

# Theoretical study on molecular and dissociative chemisorptions of an O<sub>2</sub> molecule on an Ag surface: dipped adcluster model combined with symmetry-adapted cluster-configuration interaction method

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Chemisorption of an oxygen molecule on a silver surface is studied theoretically with the use of the dipped adcluster model (DAM) for Ag<sub>x</sub>O<sub>2</sub> with  $x=2$  and 4. Electron correlation in low-lying surface states and electron transfer from bulk metal are described by combining DAM with the symmetry-adapted cluster (SAC) CI method. For chemisorption, electron transfer from the bulk metal to the adcluster and the electrostatic image force are important. They cannot be treated by the conventional cluster model, but are dealt with by the DAM. Three low-lying states, <sup>2</sup>A<sub>1</sub>, <sup>2</sup>A<sub>2</sub>, and <sup>2</sup>B<sub>1</sub>, of the adclusters Ag<sub>2</sub>O<sub>2</sub><sup>-</sup> and Ag<sub>4</sub>O<sub>2</sub><sup>-</sup> are involved in the chemisorption. In the molecular adsorption state, the <sup>2</sup>A<sub>1</sub> state is assigned to peroxide (O<sub>2</sub><sup>2-</sup>) species and the <sup>2</sup>A<sub>2</sub> and <sup>2</sup>B<sub>1</sub> states to superoxide (O<sub>2</sub><sup>-</sup>) species. The O–O stretching frequencies are in agreement with the experimental values. In the potential energy curves of Ag<sub>4</sub>O<sub>2</sub><sup>-</sup>, another potential minimum corresponding to the dissociative adsorption state is obtained for the <sup>2</sup>A<sub>1</sub> state. The energetics of the molecular and dissociative adsorptions show reasonable agreement with experiments.

Partial oxidation of ethylene on a silver surface is an important catalytic reaction, for which no catalysts except silver have been found effective [1]. However, the mechanism of this catalytic reaction is not yet clarified. We do not yet understand why only a silver surface has such a reactivity and selectivity.

Experimentally, four different species are known for the adsorbed oxygens on a silver surface [2–13]; namely, physisorbed species (O<sub>2</sub>) [2], molecularly adsorbed species, which are superoxide (O<sub>2</sub><sup>-</sup>) [3–5] and peroxide (O<sub>2</sub><sup>2-</sup>) [5–9], and dissociatively adsorbed species (O<sup>-</sup> and/or O<sup>2-</sup>) [6,10–12].

Some theoretical papers have been published on the oxygen chemisorption [14–20]. The GVB-CI study by Upton et al. [17] gave geometric and spectroscopic parameters of O<sub>2</sub> on an Ag(110) surface in good agreement with experimental data. But the molecular adsorption energies relative to the ground states were not reproduced: they were negative. Similarly negative adsorption energies have been obtained by the MP3 calculations [16] and by the GVB and correlation-consistent CI calculations [18]. All of these studies are based on the cluster model, so

that the effects of the bulk metal are only insufficiently included in the calculations. So far, no *ab initio* studies have been able to describe dissociative adsorptions of an O<sub>2</sub> molecule on an Ag surface, though recently Panas et al. successfully described the O–O dissociation on a nickel surface [21].

We report preliminary results of a theoretical study for O<sub>2</sub> chemisorption on a silver surface. We use the dipped adcluster model (DAM), in which the adcluster, which is a combined system of an admolecule and a metal cluster, is dipped onto the electron bath of the solid metal and an equilibrium is established for electron exchange between the adcluster and the bulk metal [22]. This exchange is controlled by a balance of the chemical potentials of the adcluster and the bulk metal. The electrostatic image force, characteristic of a metal surface, is considered with a modification [23] from previous work [22]. Electron correlation in lower surface states and electron transfer from the bulk metal to the adcluster are described with accuracy by the SAC [24]/SAC-CI [25] method.

We first study the energetics for the approach of

an O<sub>2</sub> molecule onto an Ag surface. The active site of an Ag surface is represented by Ag<sub>2</sub>, and an O<sub>2</sub> molecule approaches the surface in a side-on bridge form keeping C<sub>2v</sub> symmetry. This geometry was suggested by Backx et al. for O<sub>2</sub> adsorbed on an Ag(110) surface [7]. The Ag–Ag distance is fixed at 2.8894 Å, which is an equilibrium distance in solid silver [26]. Fig. 1 shows the potential energy curves of the Ag<sub>2</sub>O<sub>2</sub> adcluster as a function of the Ag<sub>2</sub>–O<sub>2</sub> distance. The curves are calculated for the O–O distance fixed at 1.35 Å, which is an equilibrium distance of an O<sub>2</sub> anion [27]. The asterisks show the energies for the optimized O–O distances.

The <sup>3</sup>B<sub>2</sub> state, which does not involve an electron transfer from the bulk metal to the adcluster, is the ground state of the separated system, namely, the <sup>1</sup>Σ<sub>g</sub><sup>+</sup> state of Ag<sub>2</sub> and the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> state of O<sub>2</sub>. The energy of the dissociation limit is estimated by optimizing the O–O distance at the Ag<sub>2</sub>–O<sub>2</sub> distance of 5.0 Å, and is shown by the asterisk in fig. 1. There, the optimized O–O length is 1.29 Å, in comparison with 1.27 Å, the optimized length for the free O<sub>2</sub> molecule (the experimental value is 1.207 Å [27]). The potential curve of the <sup>3</sup>B<sub>2</sub> state rises monotonically as O<sub>2</sub> approaches Ag<sub>2</sub>, showing that no chemisorption occurs along this state. However, when one electron transfer is admitted from the metal bulk to the adcluster, namely *n* = 1, the potential of the <sup>2</sup>A<sub>2</sub> state becomes attractive and a minimum is found at

$R(\text{Ag}_2\text{-O}_2) = 2.6 \text{ \AA}$ . When the O–O distance is further optimized at this minimum, we get  $R(\text{O-O}) = 1.50 \text{ \AA}$  and the system is stabilized up to the asterisk shown in fig. 1. This <sup>2</sup>A<sub>2</sub> state corresponds to the superoxide species, O<sub>2</sub><sup>-</sup>. There is another state, <sup>2</sup>A<sub>1</sub>, which also results from one-electron transfer from the bulk metal to the adcluster. This <sup>2</sup>A<sub>1</sub> state corresponds to the peroxide species, O<sub>2</sub><sup>2-</sup>, and has a potential minimum at  $R(\text{Ag}_2\text{-O}_2) = 2.0 \text{ \AA}$  and  $R(\text{O-O}) = 1.66 \text{ \AA}$ . The corresponding energy is shown by the asterisk in fig. 1. The calculated adsorption energies of the superoxide and peroxide species are 5.5 and 17.8 kcal/mol, respectively, in comparison with the experimental molecular adsorption energy of 9.2 kcal/mol [11].

The <sup>3</sup>A<sub>2</sub> state shown in fig. 1 is an electron transferred state from Ag<sub>2</sub> to O<sub>2</sub>, but no electron is supplied from the bulk metal (*n* = 0). The image force term is included and works to stabilize the system. Though the system is stabilized as O<sub>2</sub> approaches the surface, the energy is always higher than the free-molecule limit. This state corresponds to the molecularly adsorbed species obtained by the conventional cluster model and the adsorption energy is negative as in the previous studies [16–18]. This failure is mainly due to a limitation of the cluster model. In the cluster model, all the electrons transferred to O<sub>2</sub> must be supplied from Ag<sub>2</sub>, but in DAM some of the electrons are supplied from the bulk metal. We see that the electron transfer from the bulk metal to the adcluster is essential for the occurrence of chemisorption of an O<sub>2</sub> molecule on an Ag surface. We have confirmed that the stabilization of the charged O<sub>2</sub> admolecule by the electrostatic image force of the Ag metal is also important.

Fig. 2 shows the potential energy curves for the O–O elongation on the Ag<sub>2</sub> site. These potentials are calculated for the Ag<sub>2</sub>O<sub>2</sub> adcluster with *n* = 1 with fixing the Ag<sub>2</sub>–O<sub>2</sub> distance at 2.0 Å. As before, the <sup>2</sup>A<sub>2</sub> and <sup>2</sup>B<sub>1</sub> states correspond to the superoxide species and the <sup>2</sup>A<sub>1</sub> state to the peroxide species. The O–O bond lengths of the superoxide are calculated at 1.47 Å and that of the peroxide at 1.66 Å. The O–O vibrational frequencies of the superoxide species are calculated at 1055 (<sup>2</sup>A<sub>2</sub>) and 974 cm<sup>-1</sup> (<sup>2</sup>B<sub>1</sub>) in comparison with the experimental value of 1053 cm<sup>-1</sup> [5]. For the peroxide species, the theoretical value is 689 cm<sup>-1</sup> in comparison with the experi-

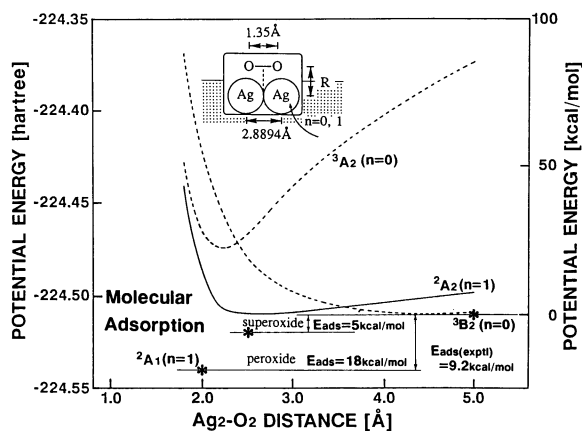


Fig. 1. Potential energy curves for the approach of O<sub>2</sub> onto Ag<sub>2</sub> in the Ag<sub>2</sub>O<sub>2</sub> adcluster. *n* denotes the number of electrons transferred from the bulk metal to the adcluster.

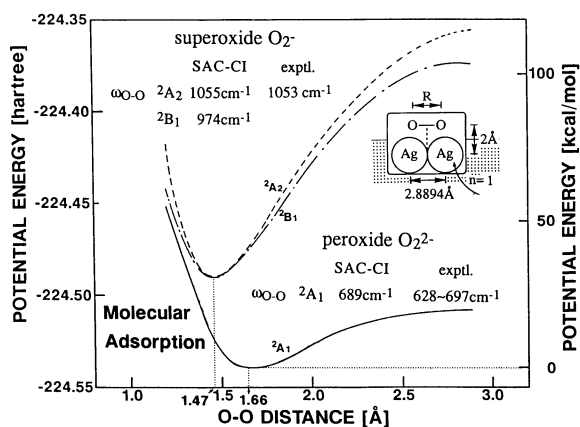


Fig. 2. Potential energy curves for the O-O elongation in the  $\text{Ag}_2\text{O}_2$  adcluster.

mental values of 628 to 697  $\text{cm}^{-1}$  [5-7]. The gross charge of the oxygen atom in superoxide is  $-0.27$  ( ${}^2\text{A}_2$ ) or  $-0.33$  ( ${}^2\text{B}_1$ ), and so  $\text{O}_2^-$  is actually  $\text{O}_2^{(0.5-0.6)-}$ . In peroxide, the gross charge on oxygen is about  $-0.7$ , and so  $\text{O}_2^{2-}$  is actually  $\text{O}_2^{1.4-}$ . Backx et al. estimated the charge of  $-1.7$  from considering the vibrational frequency as a function of the number of electrons in the  $\pi^*$  antibonding orbitals [7].

It is expected that the dissociative adsorption is led from the peroxide species ( ${}^2\text{A}_1$ ), because the curves of the superoxide species ( ${}^2\text{A}_2$ ,  ${}^2\text{B}_1$ ) rise more rapidly than that of the peroxide as the O-O distance is elongated. However, the potential curve of the peroxide rises monotonically up to  $R(\text{O}-\text{O})=2.8894$  Å, which is twice as large as the O-O distance of the free  $\text{O}_2$  molecule. We could not obtain the second minimum corresponding to the dissociatively adsorbed state. A reason is attributed to the electrostatic repulsion between the negative charges on oxygens. It is estimated as large as 60 kcal/mol from the gross charges on oxygens ( $-0.72$ ) separated by 2.8894 Å. For realizing a stabilization of the dissociative state, two oxygen atoms must be separated further on the surface. We, therefore, need a longer chain of Ag atoms so that we next consider the dissociation of  $\text{O}_2$  on the *linear*  $\text{Ag}_4$  site.

Fig. 3 shows the potential energy curves of the ground and excited states of the  $\text{Ag}_4\text{O}_2$  adcluster with  $n=1$ . Here, we get the potential minima of not only the molecular adsorption states ( ${}^2\text{A}_1$ ,  ${}^2\text{A}_2$ , and  ${}^2\text{B}_1$ ),

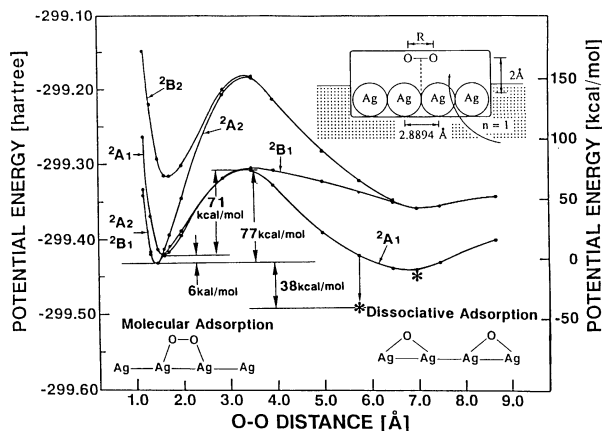


Fig. 3. Potential energy curves for the O-O dissociation process in the  $\text{Ag}_4\text{O}_2$  adcluster.

but also the dissociative adsorption state ( ${}^2\text{A}_1$ ) at  $R(\text{O}-\text{O})=7.0$  Å. When we further optimize the  $\text{Ag}_4\text{-O}_2$  distance at  $R(\text{O}-\text{O})=5.7788$  and 7.0 Å, it becomes shorter up to 1.60 and 1.90 Å, respectively, and the corresponding energies are shown by the asterisks in fig. 3. The system is most stable at  $R(\text{O}-\text{O})=5.7788$  Å and  $R(\text{Ag}_4\text{-O}_2)=1.60$  Å. The dissociated oxygens are adsorbed at the twofold bridge site of the Ag surface, as illustrated in fig. 3, and the Ag-O bond length is calculated to be 2.16 Å, which agrees with the observed distance of 2.06-2.17 Å [12]. The gross charge of oxygen at the optimized geometry is  $-0.98$  and so the dissociated oxygen is essentially  $\text{O}^-$ .

The dissociative adsorption state is lower by 38.5<sup>#1</sup> and 43.6 kcal/mol than the molecular superoxide and peroxide species, respectively. By the thermal desorption spectra of  $\text{O}_2$  adsorbed on Ag(111) and Ag(110) [11], the dissociative adsorption state is observed to be lower by 31.6 and 34.7 kcal/mol, respectively, than the molecular adsorption state. The energy barrier between the molecular and dissociative adsorptions lies at  $R(\text{O}-\text{O})=3.5$  Å with a height of 77.2 kcal/mol from the superoxide species and 71.2 kcal/mol from the peroxide species. This barrier may be too large, in comparison with that in fig. 2, and this may be attributed to the neglect of the

<sup>#1</sup> This is an average of the values, 37.6 and 39.4 for the two superoxide species,  ${}^2\text{A}_2$  and  ${}^2\text{B}_1$ , respectively.

correlations of the d electrons for the  $\text{Ag}_4\text{O}_2$  adcluster. More details of the present study will be given in ref. [28].

Lastly, we summarize the calculational method used. The Gaussian basis set for the silver atom is  $(3s3p4d)/[3s2p2d]$  and the Kr core is replaced by the relativistic effective core potential [29]. For oxygen, we use the  $(9s5p)/[4s2p]$  set of Huzinaga-Dunning [30] augmented with the diffuse anion s, p bases [31] of  $\alpha=0.059$  and the polarization d functions of  $\alpha=0.30$ . The HF calculations are carried out with the use of the program GAMESS [32]. For the SAC/SAC-CI calculations, the active occupied orbitals for the  $\text{Ag}_2\text{O}_2$  adcluster consists of the 4d and 5s orbitals of Ag and the 2p orbitals of O, and those for the  $\text{Ag}_4\text{O}_2$  adcluster the 5s orbital of Ag and the 2p orbitals of O, which do not include the 4d orbitals of Ag. The program system SAC85 [33] is used for the SAC/SAC-CI calculations.

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