THEORETICAL STUDY OF ADSORPTION ON A SiO_2 SURFACE*

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Received June 28, 1989

Abstract

Preliminary calculations of adsorption on a SiO_2 surface are presented. An open shell version of the MINDO/3 molecular orbital method is applied to a two-dimensionally periodic slab of α-quartz covered by a monolayer of hydrogens on one side. The atomic geometries and adsorption energies of a CO molecule are given for two possible molecular adsorptions.

Introduction

The investigation of the adsorption and penetration of atomic and molecular species onto and into a silica surface is of significant importance from the viewpoint of numerous practical problems. Various forms of silica serve as substrate or even active material in heterogeneous catalysis (e.g. [1]). Thermally grown vitreous silica is used in the microelectronics as a protecting/insulating surface layer subjected to various impurity adsorption and penetration phenomena throughout the technological process [e.g. 2—3].

The details of the adsorption process, such as the favoured adsorption site, the heat of adsorption, etc., as well as the chemical reactions occurring after the adsorption and/or through the indiffusion are very hard to access experimentally or theoretically. The more so in cases like that of silica where the adsorbent does not possess a two-dimensional periodicity. In this paper we present a calculational scheme based on quantum chemical methods which is simple enough to handle the problem on a personal computer, but has proven accurate enough to predict experimentally detectable properties of point defects in bulk solids. We demonstrate that our method simulates the bulk properties appropriately and we present a preliminary model calculation on the adsorption of a CO molecule on SiO_2.

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* We wish to dedicate this paper to professor János Giber who has initiated this research and launched our scientific career.

2. Calculated properties of bulk SiO_2

The problem of calculating the local structure and potential map around an adsorbate on the surface is analogous with the problem of point defects in the bulk. During the last decade we have developed [4, 5] a scheme called the cyclic cluster model (CCM) which utilizes the special **k** point theorem in choosing a large unit cell [6, 7] of the crystal and applies periodic boundary conditions. The CCM is able to provide a reasonable simulation of the bulk crystalline properties [5, 8]. The Schrödinger equation of the system is solved in a semi-empirical Hartree-Fock-Roothaan type approximation. A careful test has been carried out to choose a semi-empirical approximation from among the ones developed by chemists that works best in solid state applications [9]. The MINDO/3 (modified intermediate neglect of differential orbitals) method [10, 11] has been found the most successful regarding its overall performance, while the CNDO/S (complete neglect of differential overlap for spectroscopy) method [12, 13] has proven the most successful in describing the electronic structure. In this present study MINDO/3 will be used.

The CCM requires the choice of a symmetric multiple of the primitive unit cell as the basis of the calculation. In such a case a set of special **k** vectors of the primitive Brillouin-zone is reduced to the $K=0$ state of the large unit cell. The CCM calculation is then restricted to these states only. The better the set, the better is the simulation of the extended states.

In the case of silica, the short-range order and the short range interactions are dominant in determining the structural and electronic properties of the material as it can be seen by comparing vitreous silica and α-quartz [14]. The bands are rather dispersionless, and the electronic energies at the center of the primitive Brillouin-zone can be reproduced very well by any set of **k** states [15]; even with the $\mathbf{k}=0$ state alone, i.e. applying cyclic boundary conditions to the primitive unit cell itself.

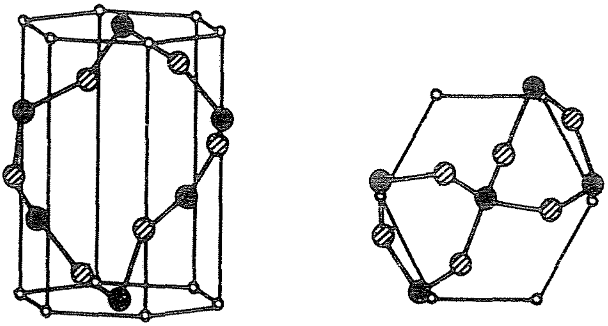

Fig. 1. The bulk unit cell of α-quartz containing Si_3O_6

A MINDO/3 calculation on the primitive unit cell of α-quartz containing an Si_3O_6 unit (see Figure 1) results in the lattice parameters

$$a = 4.954\ \text{Å} \quad (4.903\ \text{Å})$$

$$c = 5.711\ \text{Å} \quad (5.393\ \text{Å})$$

as compared with the experimental values in parentheses. This corresponds to SiO-distances of 1.637 Å and 1.661 Å in comparison with the experimental 1.604 Å and 1.608 Å, respectively for α-quartz and 1.63 Å in vitreous silica. The dipole moment of the Si—O bond is $1.94 \cdot 10^{-19}$Cm in fair agreement with the experimental value of $1.26 \cdot 10^{-19}$ Cm. The occupied energy levels are compared with the experimental photoelectron spectra in Figure 2. The first ionization energy is computed to be 9.2 eV as compared to the experimental 10.4 eV [14]. This is an error similar to what MINDO/3 shows in calculating the first IP for disiloxan [16]. The heat of formation is overestimated by about 40%.

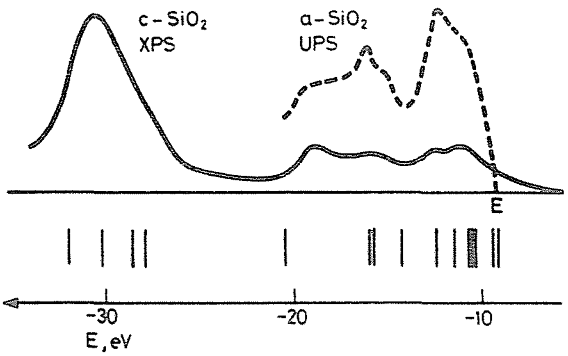

Fig. 2. The calculated occupied energy levels for Si_3O_6 compared with the experimental photoelectron spectra taken from ref. [14]

The calculation allows for only first neighbour Si—O, O—O and Si—Si interactions, and we may regard them relevant to both the crystalline and the vitreous case. The results are quite acceptable considering the fact that they have been obtained by using an IBM AT personal computer only.

3. Surface calculations

The problem of adsorption on a silica surface differs from the usual crystalline bulk case in two respects. For one, the three-dimensional periodicity is lost. This problem, in case of crystalline surfaces, is usually handled by applying the repeated slab technique. Making use of the very localized nature

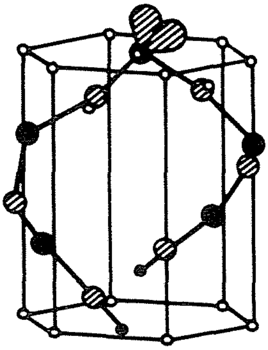

Fig. 3. The structure of the relaxed silica surface at an active Si site

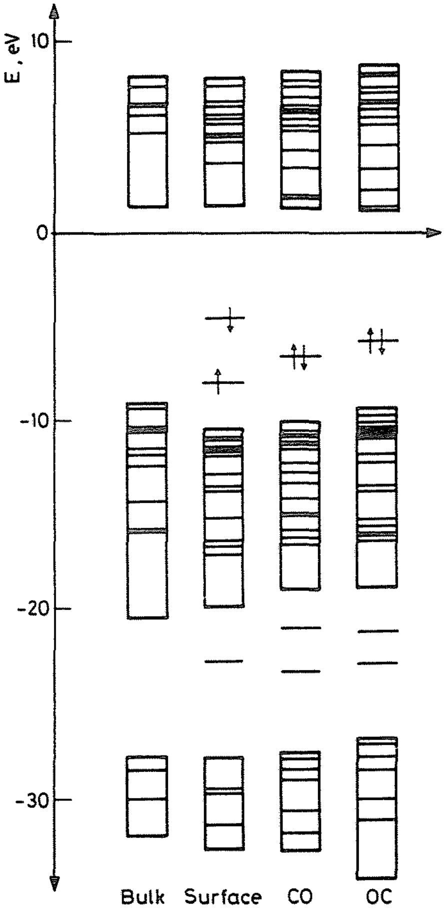

Fig. 4. The electronic structure of the silica surface at an active Si site

of bonds in silica we will not maintain an artificial periodicity perpendicular to the surface. Instead, we are going to use a single slab which is periodic in two dimensions parallel to the surface and which is saturated by a monolayer of hydrogens on one side, i.e. exhibiting just one free surface. The second problem is that the silica layers of practical interest are not even crystalline. However, as in the bulk case, we may assume that choosing a small surface unit cell (i.e. a limited number of interactions) the results will be relevant to the vitreous case as well.

Keeping this in mind, we have carried out calculations on a slab containing one $(Si_3O_6)_s + 2H$ unit. The coordinates of all but the top layer silicon and its two oxygen neighbours in the second layer have been fixed at their values obtained from the bulk calculation (with O—H distances fixed at 0.93 Å). The resulting equilibrium relaxed structure exhibiting two dangling bonds on the silicon are shown in Figure 3. The electronic structure, compared with that obtained from the bulk calculation, is shown in Figure 4.

4. Adsorption of a CO molecule on a Si site on silica

As a model calculation we have chosen to look at the adsorption of a CO molecule on a silica substrate near to a chemically active silicon site. Further work including adsorption at an active oxygen site is in progress. Calculation on the possibility of dissociative adsorption are also scheduled to be carried out.

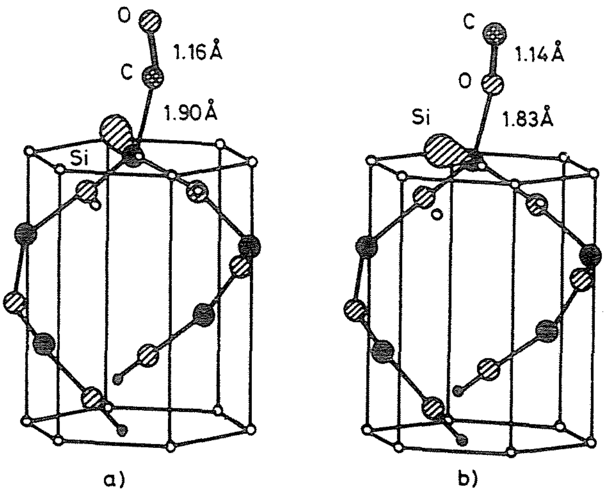

Fig. 5. Two possible molecular adsorption geometries of CO on silica

Two metastable adsorbate structures are shown in Figure 5. The adsorption energies are

$$E(SiO_2+CO)-[E(SiO_2)+E(CO)]=-1.6\,\mathrm{eV}\,(-37\,\mathrm{kcal/mol})$$

$$E(SiO_2+OC)-[E(SiO_2)+E(CO)]=-1.3\,\mathrm{eV}\,(-31\,\mathrm{kcal/mol})$$

The electronic structures reveal that in both cases the bonding configuration of the silicon atom is essentially the same as on the clean surface, i.e. the molecular adsorption leaves the silicon still chemically and electrically active.

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