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Molecular Orbital Calculations of the Chemisorption and Diffusion of Oxygen and Water on a Graphite Substrate

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Semi-empirical molecular orbital calculations have been performed using the macro-molecular orbital model to simulate the chemisorption and diffusion of oxygen and water on a graphite substrate. By comparing with previous calculations of this type we have shown that the method adopted for minimising edge effects by saturating dangling carbon bonds reproduces the surface properties adequately for our purposes. Calculations using model substrates of 16 carbon and 10 hydrogen atoms and 24 carbon and 12 hydrogen atoms have been performed.

The chemisorption and diffusion of oxygen has been studied by means of an equipotential contour map and the diffusion path and activation energy found. Less extensive calculations on water on graphite allow us to give a most probable diffusion path and activation energy. Sufficient results have been obtained to allow some qualitative remarks to be made on the inhibition of oxidation by an H_2O mechanism.

Key words: Oxygen, chemisorption and diffusion on graphite – Water, chemisorption and diffusion on graphite – Chemisorption

1. Introduction

The problem of two phase gas-surface interaction phenomena has received a good deal of attention both theoretically and experimentally in recent years. Such important effects as catalysis and oxidation are dependent upon surface effects and in particular chemisorption and interactions between atoms and molecules influenced by the presence of a substrate are of great interest. A brief glance at any experimental data on chemisorption indicates some of the difficulties involved in developing a viable theoretical model for these types of processes. For example, the geometry of the surface layer and the adsorbate is important since it is well known that a single adsorbate species on a given crystal surface will exhibit multiple binding energies [1]. This sensitivity to details of the surface geometry is also indicated by mobility measurements [2]. Therefore, a complete theoretical treatment requires a description not only of the electronic interaction between the adsorbate and the perfect crystal surface, but also the capability of investigating the properties of surfaces containing various kinds of defects.

It has been shown that it is essential to include a proper representation of the bulk properties of the material and its interaction with the adsorbate. [3–6]

This is particularly true for metallic substrates in which long range effects are most important [3, 4]. Experimentally this is shown by work function measurements which indicate that there will be a good deal of charge redistribution at the interface [7]. This indicates that a self consistent determination of the potential and charge redistribution in the theoretical model is required.

To date quantum mechanical methods have been applied to two basic substrates, metals and graphite. We shall be concerned only with the latter in these calculations but it is instructive to mention the work on metal substrates since the problems are similar, though more difficult, and a great deal of the early work was performed with these systems particularly in mind. Very early a Heitler-London valence bond method was used to investigate the adsorption of hydrogen molecules on carbon [8]. The computing limitations in 1941 meant that the extremely small, two atom substrate, severely limited the usefulness of the results. For the particular problem of metallic substrates Bennett and Falicov [4] have developed a method which treats the substrate as being free electron like and represents the atomic adsorbate in the Slater approximation [9]. The perturbation theory developed by Fano [10] for treating discrete atom level-continuum interactions was then utilized with a limited atomic basis. This led to a self-consistent scheme for the charge densities which gave promising results. A parallel scheme has been developed by Grimley [3] and Newnes [11] in which the adsorbate atomic *s* orbital interacted with the substrate via a tunnelling matrix. This scheme is difficult to use without making severe simplifying assumptions, in particular overlap integrals between substrate and adsorbate are ignored in Newnes work, a fact which makes the accurate calculation of the cohesive energy very difficult [12, 13].

In principle molecular orbital calculations avoid all of these difficulties since the interactions between all of the constituents are calculated self consistently. However, computational difficulties preclude the use of *ab initio* methods for anything but relatively small molecular systems. However, there is a class of molecular orbital methods which have been developed specifically for use in calculations on large molecules which are sufficiently economical in terms of computer requirements to allow investigations of macro-molecular models of surface interactions. These methods are semi-empirical in that certain difficult integrals are approximated by parameters obtained from experimental data or from *ab initio* calculations on small molecules containing the appropriate atomic species. Of these methods two have already been utilized for calculations on chemisorption. These are the Extended Hückel Theory (EHT) developed by Hoffman [14] and Complete Neglect of Differential Overlap (CNDO) of Pople and co-workers [15–18]. The former was applied to the chemisorption of hydrogen on graphite by Bennett and co-workers [5a]. This work also considered briefly the adsorption of CO and the formation of CH_4 on the graphite substrate. The results of this work were quite encouraging, although the lack of self consistency in the EHT method meant that the charge relocalization on adsorption was only poorly described. The same authors [5b] then consider a similar problem using the CNDO approximation. This method uses a rather more sophisticated parametrization, but more importantly includes a self consistent determination of the coupling coefficients and hence the density matrices in the approach. Calculations were performed with H, C, N, O, and F adsorbates on a graphite substrate. A further sophistication was that the graphite substrate was represented by periodically connected boundary conditions which eliminated problems of interpretation of edge sites found in their previous EHT work where the substrate was simply represented as a hexagonal array of carbon atoms. Although some quantities were not reproduced at all well by these calculations, notably the binding energy/atom, consistent results for the sequence of adsorbates were obtained and a simple scaling factor brought the results consistently into agreement with experimental data. It is well established that for ionic systems, CNDO results are in good agreement with experiment for relative quantities whilst absolute values are not well reproduced [19–21]. CNDO calculations have also been performed for the interaction of metal aggregates on a graphite substrate [6], particularly Pd, Ag, Cu, Ni, and Zn aggregates with a view to gaining some understanding of the processes involved in catalysis. Encouraging results, with similar limitations to those mentioned above, were obtained. The use of molecular orbital calculations has so far been restricted to graphite substrates since the almost free electron like properties of a metallic substrate pose a formidable problem for molecular-orbital calculations.

In this work we shall again consider a graphite substrate and its interaction with various adsorbate species. Our particular interest lies in gaining an understanding of the oxidation processes and of diffusion mechanisms for various adsorbates. This has the long term aim of aiding in the understanding of the oxidation of graphite in gas cooled reactors and its inhibition by the introduction of small amounts of various molecular species into the coolant. Naturally the experimental conditions involved are most difficult since as well as the complications involved with surface irregularities, pores etc. there is the added factor of high temperatures and radiolitic processes adding to the reactions at the surface. Needless to say, a full theoretical treatment of this situation is out of reach at the present time. However, it is our objective to consider very much simplified reactions theoretically with the hope of gaining a qualitive understanding of the relationships between the various adsorption processes for different atomic and molecular species. In order to test the usefulness of the molecular orbital method for the study of such problems we have begun with an investigation of the chemisorption of oxygen atoms on a graphite substrate and of the possible diffusion mechanisms across the surface. The inhibition processes have been investigated in a very simple way by comparing the adsorption of oxygen with that of water.

2. Method of Calculation

The CNDO method was established in order to provide a useful approximation to the Hartree-Fock equations for the treatment of valence electrons by the explicit inclusion of electron and core interactions. The method, and several extensions of it have been elucidated in detail in a recent book [18], this work also contains results of many molecular applications. Here we give only sufficient detail to highlight the approximations and the role of the empirical parameters in the method.

The wave functions are constructed from anti-symmetrized products of one electron spin orbitals

$$\chi_i(r)=\sum_\lambda C_{i\lambda}\phi_\lambda(r) \tag{1}$$

where we have suppressed the spin co-ordinates and in the following will consider only the application of the theory to closed shell systems. The extension to include open shells is straightforward. The $\phi_\lambda(r)$'s are Slater orbitals centered on atoms in the system. The coefficients $C_{i\lambda}$ and eigenvalues E_i are then determined by solution of

$$\|F_{\lambda\nu}-E_{\lambda\nu}S_{\lambda\nu}\|=0 \tag{2}$$

where $S_{\lambda\nu}$ is an element of the overlap matrix associated with orbitals ϕ_λ and ϕ_ν. The Hartree-Fock hamiltonian is then separated in the usual way into one and two electron components

$$F_{\lambda\nu}=H_{\lambda\nu}+G_{\lambda\nu} \tag{3}$$

where

$$H_{\lambda\nu}=\left\langle\lambda\left|-\frac{1}{2}\nabla^2-\sum_A\frac{Z_A}{(r-R_A)}\right|\nu\right\rangle \tag{4}$$

and

$$G_{\lambda\nu}=2\sum_{\mu\omega}P_{\mu\omega}\langle\lambda\nu|\mu\omega\rangle-\sum_{\mu\omega}P_{\mu\omega}\langle\mu\nu|\lambda\omega\rangle\,. \tag{5}$$

The density matrices are given by

$$P_{\mu\omega}=\sum_i C_{i\mu}C_{i\omega} \tag{6}$$

where i is contained in the occupied manifold of $\{\phi\}$.

The charge on atom A is given by

$$P_{AA}=\sum_\mu^A P_{\mu\mu} \tag{7}$$

Z_A and R_A are the core charge and position of atom A respectively.

The approximations made in order to solve Eq. (2) with the minimum of computational effort are as follows. Differential overlap between non-orthogonal atomic orbitals is ignored, hence the name CNDO. The terms which are ignored are of the form S_{ij} and Coulomb integrals of the form $\langle\lambda\mu|\mu\omega\rangle$ other than those of the form $\langle\lambda\lambda|\mu\mu\rangle$. Secondly, rotational invariance is retained by replacing certain integrals with average values characteristic of s orbitals for the atomic species involved. That is $\langle\lambda^A\lambda^A|\mu^B\mu^B\rangle=\gamma_{AB}$ and $\left\langle\mu^A\left|\frac{Z_B}{(r-R_B)}\right|\mu^A\right\rangle=V_{AB}$. The quantity $Z_B\gamma_{AB}-V_{AB}$ is then the penetration integral originally introduced by Geoppert-Mayer and Sklar [22]. Thirdly, one electron diagonal matrix elements are approximated as

$$\left\langle\lambda\left|-\frac{1}{2}\nabla^2-\frac{Z_A}{(r-R_A)}\right|\lambda\right\rangle=-\frac{1}{2}(I_\lambda+A_\lambda)-Z_A-\frac{1}{2}\gamma_{AA} \tag{8}$$

and the off diagonal elements are replaced by

$$\left\langle \lambda \left| -\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{(r-R_A)} \right| \mu \right\rangle = -\frac{1}{2}K(\beta_A+\beta_B)S_{\lambda\mu}\,. \tag{9}$$

The quantity $\beta_{AB}=\frac{1}{2}K(\beta_A+\beta_B)$ then represents the possible lowering of energy of an electron from being in the field of two nuclei simultaneously. For first row atoms $K=1$ and for second row atom Pople and Beveridge [18] recommend a value of $K=0.75$. In these calculations values of all the parameters are as for the CNDO/2 parametrization.

Using these approximations, the matrix elements of the Fock hamiltonian reduce to the following form,

$$F_{\mu\mu}=H_{\mu\mu}+\left(P_{AA}-\frac{1}{2}P_{\mu\mu}\right)\gamma_{AA}+\sum_{B\neq A}(P_{BB}\gamma_{AB}-V_{AB})\,, \tag{10}$$

$$F_{\mu\nu}=\beta_{AB}S_{\mu\nu}-\frac{1}{2}P_{\mu\nu}\gamma_{AB}\,. \tag{11}$$

The solution of Eq. (2) is facilitated by the use of an EHT like calculation to obtain the initial eigenvectors. These values are then used to form the P matrix which in turn is used to form the F matrix. The next estimate of the eigenvectors is obtained by diagonalizing F and so on until convergence is reached by reference to the criterion

$$\left|\frac{E^{(n+1)}-E^{(n)}}{E^{(n)}}\right|<C\,, \tag{12}$$

C may be chosen, but it usually taken as $\simeq 10^{-6}$. The subscript n refers to the n^{th} iteration in the SCF cycle. Under normal circumstances $10<n<20$ for convergence. In various calculations the convergence of the SCF cycle has been disturbed in a way which is not well understood [5]. This results in an oscillating solution which diverges. Bennett *et al.* discuss this point and have introduced a scheme whereby subsidiary interations are performed on the density matrices according to the simple prescription

$$P'^{(n+1)}=\varepsilon P^{(n)}+(1-\varepsilon)P^{(n+1)} \tag{13}$$

The new estimate $P'^{(m+1)}$ is then used to calculate a new $E'^{(n+1)}$ via $F'^{(n+1)}$. If $E^{(n+1)}<E^{(n)}$ then the calculation proceeds as normal. However, if $E^{(n+1)}$ is still $>E^{(n)}$ then further subsidiary iterations are required until the desired convergence is obtained. This procedure is open to criticism on the grounds that there is no basis for the interpolated density matrices since they do not correspond to a wave function which is the solution of Eq. (2). However, Bennett *et al.* have found no inconsistencies when using this method and transitions from normally convergent to forced convergent solutions are smooth. This procedure is only required for certain situations and in all of the calculations presented here this only occurred for the close approach of the adsorbate to the surface, i.e. $z\leqq 1$ Å. Since this did not corrspond to the region around the minima in the potential curves all of our important results were obtained with the conventional SCF procedure, although the sub iteration method has been implemented in our program.

Having thus found a set of coefficients $C_{\mu i}$ and a corresponding density matrix $P_{\mu\nu}$, the total energy of the system is obtained from

$$\mathscr{E}_{\text{total}} = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{\mathrm{A}<\mathrm{B}} \frac{Z_\mathrm{A} Z_\mathrm{B}}{R_{\mathrm{AB}}}. \tag{14}$$

Binding energies are then calculated by subtracting from this total energy the sum of the free atom energies for the system.

3. Computing Requirements

The chief concern in large scale computations on molecular systems lies in the choice of basis functions used. In general, the larger the basis, the more accurate the results but unfortunately the two electron integrals of the form $\langle \mu\nu|\kappa l\rangle$ require that the storage and time demands are proportional to n^4, where n is the number basis functions. Indeed, a considerable amount of the total effort put into molecular orbital schemes lies with deriving ingenious programming to alleviate this problem. The CNDO method removes this 4th power dependence by replacing the two electron integrals by quantities dependent only upon the nature of the atoms. The number of elements to be stored is then reduced to being proportional to $n(n-1)/2$. The actual evaluation of the two electron integrals is avoided by parameterization, thus the most time consuming part of *ab initio* SCF calculations is avoided. The result is a computational scheme which by *ab initio* standards is very rapid, for example a calculation on a typical small molecule such as H_2O requiring just a few seconds IBM 370/175 time. However, for the very large molecular systems with which we shall be concerned here, even with the CNDO approximation computing demands rapidly become prohibitive. The CNDO method uses only a valence basis set. That is, the number of orbitals is simply equal to the number of valence shells. For first row atoms (Li–F) this consists of $2s$, $2p_x$, $2p_y$, and $2p_z$, whilst second row atoms (Na–Cl) also include the five d-type functions. Cl is the largest atom for which the parametrization is automatic in the programme. However, heavier atoms may be parameterized and included in calculations using this method if desired (cf. Ref. [6]). Thus, for a calculation including 20 first row atoms, 80 basis functions would be used and the computing demands would centre upon the repeated diagonalization of an 80 × 80 matrix.

The program used was originally written by P.A. Dobosh, and is available from the Quantum Chemistry Program Exchange Scheme; program number 141. We have made alterations to the program to allow calculations on systems containing up to 50 atoms and 180 basis functions (the original limits were 35 and 80 respectively). In this form the program requires some 900 Kbytes of storage, whilst the smaller version requires < 240 Kbytes. Typical computing times would ~1 min for an 80 basis function calculation and ~1 hr for the largest possible system, in both cases the times are dependent mainly on the number of iterations required to reach self consistency in the SCF cycle. Thus, although the semi-empirical molecular orbital method embodied in the CNDO approximation represents an enormous improvement in machine requirements, of course with their limitations on accuracy, they also rapidly reach feasible limits when applied to marco-molecular calculations and the size of the model must be chosen as a compromise between computer limitations and the accuracy of their description of the system in question.

4. Results and Discussion

4.1. The Basic Graphite Substrate

Previous semi-empirical calculations [5] have used a model substrate consisting of 16 or 18 carbon atoms. In their EHT work [5a] these authors used a simple array of 16 carbon atoms arranged in the typical hexagonal lattice as shown in Fig. 1. No attempts were made to avoid the dangling carbon bonds at the edges. In their later work [5b], the same authors approached the problem of edge sites by using periodically connected boundary conditions. This method treats the pair interactions on edge atoms periodically by coupling appropriate edge sites around the lattice. The quantity which is used to indicate the degree to which the model substrate fits a perfect infinite system is the valence charge residing on each atom; this should be 4.00. Since one of the objectives in this work is to consider defect sites, the use of periodically connected boundary conditions is not useful in this case. Consequently we have adopted the scheme of saturating the dangling carbon bonds with hydrogen atoms. We argue that for an adsorption process in the center of the model substrate, edge effects will largely cancel since we shall be mainly concerned with differences in adsorbate binding energies. We have used two model substrates, the system shown in Fig. 1, containing 16 carbon and 10 hydrogen atoms, which we shall denote $C_{16}H_{10}$ and a larger array $C_{24}H_{12}$. The latter was used for testing the results obtained from the smaller system for convergence with size of substrate for only a few specific points. That this technique compares well with previous results and provides a suitable starting point for the calculations is shown in Table 1. Here we compare the valence charge distributions for EHT, 16 and 18 carbon atoms and 18 carbon atoms with periodically connected

Table 1. Comparison of valence charges on substrate lattice

Atom[a]	CNDO				
	$C_{24}H_{12}$	$C_{16}H_{10}$	18-C[b]	18-C[c]	EHT 16C[d]
2	4.00	4.00	4.00	4.05	4.27
5	3.97	3.96	4.00	3.97	3.65
6	4.00	4.01	4.00	4.00	4.19
9	3.99	3.98	3.99	4.05	3.78
10	4.01	3.99	4.00	3.89	4.00
18	4.00	–	4.01	4.03	–

[a] Atom position refer to those in Fig. 1.
[b] 18 carbon atom plane with periodically connected boundary conditions [5b].
[c] 18 carbon atom plane with no boundary conditions [5b].
[d] Extended Hückel theory for 16 atom plane with no boundary conditions [5a].

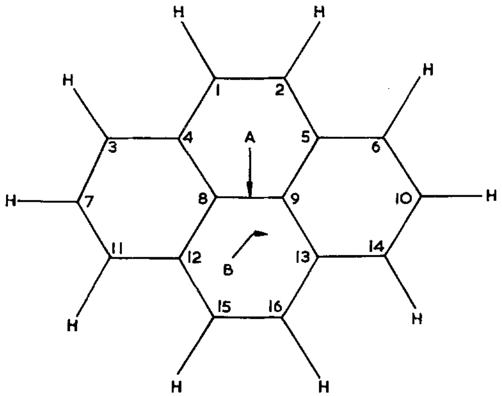

Fig. 1. Geometrical arrangement of the $C_{16}H_{10}$ model substrate. C–C bond length = 1.42 Å, C–H bond length = 1.1 Å

boundary conditions and results for the $C_{16}H_{10}$ and $C_{24}H_{12}$ systems. In this table the atom numbering refers to that of Fig. 1. Even the smaller $C_{16}H_{10}$ system compares favourably with the 18 atom connected results, whilst for the larger system the agreement is very good indeed.

Although not of prime importance in this work, it is instructive to note the cohesive energies obtained by this method since it highlights the type of inaccuracies which arise. The experimental value of the cohesive energy (the negative of the binding energy) is ~5 eV/atom [23] EHT calculations [5a] gave a result of ~4.0 eV/atom whilst CNDO calculations [5b] gave 26.33 eV/atom for the connected boundary condition case. The results of our calculations are consistent with these results in that we obtained 26.45 eV/atom for the $C_{16}H_{10}$ and 26.12 eV for the $C_{24}H_{12}$ systems, each with the internuclear separation held at 1.42 Å. It is well known that CNDO consistently overestimates the binding energy whilst the inclusion of S_{ij} in EHT tends to lower this quantity. It is hoped that calculations using INDO (intermediate neglect of differential overlap) [18] would bring the binding energies more into line with the experimental results. Such calculations are currently in hand. However, since we are primarily concerned a) with a qualitative description of diffusion paths, for which a knowledge of the absolute binding energies is not required and b) with activation energies which are themselves differences in binding energies, this consistent overestimation of binding energy will not concern us. However, for various quantities of secondary interest such as the oxygen desorption energy, we will follow the prescription given by Bennett *et al.* [5b] and Baetzold [6] in arbitrarily dividing the binding energies by a factor of ~5 for comparison with experiment.

A detailed discussion of the band structure of the graphite substrate is beyond the scope of this work. A simple relationship between the eigenvalue spectrum and the band structure at the $\Gamma(k=0)$ point as for the case of ionic crystals [19, 21] is not possible due to the high anisotropy of the band structure along the c-axis (perpendicular to the surface). A brief comparison of semi-empirical results with the $2D$ model of Bassini and Parraviccini [24] has been given by Bennett *et al.* [5a]. A description of the band structure of graphite is also available [25].

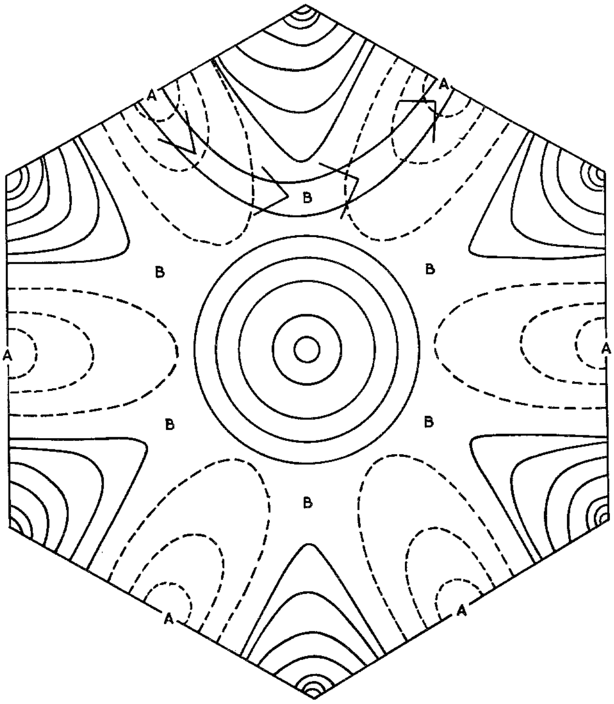

Fig. 2. Equipotential contours for oxygen 1.2 Å over a $C_{16}H_{10}$ plane. Dotted lines refer to binding energies below −1.0 eV. Full lines to binding energies above −1.0 eV. Also shown is the probable diffusion path

4.2. Oxygen Adsorption and Diffusion

The adsorption of an oxygen atom on the surface was simulated simply by calculating binding energies for the combined oxygen $+C_{16}H_{10}$ system (denoted $OC_{16}H_{10}$) with the oxygen atom in various positions above the surface. Following Bennett *et al.* [5b] we first considered a few specific positions and found, in agreement with these authors, that the most stable position was at a mid C–C bond approximately 1.25 Å above the surface, it is very satisfying that this is so since the same authors found a minimum at the centre of the hexagon for the 18 atom unconnected case labelled A in Fig. 1. This adds further weight to our assertion that the hydrogen saturated carbon bonds gives a good representation of the substrate. The binding energy of the oxygen atom at this position, using the scaling factor, is 41 kcal/mol (1.92 eV). This value lies well within the range of experimental values. A value of 40 kcal/mol was obtained at 273 K [26] whilst values up to 84 kcal/mol have been reported [27].

A subsidiary stable position was found which was along the line joining the centre of the hexagon with a carbon atom, this site is labelled B in Fig. 1. The energy surface of the oxygen adsorbate was then searched with the height above the substrate constrained at 1.2 Å and an equipotential contour map was drawn. This is shown in Fig. 2. In order to highlight the features of the surface all contours

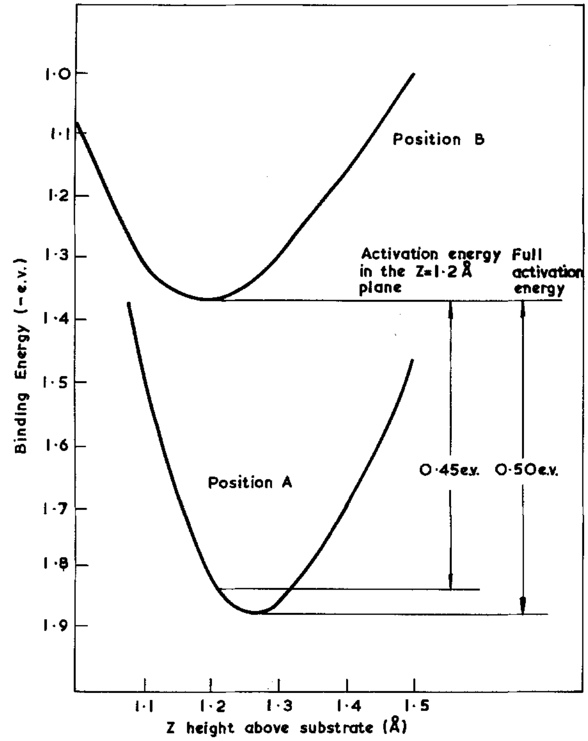

Fig. 3. Potential curves and activation energies for the system $OC_{24}H_{12}$

of binding energy above -1.0 eV are shown by full lines and those below this value by dotted lines. The saddle point nature of the minima at site B is clearly shown by this figure. From this equipotential surface the most probable diffusion path may be seen. This is shown schematically in Fig. 2 as running from position A, via position B to an equivalent site A on an adjacent C–C bond. The activation energy for this process is obtained by considering the potential curves for the oxygen atom as a function of the height above the surface for sites A and B. It should be noted that the equipotential contours shown in Fig. 2 refer to only one plane in the 4-dimensional energy surface and that the activation energy in this plane is lower than for the fully relaxed system. The potential curves for sites A and B are shown in Fig. 3 as a function of the height above the surface. For these specific positions the larger $C_{24}H_{12}$ substrate model was used. This gives $\sim$0.50 eV as the maximum value of the activation energy for migration from site A via site B to an adjacent site A.

4.3. The Adsorption and Diffusion of H_2O

A similarly detailed equipotential surface for H_2O $C_{16}H_{10}$ cannot be obtained due to the increased number of degrees of freedom for the triatomic molecule over

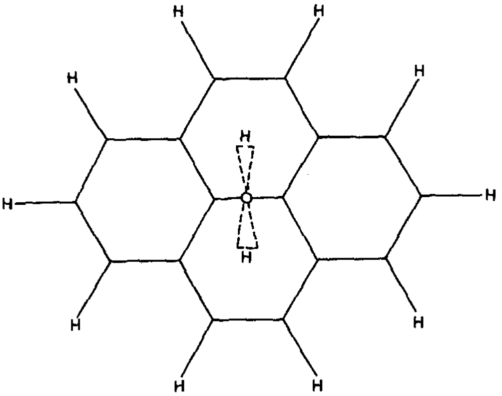

Fig. 4. Schematic representation of the equilibrium H_2O C_{16} H_{10} system. Oxygen atom lies 1.8 Å above the plane. H_2O parameters are: $\alpha = 105°$, O–H = 0.94 Å

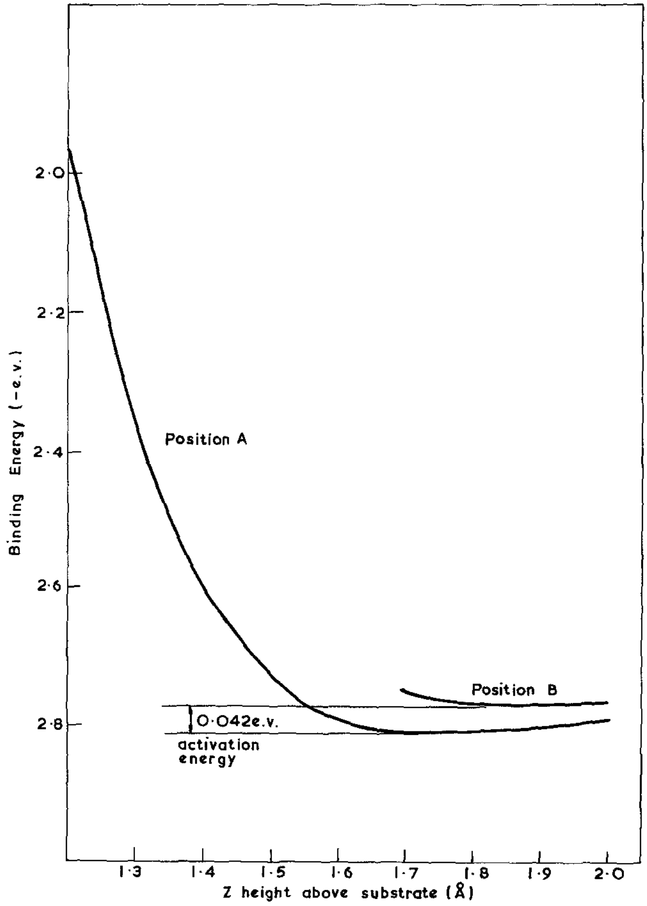

Fig. 5. Potential curves and activation energies for the system H_2O C_{24} H_{12}

the single atom. However, we performed many trial calculations and found that the most stable position for the H_2O molecules was with the oxygen atom residing in the well at point A, with the O–H bonds directed outwards from the surface, and perpendicular to the C–C axis. The position is most easily visualized by reference to Fig. 4 which gives a schematic view of this configuration. A subsidiary minimum was again found at site B, with the O–H bond similarly arranged to that at site A. We found that the H_2O molecule was more tightly bound than the oxygen atom by a factor of ~ 1.5. (60 kcal/mol compared to 41 kcal/mol). However, the activation energy has been reduced by an order of magnitude to ~ 0.04 eV. The relevant potential curves are shown in Fig. 5. Since this value is only ~ 2 KT at room temperature, it means that the water molecule is essentially free to move across the surface compared to the oxygen atom. Although no detailed calculations have been made, we believe that the diffusion path for H_2O will be similar to that for oxygen, with the oxygen member of the H_2O molecule following the same route.

Fortunately, all of the important results for both $OC_{16}H_{10}$ and $H_2O\,C_{16}H_{10}$ are contained in the range $1\,Å < z < 2\,Å$. Thus, problems associated with the lack of convergence at short distances and with the inadequacies of single determinant SCF calculations at long distances will be minimised.

4.4. *Inhibition of Oxidation*

Although this work is at a very early stage we can already make a few qualitative remarks on the oxidation inhibition mechanism. It is well known experimentally (see for example Refs. [28, 29] that small additions of various molecular species to the substrate will inhibit the oxidation process. A recent review of the processes of surface adsorption on graphite is available [30] which itself contains references to review articles. There is a wide spread of results due to the nonuniformity of the graphite sample and differences in experimental techniques. However, it has been established that both methane and water will inhibit the oxidation process, the former being the more effective of the two. The results of our work indicate first that normal oxidation takes place at sites other than on a perfect surface since the binding energies are too high. Secondly, additions of H_2O to the gas will inhibit oxidation in two ways. Firstly, the H_2O occupies the same diffusion paths as the oxygen with a very much lower activation energy, thus effectively blocking more than one site on a random walk basis. Secondly, assuming that oxidation occurs at defect sites, then the H_2O will arrive at those sites much more frequently than the oxygen since for temperatures around 600° C the water molecules are virtually free to move on the surface. As yet we have no information on the differences between the interactions of H_2O and O at edge sites (essentially with unsaturated carbon bonds). However, the fact that oxidation is reduced in the presence of H_2O would indicate that an H_2O molecule would tend to become bound to the surface at these sites whilst oxygen atoms form C–O or other species which are desorbed. A later phase of this work will include calculations on model edge sites in order to elucidate qualitatively such problems.

5. Summary and Conclusions

In these calculations we set out to investigate the usefulness of the macromolecular orbital model for examining chemisorption and surface interactions on a graphite substrate. Earlier work had indicated that useful semi-quantitative results could be obtained. We have found that this was also true for the systems studied here and that certain relative quantities could be found to a reasonable degree of accuracy.

We have shown that a model substrate containing 16 carbon atoms having the dangling carbon bonds saturated with hydrogen atoms provides an adequate basis for the calculations and that a larger system having 24 carbon atoms and 12 hydrogen atoms reproduces very well the results from calculations having periodically connected boundary conditions. Some quantities associated with the band structure are also shown to compare well with more sophisticated calculations.

The investigation of oxygen and water adsorption on the surface have already given some insight into the chemisorption of these species and also into their diffusion mechanisms across the surface. Further, qualitative conclusions could be drawn relating to the oxidation inhibition mechanisms. It is pleasing that from such a simple chemical model results may be obtained which are both consistent with accepted processes and allow the possibility of further calculations on more complicated systems. For example, we are currently investigating the chemisorption and diffusion of CO and CH_2 on graphite and hope in the near future to investigate interactions of such species with edge sites. Even though the results of these calculations are at best semi-quantitative they have the advantages of being calculable in realistic computer times, having a very simple "model" basis allowing a rather clear interpretation of the results and offering the prospect of future studies on more realistic systems with some assurance that the technique is consistent and reproduces the overall chemistry of the system accurately.

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