The interaction of potassium and oxygen, individually and as coadsorbates with graphite, was studied experimentally and theoretically. In the experiments, the sticking of oxygen was investigated at different K coverages. The extremely low sticking coefficient for chemisorption/dissociation of dioxygen on clean graphite is contrasted by the high sticking coefficient for even very dilute potassium overlayers. KO and K₂O complexes are identified as early precursors to CO₂ formation from coadsorbed potassium and oxygen. The K–O complexes formed on the surface and their transformations (as a function of increasing temperature) were followed by thermal desorption spectroscopy (TDS) and electron energy loss spectroscopy (HREELS). A theoretical study based on the tight-binding method indicates why the presence of potassium facilitates the chemisorption of dioxygen, whose sticking coefficient on clean graphite is otherwise very small. It is suggested that the potassium promotion effect is a very local one and that formation of a K–O₂ surface complex is the first step in graphite oxidation. The strongly preferred adsorption site for O₂ on a K-covered surface is on top of a potassium atom with no interaction to the graphite layer. From there the dioxygen molecule can dissociate into oxygen atoms. The stabilizing K–O₂ interaction can be traced to a localized sp-hybrid available for bonding to O₂ and the fact that the graphite π system is not distorted upon chemisorption of O₂ via the potassium spacer. Concerning the favored adsorption sites for the individual species, a slight preference is deduced for K above a hexagon (6-fold symmetry site), while O and O₂ more strongly favor a position on top of a carbon atom (O₂ in a bent end-on approach) for the undamaged surface. Surface defects, however, figure prominently in stabilizing the oxygen species and also a potassium atom in the defect area.

**Introduction**

Chemical reactions of solid carbon with oxygen, water, and carbon dioxide, known as carbon gasification reactions, have attracted considerable interest in the last decades, mainly because of their relevance in energy technology. It is well established that these reactions are catalyzed by, e.g., alkali metals and transition-metal oxides added to the carbon substrate. The reactive properties of solid surfaces are often dramatically modified by adsorption of alkali metals. It is a well-known phenomenon that potassium, or more generally, alkali metals can catalyze a myriad of reactions of gaseous substances with surfaces. Experimental observations of this phenomenon are available over the range from semiconductor (e.g., Si, GaAs) through semimetal (carbon in the form of graphite or charcoal) to metal or metal oxide surfaces, interacting with dioxygen, water, carbon monoxide, carbon dioxide, etc. Subsequently, this effect is exploited in a wide range of technological applications, e.g., in heterogeneous catalysis and semiconductor oxidation. The gasification of coal and charcoal is promoted for over a century by additives such as caustic soda (NaOH) or lime (CaO). Enhancement of reactivity by alkali metals has stimulated extensive experimental and also theoretical studies.

Various mechanisms have already been proposed for the catalytic effects of alkali additives in the form of alkali metal salts (e.g., carbonates) in the gasification of carbonaceous materials. The catalytic effect of alkali compounds in carbon gasification reactions is often explained in terms of a mechanism referred to as the oxygen transfer mechanism. According to this mechanism, the active catalyst undergoes sequential oxidation–reduction cycles on the carbon surface. Oxygen from the gas phase thus is captured on the surface by direct reaction with the catalyst. Subsequent reduction of the catalyst provides oxygen atoms, which react with the carbon surface to form CO and CO₂. This mechanism has received experimental support and is usually favored over the so-called electron transfer mechanism. In the latter mechanism, the adsorbed alkali is assumed to cause strengthening of

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carbon–oxygen bonds and weakening of the carbon–carbon bonds as a result of electron transfer to the carbon substrate.

The influence of alkali metal adsorption on the surface properties of metals, graphite (semimetal), and semiconductors is related to the electropositive nature of the alkali metals which can easily donate their single valence electron to the "surface." In the physicist's language, alkali adsorption causes a charge redistribution on the surface that effectively gives rise to a dipole field which lowers the work function of the surface.15,19 The so-called promoting effect of alkali metals in surface reactions is often discussed in terms of this (local) charge redistribution and work function decrease.20

In a previous experimental study by two of us6,6 we observed that the oxidation rate of evaporated carbon can be greatly enhanced—by up to 104 times—through a predeposited potassium layer. A theoretical model had also been proposed6 which showed that the large rate increase upon K adsorption could be explained by a K-induced increase in the dissociation rate for the O2 molecules impinging on the surface, due to a more effective coupling between the O2 antibonding σ* orbitals and the occupied σ states in the K-promoted graphite. In other words, a lower work function of K-graphite is proposed to result in more charge/electron transfer to O2, especially its half-filled σ* level. This in turn increases the dissociation probability of O2, eventually leading to chemisorption of atomic oxygen.5,21,22 For metal surfaces a work function decrease is known to affect the adsorption kinetics and the sticking coefficient of dioxygen.3

There is also an "oxygen-transfer mechanism", the essence of this model being that O2 reacts directly with K and then the KO2 complex is reduced by carbon atoms in the surface. Several chemical forms of the active potassium catalyst have been suggested for the oxygen transfer based reaction mechanisms. The potassium oxides, K2O, K2O2, and KO2, are obvious candidates, because they can undergo oxidation–reduction cycles by transformation between the different oxidation states.21,26 Mims and Pabst were able to detect the presence of a surface complex on the carbon surface during gasification conditions.27 Schlogl suggested that the presence of potassium hydroxide, KOH, on the carbon surface is essential for the catalytic effect,24 while other reaction schemes include potassium carbonate, K2CO3, as an intermediate.26 In all these experimental studies, however, the potassium catalyst was added in the form of KOH or K2CO3.

Thus, the alkali-catalyzed dioxygen–carbon reaction still presents some unsettled questions: It remains a matter of controversy whether or not the promotion effect is local or nonlocal.5,25 Local is here taken to mean that the potassium atom is a direct participant in the reaction and that it undergoes an oxidation–reduction sequence. Nonlocal implies that the increased reactivity of O2 is due solely to an electronic influence that the alkali metal has on the carbon substrate. Combinations of these mechanisms are, of course, also possible.

Concerning the mechanism of catalytic carbon oxidation, an important problem is to determine the chemical identity of the potassium catalyst under oxidation conditions. The electron transfer mechanism would be favored if atomic or intercalated potassium were present in the carbon substrate, since these potassium configurations are expected to cause large electron transfer to the carbon substrate.16 Atomic and intercalated potassium are, however, not thermally stable in the graphite substrate at gasification temperatures.4,28 Thus, it seems unlikely that these forms of potassium are important for the catalytic effect in carbon gasification.

The "potassium-on-graphite" problem is further related to alkali–graphite interaction compounds29 and to studies of other metal atoms (e.g., Cu, Ag, Au, Al, or Pd) on graphite. The chemisorption of the oxygen molecule (O2) on graphite/K is related to the adsorption of O2 on semiconductors4 or metals,30 O2 (and also N231) physisorption on graphite,23 and to the oxygen atom (O34 and also N, H,35–37 H2O,38 NO, CO, etc.39) chemisorption on graphite and other main group elements (semiconductors).40 The distinction between molecular dioxygen (O2) and atomic oxygen (O) is significant; the two species differ in their chemical behavior. While atomic oxygen apparently requires very little activation energy to react with a clean graphite surface with a high probability, molecular dioxygen reacts only at high temperature with a much smaller probability and surface defects are said to be important for the reactions.41 The dioxygen–graphite surface chemisorption is suggested to be endothermic,34,42 The binding energy of physisorbed O2 on the other hand, is about 0.1 eV, i.e. exothermic. (For the distinction between chemi- and physisorption, see below.)

The experimental studies referred to above6,6 have been extended to thermal desorption spectroscopy (TDS)16,31

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studies of K and CO₂ desorption after initial adsorption of O₂ at 138 K, and to vibrational spectroscopic studies of the K₂O complexes formed on the surface. The results most relevant to the present study are presented below. More detailed results are given elsewhere.

Previous studies have shown that the probability for dissociative adsorption of O₂ molecules impinging on a clean carbon surface, leading to the formation of CO and CO₂, is very low, at least <10⁻³ at room temperature, and that the process is thermally activated. Furthermore, the reaction probability is very sensitive to the surface structure and strongly influenced by defects. For example, the sticking coefficient for O₂ on a clean graphite surface at 673 K increased from <10⁻¹⁴ to 10⁻⁷ when a graphite surface with low defect concentration was damaged by Ar⁺ bombardment. At very low temperatures molecular oxygen is physisorbed on graphite. The monolayer desorption temperature is 47 K.

It seems generally accepted that the sticking and dissociation of dioxygen is frequently the bottleneck of surface oxidation reactions.

Note: When referring to the "graphite surface", we generally mean the basal or 0001 plane of graphite.

Experimental Methods and Procedures

The experimental details have been described elsewhere. In short the experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure in the low 10⁻¹⁰ Torr range. The system is equipped with a CMA Auger electron spectrometer for surface purity control and for work function measurements, with a high resolution electron energy loss spectrometer (HREELS) for vibrational spectroscopy, and with a mass spectrometer for thermal desorption spectroscopy. Low energy electron diffraction (LEED) is used for surface crystal structure control.

The sample was oriented graphite, exposing the basal plane. The sample was cleaned by heating, initially for several hours at 1200 K. Potassium was deposited from a break-seal glass ampule or from an alkali metal getter source. Oxygen exposures were normally made in the 10⁻⁴ Torr range by backfilling the chamber with oxygen.

Experimental Results

The results are presented in a condensed form with special emphasis on observations of relevance to the theoretical calculations. For additional information see refs 43-45. On the clean graphite surface no oxygen adsorption (sticking coefficient <10⁻⁵-10⁻⁴) was observed down to 136 K, and no reaction to form CO or CO₂ was observed in O₂ atmospheres up to 10⁻⁵ Torr and 700 K. This finding is consistent with earlier work, indicating no or very weak dioxygen chemisorption and a large activation barrier for O₂ dissociation.

In contrast the O₂ sticking coefficient on potassium-covered graphite is unity or close to unity, even at very dilute potassium coverages. The initial sticking coefficient is constantly near unity, at least down to a potassium coverage of 5% of a full monolayer (Figure 1). This behavior can be explained in terms of a direct interaction between O₂ with the graphite surface, modified by electron donation from adsorbed potassium, or as a precursor adsorption of O₂ into the physisorbed state, where it eventually reacts with potassium atoms on the surface. In the former case the mechanism is a direct charge transfer to the O₂ molecule impinging on the surface, enhanced by the lowered work function and possibly also by the increased electron density at the Fermi level.

At low temperatures, the vibrational loss peaks are fairly broad, indicating heterogeneous broadening (i.e. there is a mixture of local stoichiometries due to kinetic barriers). As the structures formed at low temperature are annealed, the peaks sharpen and undergo transformations. Some of these transformations are accompanied by desorption of potassium and/or CO₂. By variation of the surface stoichiometry (i.e. the potassium/oxygen ratio), and guided by recent XPS/HREELS results from O₂ adsorption on potassium, the loss peak at 39 meV is assigned to K₂O (for the detailed assignments, see ref 45a,b). The peak at 31 meV is not obvious in Figure 2A, the spectrum at 160 K, but clearly identifiable at different exposure and coverage conditions.

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(44) Sjövall, P.; Kasemo, B. Surf. Sci. in press.

Figure 1. Sticking coefficient of O₂ on potassium-covered graphite as a function of potassium coverage.
been studied once by theoretical methods. We want to actual chemisorption of cluster models instead. To our best knowledge the wealth of theoretical studies. Most of the calculations do graphite-adsorbate interactions has also generated a of stoichiometries, central questions in the theoretical analysis below. At low temperatures, kinetic barriers give rise to a mixture and of K-0 and C-0 bonds on the surface. These are dissociation of oxygen and potassium bonding to graphite molecules, indicating complete dissociation of dioxygen. The potassium-covered surface with unity or nearly unity sticking even at low K coverages. At low potassium a number of transformations. At temperatures up to 400 K, segregation of intercalated potassium increases the surface K:O ratio at saturation is about 2:1, indicating oxygen-rich complexes are formed. Eventually total potassium desorbs from the surface, and as a result more coverage the alkali metal desorption peaks for K and COZ. The spectra for K corresponds to metallic (unreacted) potassium, the peak around 750-800 K is coninciding with the valence and conduction bands, resulting in a nonzero energy loss.

The extensive experimental research in the area of graphite–adsorbate interactions has also generated a wealth of theoretical studies. Most of the calculations do not employ an extended, two-dimensional surface, but use cluster models instead. To our best knowledge the actual chemisorption of O2 on graphite, however, has only been studied once by theoretical methods. We want to contribute a chemical perspective to this problem. Our calculations make use of the tight-binding extended Hückel method on an infinite, two-dimensional surface. Before we can embark on a full scale calculation, some decisions need to be made.

**A One- or Two-Layer Slab?** In many studies the graphite surface is simulated with a planar C6H6 cluster model, an annulene system. In tight-binding calculations one graphite layer is typically used. A one-layer annulene or graphite-net system is reasonable, since the interlayer distance in graphite of 335 pm is close to a van der Waals contact.

The effect of going from a one-layer to a two-layer slab is for the most part negligible, as our calculations show. However, the introduction of a second layer leads to an inequivalence of the two carbon atoms within the surface unit cell. One carbon atom has a carbon directly underneath in the next layer (α site), whereas the other one is located above the center of a carbon hexagon in the next layer (β site)—illustrated in 1.

The observations above point to the key role of dissociation of oxygen and potassium bonding to graphite and of K-O and C-O bonds on the surface. These are central questions in the theoretical analysis below.

### Theoretical Preparations

The extensive experimental research in the area of graphite–adsorbate interactions has also generated a wealth of theoretical studies. Most of the calculations do not employ an extended, two-dimensional surface, but use cluster models instead. To our best knowledge the actual chemisorption of O2 on graphite, however, has only been studied once by theoretical methods. We want to contribute a chemical perspective to this problem. Our calculations make use of the tight-binding extended Hückel method on an infinite, two-dimensional surface. Before we can embark on a full scale calculation, some decisions need to be made.

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**Notes:**


(52) Note, however, that two vs one graphite layer makes a difference in the total (integrated) DOS at the Fermi level. The one layer model results in a so-called zero band gap semiconductor, i.e., zero state density at E_f, while the three-dimensional calculations yield a small overlap between the valence and conduction bands, resulting in a nonzero DOS at E_f.


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**Figure 2.** (A) HREEL spectra after 25 langmuirs O2 exposure of 2.5 monolayers (ML) potassium on graphite and after annealing the surface to the indicated temperatures in vacuum. All spectra are recorded at 160 K. Primary electron energy 15 eV, specular scattering. The elastic peak shown corresponds to the unannealed system. (B) Thermal desorption spectra of potassium, m/e = 39, and carbon dioxide, m/e = 44, (a) after 1.2 ML deposition of potassium at 160 K on graphite, and after 3, 8, and 25 langmuirs (d) oxygen exposures at 160 K. Linear heating rate of 2.5 K/s. The spectra for CO2 are shifted upward for the sake of clarity. The CO2 spectrum (a) is multiplied by a factor of 3. The arrows correspond to the annealing temperatures in Figure 2A.
have the higher DOS right at the Fermi level—in agreement with the other computational results mentioned above. Focusing on the region around K in our calculation is necessary since not all k points in the Brillouin zone contribute to the charge densities sensed by STM—only k points around the Fermi level do. For typical tunneling voltages below 1 V the part of the band structure sampled by STM near the Fermi surface is very small; the Fermi level lies close to the special point K. For a simple, pedagogically effective approach to the π-band crystal orbitals and their degeneracy lifting in two- and three-dimensional graphites near the Fermi energy; see ref. 62.

To return to the question posed at the beginning of this section, we conclude that it would be fairly safe to use only one graphite layer to model the surface. The inequivalencies between the two different carbon sites do not show up in a two-layer slab, neither on a bare surface nor with adsorbates attached to it. However, a two-layer slab allows for more options for simulation of defects (holes) in the surface which are important for the reactivity of graphite. Therefore, we opted for a two-layer slab.

**Choice of Unit Cell for Chemisorption Studies.** Potassium-promoted oxidation of graphite using pure potassium has been observed and studied experimentally for potassium submonolayer to monolayer coverages\(^\text{58}\) (see experimental section). We need a unit cell large enough to treat submonolayer coverages. This is mostly the range explored experimentally and also the one of primary interest for the theoretical work. Larger coverages are expected to represent metallic potassium rather than potassium on graphite. Actually alkali-metal overlayers are frequently reported to become metallic somewhere above 0.1 monolayer coverage\(^\text{63,64}\), reflecting the large effective radius of the alkali metal.\(^\text{6}\) For potassium, the minimum metal–metal separation in its elemental body centered cubic structure is 454.4 ppm.\(^\text{65}\) Exactly where the metallic character of the alkali overlayer is well established can be debated and most likely depends on the substrate. For example, the plasmon frequency and work function characteristic of metallic K is not established until coverages higher than 0.1 ML, typically around 0.5 ML.

We tried to simulate a low-enough coverage throughout our calculations by selecting a large unit cell (cf. ref 36; concept of a molecular unit cell\(^\text{61}\)). Our choice was a unit cell of 18 carbon atoms per layer (or 36 C’s for the two layer slab) as depicted in 3. The area spanned by this unit cell is about \(4.7 \times 10^{-15} \text{ cm}^2\). With an approximated monolayer coverage of \(5 \times 10^{14} \text{ K-atoms per cm}^2\), one alkali-metal per unit cell then corresponds to a \(\sim 40\%\) or 0.4 monolayer coverage. Note again, that here a monolayer or fraction thereof is referred to a close packed potassium layer and has no correspondence to the graphite structure, due to the incommensurate nature of the carbon and potassium atomic radii.

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(58) J. C. Hemminger, to be submitted for publication.

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We are now ready to embark on our actual surface–adsorbate calculations, which might provide us with an
understanding of the alkali-promoted oxidation of graphite. Specifically, we would like to find the preferred adsorption site for potassium and to understand the reason for the low sticking coefficient of dioxygen on a bare graphite surface, so as to comprehend the role of the potassium catalyst in enhancing the sticking and $O_2$ dissociation. The latter should help us to comment on the local versus nonlocal controversy discussed in the introduction and suggest some possible reaction mechanisms. Finally, we also want to explore how defects in the basal plane of graphite may influence its reactivity toward oxygen.

The Preferred Potassium Adsorption Site. On a graphite slab one can have four higher symmetry sites for a monoatomic adsorbate: (A) the "3-fold on-top" site, directly above a carbon atom. Since the carbon atom can be an $\alpha$ or $\beta$ carbon, as described earlier, we can, in principle, distinguish between an $A\alpha$ or an $A\beta$ site. One may also envisage (B) the "2-fold bridging" site above the center of a carbon--carbon bond and (C) the "6-fold hollow site" above the center of a hexagon. The different sites are illustrated in 4.

In this section we use an approximate molecular orbital method, the extended Hückel tight-binding procedure. This one-electron method gives only qualitative results but lends itself to the construction of simple explanations. Quantities computed by the extended Hückel methodology should be viewed as relative indications of stability of bonding.

In particular, the extended Hückel method is not expected to give reliable results as far as bond length variations are concerned. Therefore, we chose a C-K distance of 303 pm, based on structural studies of K-graphite intercalation compounds\(^{(27)}\) (305 pm found), $[\pi^2-(PhCH_2)_5C_5]K$(thf)\(^{(66)}\) (average 308.5 pm; thf = tetrahydrofuran), $[\pi^2-(Me_5Si)C_6H_4]K$\(^{(66)}\) (average 300 pm), and $[\pi^2-Me_5C_5]K$(pyridine)\(^{(66)}\) (average 303 pm). This C-K distance was kept constant throughout our studies. We only note that in potassium--fluorenyl systems\(^{(67)}\) the K--C distances are longer (range 307--332 pm) and vary directly above a carbon atom. Since the carbon atom can be an $\alpha$ or $\beta$ carbon, as described earlier, we can, in principle, distinguish between an $A\alpha$ or an $A\beta$ site. One may also envisage (B) the "2-fold bridging" site above the center of a carbon--carbon bond and (C) the "6-fold hollow site" above the center of a hexagon. The different sites are illustrated in 4.

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Table 1. Comparison between Different Potassium Adsorption Sites on Graphite As Illustrated in 4

<table>
<thead>
<tr>
<th>site</th>
<th>$E_b$ binding energy/eV</th>
<th>charge on potassium</th>
<th>C-K overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A\alpha$</td>
<td>6.14</td>
<td>+0.62</td>
<td>0.55</td>
</tr>
<tr>
<td>$A\beta$</td>
<td>6.14</td>
<td>+0.62</td>
<td>0.55</td>
</tr>
<tr>
<td>$B$</td>
<td>6.18</td>
<td>+0.81</td>
<td>0.049 (X2)</td>
</tr>
<tr>
<td>$C$</td>
<td>6.40</td>
<td>+0.83</td>
<td>0.032 (X6)</td>
</tr>
</tbody>
</table>

* See 4 for illustration; C-K distance fixed at 303 pm. $E_b = E$(bare graphite unit cell) + $E$(free K) - $E$(surface + adsorbate) = (-2556.708 eV) + (-4.34 eV) - $E$(surface + adsorbate), positive: surface--adsorbate complex more stable; Note that $E_b$ is defined relative to a free K 4s energy of -4.334 eV. The single absolute value of $E_b$ depends critically on the potassium parameters (see Appendix), so that only the trend noted here is of physical significance. $E_b$ overlap population to one carbon at a distance of 303 pm from the potassium. For the B site there are two; for C there are six carbons at this distance. To obtain a relative measure of the K-graphite bond strength, the C-K overlap population should be multiplied by this number of neighboring carbons as indicated in parentheses.

reflecting qualitatively the bond strength. In this hollow position the potassium can also transfer its electron most effectively to the graphite surface. The difference in the Fermi energy between the different adsorption sites (not shown in the table) is negligible. The small variation in binding energies for different adsorption sites may indicate that it is easy for the potassium to move around on the graphite surface. The near identity of the $A\alpha$ and $B\beta$ sites is no surprise, after what we saw for the $\alpha$ and $\beta$ sites for a bare graphite surface.

We note that this finding of a 6-fold hollow site preference for K is different than what has been observed experimentally for the coinage metals and aluminum. The coinage metals—Ou, Ag, and Au—have a similar valence configuration, namely d$^{10}$s$^1$, to the alkali metals. However, STM studies show they prefer A and B sites.\(^{(26)}\) Chemically, from a comparison with cyclopentadienyl model compounds, this does not come as a surprise: Cp-Cu$^+$, -Ag$^+$, or -Au$^+$ complexes exhibit a σ-bonded, π$^*$-Cp-metal coordination, rather than a π-, π$^*$-bonding mode.

What we did not look at was the stability of the 6-fold potassium adsorption site with respect to alkali metal clustering. A strong tendency toward formation of metal adlayer islands at low coverages (about 1% of a metal monolayer) has been observed experimentally in STM studies of Cu, Ag, Au, and Al.\(^{(28)}\) However, the potassium adsorption is accompanied by a larger charge transfer. Coulomb repulsion would then tend to keep the positively polarized K adsorbates apart at low coverages.

The Preferred Dioxygen Site on Bare Graphite. There is much geometrical freedom in the way diatomic $O_2$ can interact with the graphite surface. Relative to the surface plane the O-O bond vector might be (1) "side-on" (5), aligned parallel to the surface plane, (2) linear "end-on" (6), perpendicular to the surface plane, or (3) bent "end-on" (7), the vector forming an angle $\gamma$ with the normal to the surface plane. "Side-on" and "linear, end-on" are, of course, special positions ($\gamma = 90$ and 180°) of the general case shown in 7.
of dioxygen has not yet been found.\textsuperscript{68} If \( \text{O}_2 \) is not side-on bonded to a metal center, it assumes a bent end-on position with \( \gamma \) typically in the range between 115 and 135°. Therefore, we limited out theoretical studies also to the side-on and bent end-on cases. The higher-symmetrical adsorption sites which we studied are illustrated in 8 for the side-on and in 9 for the end-on, mode.

A refers again to on-top sites (α and β), B to sites over the center of a C-C bond, and C to sites over the center of a hexagon. Within these three basic sites one can discernmate further among various conformations. However, we elaborated on such conformational changes only for the side-on case. The most important difference occurs in the B site; we can have O-O aligned parallel to a C-C bond (ellipsoid, or \( B_1 \) conformation) or perpendicular to it (staggered, \( B_1 \)). For the C site we can make a similar distinction (\( C_1 \) or \( C_1 \), see 8). The conformational difference may be expected to be less pronounced in A and C compared to B sites, for the rotational barrier in A and C is 6-fold.

Instead of focusing on different conformations for the bent end-on mode we carried out a small angle-variation study (\( \gamma = 150, 135, \) and \( 120^\circ \)) with the second oxygen approaching the surface as shown in 9.

The O-O distance throughout most of our study was fixed at 121 pm—the separation in free \( \text{O}_2 \). While \( \text{O}_2 \) adsorption will surely result in lengthening of the O-O bond, the reason for one site being preferred over another should emerge more clearly if the O-O distance is kept fixed.

The choice of a suitable C-O distance is more problematic. In the absence of experimental studies of chemisorbed \( \text{O}_2 \) on graphite, we were left with theoretical studies of the process. We are aware of only one investigation of chemisorption of \( \text{O}_2 \) on a \( \text{C}_{10}\text{H}_{14} \) (naphtalene) molecule in which O-O distances were optimized. Different methods give a C-O distance in the range of 129–142 pm for the chemisorption product (cf. Table 3 in ref 34). However, we feel that these values correspond to an optimized C-O bond and not to a C-O distance for chemisorbed \( \text{O}_2 \).

Subsequent studies showed us that we can take the region between 175 and 200 pm as appropriate for the C-O distance for \( \text{O}_2 \) chemisorbed on the basal graphite plane. (We use the word “chemisorbed” to indicate the regime of bond distances, where there is considerable C-O interaction, but do not mean to indicate that there necessarily is a chemisorbed state.) Table II compares the binding energy and O-O overlap populations for side-on chemisorbed dioxygen on graphite in different sites, assuming C-O distances of 150, 175, and 200 pm.

The calculated binding energies are all negative, indicating the endothermic character of the interaction. As anticipated, the Aα and β sites differ only very slightly.

3.2 The Adsorption of Dioxygen on \( \text{Cu}(100) \). The choice of a suitable C-O distance is more problematic. In the absence of experimental studies of chemisorbed \( \text{O}_2 \) on graphite, we were left with theoretical studies of the process. We are aware of only one investigation of chemisorption of \( \text{O}_2 \) on a \( \text{C}_{10}\text{H}_{14} \) (naphtalene) molecule in which O-O distances were optimized. Different methods give a C-O distance in the range of 129–142 pm for the chemisorption product (cf. Table 3 in ref 34). However, we feel that these values correspond to an optimized C-O bond and not to a C-O distance for chemisorbed \( \text{O}_2 \).

Subsequent studies showed us that we can take the region between 175 and 200 pm as appropriate for the C-O distance for \( \text{O}_2 \) chemisorbed on the basal graphite plane. (We use the word “chemisorbed” to indicate the regime of bond distances, where there is considerable C-O interaction, but do not mean to indicate that there necessarily is a chemisorbed state.) Table II compares the binding energy and O-O overlap populations for side-on chemisorbed dioxygen on graphite in different sites, assuming C-O distances of 150, 175, and 200 pm.

The calculated binding energies are all negative, indicating the endothermic character of the interaction. As anticipated, the Aα and β sites differ only very slightly. Having O-O lying above a C-C bond (B1 site) seems to be the most likely side-on position. On the other hand, C sites and B1 are highly unfavorable. In all cases the O-O overlap population is lowered, compared to the free \( \text{O}_2 \) molecule, due to a filling of the dioxygen \( \pi^* \) level. A smaller overlap population should be accompanied by a lengthening of the O-O bond. The effect of C-O distance is such that at a longer separation of, e.g., 200 pm, the effects discussed here are essentially the same, albeit less pronounced. For instance, the binding energy is less negative. The increasingly negative binding energies at a shorter C-O distance of 150 pm underscore the 2-orbital/4-electron type repulsive interaction between \( \text{O}_2 \) and the graphite surface.

The respective values for the bent end-on approach in different sites and with different surface–O-O angles are compiled in Table III. While the C sites are again highly disfavored, the A position starts to become slightly exothermic. At a longer C-O separation (200 pm, results not reported here) A is even more exothermic and B also shows a positive binding energy. The angle variation is not very conclusive, its trend depending largely on the adsorption site. Again, for the bent end-on chemisorption, the O-O \( \pi^* \) level lies below the Fermi energy.

The general trend that the binding energy becomes positive at larger distances from the surface is in agreement with the readily observed physisorption of dioxygen on graphite, with surface–adsorbate distances of the order of 300 pm.\textsuperscript{34} On the other hand, dioxygen chemisorption on graphite is mostly an endothermic process. A bent end-on approach of the dioxygen molecule in the on-top site (A) is calculated as most favorable for real chemisorption. Here we note that graphite studies of \( \text{O}_2 \) indicate that there may not be such a thing as a chemisorbed \( \text{O}_2 \) but only physisorbed \( \text{O}_2 \), since to our knowledge no molecular state except the physisorbed \( \text{O}_2 \) has ever been observed experimentally. We want to emphasize that the


that in these positions \( \text{O}_2 \) interacts with the least number of carbon atoms and requires only the formation of four-coordinated carbon atoms in reasonable geometries. The \( \text{A} \) site for the side-on mode presents also an interaction with one carbon atom only, but it makes this carbon atom five-coordinated.

If we allow for a synergistic simple distortion or reconstruction around the interacting carbon atom(s), such that the atoms involved are slightly elevated above the graphite plane (12, 13), the \( \text{O}_2 \) binding energies increase somewhat, even after correcting from the reconstruction energy. An elevation of \( d = 50 \text{ pm} \) above the surface corresponds to almost tetrahedral angles around carbon.

For a small reconstruction (\( d = 25 \text{ pm} \)) the gain in binding energy is largest (0.6 eV more for \( \text{A} \), bent end-on; 1 eV more for \( \text{B} \), when compared to the undistorted case). The experimentally observed low sticking coefficient for \( \text{O}_2 \) (at temperatures higher than 50 K)\(^{32,46}\) suggests that the resulting energy for the distorted \( \text{A} \) site is still not large enough to trap an \( \text{O}_2 \) molecule effectively in a chemisorbed state (because \( kT \) is too large in comparison with the well depth). Potassium facilitates the distortion only (and to a very limited amount) if the elevated carbon atom is part of the hexagon above which the alkali metal sits. With potassium close by, the energy required for the distortion decreases by about 0.1 (\( d = 25 \text{ pm} \)) to some 0.4 eV (\( d = 50 \text{ pm} \)).

Oxygen Atoms on Graphite. The experimental findings point to a difference in reactivity between a dioxygen molecule and an oxygen atom. We need to examine theoretically oxygen atoms on a graphite surface, to check if pronounced differences do indeed exist. We start again with a comparison between different sites (cf. 9) for chemisorbed monoxygen on graphite. The results are compiled in Table IV.

For the \( \text{A} \) and \( \text{B} \) site we find rather large positive binding energies (indicating stabilization) with the on-top site being slightly favored over the bridging site. The \( \text{C} \) site or 6-fold hollow position can be excluded immediately. The stabilizing chemisorption energies for an O-atom at a C-O distance used before for dioxygen correlate with our expectations. It makes chemical sense that one obtains a “stable” chemisorption adduct from a highly reactive species such as monoxygen.

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Table II. Comparison between Different Sites for Side-on Chemisorbed Dioxygen on Graphite as Illustrated in 8 at \( \text{C-O} = 150, 175, \text{and} 200 \text{ pm} \)

<table>
<thead>
<tr>
<th>site(^{a})</th>
<th>( E_{\text{b}} ) binding energy/eV(^{b})</th>
<th>overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{A} )</td>
<td>150</td>
<td>175</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>-7.82</td>
<td>-3.88</td>
</tr>
<tr>
<td>( \beta )</td>
<td>-7.81</td>
<td>-3.88</td>
</tr>
<tr>
<td>( \beta )</td>
<td>-4.15</td>
<td>-2.06</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-13.6</td>
<td>-6.49</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-10.5</td>
<td>-5.88</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-11.8</td>
<td>-7.04</td>
</tr>
</tbody>
</table>

Table III. Comparison between Different Sites and Bending Angles for Bent End-on Chemisorbed Dioxygen on Graphite As Illustrated in 9 at \( \text{C-O} = 175 \text{ pm} \)

<table>
<thead>
<tr>
<th>site(^{a})</th>
<th>surface-O-O angle, ( \gamma ) (deg)</th>
<th>( E_{\text{b}} ) binding energy/eV(^{b})</th>
<th>overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{A} )</td>
<td>150</td>
<td>0.143</td>
<td>0.462</td>
</tr>
<tr>
<td>( \beta )</td>
<td>135</td>
<td>0.245</td>
<td>0.481</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>120</td>
<td>0.113</td>
<td>0.495</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>135</td>
<td>-0.400</td>
<td>0.468</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>120</td>
<td>-0.442</td>
<td>0.480</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>135</td>
<td>-0.833</td>
<td>0.487</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>C</td>
<td>-10.30</td>
<td>0.530</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>135</td>
<td>-11.10</td>
<td>0.527</td>
</tr>
</tbody>
</table>

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\( ^{a} \) See 8 for illustration, \( \text{O-O} \) was fixed at 121 pm. \( ^{b} \) \( E_{\text{b}} = E_0(\text{bare graphite unit cell}) + E_0(\text{free } \text{O}_2) - E_0(\text{adduct}) = (-2556.708 \text{ eV}) + (+249.681 \text{ eV}) - E_0(\text{adduct}) \). A positive binding energy indicates stabilization. \( ^{c} \) The overlap population in free \( \text{O}_2 \) with \( \text{O-C} = 121 \text{ pm} \) is calculated as 0.795. \( ^{d} \) Overlap population between one carbon and one oxygen at the distance given. For the \( \text{A} \), \( \beta \), and \( \gamma \) sites there are two, for \( \text{B} \) and \( \gamma \) there are four C-O contacts to consider for a relative measure of the \( \text{O}_2 \)-graphite bond strength.

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Figure 4. Schematic representation of the energetics of the graphite-dioxygen interaction. Physisorption is intended to mean a van der Waals interaction while chemisorption should describe a chemical (orbital) interaction. Physisorption energies are generally in the 0.1-eV range, also for \( \text{O}_2 \) on graphite.\(^{43} \) Approximate distances are from ref 34.
We can further justify the formation of gaseous oxidation products (CO, CO₂) from the monoxygen chemisorption, since the C–C overlap population of the adjacent bonds drops significantly from 1.016 for clean graphite to 0.877 for O in the on-top site. This difference in C–C overlap population becomes even larger if we distort the interacting carbon by elevating it 25 or 50 pm above the surface (cf. 12). With O on-top, the C–C overlap population to its neighbors decreases to 0.53 in both cases—down from 0.91 (50 pm above surface) to 0.99 (25 pm elevation) for the clean distorted graphite. At the same time the binding energy for monoxygen increases.

We may add that experimentally it would be of interest to explore the branching ratio CO:CO₂, when only atomic oxygen is present on the surface. As far as we know, these ratios O₂:CO:CO₂ for atomic oxygen (no potassium) on the surface have not been measured. With K on the surface there is only negligible CO and O₂ desorption. It would be of interest to deposit atomic oxygen, followed by measurement of the O₂:CO:CO₂ ratios.

**Reactivity of Defects in the Graphite Surface.**

Microscopic techniques such as STM and transmission electron microscopy as well as scanning electron microscopy (74) show clearly the formation of monolayer pits on graphite upon its gasification reaction with atomic and molecular oxygen. It is proposed that these pits start at existing defects (e.g. atomic vacancies) and can be readily expanded with atomic oxygen at about 150 °C at a rate which is several times faster than the oxidation rate in molecular oxygen at 650 °C. (40) Although some expansion of the pits with O₂ after preceding O atom exposure, is apparently possible, its extent is not clear. Work on graphite gasification by molecular oxygen is usually carried out at elevated temperatures (650 °C and above), where O₂ can thermally dissociate. It is quite possible that at these temperatures sufficient atomic oxygen is formed to dominate the reaction (41).

In our own experimental work, we also observed a reaction-induced etch pit at the center of one sample that had been used extensively in reactive experiments. We suspect that a cooperative effect of the electron beam (with energy up to 10 keV), and reactions involving coadsorbed K and O₂ was responsible for the pit formation.

We tested the influence of an atomic defect, i.e. a C vacancy on the basal graphite surface, by first removing a single carbon atom (from an a site) and then adsorbing a dioxygen molecule (bent end-on), or an oxygen atom, above the vacancy (14).

The binding energy for a vacancy with O adsorbed right above it indicated only a minor improvement, while for O₂ it was even less favorable compared to the defect-free surface. The O–O and C–O overlap populations also do not give a clear indication whether a single atom vacancy will facilitate the sticking and dissociation of an O₂ or O adsorbate.

Such a small effect on a surface defect worried us at first, especially so in light of recent STM studies that indicate the ready formation of larger pits on preexisting defects by heating highly pyrolytic graphite samples in air at 650 °C. (70) We then tried to derive an understanding of the frontier orbitals—the dangling bonds—with the use of a molecular model. A look at the molecular orbitals of 15 in comparison to 16 showed that the unsaturated σ levels are raised in energy—but so are the π levels. There is a concentration of electron density on the carbenoid carbons, but σ is still substantially below the π level (see 17).

The symmetry plane of the molecule prevents mixing between σ and π dangling bonds, so that there is little electron density in the region above the vacancy. However, things are slightly more complicated, as shown by a theoretical study which was carried out by Soto on graphite (one or two layer slab, extended Hückel tight-binding method) with a single atom vacancy. (77) The results indicate a distance dependence of the charge density directly above the vacancy. This is explained by the localized nature of the nonbonding crystal orbitals from the nearest neighbor atoms to the vacancy. In the calculated STM image the vacancy would appear as a “hole” only at low altitudes, whereas it would look like a maximum or “bump” at high altitudes, with the changeover occurring at an altitude of about 175 pm. From the orbital pictures in 17 we could expect a more pronounced defect influence if we had the O₂ or O adsorbate approach the defect site either above the rim or in the surface plane—as indicated in 18.

We thus explored putting dioxygen and monooxygen on top of a rim atom (19) and—after removing a second

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carbon atom—in the plane of the surface layer (20). Adsorbing O or O₂ in the plane of the graphite surface with one vacancy only would require C-O distances of 142 pm! We therefore decided to remove a second carbon atom which creates a large enough vacancy to accommodate an O atom with C-O = 175 pm.

![Diagram 19](image19)

Note that the in-plane approach, modeled in 20, results in simultaneous interactions with four carbon atoms with dangling bonds. For the rim position, (19) finds binding energies which are about 1.5 eV more positive than the respective values for the undamaged graphite surface. For the in-plane approach 20 the binding energies are smaller by more than 2 eV, which we, however, attribute to the square-planar environment for the oxygen atom.

Actually, we would expect a larger positive energy of chemisorption for the in-plane trajectory than for the rim-site, because of the localized nature of the dangling σ orbitals (versus π) and their better energy match with the (di)oxygenc levels. Therefore, to model a more reliable in-plane approach, we had to extend the pit even further. This could only be done by resorting to an even larger unit cell of 24 carbon atoms for the surface layer (plus 32 atoms for an eventual second layer), shown in 21.

![Diagram 20](image20)

Indeed, for this large enough defect we find in-plane binding energies which are an additional 2–3 eV more positive than for the respective rim-position. We carried out these calculations using a one- (defect surface only) and two-layer (see 21) slab. From our computational parameters we fail to see any effect on the second layer, with respect to which dioxygen is then in the physisorption range. Experimentally, the physisorption binding energy is found to be rather small, only ~0.1–0.2 eV.43

We note that surface defects (one to multiatom vacancies, 14–21) also have a stabilizing effect for potassium atoms. The binding energies for potassium adsorbed on top of a rim atom (cf. 19), or over a vacant site (cf. 14), or in an in-plane position (cf. 21) such that C–K = 303 pm, are some 0.2–0.5 eV stronger than for respective positions on the undamaged surface. This is consistent with the large increase in desorption temperature for potassium from an argon bombarded (and thus damaged) surface.44

Potassium–Dioxygen Coadsorption. We have now set the stage for an investigation of potassium–dioxygen adsorption on a graphite surface. There now enters a new parameter, the K–O₂ separation, in addition to the already mentioned different possible adsorption sites for potassium and dioxygen. The schematic drawing in 22 illustrates what is meant; having potassium in a 6-fold hollow (C) site and dioxygen coadsorbed, e.g., above a C–C bond (B₂ site), allows for four different K–O₂ chemisorption patterns, which differ in their K–O₂ separation and relative orientation (taking into account the potassium atoms in the neighboring unit cells). The same is true for dioxygen coadsorbed in the bent end-on position above a C-atom (A site). With the freedom of O–O rotating about the C–O contact, we even have various conformations in addition to three different K/O₂ chemisorption patterns (23). However, for simplicity we calculated only three conformers with the second O-atom above a C–C bond, as shown in 23.

![Diagram 21](image21)

![Diagram 22](image22)

Furthermore, we can envision an entirely new chemisorption site for the oxygen molecule when it is brought onto the potassium/graphite surface: O₂ can sit above a preadsorbed K atom, either side-on (24) or bent end-on bonded (25). These adsorption sites will be denoted K₁ and K₂, respectively.

![Diagram 23](image23)

For these sites the K–O distance was fixed at 270 pm, based on a comparison to the inorganic complexes K[Cr₂(N₂O₆)]Cl₆ (K–O ≈ 258–294 pm), K[Cr₂(C₂O₄)₂](MeOH)₉ (K–O ≈ 264–288 pm), and [(PhCH₂)₂C₂]K(OC₃H₇)₆ (K–O ≈ 269–278 pm). In Table V we compare different potassium–dioxygen chemisorption patterns with respect to the dioxygen binding energies, O–O and K–O overlap populations. The potassium position was fixed in the C site (K–C = 303 pm, and dioxygen at A).

Interaction of Potassium and Oxygen

Table V. Comparison between Different Potassium–Dioxygen Chemisorption Patterns on Graphite at C–O = 175 pm

<table>
<thead>
<tr>
<th>O2 site</th>
<th>K–O distances/pm</th>
<th>( E_b ) binding energy/eV</th>
<th>( O–O^* ) overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side-on, See 22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B11</td>
<td>365/335</td>
<td>-1.66</td>
<td>0.501/0.008</td>
</tr>
<tr>
<td>B12</td>
<td>297/317</td>
<td>+1.32</td>
<td>0.504/0.006/0.009</td>
</tr>
<tr>
<td>B3</td>
<td>167/282</td>
<td>+0.18</td>
<td>0.523/0.346/0.052</td>
</tr>
<tr>
<td>B4</td>
<td>163/153</td>
<td>+1.20</td>
<td>0.543/0.209</td>
</tr>
<tr>
<td>End-on, See 23 (135° C–O–O tilt angle)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>387/326</td>
<td>+1.14</td>
<td>0.479/0.002/0.022</td>
</tr>
<tr>
<td>A2</td>
<td>299/325</td>
<td>+3.13</td>
<td>0.488/0.078/0.008</td>
</tr>
<tr>
<td>A3</td>
<td>170/225</td>
<td>+2.88</td>
<td>0.522/0.230/0.054</td>
</tr>
<tr>
<td>Above Potassium Atom, See 24 and 25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1</td>
<td>270/270</td>
<td>+6.35</td>
<td>0.488/0.075</td>
</tr>
<tr>
<td>K2</td>
<td>270/386</td>
<td>+6.13</td>
<td>0.465/0.193/0.026</td>
</tr>
</tbody>
</table>

* O–O was fixed at 121 pm. \( b \) \( E_b = E \) (carbons + potassium) + \( E \) (free \( O_2 \) – \( E \) (surface/absorbate complex)). A positive binding energy indicates an exothermic adsorption process. The overlap population in free \( O_2 \) with \( O–O = 121 \) pm is calculated as 0.793.

see above). We include only dioxygen sites (except for the novel K sites) which were found to be most likely from our O2/graphite calculations, namely the B1 site for side-on and the A site for end-on chemisorbed \( O_2 \). The sites deemed unlikely from our earlier calculations remain so, even with potassium as a cosorbate.

For dioxygen in the B1 and A sites we note the strong shift of the binding energy toward more positive values, indicating the increased exothermic character of the \( O_2 \) adsorption on a graphite surface with a preadsorbed potassium layer. In other words, the energy lowering upon impingement of an \( O_2 \) molecule on the surface (as one condition for sticking) is enhanced drastically by a potassium cosorbate. The closer the oxygen approaches a potassium atom, the stronger the binding energy becomes.

The large binding energies for the K sites (dioxygen on top of potassium) are striking. They surpass the comparable values for all other chemisorption patterns by more than 3 eV. Moreover, the stabilization provided by potassium for the \( O_2 \) chemisorption (in the K site) is still some 1.5–2 eV higher than the already sizable stabilization derived from defects in the graphite surface (in-plane approach of \( O_2 \), \( E_b = 4.10 \) eV end-on; 4.64 eV side-on). In the following we try to rationalize the local nature of the potassium enhancement with the help of molecular models. But before we do so, we would like to show that at our level of computation, molecular models preserve the trends seen from the investigation of extended structures. Table VI compiles some molecular systems and compares binding energies and overlap populations to the values in analogous extended structures.

Even though Table VI presents a very brief list, one realizes that the overlap populations tend to be surprisingly similar in molecular and extended systems. The binding energy values may vary a little bit, but the trend in stabilization upon going from side-on bonded \( O_2 \) over bent end-on, to \( O_2 \) above a potassium, is clearly preserved.

If we now examine the interaction diagrams between \( O_2 \) and the molecular \( C_6 \) fragments (not shown here), we note some subtle differences in the orbital interactions: For \( O_2 \) side-on bonded to \( C_{6}H_{10} \) we have a very strong perturbation of the carbon \( \pi \) system through a repulsive \( O_2 \) \( \pi \)/\( C \) \( \pi \) interaction. Such a repulsive interaction gives rise to the destabilization of side-on adsorbed \( O_2 \) on graphite (see above). For \( O_2 \) end-on bound to \( C_{6}H_{10} \), on the other hand, the repulsive \( O_2 \) \( \pi \)/\( C \) \( \pi \) interaction is rather weak and a 2-orbital/2-electron \( O_2 \) \( \sigma \)/\( C \) \( \sigma \) interaction becomes predominant with a smaller carbon \( \pi \)-level perturbation.

When \( O_2 \) is adsorbed on top of a potassium, sitting in turn above a \( C_{6}H_{5} \) ring, one sees only a very small perturbation for the benzenoid \( \pi \) system and the \( O_2 \) \( \pi^* \) level—illustrated in Figure 5. We see again an important role of the \( O_2 \) \( \sigma \) and \( O_2 \) \( \pi \) orbital as they interact with the potassium s-p hybrid. It is this hybrid pointing away from the surface which mediates the sticking and chemical interaction of \( O_2 \) with the graphite surface at a C–O distance which is normally in the physisorption region. The large positive binding energy for \( O_2 \) on top of the potassium can be traced to the transfer of the remaining electron density on potassium into the \( O_2 \) \( \pi^* \) level.

Dioxygen Dissociation. It is generally accepted that the gasification of graphite is preceded by chemisorption (sticking) of the dioxygen molecule on the surface, followed by its dissociation to oxygen atoms. In our investigation we emphasized the (dissociative) sticking component as the apparent bottleneck in the reaction process. And indeed, as the \( O–O \) overlap population in all of the tables shows, the \( O–O \) bond strength is substantially lowered when the dioxygen molecule interacts with the surface—even in cases with a negative binding energy. From much experience a lowered overlap population correlates with a weaker bond. Thus, a lengthening of the \( O–O \) bond should occur. This may eventually lead to bond dissociation. Let us explore this dissociation in some more detail.

Figure 6 shows the Walsh diagram (orbital energies versus atomic separation) for the \( O–O \) bond stretch in a free dioxygen molecule. The left-hand value on the abscissa—121 pm—is the equilibrium distance in free \( O_2 \). The doubly degenerate \( \pi^* \) level is half filled with two electrons, giving rise to the well-known paramagnetic character of dioxygen in its triplet \( 3^2\text{g} \) ground state.

The lowering of the overlap population upon chemisorption stems from the filling of the antibonding \( \pi^* \) level. The oxygen \( \pi^* \) (at about \(-13 \text{ eV} \)) lies below the Fermi level of the graphite slab, around \(-11 \text{ eV} \). One has, of course, to be careful here since in our simple one-electron approximation the \( O_2 \) \( \pi^* \) would be filled even at large separation from the surface. However, if one is in a region where adsorbate–substrate interaction is likely to occur (cf. C–O = 200 or 175 pm), we may rely on these results.

Putting two more electrons into an antibonding orbital will, of course, weaken the corresponding bond. Occupying the \( \pi^* \) level in \( O_2 \) (\( \leftrightarrow \) \( O_2^2 \)) is not yet, by itself, sufficient to break the bond. With the overlap population dropping from 0.79 to ca. 0.46–0.50 (cf. Tables II–VI) the atoms can still be considred to be held together by the \( \sigma \) bond. However, from molecular dioxygen–metal complexes it is known that as the number of antibonding electrons rises from \( O_2 \) through \( O_2^- \) to \( O_2^{2-} \), the \( O–O \) distance increases from 121 over 133 to 149 pm (accompanied by a distinct lowering of the Fermi stretching frequency). As pointed out above, such a bond lengthening—possibly to approximtely 150 pm, depending on the adsorption site—will also occur with dioxygen on the graphite surface.

Returning now to Figure 6 we realize that the strongly antibonding \( \sigma^* \) level experiences a dramatic decrease in energy upon lengthening of the \( O–O \) bond. Our qualitative calculations show that the energy of \( \sigma^* \) approaches the Fermi level of the surface at an \( O–O \) separation of about 150–160 pm. Once it sinks below the Fermi energy \( (\epsilon_f) \) it will be filled by two electrons from the slab (26), giving rise to a dissociation of the molecule into oxygen atoms.

An additional experiment to test for chemisorbed active monooxygen may be the use of carbon monoxide as a reducing material. A recent study indicated that the (80) Vaska, L. Acc. Chem. Res. 1976, 9, 175.
Table VI. Comparison between Molecular Surface-Adsorbate Models and the Analogous Extended Structure System

<table>
<thead>
<tr>
<th>molecular system</th>
<th>analogous extended structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_b$ overlap population</td>
<td>$E_b$ overlap population</td>
</tr>
<tr>
<td>$E_b$ overlap population</td>
<td>$E_b$ overlap population</td>
</tr>
</tbody>
</table>

- $E_b = E(\text{substrate}) + E(\text{free } O_2) - E(\text{adduct})$. A positive binding energy indicates an exothermic adsorption process.

oxidation of CO may be used as a probe reaction to detect some forms of chemisorbed oxygen in coals. We have focused here on the $O_2$ dissociation step, since it seems to be the more important rate limiting step in CO and CO$_2$ formation of graphite. We did not explore in any detail the C–O bond formation nor the detachment of CO/CO$_2$ from the surface. Also left for a later study are

Theoretical Conclusions

Supplementing the experimental results, we have tried to provide a possible understanding of parts of a graphite gasification mechanism, especially the dioxygen adsorption and dissociation. We attempted to work out the differences between $O_2$ adsorption on clean or potassium-covered graphite in a chemical, molecular orbital picture. We found that in the absence of potassium on the surface there is no deep potential energy well in $O_2$ chemisorption, allowing only physisorption of $O_2$ molecules with low kinetic energy. A deep potential minimum develops only for oxygen atoms. However, experimentally this requires substantial kinetic energy input in the appropriate degrees of freedom (translational, vibrational and/or rotational energy), either by raising the temperature or providing the $O_2$ with kinetic energy using molecular beam techniques to overcome the $O_2 \rightarrow 2O$ dissociation barrier. With potassium on the surface this dissociation barrier is

Interaction of Potassium and Oxygen

Langmuir, Vol. 9, No. 12, 1993 3439

Acknowledgment. C.J. thanks the Deutsche Forschungsgemeinschaft (DFG) for the award of a postdoctoral and a Habilitation fellowship. The theoretical work carried out by C.J. initiated during a postdoctoral stay at Cornell in the group of R.H. and was finished upon return to Berlin. At Cornell our work was supported by the Office of Naval Research and the National Science Foundation through the Materials Science Center at Cornell, Grant DMR-9121654. The TU Berlin is thanked for providing computer time, the “Fonds der chemischen Industrie”, and the “Freunde der TU” for additional support.

We thank John Lowe for helpful suggestions and for bringing some of the theoretical work on graphite to our attention and one of the reviewers for his or her very constructive comments. Furthermore, we are grateful to Dinko Chakarov for valuable discussions and for help with the HREELS measurements.

Appendix

The computations were performed within the extended Hückel formalism with weighted H_{ij} values. The atomic parameters for the elements involved in our calculations were as \(H_{ii}, v\): C 2s, -21.4 eV, 1.625; 2p, -11.4 eV, 1.625; O 2s, -32.3 eV, 2.275; 2p, -14.8 eV, 2.275; K 4s, -10.49 eV, 1.2; 4p, -7.37 eV, 1.2; from charge iteration, see text. The parameters for the charge iteration of the potassium atom were \(A = 1.00304/1.34340; B = 6.63321/4.49320; C = 4.30229/2.72900\). Geometrical parameters and k-point sets are referred to in the appropriate tables or in the text. The intralayer C–C distance in the undistorted graphite net was fixed at 142 pm, the interlayer contact at 335 pm.

Chosing the Brillouin Zone and k-Point Set. Our bare graphite slab in 3 still has 3-fold symmetry. Together with the inversion symmetry of the Hückel Hamiltonian the irreducible part of the Brillouin zone is \(1/12\) of the full zone. However, bringing in an adsorbate, such as potassium or O_2 above a C–C bond, already reduces the symmetry to 2-fold, with the irreducible Brillouin zone (IBZ) then occupying one-quarter of the full first Brillouin zone \((27)^{37}\). Coadsorption of K and O_2 \((28)\) may leave no symmetry at all, thus giving only an oblique coadsorbate/substrate unit cell.

For the special case of an oblique lattice with \(\angle a_1b_2 = 60^\circ\) and \(\angle b_1b_2 = 120^\circ\), respectively, the unit cell in reciprocal

![Figure 5. Partial interaction diagram for dioxygen bonded side-on to a benzene-potassium fragment (K1 site). Lack of perturbation of the benzenoid \(\pi\) system together with a good overlap between the dioxygen \(\sigma^*\) and \(\pi\) level and a potassium sp hybrid explains the large energy of interaction. A vertical bar indicates the occupation of the HOMO.](image)

![Figure 6. Partial Walsh diagram for the stretching of the O–O bond in the dioxygen molecule. 121 pm is the medium distance in free O_2. The doubly degenerate \(\pi^*\) level is the half-filled, highest occupied MO.](image)
space of the oblique lattice corresponds to the full Brillouin zone (BZ) of the hexagonal lattice, as depicted in 29. The shaded or lined areas of the oblique BZ can be mapped onto an area of the hexagonal lattice by means of an inversion center (O). Therefore, there is no problem in using the k-point sets for an oblique lattice also in cases of higher hexagonal symmetry. Actually, even in 6-fold symmetrical hexagonal lattices it is safer to average over the whole BZ (shown in 29) instead of just the irreducible BZ (given in 2), to ensure a reliable calculation of properties.

In order to be consistent in average property calculations, and to be able to compare results for different systems, one has to use the same k-point set for both low- and high-symmetry systems. Due to computational constraints, we decided on using a grid with only eight k-points—though a highly efficient one shown in 30 (the k-points are indicated by + − labels), throughout our average property calculations. The efficiency of the small k-point set in 30 was verified through a comparative average property calculation on graphite using 18 and 72 k-point sets.

The Potassium Parameters. The parameters of the extended Hückel method are the Coulomb integrals $H_{ii}$ and Slater orbital exponents $\xi$. The choice of these for systems spanning a range of ionic and covalent bonding is always a problem. For carbon and oxygen there exist well-established literature parameters. However, taking a set of potassium parameters for neutral K, which we found in the literature ($H_{\text{K}} = -4.34$ eV, $H_{\text{sp}} = -2.73$ eV, $\xi_{\text{Ksp}} = 0.87$) creates serious problems, as it gives rise to strong counterintuitive orbital mixing (COM) in our semiempirical calculations. COM has been described before, and the conditions for its occurrence were analyzed in detail. We just mention briefly the features of this phenomenon in our problem. The effect is easiest illustrated by using a molecular model for our extended surface system.

If we carry out a molecular calculation on a neutral benzene–potassium model (31) using the potassium parameters given above and a reasonable C–K distance of 303 pm (see above), we compute an atomic charge on potassium of $+1.21$ (1), a K–C overlap population of $0.08$, and gross atomic orbital populations for the potassium $s$, $p$, and $x/z$ orbitals of $-0.25$, $-0.13$, and $-0.01$, respectively (despite using the weighted Wolfsberg–Helmholtz formula). A calculation with potassium on the extended graphite surface gives very similar values. These unrealistic values can be attributed to the above mentioned counterintuitive orbital mixing, the out-of-phase admixture of an energetically high-lying metal orbital into a very low lying ligand combination. In our case the main interaction responsible for COM takes place between the potassium $p_y$ and the benzene $a_1$ carbon $2s$ combination graphically illustrated in (32) (the numbers denote the orbital energies in eV). To a smaller extent the potassium $s$ orbital is also involved.

The potassium $y$ and $s$ orbitals overlap substantially with the $C_6H_6 a_1$ combination (overlap matrix element $-0.56$ for $y$ and $0.40$ for $s$), while they differ much in ionization potentials (see 32). These are the conditions leading to COM within the extended Hückel framework.

To obtain a better set of parameters, we therefore performed a charge iteration on potassium on an extended graphite surface. For the charge iteration the potassium–graphite geometry was kept constant with C–K = 303 pm and potassium placed above a 6-fold site at 0.4 ML coverage (1K/18C atoms). A one-layer graphite surface had to be used in the charge iteration procedure, due to computational constraints. In addition we carried out charge iterations for different exponents ($0.87 < \xi_{\text{sp}} < 1.40$) to find an optimum parameter set which would give a small positive C–K overlap population and a potassium charge as close to $+1$ as possible, yet still having diffuse potassium orbitals ($\xi_{\text{Ksp}}$ as small as possible). The set with an exponent $\xi_{\text{Ksp}} = 1.20$ with $H_{\text{K}} = -10.49$ and $H_{\text{sp}} = -7.37$ eV was then our final choice and the basis for the subsequent calculations involving potassium on graphite.