz, Chem. Phys. Chem. **4**, 1233 (2003)
21. Y.D. Kim, G. Ganteför, Chem. Phys. Lett. **382**, 644 (2003)
22. Y.D. Kim, D. Stolcic, M. Fischer, G. Ganteför, J. Chem. Phys. **119**, 10307 (2003)
23. Y.D. Kim, D. Stolcic, M. Fischer, G. Ganteför, Chem. Phys. Lett. **380**, 359 (2003)
24. Y.D. Kim, G. Ganteför, Q. Sun, P. Jena, Chem. Phys. Lett. **396**, 69 (2004)
25. C.T. Campbell, K.A. Daube, J.M. White, Surf. Sci. **182**, 458 (1987)
26. S. Tsuyoshi, T. Saski, Y. Iwasawa, Surf. Sci. **365**, 310 (1996)
27. F.v. Gynz-Rekowski, N. Bertram, G. Ganteför, Y.D. Kim, J. Phys. Chem. A **108**, 18916 (2004)
28. C.Y. Cha, G. Ganteför, W. Eberhardt, Rev. Sci. Instrm. **63**, 5661 (1992)
29. F. von Gynz-Rekowski, N. Bertram, G. Ganteför, Y.D. Kim, J. Phys. Chem. B **108**, 18916 (2004)
30. L.S. Wang, H. Wu, S. R. Desai, L. Lou, Phys. Rev. B **53**, 8028 (1996)
31. H. Wu, S.R. Desai, L.S. Wang, J. Phys. Chem. **101**, 2103 (1997)
32. L. Holmgren, M. Andersson, A. Rosen, Chem. Phys. Lett. **296**, 167 (1998)
33. L. Holmgren, H. Gronbeck, M. Andersson, A. Rosen, Phys. Rev. B **53**, 16644 (1996)