

Theoretical Dynamics Study of Atomic Oxygen over β -Cristobalite (100)

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Abstract. In this work we examine the interaction of $O(^3P)$ atoms with β -cristobalite (100) surface. We derived a potential energy surface for the ground O/SiO_2 state based in density functional theory calculations along with some empirical data. We study the adsorption and reflection dynamics considering a 9-layer slab (2x2) cell coupled to several generalized Langevin oscillators to control the surface temperature (T_s). We obtained high adsorption probabilities (85-98%) in comparison with reflection at all initial conditions, which also decrease slightly when O kinetic energy or T_s are augmented. Adsorption processes correspond to a rapid O sticking over Si first-layer sites of β -cristobalite (100) surface. Our calculated thermal initial sticking coefficients are much bigger than indirect values used in some published kinetic models about O recombination reactions on other type of silica surfaces.

Keywords: Adsorption, density functional theory, atomic oxygen, cristobalite, sticking coefficient, classical dynamics

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INTRODUCTION

The interaction of atomic and molecular oxygen with SiO_2 -based materials plays an important role in the chemical processes that take place over the thermal protection system (TPS) of some Shuttle-like orbital vehicles (e.g., American Shuttle, Russian Buran, Japanese Hope,...) during their atmospheric re-entry [1]. For example, reaction-cured glass (RCG) with 94 % of SiO_2 , 4% of B_2O_3 and 2 % of SiB_4 is used in coating materials for some parts of these vehicles. The most important processes involving the TPSs and the dissociated air (e.g., in Earth's atmosphere) are oxidation, formation of an oxide layer and catalytic atom recombination. The heterogeneous atom recombination considerably influences the heat transfer to the vehicle at hypersonic flight velocities. TPSs with materials as little catalytic as possible are searched because they prevent from recombination of the dissociating atoms on the surface and the release of large diatomic dissociation energy. For this purpose, SiO_2 -based materials are used although the slight catalysis of these materials is significant enough compared with an ideal non-catalytic surface assumption. The mechanisms and the rates of the different gas-surface processes in such non-equilibrium conditions (i.e., hypersonic flows) are not well known [2]. In fact, much of these processes have neither been well characterized even at room temperature. Therefore, accurate theoretical and experimental data are necessary to simulate (e.g., via computational fluid dynamics (CFD) codes) hypersonic flights with several TPS systems.

Among the different heterogeneous processes that can occur in the mentioned conditions, $O + O \rightarrow O_2$ recombination (via Eley-Rideal (ER) or Langmuir-Hinshelwood (LH) mechanisms) is one of the most important reactions because of the major amount of oxygen atoms in dissociate air. However, in a previous elementary step to this reaction, one (for ER reaction) or two (for LH reaction) atomic oxygen have to become adsorbed over the TPS. Limited experimental data is available about atomic oxygen adsorption over silica surfaces. An average adsorption energy of 3.5 eV, regardless of the kind of silica surface (e.g., Pyrex, quartz, RCG,...), have been used in some kinetic models that fit some empirical data, deriving as well some oxygen initial sticking coefficients (e.g., $S_0 = 0.05e^{-0.002T}$ on SiO_2 or $1.0e^{-0.002T}$ on RCG), 300-2000 K [1]). In a recent theoretical study [3], we have studied the O interaction with β -cristobalite by means of the density functional theory. β -cristobalite is the most stable polymorph

of silica at high temperatures (as can be reached during the Earth's atmospheric re-entry phase) although is also metaestable at room conditions. Moreover, this crystalline phase of silica presents similar properties (e.g., density, refractive index, band structure,...) to amorphous silica, which seems to be used in TPSs. Thus, we initially calculated its bulk properties and after that we studied the O and N adsorption over β -cristobalite (100) face. We found that O and N were strongly adsorbed, mainly in two sites: directly on top Si and also over a bridge between two Si atoms for the first Si layer of the fcc unit cell. The calculated average adsorption energies of O were equal to 5.89 eV (singlet state) and 4.87 eV (triplet state), much higher than the usual assumed value of 3.5 eV.

The main goal of the present work is to analyse the dynamics of the O collisions with β -cristobalite in order to ascertain the importance of the DFT calculated properties (e.g., adsorption energy, geometry of the adsorption site...) on the different processes (i.e., sticking and reflection) depending on the incidence collision energy and the surface temperature. These dynamical data and the analytical (or interpolated) potential energy surface (PES) will be necessary in a next theoretical study for both ER and LH oxygen atomic recombination reactions. Furthermore, the dynamics study (classical or quantum) of these processes for non-equilibrium conditions (e.g., high collision energies and low surface temperatures) would be very useful in CFD calculations aimed at simulating the hypersonic flights of several space vehicles.

COMPUTATIONAL PROCEDURE

Potential Energy Surface

We have performed density functional theory (DFT) calculations by means of the VASP code [4-6] to determine the atomic oxygen interaction with a Fdd2 β -cristobalite (100) surface at several sites, following the same procedure that was explained in more detail in our previous work [3]. Thus, calculations were based on the generalized gradient correction functional Perdew-Wang 91 (PW91). The electron-ion interactions were described by using the projector-augmented-wave technique. For the plane wave basis set, an energy cut-off of 400 eV was accurate enough to obtain converged properties. Spin-polarized calculations were carried out for both total spin states (i.e., singlet and triplet) deriving from ground atomic oxygen (triplet) and β -cristobalite (singlet). Integration over the Brillouin zone was made by means of a $3 \times 3 \times 1$ k-points mesh by using the Monkhorst-Pack method.

We used a 1×1 surface unit cell and a SiO_2 slab model including 6 layers for the Fdd2 β -cristobalite (100) face, with a silicon first layer. An additional hydrogen bottom layer was added to saturate the O dangling bonds of the inner layer. The distance between slabs (ca. $z = 17\text{-}18$ Å) was large enough to prevent significant interactions between them. The atomic oxygen energy was calculated with the atom inside a large broken symmetry box (i.e., $8 \times 7.5 \times 7.6$ Å³). Around 50 DFT points were calculated for every of the two sites: on top Si of the first layer (T1) and on top O of the second layer (S2), keeping fixed the slab geometry for its most stable configuration in absence of O atom. The ground interaction curves were constructed by using the lowest energy (singlet or triplet) and then a 1D cubic spline interpolation was carried out to improve the quality of both energy curves. Mostly, at large O-slab distances the triplet energies were chosen. Figure 1 shows the β -cristobalite surface unit cell and several sites and their DFT energies used to check the goodness of the analytical PES1, apart from T1 and S2 curves.

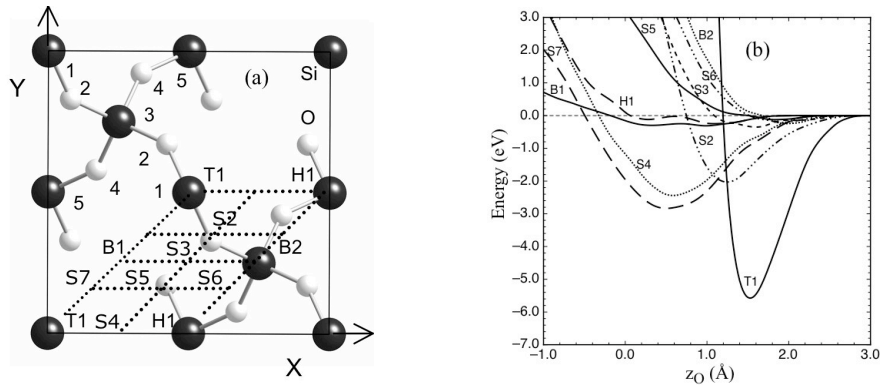


FIGURE 1. (a) Surface unit cell, sites and atom positions in each layer and (b) Energy curves ($V^{\text{O-slab}}$) for these sites.

The PES is expressed as a sum of two potentials:

$$V(\vec{R}_O, \{\vec{R}_{slab}\}) = V^{slab}(\{\vec{R}_{slab}\}) + V^{O-slab}(\vec{R}_O, \{\vec{R}_{slab}\}) \quad (1)$$

where \vec{R}_O is the oxygen atom position vector and $\{\vec{R}_{slab}\}$ indicates the atomic slab positions of all O and Si atoms

$$\{\vec{R}_{slab}\} = \{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_s}\} \text{ and } N_s = N_{Si} + N_O \text{ (number of slab atoms)} \quad (2)$$

The V^{slab} potential describes the slab interactions in absence of adsorbate. It is a sum for all kind of pair-interactions in silica:

$$V^{slab}(\{\vec{R}_{slab}\}) = \sum_{i=1}^{N_O} \sum_{j=1}^{N_O} \phi_{ij}(R_{ij}) + \sum_{i=1}^{N_{Si}} \sum_{j=1}^{N_{Si}} \phi_{ij}(R_{ij}) + \sum_{i=1}^{N_{Si}} \sum_{j=1}^{N_O} \phi_{ij}(R_{ij}) \quad (3)$$

and we use a modified form of the Born-Mayer-Huggins ionic potential [7] for each pair interaction:

$$\phi_{ij}(R_{ij}) = A_{ij} e^{-R_{ij}/\rho} + \frac{Z_i Z_j}{R_{ij}} \operatorname{erfc}\left(\frac{R_{ij}}{\beta_{ij}}\right) \text{ (in a.u.)} \quad (4)$$

where R_{ij} is the interatomic distance, Z_i is the formal ionic charge, and, A_{ij} , β_{ij} and ρ are parameters. These potentials have been successfully employed in previous molecular dynamics simulations of silica and silicate systems [7].

The V^{O-slab} potential includes the O-surface interactions

$$V^{O-slab}(\vec{R}_O, \{\vec{R}_{slab}\}) = \sum_{i=1}^{N_{Si}} V_{SiO}(R_{Oi}) + \sum_{j=1}^{N_O} V_{OO}(R_{Oj}) \quad (5)$$

and we employ the above mentioned DFT interpolated curves at T1 and S2 sites with the DFT relaxed slab geometry for the V_{SiO} and V_{OO} potentials, respectively. Both potentials become zero at long distances (i.e., $\geq 3\text{\AA}$). For the total V energies, the zero of energies (V_{zero}) is taken for slab at its optimal geometry with O atom at infinite separation. Figure 1b illustrates the large corrugation of the constructed surface for several O positions over the optimum DFT slab geometry. The use of the empirical V^{slab} , which presents only small geometrical differences with respect to the DFT slab, maintains almost the same properties of the main adsorption minimum. Thus, this minimum in PES1 is at the T1 site with $V = -5.21$ eV and $R_{SiO} = 1.559$ Å. Harmonic vibrational analysis verifies that it is a true minimum ($\nu = 964.1, 278.8$ and 91.3 cm⁻¹). These values are very close to the reported DFT ones [3].

Classical trajectory method

We have performed a classical molecular dynamics study of the atomic oxygen adsorption or reflection processes over a β -cristobalite (100) surface. We included the motion of all atoms in a 9-layer (100) slab, using a 2x2 surface unit cell (104 atoms in all) with a cell parameter of 7.348 Å. The temperature of slab ($T_s = 300 - 1100$ K) was controlled by means of a Generalized Langevin equation (GLE) approach [8]. The friction coefficient and the frequency of the oscillators in each direction were selected for several temperatures to obtain a fast thermalised slab with small thermal fluctuations. Thus, the energy distribution of slab atoms corresponded to a Boltzmann one after quick equilibration (e.g., $\langle V \rangle \approx \langle K \rangle = 3N_s k_B T_s$), with an uncertainty ≤ 50 K for all surface temperatures.

The Hamilton's equations were integrated by using a modified fixed step (0.1 fs) Beeman algorithm. Energy was conserved within an error of 10^{-4} - 10^{-5} eV in absence of the GLE bath. The initial O atom distance to the slab was around 4-6 Å and the oxygen kinetic energies (E_i) were within 0.1 - 1 eV. Collision of atomic oxygen was studied for different initial incidence angles of the O velocity vector respect to the negative Z axis cell (i.e., $\theta_i = 0^\circ$ and 45°).

This aiming point (X_0, Y_0), i.e., the point at the 1x1 surface unit cell which would be hit in absence of potential interaction, was generated by using a random uniform sampling of this cell. Moreover, the angle between the X-axis and the projection of the O velocity vector in the X-Y plane (ϕ_i) was uniformly distributed over the interval $0-2\pi$.

Approximately, batches of 1000-5000 trajectories were run for each initial condition (i.e., E_i , θ_i and T_S), reaching reaction probabilities with statistical relative errors lower than 1%.

The analysis of the trajectories was carried out on the basis of two possible events: reflection and adsorption. Trajectories were classified as reflection when atom reaches a final $Z_0 > 4 \text{ \AA}$ with a final Z velocity component pointing toward vacuum. The small amount of adsorption trajectories that penetrated into the slab (i.e., final $Z_0 < 0$) was also labelled as absorption. Integration was usually computed for collision times until 5 ps, although for several conditions we checked that final probabilities at longer collision times (e.g., 10 ps) were the same.

RESULTS OF THE DYNAMICS STUDY

The adsorption (P_{ads}) and reflection (P_{ref}) probabilities are plotted in Fig. 2. Adsorption probabilities (85-98%) are much more higher than reflection ones for all oxygen kinetic energies (Fig. 2a) and surface temperatures (Fig. 2b), with a small but clear trend for adsorption probabilities at normal incidence ($\theta_i = 0^\circ$) to be smaller than at non-normal incidence ($\theta_i = 45^\circ$). All adsorption curves show a typical behaviour, namely its fall with increasing the kinetic energy, which can be explained in terms of the less efficient energy transfer to the surface at higher E_i . Figure 2c shows the adsorption probabilities (or initial sticking coefficients) for both incidence angles at $T_S = 500 \text{ K}$, in comparison with simple models of gas-surface collisions. Thus, a hard-cube model (HCM) prediction [11] is shown, where it is assumed an atom collision with a surface, which is described as a cube of effective mass (optimal $m_c = 266 \text{ amu}$) moving at a thermal distribution (T_S). An improved Baule model (ion cores in jellium model) [10], assuming a hard sphere collision between an adsorbate and an isolated surface atom at rest, allows the introduction of the incidence angle, not present in HCM. Both models were applied using a fixed adsorption energy of 5.2 eV. Improved Baule model reproduces quite well the trajectory results respect E_i and θ_i dependency.

Adsorption probabilities scale as E_i (i.e., $E_i \cos^n \theta_i$ with $n \approx 0$), which corresponds to a *total energy scaling*, as could be expected due to the high corrugation of PES1 (Fig. 1b). This fact can also justify the slight differences observed with the incidence angle, as there will be more x-y momentum to be transferred at grazing incidence than at normal incidence, originating a larger trapping probability.

The hard-cube model decay of P_{ads} vs. T_S at two E_i values (i.e., 0.1 and 1 eV) agrees very well with trajectory results in all temperature range (300-1100 K), giving place to higher P_{ads} values for the lower kinetic energy, which allows a longer time for energy transfer and therefore can facilitate the adsorption process. The P_{ads} fall with T_S is consistent as usually desorption increases at higher temperatures.

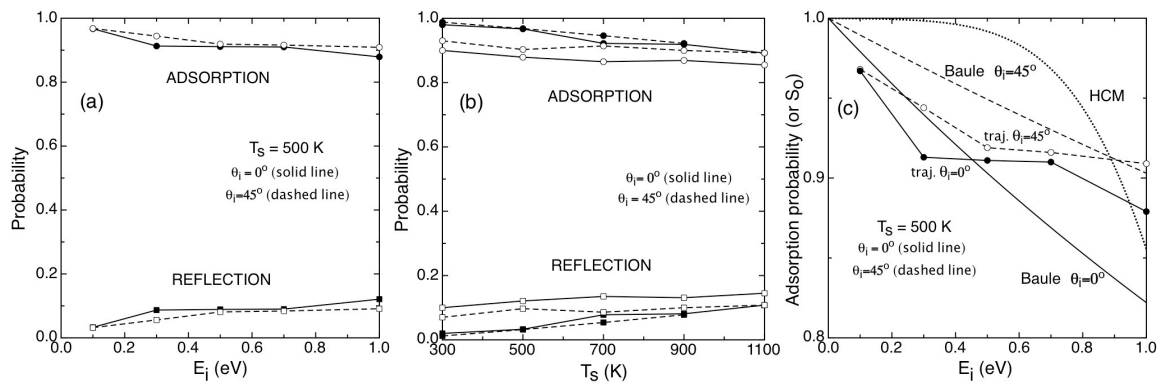


FIGURE 2. Adsorption (upper) and reflection (lower) probabilities: (a) vs. O kinetic energy at $T_S = 500 \text{ K}$, (b) vs. surface temperature at $E_i = 0.1$ (black symbols) and 1 eV (white symbols) and (c) adsorption probabilities compared with improved Baule or hard-cube model predictions. Two initial incidence angles (0° and 45°) were considered.

We have also calculated thermal initial sticking coefficients, taking the same temperature for gas and surface atoms ($T_g = T_S$). Figure 3 shows our results for β -cristobalite (100) compared with indirect values derived from experimental data by means of kinetic models about oxygen recombination on RCG or pure silica [1,11]. There is a

significant difference between these curves, with much higher values for β -cristobalite; a small temperature dependency is also observed. Despite the differences in silica structures (e.g., crystalline or amorphous structures, the face,...) are also relevant for S_0 values, the important assumptions made in these kinetic models (e.g., $E_{ad} = 3.5$ eV) should be also taken into account in this comparison. Moreover, the use of simple $S_0(T)$ expressions in these models, which are based partially in standard Transition State Theory, can produce very small S_0 values, which increase a little with T though the use of high adsorption DFT energies for these calculations [3]. Therefore, the classical dynamics treatment with a quite accurate PES seems to us more reliable to determine S_0 and another properties than simpler theoretical approaches with adjustable parameters.

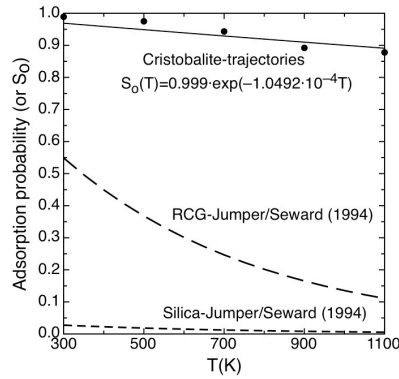


FIGURE 3. Comparison of calculated thermal initial sticking coefficients for β -cristobalite (100) with indirect experimental data derived by using kinetic models for oxygen recombination on RCG and pure silica [11].

Energy dissipation during the oxygen collision with the surface is quite fast for all initial conditions (Fig. 4a). Typically, in less than 0.5 ps the initial kinetic energy has fully released, getting a large negative potential energy as should be expected for O adsorption close to a T1 site ($V = -5.2$ eV in PES1). This fact is also shown in the plot of the average final Z_O coordinate (Fig. 4b), reaching values ($\langle Z_O \rangle = 1.0$ - 1.4 Å) close to the R_{SiO} distance (i.e., 1.56 Å) in T1 minimum. The trajectories that penetrate into the slab (i.e., absorption) along with the final angle (θ) for adsorption ones can explain this decrease in $\langle Z_O \rangle$ values. We have also monitored the average parallel displacement of the O atoms ($\langle R_{||} \rangle$) along the surface (Fig. 4c). This displacement is always lower than aprox. 2.5 Å, whose value is similar to the neighbour Si distance of 2.6 Å in the unit cell. Thus, it seems that O atoms get trapped to the closest Si atom respect the initial aiming point. The visualization of several trajectories seems to confirm this microscopic behaviour for the most part of the adsorption processes.

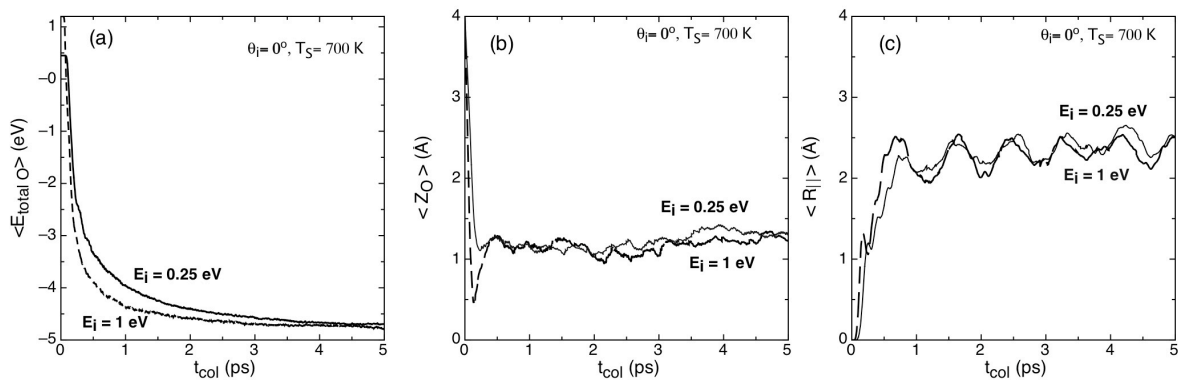


FIGURE 4. (a) Average total oxygen energy, (b) average final Z_O coordinate and (c) average parallel displacement of O, along the collision time for all adsorption trajectories with $T_S = 700$ K, $E_i = 0.25$ or 1 eV and $\theta_i = 0^\circ$.

Figure 5a shows the X-Y final position of oxygen adsorbed atoms on the surface unit cell with a major density around the lower-left to higher-right diagonal, in spite of starting from an initial uniform distribution over the unit cell. This fact can be explained in terms of the potential energy (PES1) as is shown in Figure 5b. The absence of O

in the second layer along this diagonal in comparison with the other one favours the penetration of O into the slab. We have checked that "pure" adsorption trajectories are concentrated in a similar way around all 5 Si atoms, and this increase in one diagonal arises mainly from "absorption" trajectories. Reflection trajectories (not indicated in the plot) correspond to hollow sites of the unit cell.

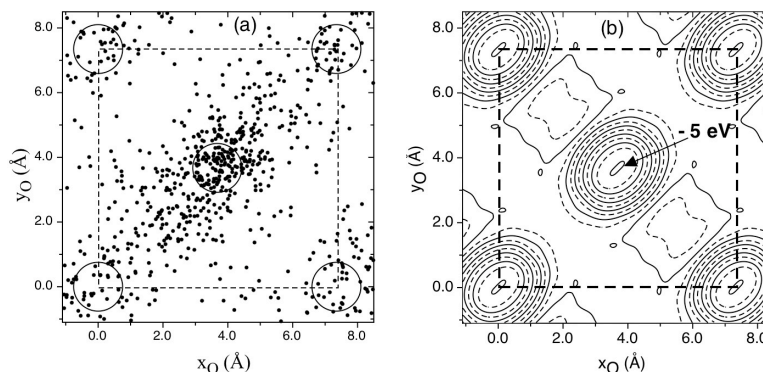


FIGURE 5. (a) X-Y final oxygen positions over the unit cell (big circles show the Si atoms) corresponding to all adsorption processes at $T_s = 700$ K, $E_i = 0.1$ eV, $\theta_i = 0^\circ$, and (b) contour plots of PES1 at $Z_O = 1.56$ Å for fixed clean slab optimum geometry.

CONCLUSIONS

In this study we present a classical dynamics study about the $O(^3P)$ collisions with a β -cristobalite (100) surface, using a new analytical PES based in DFT data and some empirical information. We observe that the adsorption (sticking) process is predominant (85-98 %) at all conditions (i.e., E_i , T_s , θ_i). The adsorption probability decreases with collision energy or surface temperature increments, and also is lower for normal incidence angles. This behaviour can be interpreted with simple collision models (e.g., improved Baule or hard-cube models) and also taking into account the high corrugation of the surface. The adsorption microscopic mechanism corresponds to a rapid O sticking around Si first-layer sites, with a fast energy release to the slab. Trajectories that enter into the slab (absorption) are concentrated along the diagonal of the unit cell without O atoms in the second layer. Thermal initial O sticking coefficients over silica based-materials, used in published kinetic models for air recombination, should be revised as possibly they are very low.

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