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. 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. Configuration Fig. 1(b) leads to triplet ($^3\Sigma^+$) and singlet ($^1\Delta$) states of which the triplet state is lower (due to the exchange interaction). The other way of pairing these orbitals, Fig. 1(c), leads to excited singlet states of O$_2$ ($^1\Sigma^+$ and the other component of $^1\Delta$). 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 $\sigma$ 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 SiO$\cdot$plane and hence 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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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 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 silicon atoms 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 O₂–Si₃H₆ complex. Ionizations involving simultaneous excitation of an electron are omitted as are ionizations involving the SiH bonds. All energies are in eV

<table>
<thead>
<tr>
<th>State</th>
<th>Calculated Energy (GVB–CI)ᵃ</th>
<th>Experimental Resultsᵈ</th>
<th>Corresponding values for O₂ᵉ for HO₂ᵉ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si₃H₆O₂</td>
<td>Si₃H₆O₂</td>
<td>O₂ on Si</td>
</tr>
<tr>
<td>Ground State</td>
<td>0.00</td>
<td>0.00, 0.007</td>
<td></td>
</tr>
<tr>
<td>pₓᵧ → pₓᵣ</td>
<td>0.84</td>
<td>0.92, 0.95</td>
<td></td>
</tr>
<tr>
<td>pₛᵣ → pₓᵣ</td>
<td>6.65</td>
<td>6.19, 6.19</td>
<td></td>
</tr>
<tr>
<td>OΟₒ → pₓᵣ</td>
<td>6.51</td>
<td>6.54, 6.55</td>
<td></td>
</tr>
<tr>
<td>SURFᵇ → pₓᵣ</td>
<td>–</td>
<td>7.68</td>
<td></td>
</tr>
<tr>
<td>SiO → pₓᵣ</td>
<td>7.96</td>
<td>7.90, 8.17</td>
<td></td>
</tr>
<tr>
<td>pₓᵧ → SURFᵇ</td>
<td>–</td>
<td>9.98</td>
<td></td>
</tr>
</tbody>
</table>

Ionization

| pₓᵧ → vac              | 10.81, 11.82                 | 11.00, 11.08, 11.99 | 11.9 | 16.7 |
| pₓᵣ → vac              | 11.51                       | 11.3/                 |      | 12.3 |
| pₛᵣ → vac              | 14.4                        | 14.23, 14.23         | 15.1 | 16.7 |
| SiΟₒ → vac             | 14.73, 14.78                | 15.00, 15.04, 15.28  |      |      |
| OΟₒ → 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 O₂. 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.


ᵈ Reference 6, assignments are tentative.


other oxygen systems²,³), the O₂s 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) calculations⁴ on the excited states and positive ion states as reported in Table 1.

As indicated in Table 1, the calculated excitation energies and ionization potentials of the H₆Si₃O₂ complex are close to what would be predicted using our model and the known values for O₂ or HO₂. The main changes occur in (i) the singly-occupied oxygen orbital (pₓᵣ) whose IP increases from 12.3 to 15 eV upon bonding to the Si and (ii) the doubly-occupied orbital (pₓᵧ), which is a bonding orbital in O₂ (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 Si₃H₆ unit with an SiH₃ 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 O₂ molecule and a free silicon surface, our best estimates for the energetics are as follows: The O₂ bonded to the silicon surface (in the peroxy radical form) is at −2.2 to −2.5 eV; the dissociative adsorption of the O₂ leaving a single oxygen bonded to the surface and the other oxygen free is at +0.5−0.3 eV. The state with the O₂ 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 O₂ is at +1.0 eV. The state with the O₂ 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 O₂ 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. 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 are in fair agreement with our calculated ionization potentials. The IP’s calculated at 11—12 eV arise from orbitals ($p_{xy}$ and $p_{xy}$) 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 ($\sim 0.1$) broad ($\sim 2$ 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 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 (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.

REFERENCES

4. The basis set is of “double zeta” quality. The SiH, SiSi, and SiO bond lengths are standard values. The SiOO angle and OO bond lengths were optimized for the corresponding SiH$_2$O$_2$ complex, $R_{OO} = 1.366$ Å and SiOO = 125.9°. The GVB–CI calculations involve 646—1004 determinants for the cases considered here.
7. LÜDEKE R. & KOMA A., Phys. Rev. Lett. 34, 1170 (1975). This paper proposes that $O_2$ chemisorbs as atoms double bonded to surface silicon atoms. This is contrary to our calculations on O atom bonded to (111) surface complexes (the experimental evidence is quite weak).