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THE PEROXY RADICAL MODEL FOR THE CHEMISORPTION OF O_2 ONTO SILICON SURFACES*

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We propose that an oxygen molecule chemisorbed onto the silicon surface has an electronic structure corresponding to a peroxy radical. Using this model we carried out extensive theoretical calculations including electron correlation (generalized valence bond with configuration interaction) obtaining excitation energies and ionization potentials.

A MAJOR DIFFICULTY in the design of heterogeneous catalysts is the lack of clear, conceptual principles suitable for distinguishing between various bonding configurations and useful for predicting the subsequent reactions.[1] With the goal of developing such principles for bonding of molecules on surfaces, we have examined the case of O_2 chemisorbed onto the (111) surface of silicon as described herein.

An oxygen atom can be pictured as in Fig. 1(a). Pairing two oxygen atoms to form the O_2 molecule leads to Fig. 1 (b) as the ground state.[2] Configuration Fig. 1(b) leads to triplet ($^3\Sigma_g^-$) and singlet ($^1\Delta_g$) states of which the triplet state is lower (due to the exchange interaction). The other way of pairing these orbitals,[2] Fig. 1(c), leads to excited singlet states of O_2 ($^1\Sigma_g^+$ and the other component of $^1\Delta_g$). Solving self-consistently for the orbitals of O_2 leads to significant delocalization of the orbitals but the qualitative picture still applies. The basic reason why the configuration of Fig. 1(b) is better that Fig. 1(c) is that the doubly-occupied $p\pi$ orbitals can delocalize onto the other center for Fig. 1(b) (where there is a single-occupied orbital on this center) but not for Fig. 1(c) (where there is a doubly-occupied orbital on this center).

Now consider bonding the O_2 to a dangling bond orbital of the (111) surface, as in Fig. 1(d). After bonding one end of the O_2 to a surface silicon atom, there is a remaining unpaired orbital on the O_2. However, this orbital is *perpendicular* to the SiOO plane and hence

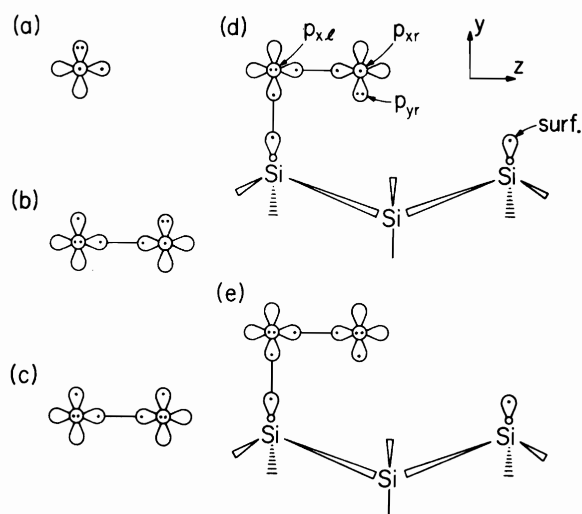

Fig. 1. The orbital diagrams for (a) oxygen atom (^3P), (b) ground state O_2, (c) excited state O_2, (d) ground state of chemisorbed O_2, (e) excited state of chemisorbed O_2. Here the 1*s* and 2*s* orbitals have been ignored and *p* orbitals paralled and perpendicular to the plane are indicated as ∞ and ○, respectively. The dots indicate how many electrons are in each orbital. Orbitals combined into a singlet pair are indicated by a connecting line.

parallel to the surface so that it cannot (for the perfect surface) bond to another surface atom to form a bridged structure. That is, the chemisorbed O_2 is a *peroxy radical*.

On the other hand, the excited state of O_2, Fig. 1(c), leads to Fig. 1(e) upon bonding to the surface. In this case it *is* possible for the unpaired orbital of the O_2 to pair up with the dangling bond orbital of the silicon to form a bridged O_2 bond. Given the strong SiO bond combined with the strained configuration, the weak OO bond of the bridged species should fission, leading to two chemisorbed oxygen atoms or to insertion of an O into a Si–Si bond. (This could be tested

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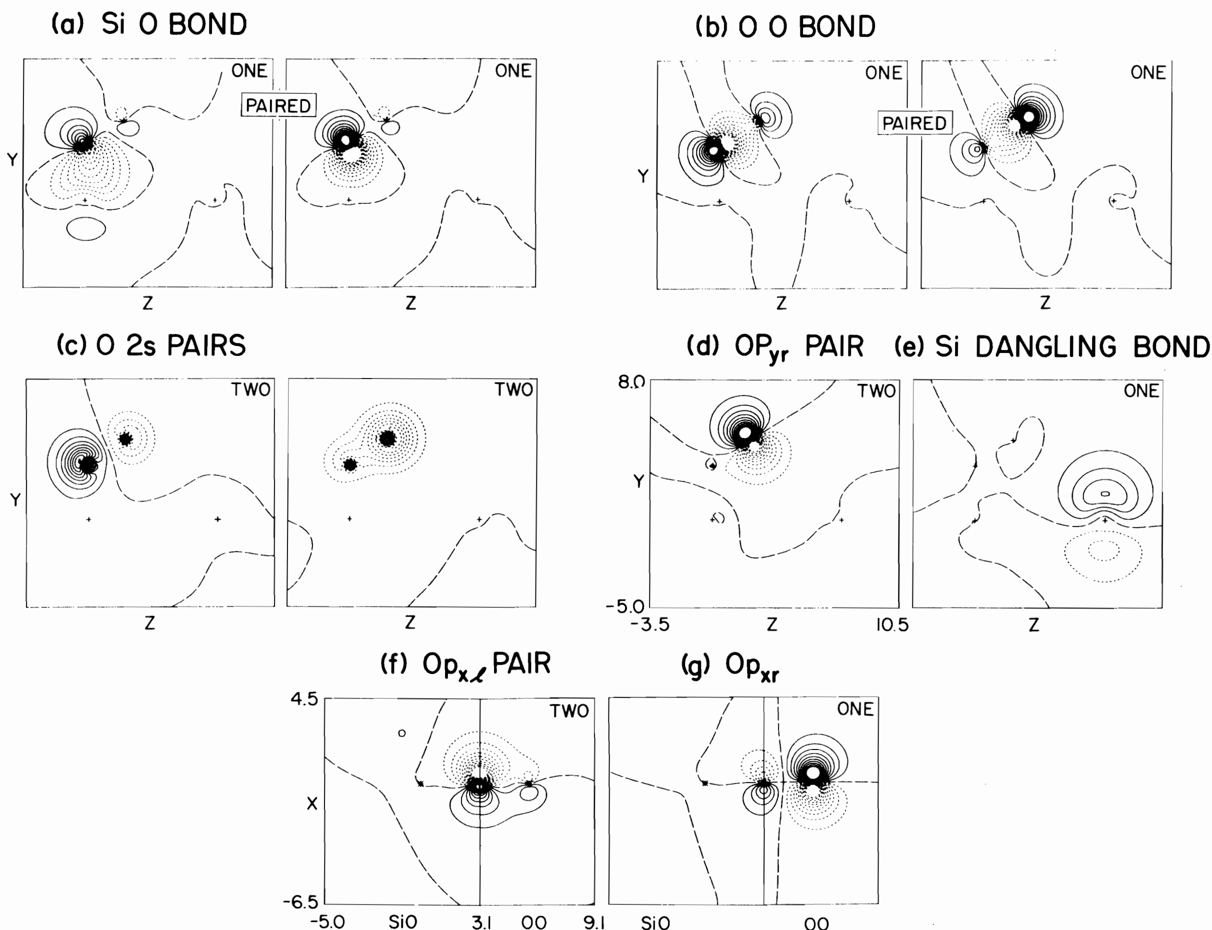

Fig. 2. The GVB orbitals of the $Si_3H_6O_2$ complex, where the O_2 is in the plane passing through two surface atoms and perpendicular to the surface (the atom positions are indicated by +). Band orbitals and O1*s*-like orbitals are not shown. Long dashes indicate nodal planes; the separation between contours is 0.05 a.u. Parts (a)–(e) are plotted in the SiOO plane; (f) and (g) are each composite plots in planes perpendicular to the SiOO plane and passing through the SiO and OO bonds, respectively.

experimentally by passing the O_2 through a microwave discharge to convert a significant fraction to singlet O_2.) The vertical excitation energy from Fig. 1 (d) to (e) should be similar to that from Fig. 1(b) to (c), about 1 eV.

To test such ideas and to allow detailed comparison with experiment, we carried out theoretical calculations. An important consideration here is the method of calculating the states. The usual approach is the Hartree–Fock (HF) method (e.g., band theory) in which a set of doubly-occupied orbitals is solved for self-consistently. However, the HF method is not adequate for these studies (accounting, for example, for only 0.9 eV of the 5.2 eV bond energy of O_2), and we have instead used the generalized valence bond (GVB) method, which allows singly-occupied, overlapping orbitals and consists of solving self-consistently for the optimum correlating orbitals simultaneously with the other occupied orbitals. For example, including a configuration interaction over just the GVB orbitals (GVB–CI) accounts for 4.9 eV[3] of the 5.2 eV bond energy of O_2.

Currently it is not possible to carry out GVB calculations on the infinite solid; hence, we have used a molecular complex to represent the surface. We concluded that the simplest adequate model of the surface is as follows: Three silicon atoms are placed at the positions of a silicon lattice, as in Fig. 1(d, e). Each of these silicon atoms should be bonded to two additional silicons not shown; however, we have replaced these bonds with Si–H bonds. Thus the surface is represented by a complex of three silicon atoms and six hydrogen atoms; two of the Si atoms are at the surface. Including a chemisorbed O_2 leads to a total complex of composition $Si_3H_6O_2$. With this system we could examine highly correlated wavefunctions and test the basic validity of our model.

The resulting wavefunction[4] is shown in Fig. 2. Just as assumed in the above discussion (and found for

Table 1. Excitation energies and ionization potentials for the O_2–Si_3H_6 complex. Ionizations involving simultaneous excitation of an electron are omitted as are ionizations involving the SiH bonds. All energies are in eV

State	Calculated Energy (GVB–CI)[a]		Experimental Results[d]	Corresponding values	
				for O_2[e]	for HO_2[c]
Excitation	SiH_3O_2	$Si_3H_6O_2$	O_2 on Si		
Ground State	0.00	0.00, 0.007	0.00	0.00	0.00
$p_{yr} \rightarrow p_{xr}$	0.84	0.92, 0.95		0.98	0.93
$p_{xl} \rightarrow p_{xr}$	6.65	6.19, 6.19		8.6	6.40
$OO\sigma \rightarrow p_{xr}$	6.51	6.54, 6.55		–	7.54
SURF[b] $\rightarrow p_{xr}$	–	7.68		–	
SiO $\rightarrow p_{xr}$	7.96	7.90, 8.17		–	
$p_{yr} \rightarrow$ SURF[b]	–	9.98		–	
Ionization					
$p_{yr} \rightarrow$ vac	10.81, 11.82	11.00, 11.08, 11.99	11.9 (brace: p_{yr}, p_{xr})	16.7	
$p_{xr} \rightarrow$ vac	11.51	11.37		12.3	
$p_{xl} \rightarrow$ vac	14.4	14.23, 14.23	15.1 (brace: p_{xl}, SiOσ)	16.7	
SiO$\sigma \rightarrow$ vac	14.73, 14.78	15.00, 15.04, 15.28		–	
OO$\sigma \rightarrow$ vac	17.42	17.54, 18.02, 18.06	18.4	18.2	

[a] For the states of the neutral system, the two entries correspond to the triplet and singlet states resulting from the coupling of the surface orbital with the singly-occupied orbital of the O_2. For the infinite solid, one expects a narrow band of states corresponding to each of these pairs of states. For the ion states there are generally two doublet states and one quartet for each configuration.

[b] Here SURF indicates the surface dangling bond orbital.

[c] GODDARD W.A., III & DUNNING T.H., Jr. (unpublished calculations).

[d] Reference 6, assignments are tentative.

[e] HERZBERG G., *Spectra of Diatomic Molecules.* Van Nostrand, NY (1950); TURNER D.W., *Molecular Photoelectron Spectroscopy.* Wiley, NY (1970).

other oxygen systems[2,3]), the O2*s* orbitals are only changed slightly [Fig. 2(c)]. The other orbitals are much as pictured in Fig. 1(d), supporting the peroxy radical model. Using these self-consistent GVB orbitals, we carried out extensive configuration interaction (CI) calculations[4] on the excited states and positive ion states states, as reported in Table 1.

As indicated in Table 1, the calculated excitation energies and ionization potentials of the $H_6Si_3O_2$ complex are close to what would be predicted using our model and the known values for O_2 or HO_2. The main changes occur in (i) the singly-occupied oxygen orbital (p_{xr}) whose IP increases from 12.3 to 15 eV upon bonding to the Si and (ii) the doubly-occupied orbital (p_{yr}), which is a bonding orbital in O_2 (IP = 16.7 eV) but which must localize onto the right oxygen (thereby decreasing the IP to ~ 11.5 eV) as the left oxygen bonds to the Si. Replacing the Si_3H_6 unit with an SiH_3 unit leads to small changes, indicating that these excitations energies and ionization potentials are not sensitive to the size of the complex. Corrections due to the polarizability of the semi-infinite solid are estimated to be of the order of 0.2–0.4 eV.

Referencing all the bond energies to an O_2 molecule and a free silicon surface, our best estimates for the energetics are as follows: The O_2 bonded to the silicon surface (in the peroxy radical form) is at – 2.2 to – 2.5 eV; the dissociative adsorption of the O_2 leaving a single oxygen bonded to the surfacc and the other oxygen free is at + 0.5–0.3 eV. The state with the O_2 bond broken and the two oxygen atoms independently bonded to two separate sites on the silicon surface is at – 4.1 to – 4.5 eV; however, the barrier separating this state from the peroxy radical is expected to be large. The excited state of the O_2 is at + 1.0 eV. The state with the O_2 in an excited state and bonded to the silicon surface in the peroxy radical form is at – 1.3 to – 1.5 eV. The barrier between this state and that with the two oxygen atoms separately bonded to the surface should be much smaller than the comparable barrier for the ground state of O_2 bonded to the surface.

There is some experimental evidence that the O–O

bond remains intact upon chemisorption onto silicon. Using high resolution electron spectroscopy, Ibach *et al.*[5] found three infrared transitions due to O_2 on the surface. They conclude that these transitions must have a component perpendicular to the surface and suggest from an analysis of several models that the O_2 might bridge two surface silicons. Our peroxy radical model is also consistent with these experimental results since it leads to three vibrational modes with significant components perpendicular to the surface.

As indicated in Table 1, the recent photoemission experiments of Ibach and Rowe[6] are in fair agreement with our calculated ionization potentials. The IP's calculated at 11–12 eV arise from orbitals (p_{xr} and p_{yr}) that are only weakly involved in bonding and hence should give the sharpest line (as observed at 11.9 eV).

A characteristic feature of peroxy radicals is a strong ($f \sim 0.1$) broad (~ 2 eV) absorption around 6–7 eV (the calculated value for O_2 on Si is 6.2 eV). This transition should result in dissociation of the O_2 bond leading to a chemisorbed atom plus a free oxygen atom, with a significant probability of the O atom being in the singlet state. Experimental tests of our model would be possible here (some electron energy loss experiments have been carried out;[6,7] however, only second derivative spectra were reported).

The peroxy radical model could also be tested by appropriate ESR studies. The ESR of peroxy radicals has been observed in other systems[8] (usually the peroxy radical is referred to as O_2^-).

In summary, general bonding considerations suggest that chemisorption of O_2 onto simple silicon surface leads to formation of a peroxy radical as the initial state. Our theoretical studies of this model are in agreement with established experimental results. Subsequent excitation (thermally or otherwise) to the excited state corresponding to singlet O_2 would likely lead to attack of the second O atom onto the surface and perhaps subsequent formation of normal SiO_2-like configurations. Similar results are expected for bonding of O_2 to germanium and similar semiconductors. Work is now in progress to investigate the potential surfaces for the initial steps of oxide formation, to examine reconstruction of the silicon surface, and to learn about the new effects occurring at steps on the surface.

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