

# Potential energy curves of dioxygen anion species, $O_2^-$ and $O_2^{2-}$

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The bondings and the potential energy curves of the ground states of the dioxygen anion species,  $O_2^-$  ( $^2\Pi_g$ ) and  $O_2^{2-}$  ( $^1\Sigma_g^+$ ) are studied by the single and double excitation configuration interaction (SD-CI) and the symmetry adapted cluster (SAC)/SAC-CI methods. For  $O_2^-$ , the spectroscopic constants calculated by the SD-CI and SAC-CI methods are in reasonable agreement with experiment. For  $O_2^{2-}$ , we have found a metastable state in the potential curve, for which the SD-CI calculation gives an equilibrium distance of 1.64 Å and vibrational frequency of 615  $cm^{-1}$ , and the SAC/SAC-CI calculation gives 1.67 Å and 545  $cm^{-1}$ , respectively. The free  $O_2^-$  and  $O_2^{2-}$  molecules are compared with the superoxide and peroxide species adsorbed on an Ag surface, respectively.

## 1. Introduction

Dioxygen species play a key role in many important oxidation processes, particularly on conductor and semiconductor surfaces. In surface chemistry, the anion species, superoxide  $O_2^-$  and peroxide  $O_2^{2-}$ , are more important than the neutral species  $O_2$ , and these anions have been observed by many experimental techniques.

Several electron-spin resonance (ESR) signals due to  $O_2^-$  have been reported on the surfaces of alkali-halide crystals [1], zeolites [2], ZnO, MgO [3], single crystals of hydrogen peroxide-urea addition compounds [4] and alcohols [5], and Ag [6]. Molecularly adsorbed oxygen has been observed on many metals, particularly on well-defined surfaces such as Cu(100) [7], Cu(110) [7,8], Ag(110) [6,9-15], Ag(111) [16], Pd(100) [17], Pt(110) [18], Pt(111) [13,19,20], and Cr(110) [21]. The O-O stretching vibrational frequency for the adsorbed oxygen has been measured for a few different metal surfaces by several spectroscopic techniques, namely, electron energy-loss spectroscopy (EELS), surface-enhanced Raman scattering (SERS), etc. The results

fall into two categories; one with frequencies in the range 740-932  $cm^{-1}$  and the other in the range 1075-1195  $cm^{-1}$  as mentioned by Jones et al. [22]. The first one was assigned to peroxide species  $O_2^{2-}$ , and the second one to superoxide species  $O_2^-$ . The frequencies 640  $cm^{-1}$  obtained for  $O_2$  on Ag(110) and 660  $cm^{-1}$  on Cu(110) were therefore thought to be due to the electron donation from the metal to the oxygen  $2p\sigma^*$  orbital. Panas and Siegbahn, on the other hand, have considered from theoretical studies that the ones with frequencies 610-660  $cm^{-1}$  are due to peroxide species and those at 870-1020  $cm^{-1}$  are due to superoxide species [23].

There are also some observations of the bond length for the chemisorbed  $O_2$  species, mainly by the near edge X-ray absorption fine structure (NEXAFS) method. For example, the bond length of  $O_2$  on Pt(111) is  $1.32 \pm 0.05$  Å, and that of  $O_2$  on Ag(110) is  $1.47 \pm 0.05$  Å [13], which may show the difference between the superoxide and peroxide species.

In the separate papers [24,25] we have investigated the adsorption mechanism of  $O_2$  on an Ag surface by using the dipped adcluster model (DAM) [26,27]. The existence of both molecular superoxide and peroxide species was shown theoretically. For the occurrence of chemisorption, the electron transfer from the bulk metal to the adsorbate and the elec-

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trostatic image force between them were shown to be very important. Furthermore, we have shown that the molecular peroxide species, not the superoxide species, is the direct precursor state for the dissociative adsorption of  $O_2$  on a silver surface.

For further understanding the bonding of such adsorbed dioxygen species, it is very important to investigate the electronic structures of the free anion species  $O_2^-$  and  $O_2^{2-}$ . For  $O_2$  and  $O_2^-$ , many experimental works have been reported: for example, Krupenie reviewed the electronic structures and the electronic spectra of  $O_2$  and  $O_2^-$ , and gave the potential energy curves of the ground state and some low-lying excited states [28]. On the other hand, no measurements have been made for  $O_2^{2-}$  in the gas phase. Though a few theoretical studies are reported for  $O_2^{2-}$  [29–32], no studies are reported on the potential energy curve of  $O_2^{2-}$ , and no discussions are made about the comparison between the free anion species  $O_2^{2-}$  and the peroxide species observed on a metal surface. In the present letter, we report an ab initio calculation of the potential energy curves of  $O_2^-$  and  $O_2^{2-}$  and compare them with the dioxygen species on a metal surface, mainly on a silver surface.

## 2. Gaussian basis set

The purpose of this work is to investigate the electronic structures of the free anion species  $O_2^-$  and  $O_2^{2-}$  and to compare them with the dioxygen species, superoxide and peroxide, on a silver surface. We therefore use the same basis set as that used for the studies of  $O_2$  adsorbed on a silver surface [24,25]; namely, the Huzinaga–Dunning [4s2p] set [33] augmented by the diffuse s, p functions of  $\alpha=0.059$  [34] and the polarization d function of  $\alpha=0.30$ .

We first examine the electron affinity (EA) of the oxygen atom. The EA calculated by the delta-self-consistent-field ( $\Delta$ SCF) procedure is a negative value of  $-0.52$  eV, and does not explain the experimental value of  $1.46$  eV even in sign. On the other hand, the result of the single and double excitation configuration interaction (SD-CI) method is a positive value of  $0.97$  eV, which shows that electron correlation is essential for calculating the EA of the oxygen atom. However, the agreement with the experimental value is not particularly good in comparison with the pre-

vious works [35–41]. For obtaining further agreement, it is necessary to use larger basis sets and a larger expansion of the configuration space. For example, Sasaki and Yoshimine used the (8s7p6d5f4g3h2i) Slater type basis set and obtained an EA of  $1.04$  eV by the SD-CI calculations. Feller and Davidson used the (23s12p10d5f3g) uncontracted basis set containing a total of 171 functions, and adopted more than 200000 and 300000 configurations for the neutral and anion atoms, respectively, in the multi-reference (MR) SD-CI calculations. The calculated EA was  $1.31$  eV, which differs from the experimental value by only  $0.15$  eV.

## 3. Potential energy curves of dioxygen anion species

The electronic structures and the potential energy curves of the ground states of the dioxygen species  $O_2(^3\Sigma_g^-)$ ,  $O_2(^2\Pi_g)$ , and  $O_2^{2-}(^1\Sigma_g^+)$  are calculated by the restricted Hartree–Fock (HF) and the SD-CI methods. Furthermore, symmetry adapted cluster (SAC)/SAC-CI calculations [42,43] are performed for the anion species  $O_2^-$  and  $O_2^{2-}$ , and the calculated potential energy curves are shown in fig. 1.

The  $1\sigma_g$ ,  $1\sigma_u$ ,  $2\sigma_g$  and  $2\sigma_u$  molecular orbitals

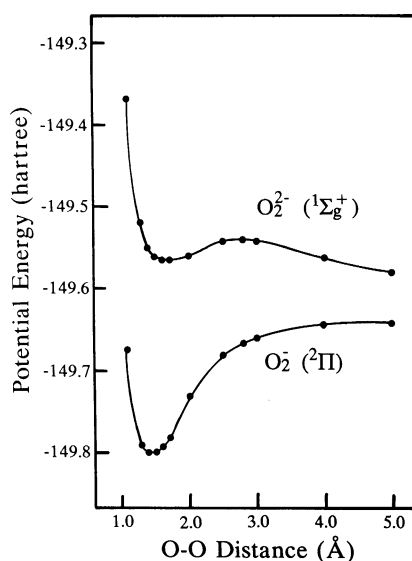


Fig. 1. Potential energy curves of the ground state of the dioxygen anion species,  $O_2^-$  and  $O_2^{2-}$  calculated by the SAC/SAC-CI method.

(MOs), which correspond to the 1s and 2s atomic orbitals (AOs), are frozen in the CI and SAC/SAC-CI calculations, and five higher occupied orbitals are used in the active space. In the previous studies for the oxygen adsorption onto an Ag surface [24,25], the 1s and 2s AOs of oxygen were also treated as frozen core orbitals. Since the energies of the highest four unoccupied orbitals, which are mainly composed of the s AOs, are higher than 3.5 hartree and almost constant at all the separations, they are also frozen in the present calculations.

No configuration selections for the linked operators are made in the SAC/SAC-CI calculations. In the SAC calculations of  $O_2^{2-}$ , all single and double excitation operators are used as the linked operators, and therefore the dimension of the SAC Hamiltonian matrix is equal to that of the SD-CI matrix. In the SAC-CI calculations of the  $O_2^-$  species, it is expressed as the ionized state of the dianion species. Because of the merit of the SAC/SAC-CI theory, the dimension of the linked terms in the SAC-CI calculation is notably small compared with the usual CI method: namely, 82 and 1234 in the SAC-CI and SD-CI calculations, respectively. The HF and CI calculations are carried out by the GAMESS program

[44], and the SAC/SAC-CI calculations by the SAC85 program [45].

Table 1 shows the equilibrium distance, the vibrational frequency, and the dissociation energy of the dioxygen species. The quantities calculated for the superoxide and peroxide on an Ag surface [24] are also shown for comparison. These spectroscopic constants are calculated by analytically fitting the present theoretical curve to the extended Morse function [46], and the vibrational energy levels are given by [47]

$$E_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4. \quad (1)$$

Since  $O_2$  and  $O_2^-$  have unpaired spins in the  $1\pi_g$  orbitals, they have permanent magnetic moments. The bond order of the dioxygen species decreases as the occupation of the  $1\pi_g$  orbital increases, and therefore the bond lengths are calculated to be longer and the vibrational frequencies to be smaller as the  $1\pi_g$  occupation increases.

The bond lengths of  $O_2$  and  $O_2^-$  calculated by the HF method are closer to the experimental values than those calculated by the SD-CI method. A reason

Table 1

The bond lengths  $R_e$ , vibrational frequencies  $\omega_e$ , dissociation energies  $D_e$ , electron affinities EA, and gross charges of the  $O_2$ ,  $O_2^-$ , and  $O_2^{2-}$  molecules in the gas phase and the superoxide  $O_2^-$  and peroxide  $O_2^{2-}$  species on a silver surface

Species	Method	$R_e$ (Å)	$\omega_e$ ( $cm^{-1}$ )	$D_e$ (eV)	EA (eV)	Gross charge (per $O_2$ )
$O_2$	HF	1.20	1856	16.64	-0.06	0
	SD-CI	1.27	1445	7.25	0.52	0
	exp.	1.21	1580	5.12	0.44	0
$O_2^-$	HF	1.33	1420	10.61	-7.76	-1
	SD-CI	1.42	1078	5.38	-6.68	-1
	SAC-CI	1.44	1010	4.00	-6.24	-1
	exp.	1.35	1090	4.09		-1
$O_2^{2-}$	HF	1.53	836	2.91		-2
	SD-CI	1.64	615	-2.21 (1.14) <sup>b)</sup>		-2
	SAC	1.67	545	-2.94 (0.703) <sup>b)</sup>		-2
$O_2^-$ on Ag <sup>a)</sup>	SAC-CI	1.47	974, 1055			-0.54, -0.65
	exp.		1053			
$O_2^{2-}$ on Ag <sup>a)</sup>	SAC-CI	1.66	689			-1.4
	exp.	1.47 ± 0.05	628-697			

<sup>a)</sup> Ref. [24].

<sup>b)</sup> Values in parentheses are the hump heights.

would be a lack of harder polarization  $d$  functions, which are expected to shorten the O–O length. On the other hand, the overestimation of the vibrational frequencies by the HF method is improved by including electron correlations.

In the previous study of the adsorbed oxygen species on an Ag surface [24], we used the SAC/SAC-CI method. The existence of the two superoxide species was shown for the side-on form; one has an unpaired electron in the  $\pi^*$  orbital parallel to the surface and the other in the perpendicular  $\pi^*$  orbital. The calculated bond lengths are 1.47 Å together and the vibrational frequencies are 1055 and 974  $\text{cm}^{-1}$ , respectively. These values are similar to those of the free  $\text{O}_2^-$  molecule calculated by the SAC-CI method, suggesting that the bonding in the molecular superoxide species absorbed on an Ag surface is similar to that of the free  $\text{O}_2^-$  molecule. The cross charges of the superoxide species are  $-0.54$  and  $-0.65$ , respectively, in contrast to  $-1.0$  for a free molecule, by the back-donation from  $\text{O}_2$  to an Ag surface.

The EA of  $\text{O}_2$  is also shown in table 1. While the EA calculated by the  $\Delta\text{SCF}$  procedure is negative as for the oxygen atom, that calculated by the SD-CI method is properly positive. The discrepancy from the experimental value is  $+0.12$  eV, which is comparatively small. The previous study [48] using the Møller–Plesset (MP) perturbation method gave an EA of  $-1.03$  to  $+1.15$  eV with several Gaussian basis sets.

At the dissociation limit,  $\text{O}_2$  and  $\text{O}_2^-$  become  $\text{O}(^3\text{P})+\text{O}(^3\text{P})$  and  $\text{O}(^3\text{P})+\text{O}(^2\text{P})$ , respectively, and the energy difference between them corresponds to the EA of an oxygen atom. The SD-CI calculations give a difference of 2.43 eV in comparison with the experimental value of 1.46 eV, and the disagreement of  $+0.97$  eV is very large. The dissociation energies of  $\text{O}_2$  and  $\text{O}_2^-$  are calculated to be larger than the experimental values by  $+2.08$  and  $+1.29$  eV, respectively. These large disagreements are due to the truncated and size-inconsistent nature of the CI method. On the other hand, the dissociation energy of  $\text{O}_2^-$  is calculated to be 4.00 eV by the SAC-CI method. The discrepancy from the experimental value is  $+0.09$  eV, which is very small.

The anharmonicity terms  $\omega_e x_e$ ,  $\omega_e y_e$ , and  $\omega_e z_e$  of  $\text{O}_2^-$  estimated from the SAC-CI calculations are 7.31,  $3.01 \times 10^{-3}$ , and  $1.25 \times 10^{-4}$   $\text{cm}^{-1}$ , respectively,

while the experimental value of  $\omega_e x_e$  is  $11.7 \pm 4$   $\text{cm}^{-1}$  [28]. From eq. (1), 47 vibrational levels ( $\nu=0-46$ ) are obtained for the bound state of  $\text{O}_2^-$ , of which the lowest 16 and the highest 10 levels are shown in table 2. The level spacing between  $\nu=0$  and 1 is  $995$   $\text{cm}^{-1}$ , which is not equal to the vibrational frequency shown in table 1, because of the anharmonicity of the curve: see eq. (1).

Different from  $\text{O}_2$  and  $\text{O}_2^-$ , the  $\text{O}_2^{2-}$  molecule has no unpaired spins and, therefore, no permanent magnetic moments. While  $\text{O}_2^{2-}$  is a closed-shell molecule, it shows a Hartree–Fock instability at longer bond length: namely, the unrestricted HF solution is lower than the restricted HF one. The potential energy curve calculated by the HF method does not have a hump due to the electrostatic interaction between the two negative oxygen atoms. On the other hand, the potential energy curves calculated by the SD-CI and SAC methods have humps around the O–O distance of 2.8 Å. The metastable state around the O–O distance of 1.6 Å is based on the  $3\sigma_g$  bond. By fitting the present curve to the extended Morse function at the region shorter than the O–O distance of 2.8 Å, the length is calculated to be 1.64 and 1.67 Å by the SD-CI and SAC methods, respectively, and the O–O vibrational frequency to be 615 and 545  $\text{cm}^{-1}$ , respectively. The anharmonicity terms  $\omega_e x_e$ ,  $\omega_e y_e$ , and  $\omega_e z_e$  of  $\text{O}_2^{2-}$  estimated by the SAC calculation are 10.9,  $6.48 \times 10^{-3}$ , and  $-2.99 \times 10^{-4}$   $\text{cm}^{-1}$ , respectively. The hump height from the potential minimum at the O–O distance of 1.67 Å is calculated to be 0.703 eV ( $5670$   $\text{cm}^{-1}$ ) by the SAC method. For the metastable state of  $\text{O}_2^{2-}$ , we obtain 15 vibrational levels ( $\nu=0-14$ ), and the results are shown in table 2.

The calculated bond length of the peroxide species on an Ag surface is similar to that for the free  $\text{O}_2^{2-}$  molecule, though the experimental value is  $1.47 \pm 0.05$  Å. The vibrational frequency, on the other hand, is different: that of the free molecule is smaller than that on a silver surface. This is in accordance with the fact that  $\text{O}_2^{2-}$  is stable on the surface, but only metastable in the gas phase. The gross charge of the peroxide species on the surface is  $-1.4$  by the back-donation from  $\text{O}_2$  to the Ag surface, in contrast to 2.0 in the gas phase.

At the region longer than the O–O distance of 2.8 Å, the potential energy curve of  $\text{O}_2^{2-}$  is repulsive due

Table 2  
Vibrational levels of the ground states of  $O_2^-$  and  $O_2^{2-}$

Vibrational level $\nu$	$O_2^-$		$O_2^{2-}$	
	wave number $E_\nu$ ( $cm^{-1}$ )	level spacing $E_\nu - E_{\nu-1}$ ( $cm^{-1}$ )	wave number $E_\nu$ ( $cm^{-1}$ )	level spacing $E_\nu - E_{\nu-1}$ ( $cm^{-1}$ )
0	503		270	
1	1498	995	793	523
2	2479	981	1295	502
3	3444	965	1774	479
4	4396	952	2233	459
5	5333	937	2669	436
6	6255	922	3084	415
7	7163	908	3477	393
8	8057	894	3849	372
9	8936	879	4199	350
10	9801	865	4527	328
11	10651	850	4833	306
12	11488	837	5118	285
13	12310	822	5381	263
14	13118	808	5622	241
15	13912	794		
37	27991	507		
38	28486	495		
39	28969	483		
40	29440	471		
41	29900	460		
42	30349	449		
43	30787	438		
44	31213	426		
45	31629	416		
46	32034	405		

to the interaction between negatively charged atoms as mentioned above. Fig. 2 shows the potential energy curve plotted against the reciprocal of the O–O distance in au. The points in the figure correspond to O–O distances of 2.8, 3.0, 4.0, 5.0, and 10.0 Å, respectively. This figure shows that the slope of the curve asymptotically approaches unity as the distance is elongated, which means that the interaction is due only to the electrostatic repulsion. The energy at the dissociation limit, which is used for calculating the dissociation energy of  $O_2^{2-}$  as shown in table 1, is estimated by subtracting the electrostatic energy from the potential energy. The difference between the energies of  $O_2^-$  and  $O_2^{2-}$  at the dissociation limit, which corresponds to the EA of the oxygen atom as mentioned before, is calculated to be 0.82 eV. This

value is closer to and a little smaller than the EA of the oxygen atom calculated in the present study, i.e. 0.97 eV. A reason of this underestimation is that the 2s orbital is frozen in the molecular calculations, while it was not in the atomic calculations.

The  $O_2^{2-}$  molecule is less stable than the  $O_2^-$  molecule by 6.19 eV, and does not exist, as a stable species, in the gas phase. This calculated valence state of  $O_2^{2-}$ , which is an electron-attached state of  $O_2^-$ , is embedded in the continuum of the  $O_2^-$ . On the Ag surface, on the other hand, the peroxide  $O_2^{2-}$  species is more stable than the superoxide  $O_2^-$  species. The main difference of the metal surface from the gas phase is that the  $O_2^{2-}$  species is stabilized by the dangling bonds of the surface atoms and by the electrostatic image force. The image force stabilizes both

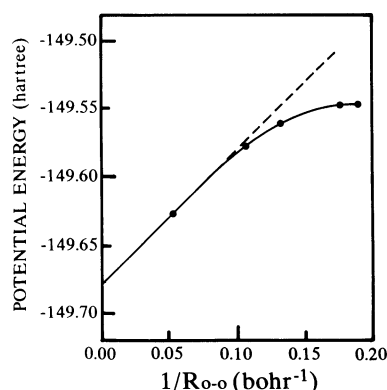


Fig. 2. Potential energy curves of the ground state of  $O_2^-$  calculated by the SAC method. The horizontal axis shows the reciprocal of the O–O distance in au. The dashed line with the slope of unity means that the electrostatic repulsion is a main interaction between negatively charged oxygen atoms.

$O_2^-$  and  $O_2^{2-}$  species, but the stabilization of  $O_2^{2-}$  is larger than that of  $O_2^-$ . Therefore, the adsorption energy calculated for the peroxide species on an Ag surface is larger than that for the superoxide species [24]. The image force does not affect the geometries of the adsorbed species much because it is a long-range force in comparison with the force for chemical bonding. Further, the potential curves of dioxygen species shown in fig. 1 correspond well with the fact that the molecular peroxide species, not the superoxide species, is the direct precursor state for the dissociatively adsorbed oxygens on an Ag surface [24].

#### 4. Concluding remarks

In the present Letter, we have theoretically studied the electronic structures of the ground state of the free dioxygen species  $O_2(^3\Sigma_g^-)$ ,  $O_2(^2\Pi)$ , and  $O_2^{2-}(^1\Sigma_g^+)$ . We first examine the electron affinity (EA) of the oxygen atom, in which all of the diffuse s, p and polarization d functions are necessary for describing the EA. A reasonable value for the EA is obtained only after including electron correlations; the EA of O calculated by the  $\Delta$ SCF procedure does not agree with the experimental value even in sign.

For  $O_2^-$ , the spectroscopic constants calculated by

the SAC-CI method agree well with the experiments. In the potential curves of  $O_2^{2-}$  obtained by the SD-CI and the SAC calculations, there is a metastable state which reflects the  $3\sigma_g$  bond. The equilibrium distance of this state is calculated to be 1.64 and 1.67 Å and the vibrational frequency to be 615 and 545  $cm^{-1}$  by the SD-CI and SAC methods, respectively.

The bonding of the free  $O_2^-$  molecule is similar to that of the molecular superoxide species on a silver surface. However, the bonding of the  $O_2^{2-}$  in the gas phase is somewhat different from that of the peroxide species on the surface. The stabilities of the superoxide and peroxide species on the surface are opposite to those of the free  $O_2^-$  and  $O_2^{2-}$  molecules, because of the effects of the dangling bonds and the image force on the surface.  $O_2^{2-}$  receives a larger image force than  $O_2^-$  on the surface. We note that the image force is a long-range force, in comparison with the force for chemical bonding, so that it does not affect the geometries and vibrational frequencies of the adsorbed species much, but affects the adsorption energy and stability more.

We expect that the knowledge of the electronic structures and potential energy curves of the free dioxygen species as shown in the present study gives insight for studying the dioxygen species adsorbed on metal surfaces.

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