PHYSICAL REVIEW B **76**, 073406 (2007)

Adsorption of gold clusters on metal-supported MgO: Correlation to electron affinity of gold

Pentti Frondelius,[1] Hannu Häkkinen,[1,2] and Karoliina Honkala[1,2]
[1]*Department of Physics, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland*
[2]*Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland*

(Received 18 June 2007; published 13 August 2007)

Adsorption of Au_N clusters ($N=1-6$) on a bulk MgO(001) surface and on an ultrathin (3 ML) MgO(001) film supported by Mo metal is investigated via density-functional theory calculations. Comparison of the two substrates unambiguously shows that the gold clusters adsorbed on MgO/Mo turn into singly charged cluster anions Au_N^{δ}, $\delta\approx-1$. Their structures and internal charging patterns are analogous to singly charged, planar, gas-phase cluster anions Au_N^-. The adsorption energy has prominent size-dependent odd-even oscillations, correlating fully with the known electron affinity of gas-phase Au clusters in this size range.

DOI: 10.1103/PhysRevB.76.073406 PACS number(s): 68.47.Jn, 36.40.−c, 61.46.Bc

The past two decades have witnessed a surge of interest in investigations of physical and chemical properties of small metal clusters.[1–3] Aside from the traditional viewpoint of clusters providing a “laboratory,” where size evolution of properties of aggregates from atom to bulk can be conveniently investigated, many such studies now are motivated by the increasing drive to learn to control and utilize matter in nanometer scale. In general, this endeavor aims at gaining (i) an understanding of the cluster formation processes, in particular, those that lead to the extra stable or “magic” sizes, and (ii) a profound knowledge of their interaction with the pertinent environment, where their electronic, magnetic, optical, or chemical properties are expected to be utilized.

It has been well known for decades that a single gold atom has rich chemistry as it supports remarkably many oxidation states from −1 to +5 and its $5d^{10}$ shell participates actively in bonding coordination in various compounds.[4,5] Gold clusters and nanoparticles have attracted much attention recently as they are considered promising candidates for applications, e.g., in heterogeneous catalysis,[6–10] bioelectrocatalysis,[11] labeling,[12] and photonics.[13] Recent catalysis investigations have focused on low-temperature oxidation and epoxidation reactions, catalyzed by nanometer- or subnanometer-sized, metal-oxide-supported gold clusters.[6–9] The oxidation state of catalytically active gold in these systems is currently a much debated issue.

Models of bulk magnesia as a substrate for gold have become popular[14–18] due to their simple rocksalt oxide structure that simplifies the theoretical treatments. Less attention[19–22] has been paid to the fact that in the experiments, the gold clusters are supported by a few monolayer (ML) thick MgO films that are grown, e.g., on Ag (Ref. 23) or Mo.[24] At equilibrium, these systems must therefore be considered as an ultrathin insulator sandwiched between two metals. At this limit, current tunnels through the MgO film under scanning tunneling microscopy (STM) imaging conditions, and the first STM data on nanometer-sized gold clusters grown at color centers of MgO/Ag has recently been published.[25] Characterization of charge states of these aggregates, as well as their chemical properties, continues to be a challenging task for high-level theory. It has been recently shown theoretically that single Au atoms[19,26] and interfacial Au atoms[20] in large clusters are negatively charged on regular metal-supported thin MgO films.

In this Brief Report, we unambiguously show from systematic density-functional theory (DFT) calculations that the gold clusters with one to six atoms, adsorbed on a regular MgO(3 ML)/Mo surface, turn into *singly charged* cluster anions Au_N^{δ}, $\delta\approx-1$. Three results are presented in this work: First, the optimal structure of the adsorbed clusters is analogous to the corresponding singly charged gas-phase cluster anions. Second, the internal charge analysis of the adsorbed clusters by the Bader method gives almost an identical correspondence to the atomic charge decomposition of the reference singly charged gas-phase cluster anions. Third, the prominent odd-even variations of the adsorption energy $E_{ads}(N)$ as a function of cluster size, where $N=1,3,5$ correspond to local maxima, correlate fully with the well-known maxima of electron affinity of the reference gas-phase clusters. We demonstrate for Au_2/MgO/Mo how charging of the gold, that arises from the alignment of the Fermi levels of the gold cluster and the Mo support, induces a spatially varying polarization pattern inside the ultrathin MgO(3 ML) insulator.

The DFT calculations were performed with the DACAPO code,[27] with a plane wave basis restricted by a kinetic energy cutoff of 25 Ry. We employed the revised Perdew-Burke-Ernzerhof[28] (RPBE) generalized gradient correction self-consistently, and the core electrons of all the atoms were treated with Vanderbilt ultrasoft pseudopotentials.[29] The sampling of four (one) special *k* points were used for MgO/Mo and MgO, respectively. A spin-unpolarized approach was used for all the calculations. This choice was checked for the adsorption energies of Au_1 and Au_3 on MgO(3 ML)/Mo and Au_3 on MgO(3 ML). We found that the difference in the spin-polarized and -unpolarized adsorption energies is at most 0.05 eV. In electron affinities, the difference is less than 0.06 eV. We modeled the Mo-supported MgO film with a six-layer-thick slab, where the three undermost layers are made of Mo and the three topmost ones of MgO. The slab is repeated periodically with a (3×3) or (4×3) unit cell and at least 10 Å of vacuum between the slabs. The MgO-Mo interface structure and applied lattice constants are taken from Ref. 26. Three ML of MgO have been shown to be enough to form an insulating film.[23,26] The bottom Mo layer was frozen at the bulk geometry, while all the other atoms were free to relax.

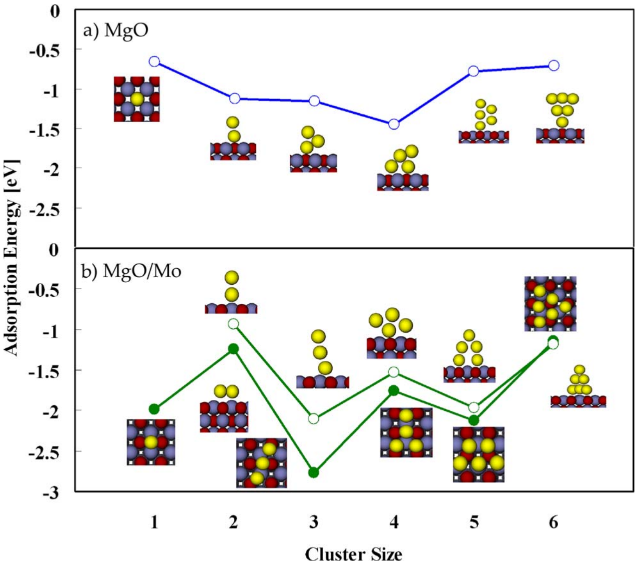

FIG. 1. (Color online) The adsorption energies and geometries of the optimal clusters on (a) bulk MgO and on (b) MgO/Mo as a function of cluster size. In (b), two different planar structures, upright (open circles) and flat (solid circles), are given. Au atoms are yellow (light gray), O atoms are red (dark gray), and Mg atoms are blue (medium gray). Mo atoms are not shown in (b).

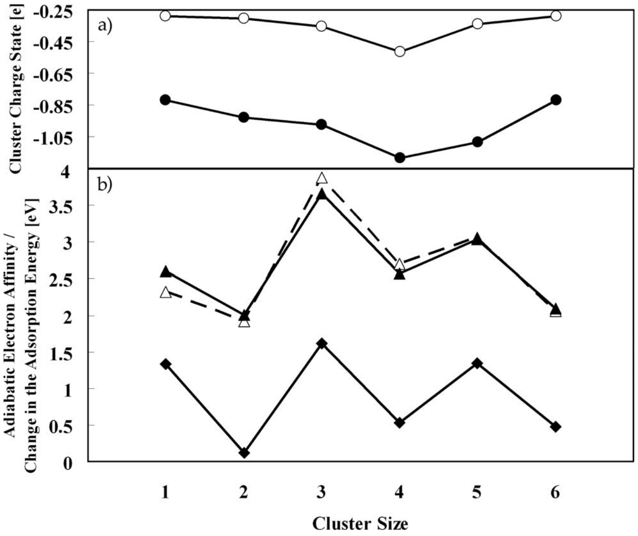

FIG. 2. (a) The calculated cluster charge as a function of size on MgO (open circles) and MgO/Mo (solid circles). (b) The measured (Ref. 39) (open triangles) and calculated (solid triangles) electron affinities of gas-phase Au clusters compared to the enhancement in Au cluster adsorption energy induced by the Mo support below MgO (solid diamonds).

The gas-phase clusters were calculated in large supercells with volume larger than 16^3 Å^3 to isolate the periodic images from each other. Analysis of spatial distribution of charge in the system was done via the Bader approach.[30] For the details of the implementation of the method, see Ref. 31, and for the recent applications, see Refs. 26 and 32. We define adsorption energies through $E_{ads}=E_t(\mathrm{Au}_N/\mathrm{subs})-E_t(\mathrm{subs})-E_t(\mathrm{Au}_N)$, where $E_t(\mathrm{Au}_N/\mathrm{subs})$ is the total energy of the cluster and the substrate, and $E_t(\mathrm{subs})$ and $E_t(\mathrm{Au}_N)$ stand for the total energies of the substrate and the gas-phase cluster, respectively.

Figure 1 compares the optimal adsorption geometries and adsorption energies for clusters with $N=1-6$ on bulk MgO and MgO/Mo surfaces. Aside from testing a number of candidate structures for each size and substrate, we systematically explored two structure "families:" one with the minimal wetting contact: one atom, and one with maximal wetting: a flat structure parallel to the surface. As Fig. 1(a) shows, the optimal adsorption geometry on the bulk MgO surface favors minimal wetting with one or two Au atoms in contact with oxide ions. This trend agrees with the previously reported data for small noble metal clusters on bulk MgO.[17,19,33–36] For gold cluster with $N=3-6$, the internal atomic structure follows the calculated structures of corresponding neutral gas-phase species.[37] Adsorption energies are rather weak from -0.6 to -1.4 eV, without clear size dependence. Previously, the nature of the weak gold-MgO "bond" has been characterized as being of polarization type.[38]

The situation changes rather dramatically for the Mo-supported MgO film, given in Fig. 1(b), where we show for each size two low-energy structures that follow the above-mentioned classification. Generally, flat structures with maximal wetting give a better adsorption configuration than the upright ones. Note that for $N=6$, we find two quasidegenerate low-energy isomers: upright triangular-shaped cluster with a three-atom contact to the film and the flat structure. From comparison between Figs. 1(a) and 1(b), we see that the structure of the gold cluster changes from the bulk MgO adsorption for $N=3,4$, with the trimer being linear and tetramer a "Y-shaped" cluster. The adsorption energy shows strong odd-even variations on MgO/Mo in the range from -1.2 to -2.8 eV, with local maxima at $N=1,3,5$. The stronger contact to the surface induces reoptimization and straining in the internal cluster geometry, each gold atom tending to attach to a fourfold Mg-O hollow site, which was recently shown to be the best adsorption site for a single Au adatom on this substrate.[26]

The fact that the MgO-film-adsorbed Au_3 and Au_4 clusters are structural analogs to the corresponding gas-phase anions[37] prompted us to examine in more detail the adsorption-induced charging effects in the clusters through the Bader analysis. Figure 2(a) shows the local cluster charges as a function of size for both MgO and MgO/Mo substrates, which depend only slightly on the aggregate size. On bulk MgO, the clusters are close to neutral, while on MgO/Mo, they are on average charged by one electron, with the cluster charge varying from $-0.8\,e$ to $-1.2\,e$. More detailed Bader analysis of the substrate layers shows that the extra adsorbate charge on MgO/Mo compared to bulk MgO mainly originates from the Mo metal below the oxide. No obvious correlation between the adsorption energy and the cluster charge state is found for MgO/Mo, the system, where the adsorption energy itself was found to be a strongly size-dependent oscillating quantity.

Central to the conclusions of this work is the examination of Fig. 2(b). It shows an unambiguous correlation between

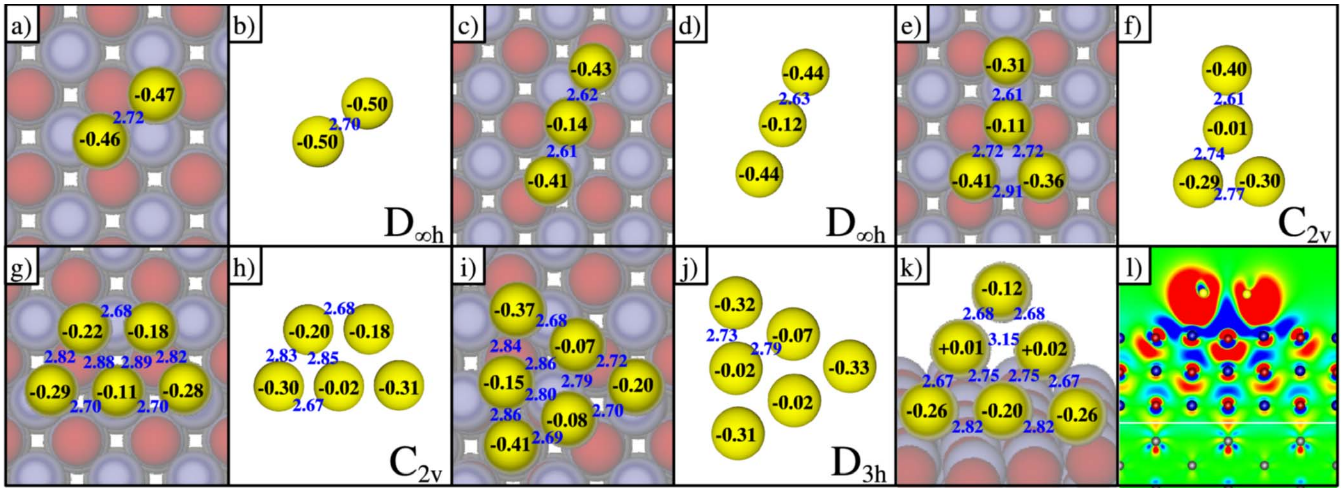

FIG. 3. (Color online) The Bader charges of the individual cluster atoms in electrons (numbers on atoms) and the bond lengths in Å (numbers between atoms) for $\mathrm{Au}_N/\mathrm{MgO}/\mathrm{Mo}$ in (a), (c), (e), (g), (i), and (k), and for anionic gas-phase clusters in (b), (d), (f), (h), and (j) with the given symmetries. Yellow (lightest gray), red (darkest gray), blue (medium gray), and gray balls [the bottom most ones in (l)] mark Au, O, Mg, and Mo atoms, respectively. (l) gives a density difference plot of Au_2 on MgO/Mo shown in (a). Note that the cut plane is (110), which does not coincide with the symmetry planes of Mo *d* orbitals, hence the charge depletion from Mo atoms is not clearly visible. Blue or darkest gray (red or second darkest gray) regions indicate charge depletion (accumulation). The MgO-Mo interface is marked with the white line.

the *increase* of E_{ads} *induced* by the Mo support and the electron affinity of the gold clusters. By the increase of E_{ads} we mean the difference in Au_N adsorption energies on MgO and MgO/Mo surfaces, i.e., $\Delta E_{ads}=E_{ads}^{\mathrm{MgO}}-E_{ads}^{\mathrm{MgO/Mo}}$, see the lowest curve in Fig. 2(b). Theoretical and experimental electron affinities are also shown in Fig. 2(b). Measured affinities are taken from Ref. 39, whereas theoretical affinities E_A are determined from the ground-state total energies of neutral and anionic gas-phase clusters:[40] $E_A(N)=E_t(\mathrm{Au}_N)-E_t(\mathrm{Au}_N^-)$. The calculated values agree very well with the experimental numbers[39] and those calculated previously by one of us, using a non-periodic-cell approach.[37] Small gas-phase gold clusters are known to feature exceptionally large size-dependent E_A variations.[39,41] Figure 2(b) implies that the obvious role of the Mo support is to increase the basicity of the substrate. This leads to an enhanced but size-independent donation of approximately one electron to the gold, which in turn is strongly reflected in the adsorption energy as the high-E_A clusters $N=1,3,5$ are able to accommodate the extra anionic charge better upon adsorption.

To discuss the structural and internal charging patterns of the MgO/Mo adsorbed clusters, we display in Fig. 3 the detailed comparison between the $\mathrm{Au}_N/\mathrm{MgO}/\mathrm{Mo}$ clusters and the corresponding optimized gas-phase Au_N^- anions. We point out the amazingly good correspondence in the internal bond lengths for the smallest clusters, $N=2-4$, where the deviation is less than 0.02 Å. For larger clusters, Au-Au distances are elongated from 0.05 to 0.1 Å compared to their anionic gas-phase counterparts, introducing internal strain to the cluster. This is due to the slight preference of Au to adsorb on a hollow site on MgO/Mo.[26]

Figure 3 shows also the Bader analysis of the internal charge distribution in the adsorbed and gas-phase anionic clusters. The results reveal that the charging patterns inside the flat $\mathrm{Au}_N/\mathrm{MgO}/\mathrm{Mo}$ clusters bear a close analogy to their gas-phase anionic counterparts, Au_N^-. Prominent examples are the trimer, tetramer, and flat hexamer, where the "inner" atoms are close to neutral both for adsorbed and gas-phase clusters. The extra anionic charge is located at the corners and end atoms as in our anionic gas-phase reference clusters and in agreement to a previous study for gas-phase Au_6^-.[41] Experimentally, the internal charge distribution of the supported cluster could be investigated via CO adsorption and local spectroscopy (STM, scanning tunneling spectroscopy, or Fourier transform infrared). For the upright hexamer, the three Au atoms that make contact to the surface are all appreciably negatively charged, in qualitative agreement with recent findings for Au_8, Au_{16}, and Au_{20} on MgO/Mo.[20]

The anionic charging originates from the alignment of Fermi levels at both metal/MgO interfaces,[26] which in turn induces a rich, spatially varying polarization pattern through the ultrathin oxide film. This is illustrated in Fig. 3(l), where we show the density difference, $\Delta\rho=\rho(\mathrm{Au}_N)+\rho(\mathrm{MgO}/\mathrm{Mo})-\rho(\mathrm{Au}_N/\mathrm{MgO}/\mathrm{Mo})$, for $N=2$, projected on the plane parallel to the Au_2 dimer. Note that the spatial pattern of the excess anionic charge has a local σ^* symmetry on gold, as would be expected from the electronic level structure of the gas-phase anion.

We have shown that the Mo support below an ultrathin MgO(3 ML) film increases the basicity of the substrate and induces the donation of the excess negative charge to electrophilic gold adsorbed on the film. The adsorbed gold clusters with one to six atoms show structural and charging patterns that are analogous to singly negatively charged cluster anions in the gas-phase. In this sense, the gold clusters function in the same way as electrophilic molecules, such as NO_2, on metal-supported oxides.[42] The interface between gold and oxide has a rich vertical and horizontal charging pattern, which should lead to preference of certain adsorption sites for polar reactants, such as CO, due to charge-dipole interaction, as well as the existence of excess anionic sites for the adsorption of electrophilic molecules, such as oxygen.

We acknowledge fruitful discussions with M. Manninen and M. Walter. This work was financially supported by the Academy of Finland through Projects No. 106372, No. 110653, No. 113419, and No. 110013. The computational resources were provided by the Finnish IT Center for Science (CSC).

---

[1] W. A. deHeer, Rev. Mod. Phys. **65**, 611 (1993).

[2] *Clusters of Atoms and Molecules I+II*, edited by H. Haberland (Springer, Berlin, 1994).

[3] *Metal Clusters at Surfaces*, edited by K. H. Meiwes-Broer (Springer, Berlin, 2000).

[4] *Gold: Progress in Chemistry, Biochemistry and Technology*, edited by H. Schmidbaur (Wiley, Chichester, England, 1999).

[5] P. Pyykkö, Angew. Chem., Int. Ed. **43**, 4412 (2004).

[6] B. Gates, Chem. Rev. (Washington, D.C.) **95**, 511 (1995).

[7] M. Haruta, Catal. Today **36**, 153 (1997).

[8] G. Bond and D. Thompson, Catal. Rev. - Sci. Eng. **41**, 319 (1999).

[9] R. Meyer, C. Lemire, S. K. Shaikhutdinov, and H. J. Freund, Gold Bull. **29**, 72 (2004).

[10] C. R. Henry, Prog. Surf. Sci. **80**, 92 (2005).

[11] Y. Xiao, F. Patolsky, E. Katz, J. Hainfeld, and I. Willner, Science **299**, 1877 (2003).

[12] J. Zheng, C. Zhang, and R. M. Dickson, Phys. Rev. Lett. **93**, 077402 (2004).

[13] W. L. Barnes, A. Dereux, and T. W. Ebbesen, Nature (London) **424**, 824 (2003).

[14] A. Sanchez, S. Abbet, U. Heiz, W. Schneider, H. Häkkinen, R. Barnett, and U. Landman, J. Phys. Chem. A **103**, 9573 (1999).

[15] H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz, and U. Landman, Angew. Chem., Int. Ed. **42**, 1297 (2003).

[16] L. M. Molina and B. Hammer, Phys. Rev. Lett. **90**, 206102 (2003).

[17] L. M. Molina and B. Hammer, Phys. Rev. B **69**, 155424 (2004).

[18] B. Yoon, H. Häkkinen, U. Landman, A. Worz, J. Antonietti, S. Abbet, K. Judai, and U. Heiz, Science **307**, 403 (2005).

[19] G. Pacchioni, L. Giordano, and M. Baistrocchi, Phys. Rev. Lett. **94**, 226104 (2005).

[20] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. **97**, 036106 (2006).

[21] L. Giordano and G. Pacchioni, Phys. Chem. Chem. Phys. **8**, 3335 (2006).

[22] C. Zhang, B. Yoon, and U. Landman, J. Am. Chem. Soc. **129**, 2228 (2007).

[23] S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, and W.-D. Schneider, Phys. Rev. Lett. **87**, 276801 (2001).

[24] M. Sterrer, E. Fischbach, T. Risse, and H.-J. Freund, Phys. Rev. Lett. **94**, 186101 (2005).

[25] M. Sterrer, M. Yulikov, E. Fischbach, M. Heyde, H. P. Rust, G. Pacchioni, T. Risse, and H. Freund, Angew. Chem., Int. Ed. **45**, 2630 (2006).

[26] K. Honkala and H. Häkkinen, J. Phys. Chem. C. **111**, 4319 (2007).

[27] http://dcwww.fysik.dtu.dk/software/

[28] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).

[29] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[30] R. Bader, *Atoms in Molecules* (Oxford University Press, New York, 1990).

[31] G. Henkelman, A. Arnaldsson, and H. Jónsson, Comput. Mater. Sci. **36**, 354 (2006).

[32] G. Henkelman, B. P. Uberuaga, D. J. Harris, J. H. Harding, and N. L. Allan, Phys. Rev. B **72**, 115437 (2005).

[33] A. D. Vitto, G. Pacchioni, F. Delbecq, and P. Sautet, J. Phys. Chem. B **109**, 8040 (2005).

[34] M. Walter and H. Häkkinen, Phys. Rev. B **72**, 205440 (2005).

[35] A. Bogicevic and D. Jennison, Surf. Sci. **515**, L481 (2002).

[36] V. Musolino, A. Selloni, and R. Car, Phys. Rev. Lett. **83**, 3242 (1999).

[37] H. Häkkinen and U. Landman, Phys. Rev. B **62**, 2287(R) (2000).

[38] I. Yudanov, G. Pacchioni, K. Neyman, and N. Rösch, J. Phys. Chem. B **101**, 2786 (1997).

[39] K. Taylor, C. Pettiette-Hall, O. Cheshnovsky, and R. Smalley, J. Chem. Phys. **96**, 3319 (1992).

[40] The anionic clusters were treated in the supercell that included a neutralizing homogeneous background charge, the effects of which were removed from the calculated total energy by a leading correction term $\Delta E \propto \Omega^{-1/3}$.

[41] H. Häkkinen, B. Yoon, U. Landman, X. Li, H.-J. Zhai, and L.-S. Wang, J. Phys. Chem. **107**, 6168 (2003).

[42] H. Grönbeck, J. Phys. Chem. B **110**, 11977 (2006).