Molecular Dynamics Simulations of Surface Processes: Oxygen Recombination on Silica Surfaces at High Temperature

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A) GENERAL CONSIDERATIONS

The interaction between a molecule and a solid surface can lead to a great variety of elementary processes such as elastic, inelastic and reactive. Of particular importance is the dissociative chemisorption of a diatomic molecule

$$O_2(v,j) + wall --> [O_2(v',j')]_{ad} * wall --> O + O + wall \qquad (1)$$
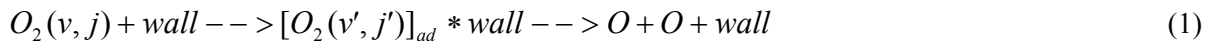
where a molecule chemisorbed at the surface in a specific roto-vibrational state (v,j) dissociates with the two atoms adsorbed or scattered into the gas-phase. Of great importance is also the atom recombination on surfaces:

$$O + O + wall \rightarrow O_2(v,j) + wall \qquad (2)$$

here two atoms recombine thus forming a diatomic molecule that can be either chemisorbed or reflected in the gas-phase in a given internal energy state. Reactions (1)-(2) are very often the rate determining step of complex heterogeneous systems of interest in different branches of industrial and technological applications, as for example in the ammonia synthesis, hydrocarbon production, chemical vapour deposition, etching and thin solid film deposition via plasma, nuclear rector technologies [1].

Both processes are of central importance in aerothermodynamics and the chemistry of interstellar media. Thus, the recombination of atomic O and N on silica and UHTC materials plays a central role for the thermal protection system of the space shuttles entering into the terrestrial atmosphere, whereas the recombination of hydrogen atoms on ice grains covered by carbon is, very likely, the main source of molecular hydrogen observed in the interstellar media.

The interaction of chemical species with surfaces can lead to other non-reactive chemico-physical processes such as the inelastic processes and adsorption. The adsorption processes occur when the particle is trapped in a chemisorption site and its available energy is not enough to escape from the chemisorption potential well. The inelastic processes can be of two types: direct and indirect. In the first case the molecule hits the surface and it is scattered in the gas-phase after few bounces. Due to the interaction, the internal energy state of the molecule leaving the surface is different with respect to its state before the collision.

In the indirect scattering, or adsorption/desorption collisions, the interaction occurs on a longer time scale and the collision is more involved: in fact, the molecule hits the surface several times, it is temporarily adsorbed eventually forming a surface activated complex before desorbing in the gas-phase. The energy distribution of the scattered molecules is different according to the different mechanism followed in the interaction.

A further class of surface processes are: surface oxidation, chemical and physical sputtering, ion implantation, etc. In these cases atomic and molecular radicals react with the atoms of the substrate, thus forming volatile compounds. These processes, not discussed in this lecture, are effective in the energy regime of several eV, or KeV, that is higher compared to the collisional energy regime of the processes (1)-(2).

The dynamical quantity typically associated to the process (1) is the state-to-state sticking coefficient S_0 which corresponds to the dissociation probability. S_0 is a function of the several variables: $S_0 = S_0 (E_{kin}|\{\theta_i, \varphi_i\}|v,j,T_S)$, where E_{kin} is the impact kinetic energy, v and j the vibrational and rotational quantum number of the incident molecule respectively, T_S is the surface temperature. $\{\theta_i, \varphi_i\}$ are the angles that define the relative orientation of the molecule with respect to the surface plane (the collisional system, sketched in Fig.1, is described in a cartesian frame of reference having the Z axis orthogonal to the surface plane and the (X,Y) axis laying on the surface top layer).
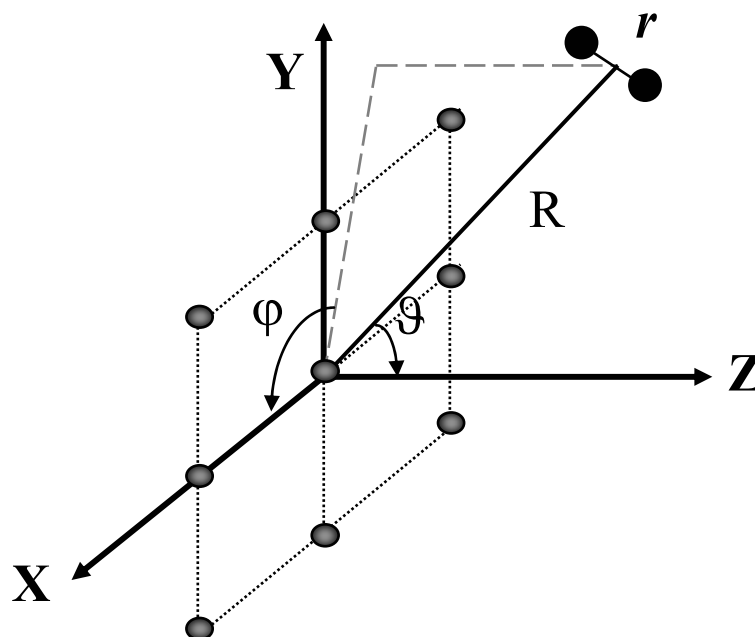

Fig. 1: The collisional system is sketched. The dynamics is described with respect
to a cartesian frame of reference having the Z axis orthogonal to the surface
plane and the (X,Y) axis laying on the surface top layer.

Different averaged quantities can be obtained from the state-to-state sticking coefficient. Thus the state-average sticking coefficient $<S_0(E_{kin}|\{\theta_i, \varphi_i\}|T_S)>$, usually measured in molecular beam experiments, is obtained by averaging S_0 over a known, not necessarily Boltzmann population distribution for the v and j states. The statistical rate constant $K(T_S)$ used in kinetic modelling can be obtained by further averaging S_0 over the incident angles and the Maxwell energy distribution function of the gas-phase molecule.Then we get $K(T_S)=K_{coll} *< S_0 (T_S)>$.

In addition to S_0, other collisional data needed to characterize the surface reactions and to include them in kinetic modelling are: the energy accommodation coefficient $\beta(T_S)$, the roto-vibrational distribution of the scattered particles $N(v,j|T_S)$, the angular distribution in intensity and energy $I(\vartheta,\varphi|T_S)$, the lifetimes of the adsorbed species.

Collisional data can be determined by using a large variety of experimental techniques that have been developed to probe directly or indirectly surface processes. Nevertheless, the observation of surface

processes is not an easy task and in fact it is a matter of fact that collisional data for heterogeneous processes are very sparse (if not absent) despite the large amount of information emerged from different experimental works. Rate coefficients are still poorly known and somehow dubious, particularly for wall processes occurring under extreme thermal conditions as those met in aerothermodynamics.

In Fig. 2 some of the experimental results reported in the literature for the recombination coefficient γ for O atoms recombination on silica-based materials are reported in a large range of the surface temperature [2-4].
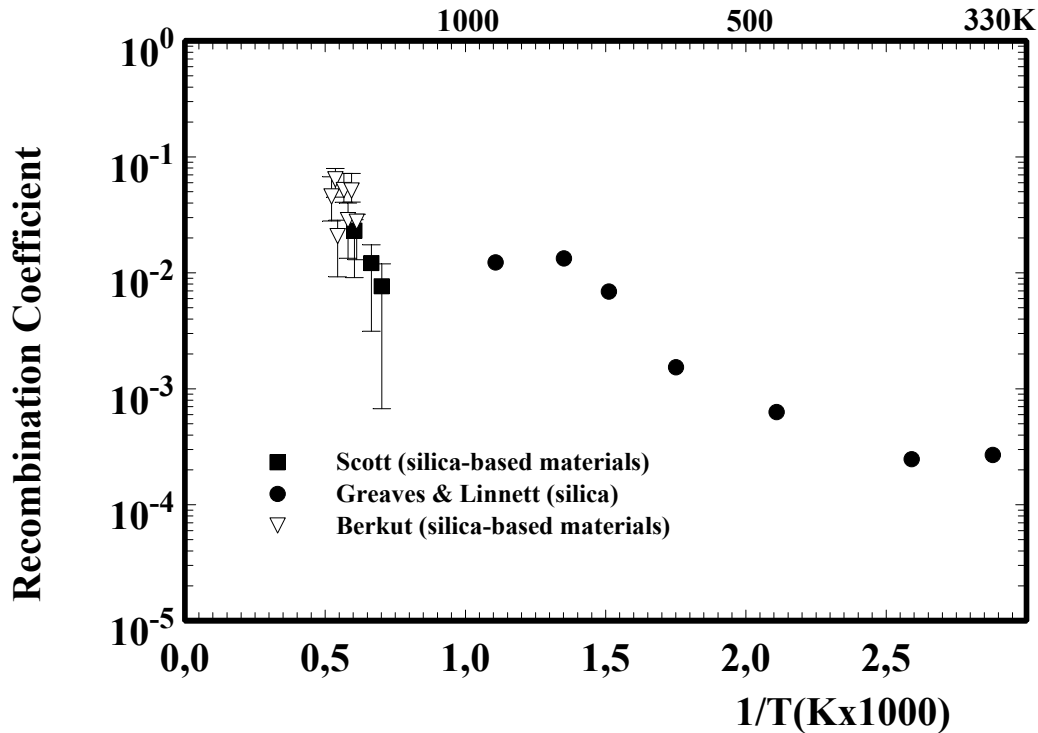

Fig. 2: The recombination coefficient γ for O atom recombination on silica-based materials is reported as a function of the surface temperature.

In the high temperature regime the results are somehow contrasting, also due to the large experimental uncertainties. From the theoretical point of view various kinetics schemes have been developed to describe the kinetics of this reaction [5,6,7].

In these studies some physical quantities, typically the activation energy, surface coverage, the number of active sites and the so-called 'steric factor', are treated as unknown parameters and varied to fit the experimental data.

Due to the lack of accurate collisional data, a complete understanding of elementary surface processes involving O, N, C, CO on silica-based materials has not yet completely achieved and a number of fundamental aspects are open to question. Among the others, the most critical aspects discussed in molecule-surface interaction studies concern, on the one hand the internal state selectivity of the collisional coefficient and, on the other hand the energy transfer mechanisms that control the surface processes. Further elements of complexity are introduced by the surface structure and surface coverage effects on the catalytic activity of the substrate.

Possible answers to these issues can be given by performing Molecular Dynamics (MD) calculations [8,9,10]. The MD approach has some important features in that predicts quantities that cannot be easily measured in experiments: quite often, the state-selected sticking coefficient S_0, or the energy accommodation coefficient β can be established only on a theoretical ground.

The MD simulation of surface chemical processes is quite complex both from the formal and the computational point of view. The multidimensional nature of the collisional system, and thus the large number of degrees of freedom introduced by the presence of the solid, increases considerably the complexity of the dynamics. As a consequence, in the last few years a variety of collisional methods [8,9] have been developed to simulate reactive surface processes, ranging from ab initio quantum mechanics calculations of reduced dimension, semiclassical and mixed semiclassical-wave packet propagation techniques, statistical simulations, classical and quasi-classical methods. MD simulations imply the solution of three main problems: i.) the first, probably the most critical one that would prevent an accurate description of the surface processes concerns the determination of the potential energy surface (PES) where the dynamics takes place, that is the determination of the forces exerted between the atoms in the gas-phase and the atoms of the surface. ii.) The second concerns the building up of a 'model' sample of the solid substrate. iii.) Finally the third aspect to solve concerns the development of a suitable collisional model to follow the nuclear motions of the particles propagating in the gas phase and interacting with the solid surface.

In the following sections some interesting results obtained from MD simulations of atom recombination processes over model silica surfaces that could be of interest in aerothermodynamics are briefly reviewed and discussed.

B) INTERACTION POTENTIAL DETERMINATION FOR O,N/SILICA

B.1) *Ab initio* methods

Determining the PES where the reaction takes place is a prerequisite for any MD calculations. In principle, this issue is addressed using computational methods developed in quantum chemistry [10]. Among the proposed approximate schemes, the most promising approach is the density functional theory (DFT) [9,11-13], which is accurate near the chemisorption well, but less accurate for long-range/weakly bound interactions. The accurate determination of the interaction potential for heterogeneous systems poses different problems, both from the theoretical and the computational point of view. Assuming that the relaxation of the lattice atoms can be neglected, the PES is, in principle, a multidimensional function which depends for diatom-surface interaction, upon six coordinates, that is the surface is too much complex and the number of interactions is too large for ab initio electronic structure calculations, either cluster or slab calculations, involving a large number of atoms and electrons. As a consequence, also due to the large computational time demanded to assure the convergence of calculated energies, complete fully dimension electronic structure calculations have been performed for few elementary systems, notably those involving H_2, CO, O_2 and others diatomics on noble and transition metals. The 'true' interaction potential remains rather unknown for a large class of heterogeneous systems, in particular for the catalytic systems of interest in aerothermodynamics. In fact uncertainties exist on: the adsorption energies and their dependence on the chemisorption site, the size and the nature of the activation energies, the energy barriers to surface diffusion.

Due to the lack of ab initio calculations one has, quite often, to rely on low-dimension ab initio 'model' potentials where the dependence of the interaction potential upon the intramolecular distance of the diatom and the distance from the surface is considered. PES of reduced dimension can be useful for understanding the qualitative aspects of dissociation/recombination processes, but for a quantitative description a PES that includes the dependence on the two (X,Y) surface plane coordinates is necessary.

An accurate two-dimensional adiabatic PES for N,N_2 interacting with a silica surface has been recently calculated [14] using the *size-scalable* cluster approach with Si_xO_y clusters of increasing size cleaved from the β-cristobalite unit cell. In this study the hybrid Hartree-Fock Self Consistent Field (HF-SCF) and the DFT method was applied and the B3LYP functions [15] used in order to take into account the exchange and the electron correlation contribution in the interaction. The interaction potential is calculated by keeping the SiO_2 geometry fixed at the experimental values of the β-cristobalite cell and extending the

N/N$_2$-Si$_x$O$_y$H$_z$ cluster model in the intervals (x=1,3,7; y=2,4,6,14; z=2,6,14). All the calculations were carried out with the Gaussian 03 package [16]. Complete scans of the R$_{N-Si}$ distance in the whole range of energy interaction (R$_{N-Si}$ = 0.90 Å, R$_{N-Si}$ =4.00 Å) for just the perpendicular configuration (that is, with the N-surface angles fixed to 90º) were performed. The N-N distance used in all N$_2$-surface PES calculations was kept fixed to 1.10 Å, close to the spectroscopic value [17]. As far as the N-Si$_x$O$_y$H$_z$ interaction is concerned, both doublet and quartet total electronic spin states were considered along the PES scan, since the electronic spin state induced by chemisorption is not known. The calculated binding energies are reported in Fig. 3. As expected, N is chemisorbed with a binding energy of about 2.79eV at a minimum N-Si distance around 1.65 Å. N$_2$ is slightly physisorbed.
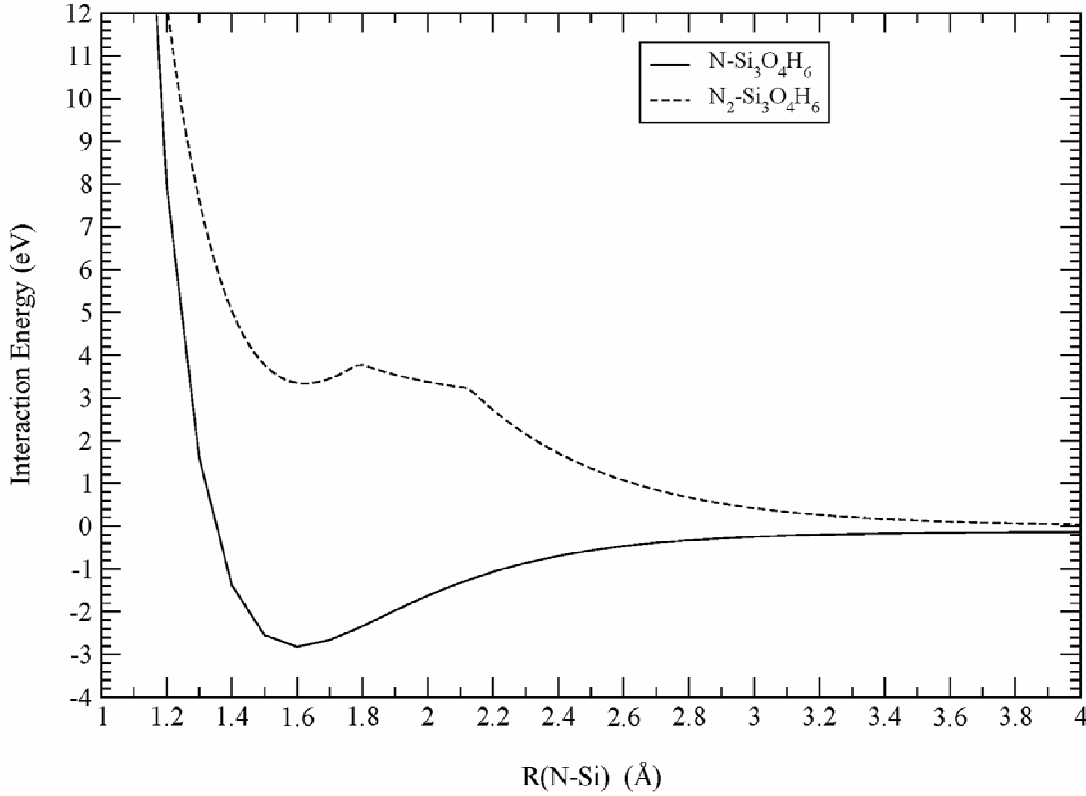

Fig. 3: Full line: the interaction potential for N interacting with Si$_3$O$_4$H$_6$ cleaved from the β-cristobalite surface is reported as a function of the distance of the N atom from the Si active atom. The dashed line shows the interaction potential of N$_2$(r$_{eq}$) approaching the silica cluster in the perpendicular configuration on top of the Si active atom. Results obtained at the DFT-B3LYP/6-311+G* level.

From the calculated quantum mechanical interaction energies a LEPS-type interaction potential can be obtained [18,19]. In order to account for the motion of the lattice atoms explicitly considered in the collision dynamics, the LEPS potential is, in this case, obtained as a sum of pair-wise N/silica atom interaction and it is given by:

$$V = \sum_{i=1}^{\mathcal{N}} U_1(r) + U_2(R_{a,i}) + U_3(R_{b,i}) - \sqrt{A_1^2(r) + (A_2(R_{a,i}) + A_3(R_{b,i}))^2 - A_1(r)(A_2(R_{a,i}) + A_3(R_{b,i}))} \quad (3)$$

where the sum is over the lattice atoms, $\mathcal{N}$ being the total number of atoms in the silica surface, r is the N-N interatomic distance, $R_{a,i}$ and $R_{b,i}$ are the distances of nitrogen atom a and nitrogen atom b from the i-th atom in the lattice, respectively. U_k (k=1,3) and A_k (k=1,3) are related to the two-body Coulomb and

exchange integrals, respectively, in the energy expression for the interaction of the solid surface with the molecule [18,19] and are given as a combination of modified Morse functions with the two additional Sato parameters. The corresponding potential parameters are obtained by fitting the full potential given by Eq. (3) to the *ab initio* DFT-B3LYP energies (Fig.3). Since the determination of the activation barrier for the N_2 formation would imply massive multidimensional DFT calculations, planned for the near future, the Sato parameters are taken as a free parameters and changed in order to get PES's with different barriers in the recombination reaction channel. This allows to study the sensitivity of the calculated collisional reaction coefficients upon the reaction barrier height.

In Fig. 4 the potential contour map of the PES for N_2 interacting in the perpendicular geometry with the active Si surface atom is shown. The interaction potential is plotted as a function of the distance from the N atom closest to the surface, and the N-N bond distance. The PES shown is obtained assuming a value of the Sato parameters that gives zero activation energy.
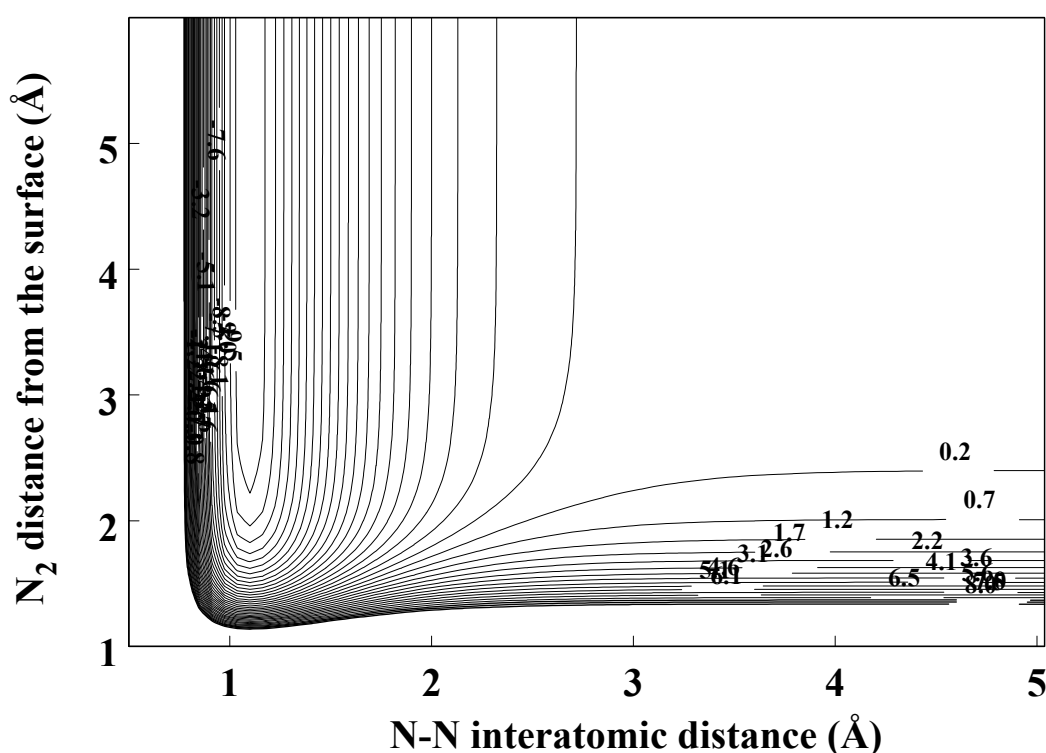

Fig. 4: PES for N_2 interacting in the perpendicular geometry with the active Si surface atom.
The interaction potential (in eV) is plotted as a function of the distance from
the N atom closest to the surface and the N-N bond distance.

The DFT cluster approach has been recently extended to the $O,O_2/ZrB_2$ system and preliminary results for O chemisorbed on top of a Zr atom have been obtained by us.

B.2) Approximate semiempirical methods

For molecule-surface systems potential surfaces can be inferred following a semiempirical approach by using the spectroscopic data available for the chemisorbed species, i.e. equilibrium geometries, adsorption energies, inter and intra-molecular vibrational frequencies. The idea is to start with a parametric interaction potential and to calculate the potential parameters such that the potential is able to reproduce all the observed spectroscopic constants. This approach has been followed to derive a realistic interaction potential for CO/Pt(111) [20], a system considered as a prototype in heterogeneous catalysis.

Unfortunately, due to the lack of spectroscopic data for the O,O$_2$/silica system, this approach cannot be followed. However a tentative interaction potential can be constructed semiempirically on the ground of reliable physical considerations. The method, developed to study the interaction of O with two silica polymorphs [21,22], β-cristobalite and β-quartz, although quite crude has been successful in predicting the recombination coefficient γ for the O+O/silica system at high temperature. As usual, the O-silica potential is expressed as a sum of pair-wise interactions, assuming that the O$_{gas}$-Si interaction is the same as the O-Si interaction in the lattice, while the interaction between the O atom in the gas-phase and the O of the quartz surface is assumed as that known for the O-O interaction in the gas-phase. The validity of this latter assumption is discussed later in the paper .Thus we have:

$$V_{G-S} = \sum_{\alpha=1,2} \left[\sum_{j=1}^{N_{Si}} V_{BKS}(R_{\alpha j}) + \sum_{j'=1}^{N_O} V_{O-O}(R_{\alpha j'}) \right] + V_C \qquad (4)$$

where the first term is the BKS potential [23] for the interaction of the gaseous O atoms and the Si lattice atoms. Moreover, since the BKS potential at O-Si distances shorter than 1.5 Å is attractive, in order to get the expected correct behaviour, the following potential is taken for the O$_{gas}$-Si interaction:

$$V_{O-Si} = A_{O-Si}\, e^{-b_{O-Si}\, R_{O-Si}} - \frac{C_{O-Si}}{R_{O-Si}^6} \left[1 + tanh\left(\frac{R_{O-Si} - R_0}{R_{O-Si}} \right) \right] \qquad (5)$$

where the repulsive and the attractive part of the BKS have been retained (and the Coulomb charge-charge interaction dropped out). An appropriate switching function has been introduced in order to smooth the repulsive potential to the C$_6$ attractive interaction at the larger distances. R$_0$ was set to 2.5 Å. The second term in Eq. (4) is the interaction potential between the gaseous O atoms and the O lattice atoms and it is given as:

$$V_{O-O} = A_{O-O}\, e^{-b_{O-O}\, R_{O-O}} \qquad (6)$$

where the parameters A$_{O-O}$ and b_{O-O} are those known from the O-O interaction in the gas-phase [21]. Finally, the last term in Eq. (4) represents the Coulomb interaction between the charge on the Si and O lattice atoms and the charges of the molecular oxygen due to the quadrupole charge separation in O$_2$. Further details about these two last terms of the potential can be found in Ref. [21].

In Fig.5, the two-dimensional interaction potential is shown for O$_2$ interacting in the perpendicular orientation on top of a Si atom. The potential is plotted as a function of the O-O internuclear distance and the distance of the closest O to the surface. In this configuration, the PES shows that the O$_2$ formation occurs without activation energy so that this configuration is very likely the most effective for the recombination process.
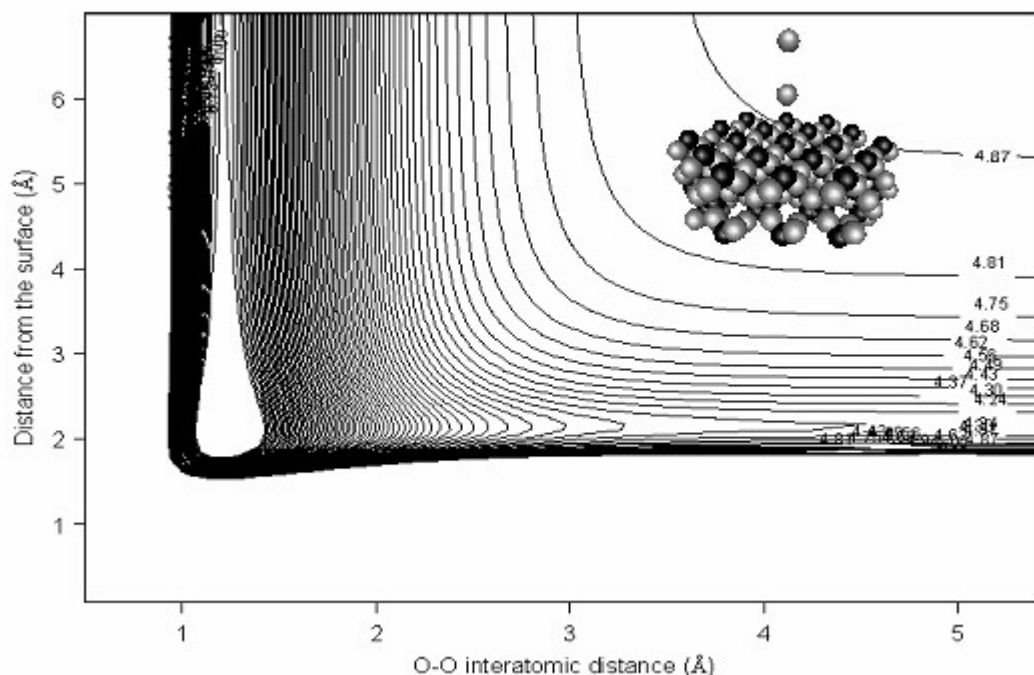
Fig. 5: Two-dimensional interaction potential for O₂ interacting in the perpendicular orientation on top of a Si atom of a β-quartz surface. The potential (in eV) is plotted as a function of the O-O internuclear distance and the distance of the closest O atom to the surface.

C) RECOMBINATION DYNAMICS OF O ON 'MODEL' SILICA SURFACES

C.1) The semiclassical collisional method

In this section two aspects relevant to the MD approach to catalysis are discussed: firstly we briefly discuss the semiclassical collisional model developed to describe the dynamics of the O atom recombination and the O₂ dissociation on silica, secondly the static properties of a silica surface are examined. Compared to a fully classical MC simulation, a much detailed and physically coherent description of the surface phenomena can be reached using the semiclassical time-dependent collisional method [24]. This method is able to describe the most fundamental features of the molecule/surface interaction: desorption (inelastic scattering) and sticking, diffusion, dissociation and atom recombination. The following aspects can be incorporated in the model: lattice geometry, force constants, electronic structure (band gap, Fermi level, etc).

The method is semiclassical in that, while the nuclear motions of the atoms/molecules approaching the surface are treated classically, the vibrational motions of the lattice atoms and the electrons are treated quantum-mechanically. Thus, the classical Hamilton's equations of motion for the gas-phase species and the time-dependent Schrödinger equations of motion for the phonons and the electrons of the substrate are solved self-consistently. The time evolution of the phonons/electrons is dynamically coupled to the time evolution of the chemical species through the definition and calculation of the effective Hamiltonian $H_{eff}(\text{t})$:

$$H_{eff} = \left\langle \Psi | V_I | \Psi \right\rangle = H_{eff}^{ph} + H_{eff}^{e-h} \tag{7}$$

H_{eff}^{ph} is contribution due to the excitation/deexcitation processes of the surface phonons and it is defined as the expectation value of the interaction potential over the total wave function of the phonon state at a

given temperature. Similarly, the effective Hamiltonian due to the excitation/de-excitation of the electron holes in the substrate, H_{eff}^{e-h}, is given by averaging the coulomb potential over the wave function of the electrons:

$$H_{eff}^{ph} = \langle \Psi_{ph}(t) | V_{int}(r, R) | \Psi_{ph}(t) \rangle \qquad\qquad H_{eff}^{e-h} = \langle \Psi_{e-h}(t) | V_C(r, R) | \Psi_{e-h}(t) \rangle \qquad (8)$$

where t is the interaction time, $V_{int}(r, R)$ is the interaction potential between the gas-phase species and the surface atoms determined as described in the previous section, $|\Psi_{ph}\rangle$ is the total wave function of the phonon state at a given surface temperature T_S, $V_C(r,R)$ is the coulomb potential due to the interaction between the electron charge in the solid and the charge temporally transferred to the molecule, $|\Psi_{e-h}\rangle$ is the total wave function of the electrons perturbed by the external coulomb force.

The total hamiltonian for the molecular motion of a diatomic molecule is obtained by adding to the usual hamiltonian for the free molecule the effective hamiltonian arising from the molecule-surface interactions:

$$H_{cl} = \frac{1}{2} \sum_{i,\alpha} \frac{P_{i\alpha}^2}{m_i} + V(r) + H_{eff}^{ph} + H_{eff}^{e-h} + \Delta E_{ph} + \Delta E_{e-h} \qquad (9)$$

where $P_{i\alpha}$ is the α-th cartesian component of the momentum of atom i and m_i the corresponding mass. ΔE_{ph} and ΔE_{e-h} are the energy exchanged with the phonons and the electrons respectively, $V(r)$ is the intra-molecular potential of the gas-phase molecule.

The effective Hamiltonian H_{eff}^{ph} due to the phonon interaction can be obtained within the well known linearly and quadratically forced harmonic oscillator model [24]. This leads to an analytical solution for the time evolution of the phonon wave function and, consequently, for the excitation/de-excitation amplitudes of the phonons in each normal modes. Finally, an analytical expression of H_{eff}^{ph} is obtained in terms of the 'phonon excitation strengths' $\eta_k(t)$:

$$H_{eff}^{ph} = \sum_k V_k^{(1)}(R(t))\eta_k(t) \qquad (10)$$

where $V_k^{(1)}$ is the linear external force exerted on the k-th normal mode, $R(t)$ is the position vector of the incoming particle at t time. $R(t)$ is the classical trajectory that is solution of the Hamilton's equations of motion. $\eta_k(t)$ are given in terms of the Fourier components of the forces exerted between the gaseous species and the surface.

$$\eta_k(t) = -\int dt' \frac{1}{\hbar \omega k} \frac{d(\Delta E_{ph})}{d\rho_k} \left[I_{c,k} \cos(\omega_k t) + I_{s,k} \sin(\omega_k t) \right] \qquad (11)$$

$$I_{c,k} = \int_{-\infty}^{+\infty} dt V_k^{(1)}(R(t)) \cos(\omega_k t) \qquad (12)$$

ω_k are the frequencies of the phonon normal modes.

The method outlined here has two important features: firstly, since the quantum phonon dynamics is solved exactly both the single and the multi-phonon processes are accounted for in the collisional model, and secondly the effective Hamiltonian depends explicitly upon the temperature of the solid. This later effect is due to the energy symmetrization and to the use of a thermal phonon distribution instead of a pure phonon eigenstate for the initial phonon state.

A further important feature is the energy exchanged between the solid substrate (phonons and/or electrons) and the chemical particles. In the case of surface processes assisted by the phonon excitation mechanism, the exchanged energy is given as:

$$\Delta E_{ph} = \sum_k \sum_{n_k} \sum_{n_k^0} p_{n_k^0} (E_{n_k} - E_{n_k^0}) P_{n_k^0 \rightarrow n_k} = \sum_k (\Delta E_k^+ + \Delta E_k^-) \tag{13}$$

where $(E_{n_k} - E_{n_k^0})$ is the energy exchanged in the transition $n_k \leftarrow n_k^0$ between the quantum state n_k^0 and n_k of the k-th phonon mode. $p_{n_k^0}$ is the Boltzmann distribution of the phonon energies, $P_{n_k^0 \rightarrow n_k}$ is the transition probability.

$\Delta E_k^\pm$ is the energy loss (+) or gained (-) from the molecule due to the excitation/de-excitation phonon processes in the substrate.

The method is formally rather involved, but nevertheless it is computationally affordable still providing a realistic description of the gas-surface interactions in their full dimension. The method has been applied to several heterogeneous systems, including the CO and CO_2 formation on a platinum surface [25,26] and the inelastic scattering of Xe atoms from a corrugated GaSe(001) surface [27].

C.2) Model silica surfaces and phonon dynamics

In order to perform MD calculations a sample of the solid substrate where the surface reactions occur must be built up and incorporated in the collisional model. Model surfaces can be constructed starting from the known arrangement of the Si and O atoms in the unitary cell of a specific silica polymorph [28], then the unitary cell is repeated several times in the 3D space in order to have a sufficiently large sample. The obtained surface can be considered as an ideal, perfect surface. In fact, while the bulk structure of real surface is known, the atom arrangement on the top most layers is not due to the covalent character of silica. Indeed, MD simulations of the static properties of silica have revealed a very complex structure of the surface layers which appear reconstructed with structural and bond defects(see Fig. 6) [29].
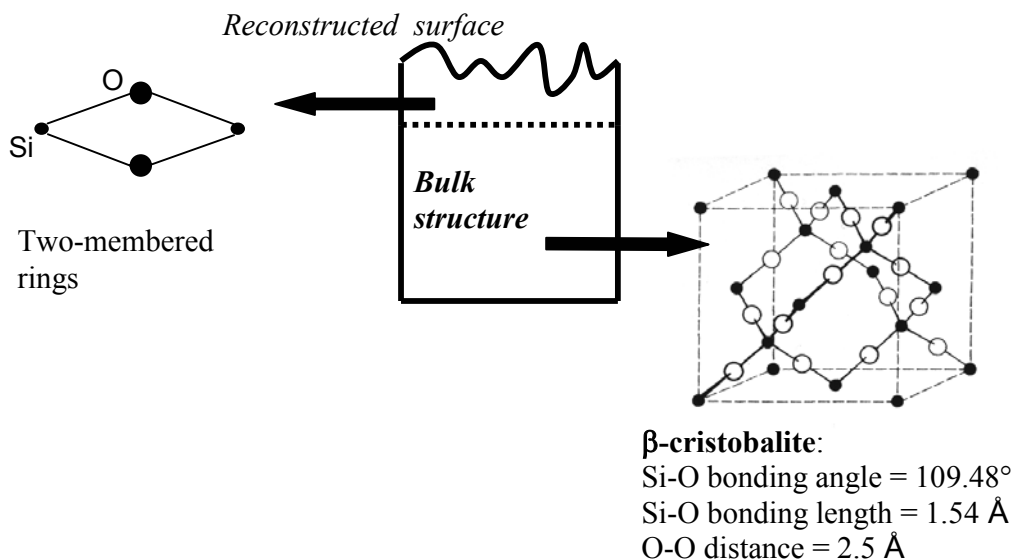

Two-membered rings

Bulk structure

β-cristobalite:
Si-O bonding angle = 109.48°
Si-O bonding length = 1.54 Å
O-O distance = 2.5 Å

Fig. 6: A reconstructed surface is depicted.

In addition to that, the chemical and structural properties of silica targets used in cell experiments, or in real systems, can be strongly connected to the chemistry and the physics of the plasma environment. As a consequence, the surface reactivity can be different under different operative plasma conditions. Since the real structure of silica surfaces cannot be easily modelled, also due to the lack of structural data determined from in situ observation, practically all the MD simulations are carried out on flat and perfect surfaces. This poses some problems when the collisional data obtained in MD studies are compared with those determined in cell experiments. On the other hand, MD data can be directly compared (and validated) with data measured in molecular beam experiments, where a molecule/atom in a well defined internal state hits a well defined single crystal surface (as in the MD simulations).

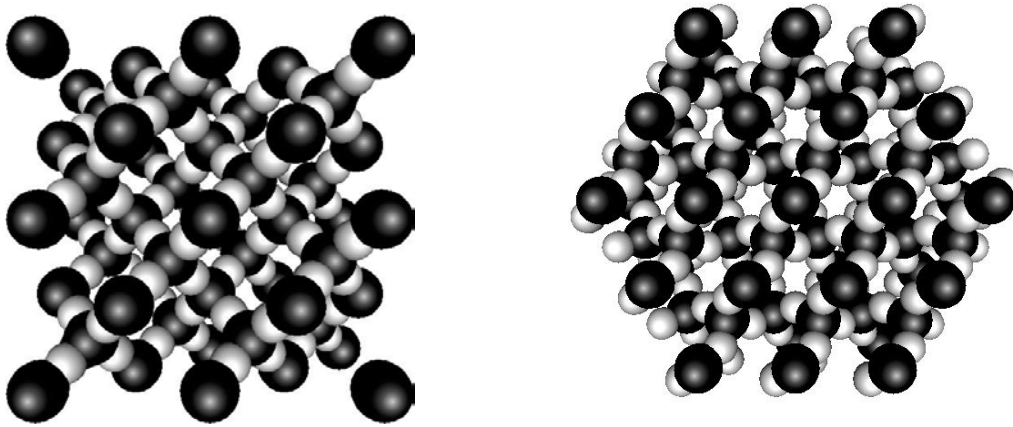In Fig.7 the top view of the β-quartz and β-cristobalite surfaces used in recent MD calculations are shown.

Fig. 7: Top view of the β-cristobalite (left) and β-quartz (right)
surfaces recently used in MD calculations.

In order to describe the phonons dynamics of the silica surface a reliable interatomic potential is necessary. Several interatomic potentials for silica polymorphs are available in the literature each of them being able to reproduce on a quite good level different structural properties of the materials. The semi-empirical BKS potential [23] is among the prime potentials used for silica polymorphs. The BKS potential is a pair-wise potential given by:

$$V_{BKS}(R_{ij}) = A_{ij}e^{-b_{ij}R_{ij}} - \frac{C_{ij}}{R_{ij}^6} + 14.4\frac{q_i q_j}{R_{ij}} \tag{14}$$

where the first term describes the purely repulsive interaction between two lattice atoms, i and j, R_{ij} being the distance between the two atoms. The second term is the C_6 attractive dispersion term, while the last term is the coulomb interaction between the charged Si and O atoms. Being the BKS potential a two-body interaction potential with few parameters, the computational time needed to describe the dynamics of the lattice phonons is lower than that required by other interaction potentials and its results in reproducing various structural material properties are often better.

The phonon frequency spectrum,$\{\omega_k\}$, for the assumed silica surface can be deduced from the normal mode analysis of the 3D lattice atom vibrations. The dynamical matrix H of the potential force constants is constructed by calculating the second derivatives of the pair-wise BKS potential applied to the first nearest atoms of the lattice

$$\left[\frac{K_{i\alpha,j\beta}}{m_{ij}}\right]_{i<j<N} = \left[\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V_{BKS}(R_{ij})}{\partial R_{i\alpha}\partial R_{i\beta}}\right] \tag{15}$$

where $K_{i\alpha,j\beta}$ stands for the inter-atomic force constants between the two nearest lattice atoms i and j, α and β are the components of their respective cartesian coordinates. N is the total number of atoms in the lattice. Then the secular equation is solved:

$$|H - E\omega| = 0 \tag{16}$$

and the eigenvalues $\{\omega_k\}$ corresponding to the frequencies for the localized vibrational normal modes of the lattice are obtained (E is the unitary matrix).

In Fig. 8, the frequency distribution calculated for a model β-quartz surface is shown for a 3D crystal consisting of 198 atoms displayed over 8 layers [22].
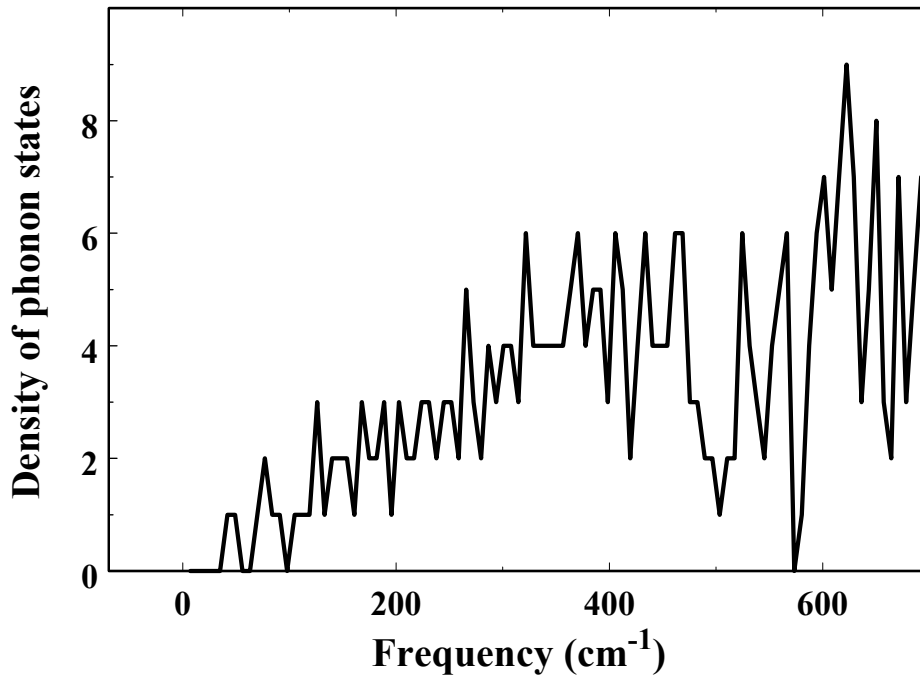

Fig. 8: Frequency distribution calculated for a 3D model crystal
of β-quartz consisting of 198 atoms displayed over 8 layers.

C.3) E-R and L-H Oxygen recombination dynamics on silica

The oxygen atom recombination on surfaces is generally described according to two extreme collisional mechanisms, the so-called E-R and L-H mechanism. The E-R reaction is a two steps process, firstly the oxygen is adsorbed at the surface in a specific surface site:

O + silica -------> O_{ad} + silica (17)

Then the adsorbed oxygen reacts with an oxygen atom approaching the surface from the gas-phase.

O + O_{ad} + silica -------> $O_2(v,j)$ + silica (18)

The first step is a thermal equilibrium process, the second reaction is the rate-determining step.

According to the L-H mechanism the reaction occurs between two adsorbed atoms which propagate on the surface from site to site and then, eventually, recombine.

$$O_{ad} + O_{ad} + silica \text{ -------> } O_2(v,j) + silica \tag{19}$$

MD simulations have been performed for both reactions catalysed by β-cristobalite in the temperature range from Ts=600K to Ts=1600K, using a semiempirical interaction potential determined according to the basic considerations discussed in a previous section. Details can be found in Ref.s [21,30]. In Ref.[21] the effect of first layer composition on the recombination reaction was also explored. In Fig. 9.a the E-R recombination probability at Ts=1000K is reported for an oxygen covered and a clean β-cristobalite surface, full dot and open dot respectively.

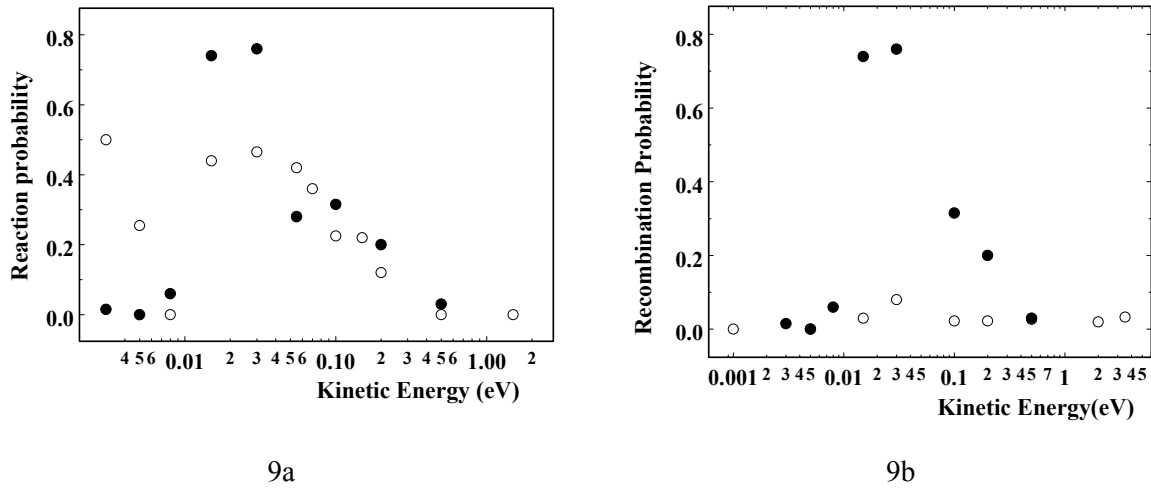9a   9b

Fig. 9: (a) The E-R oxygen recombination probability at Ts=1000K is reported for a clean (open dots) and oxygen covered (full dots) model surfaces of β-cristobalite. (b) The E-R recombination probability of O on β-cristobalite (full dot) and β-quartz (open dot) is reported as a function of the impact energy of the gas-phase oxygen atom. The surface temperature is Ts=1000K.

In Fig.9b the E-R recombination probability of O on β-cristobalite (full dot) and on β-quartz (open dot) is shown as a function of the impact energy of the gas-phase oxygen. The surface temperature is Ts=1000K.

In the trajectory simulations the oxygen atom sitting on the surface is in thermal equilibrium with the surface and randomly adsorbed within the unit cell area, the initial O_{ad}-surface distance being 2.Å. The incoming gas-phase O atom approaches the silica surface in the perpendicular orientation, the initial (X,Y) position coordinates are randomized within the unit silica cell and Z far in the asymptotic region (Z=10 Å at t=0).

From the calculated recombination probabilities the recombination coefficient γ(Ts) is calculated assuming that a flux of oxygen atoms hits the surface with a maxwellian kinetic energy distribution corresponding to the surface temperature.

The γ(Ts) coefficient is obtained by averaging the calculated recombination probabilities over a flux of O atoms having a Maxwellian kinetic energy distribution at a given temperature (usually the temperature of the surface):

$$\gamma_{E-R} = \frac{2}{K_B T_S \sqrt{\pi}} \int_0^\infty P_{E-R}\left(E_{kin}\right) \sqrt{\frac{E_{kin}}{K_B T_S}} e^{-\frac{E_{kin}}{K_B T_S}} \, dE_{kin} \tag{20}$$

where K_B is the Boltzmann constant.

The L-H reaction mechanism was also simulated and the recombination probabilities calculated for different adsorption geometries of the two ad-atoms (see Ref. [21] for details). The L-H simulation was performed at three different temperatures of the substrate: Ts=600K,800K,1000K.

The semiclassical recombination coefficient γ for the E-R and the L-H recombination is reported in Fig. 10, together with the high temperature experimental data determined recently by M.Balat et coll. on β-cristobalite using the MESOX set up [31,32].
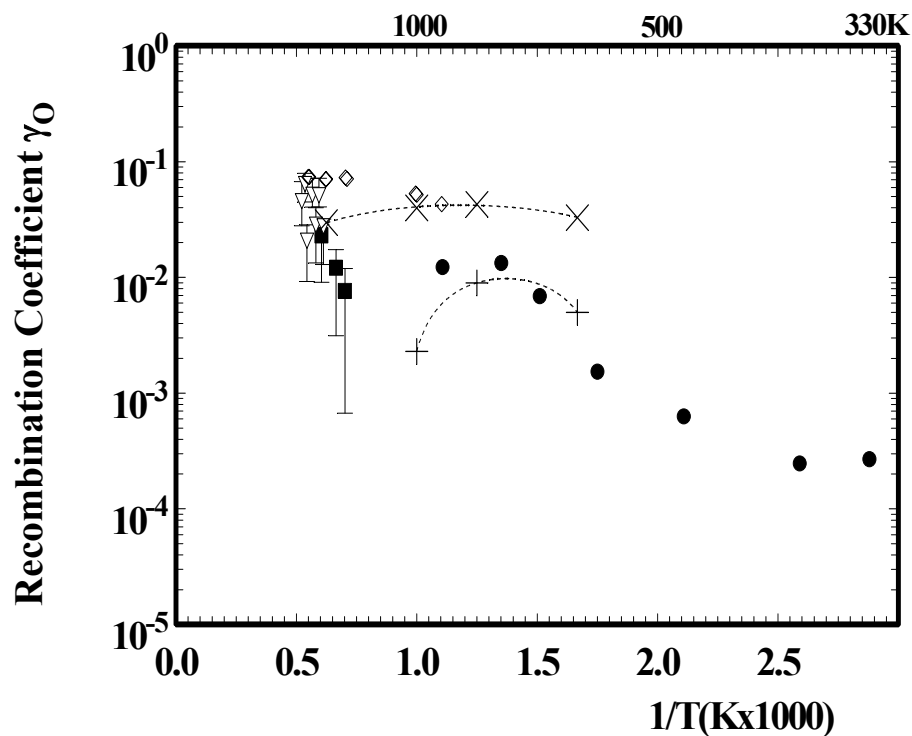

Fig. 10 : The semiclassical recombination coefficient γ for the E-R (X) and the L-H (+)
recombination reaction [21] is reported together with the experimental data
(■Scott (silica-based materials)Ref. [3]; ● Greaves et al. (silica) Ref. [4] ; Berkut et al.
(silica-based materials) Ref. [2] ; ◊ Balat et al. (β-cristobalite) Ref. [31]).

A cross-comparison between the experimental and the semiclassical results shows that a good agreement is reached between the E-R γ values and the experimental values, whereas at the lower temperature the L-H recombination probabilities match the experimental measurements. Note that a large surface temperature effect is found for the L-H recombination process, whereas T_S has only a weak impact on the E-R reaction.

The theoretical γ values should not be directly compared with the cell measurements (see the previous discussion on this point), nevertheless the agreement between theory and experiments is very encouraging.
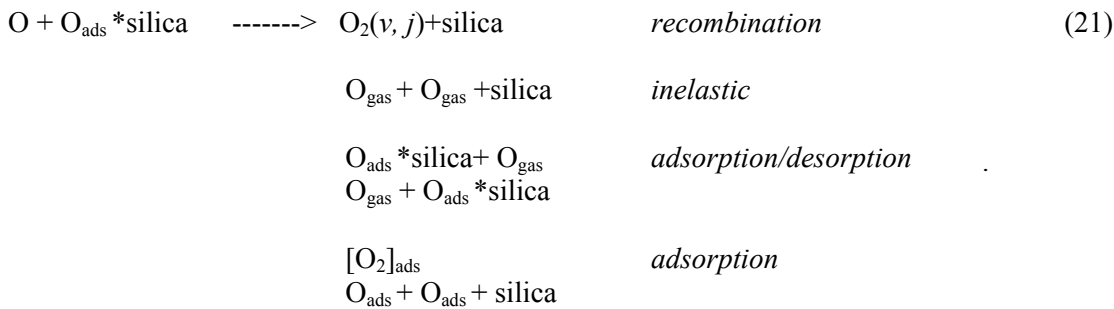
The reliability of the semiclassical approach followed in the MD simulation has been demonstrated in a combined experimental and theoretical investigation [22] recently carried out on the catalytic activity of the β-quartz. In the table below the theoretical and experimental recombination coefficient γ for oxygen recombination on β-quartz are reported at T_S=1000K and compared with the corresponding data for β-cristobalite.

SURFACE (T_s=1000K)	γ_{th}	γ_{exp}
β-quartz	0.008	0.008
β-cristobalite	0.03	0.027

Such agreement gives support to the E-R recombination mechanism as the mechanism followed in the recombination reaction process monitored in the experiments and gives further evidence of the large effect the surface crystallographic structure has on the catalytic activity of silica-based surfaces.

It is worth noticing that the semiclassical recombination coefficients reported in the table above were obtained assuming that in the initial conditions the O ad-atom is randomly adsorbed within the unit cell. The same trend is observed when the O ad-atom is chemisorbed in a specific silica site, on top of a Si surface atom. In this case in fact we get γ= 0.04 and γ=0.3 for O recombination on β-quartz and β-cristobalite at Ts=1000K, respectively. That is, although the recombination coefficients are higher than that measured in the experiments, the ratio γ(cristobalite)/γ(quartz) is about a factor two higher compared to the ratio observed in the experiments.

The semiclassical MD calculations have revealed some aspects that cannot be observed directly in the experiments. The dynamics is, in fact, quite complex with several collisional processes that are in competition with the O_2 formation at the surface.

O + O_{ads}*silica   -------> O_2(*v, j*)+silica   *recombination*   (21)

                                         O_{gas} + O_{gas} +silica   *inelastic*

                                         O_{ads}*silica+ O_{gas} *adsorption/desorption*   .
                                         O_{gas} + O_{ads}*silica

                                         $[O_2]_{ads}$ *adsorption*
                                         O_{ads} + O_{ads} + silica

In particular, the adsorption and adsorption/desorption processes of the oxygen atoms are quite effective in a large collisional energy range. This is shown in Fig.11 where the probabilities for the different surface processes active on β-cristobalite are reported at T_S=1000K.
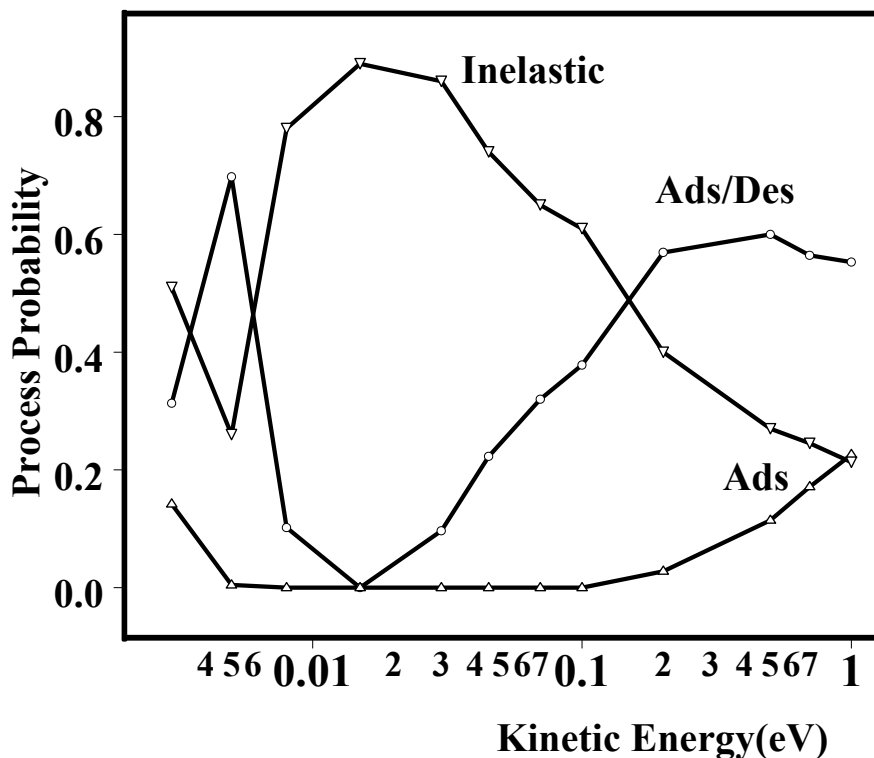
Fig. 11: Probability for the different surface processes of Eq. (21) on β-cristobalite. T_S=1000K.

In the full range of the explored energies the adsorption and adsorption/desorption processes are quite effective. This is an interesting result that could be of some relevance for the surface damage problem. The residence time for these processes is large so that chemical reactions between the adsorbed atoms and the surface Si/O atoms can be eventually be promoted (with the formation of SiO_x volatile compounds).

In Fig. 12 the probability for the different reaction channels of Eq. (21) is reported but for the interaction of N atoms with β-cristobalite. In the initial conditions the N ad-atom is chemisorbed in a specific chemisorption site, that is on top of a Si surface atom, in thermal equilibrium with the silica surface at Ts=1000K. The gas-phase N hits the surface in the normal configuration, with the (X,Y) coordinates randomly varied within the unit silica cell of the β-cristobalite. The potential energy surface assumed in the dynamics is the LEPS surface of Fig. 4 obtained from DFT calculations. A further aspect of great relevance for the surface heating problem concerns the energetics of the recombination process. Reactions (18), (19) are both strongly exothermic so that part of the exothermic energy can be gained by the formed O_2 molecules while the remaining part can be transferred to the substrate as heat flux. The energy flux pathways are shown in Fig 13. Here the energy partitioning among the translational (E_{tr}), rotational (E_{rot}) and vibrational motions (E_{vib}) of the O_2 molecules and the surface phonons (ΔE_{ph}) is shown as a function of the impact kinetic energy for oxygen formation on β-cristobalite at Ts=1000K (a) and Ts=1600K, respectively.
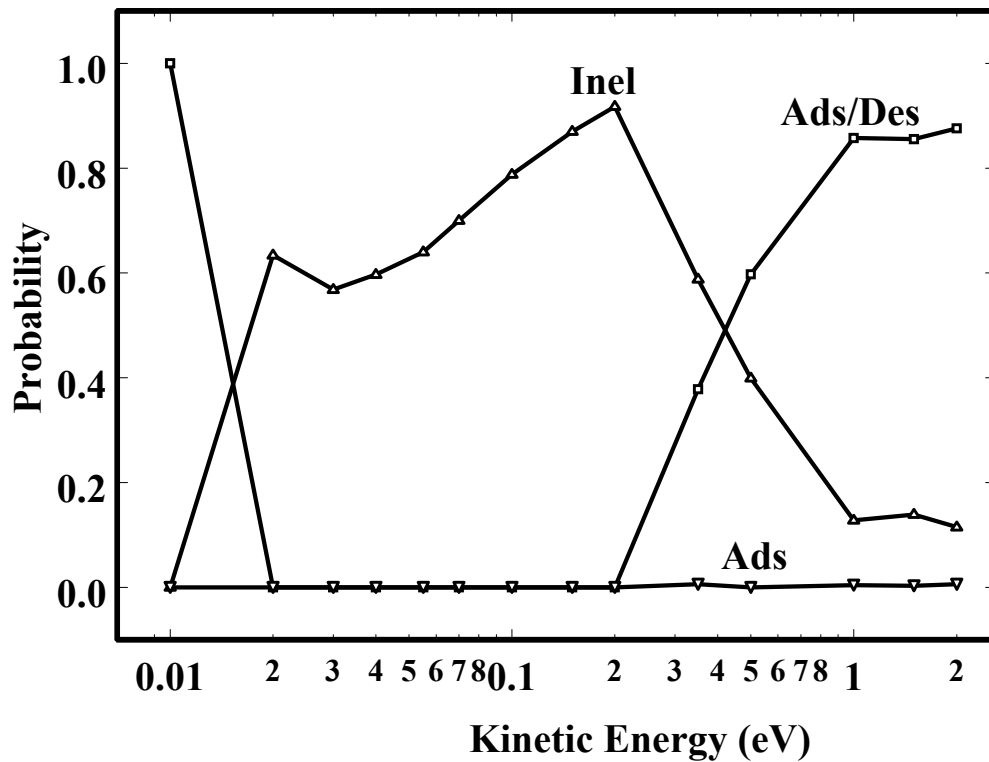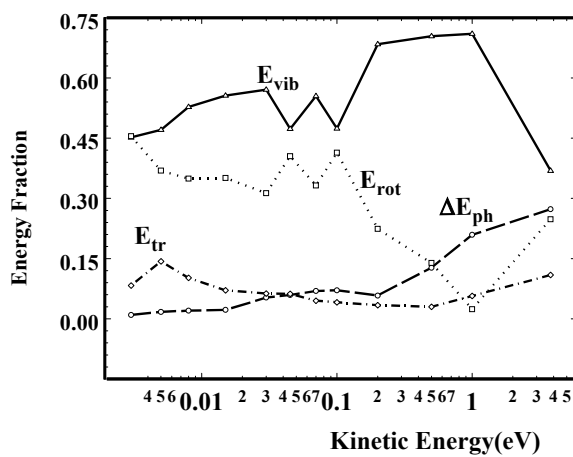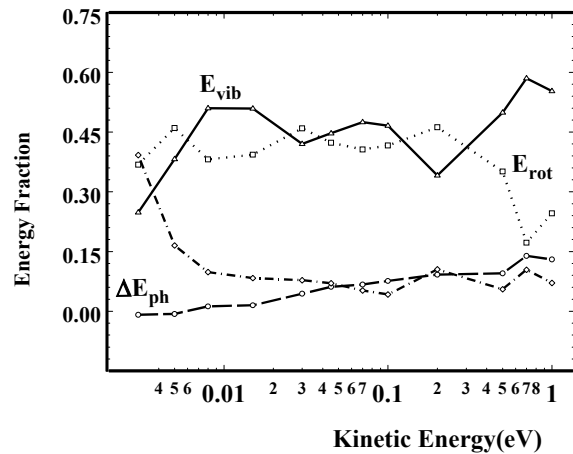
Fig. 12: The same as for Fig.11 but for N + N_{ad} on β-cristobalite. N_{ad} is initially adsorbed on top of a Si surface atom. The PES of Fig. 4 was assumed in the dynamics.

13a

13b

Fig.: 13: Energy partitioning among the translational (E_{tr}), rotational (E_{rot}), vibrational (E_{vib}) motions of the O_2 molecules and the surface phonons (ΔE_{ph}) as a function of the impact kinetic energy in the reaction: O + O_{ad} *silica ---> O_2(v,j) + silica . (a) Ts=1000K and (b) Ts=1600K.

It is evident that the largest fraction is primarily shared among the vibrational and rotational motion of O_2, while only a small fraction of the total energy is transferred to the silica surface as phonon excitation energy. However, at the higher energies and Ts=1000K almost 30% of the exothermic energy appears as

phonon energy. Interesting different behaviours of the reaction energetics can be pointed out by comparing the results reported at the two different surface temperatures. As a consequence of the energy sharing mechanism, the O_2 molecules are formed in highly vibrationally excited state.

This is shown in Fig.14 where a typical vibrational distribution is reported for the recombination reaction over β-cristobalite at E_{kin}= 0.003eV, Ts=1000K.
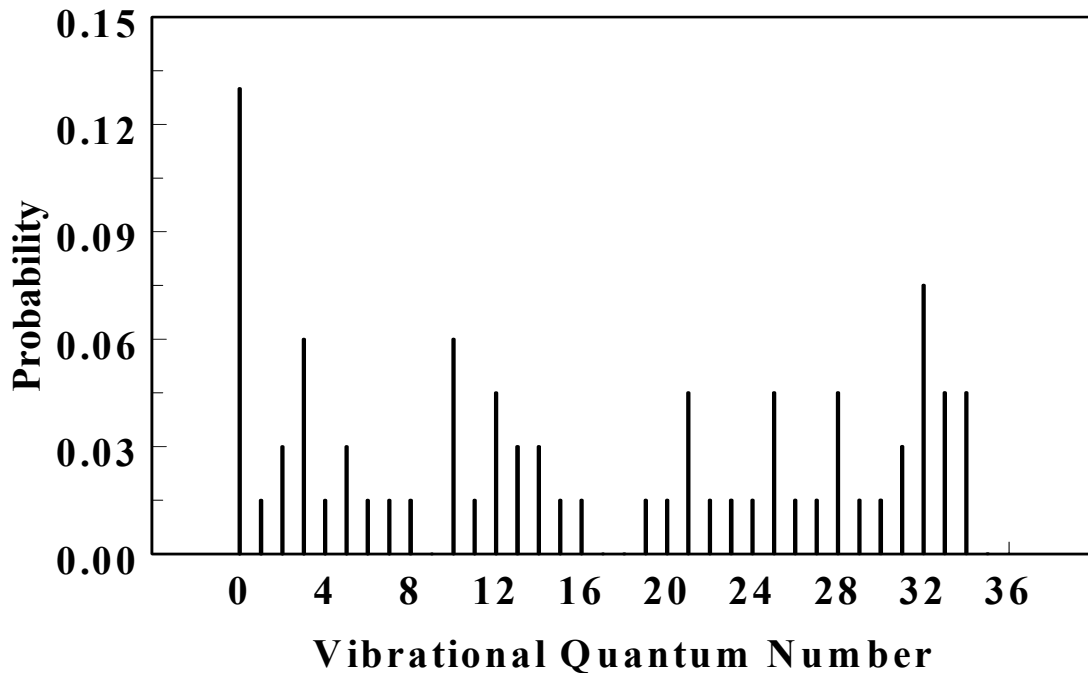

Fig.14: A typical vibrational distribution of the O_2 molecules formed after atom recombination over β-cristobalite at E_{kin}= 0.003eV and T_S=1000K.

The distributions are characterized by a peak in v=0, but virtually all the vibrational levels are populated and involved in the surface process. The distributions are in non-thermal equilibrium.

From the calculated vibrational distribution, the vibrational state-selected recombination coefficient γ(v,Ts) can be easily obtained. The spectral distribution of γ for O recombining on β-cristobalite at Ts=1000K is shown in the Fig.15. The γ(v) coefficients are an important ingredient for the kinetic modelling of the chemistry of the boundary layer [33-34] where, very likely, a non-thermal equilibrium condition is established due to the fluodynamics conditions.
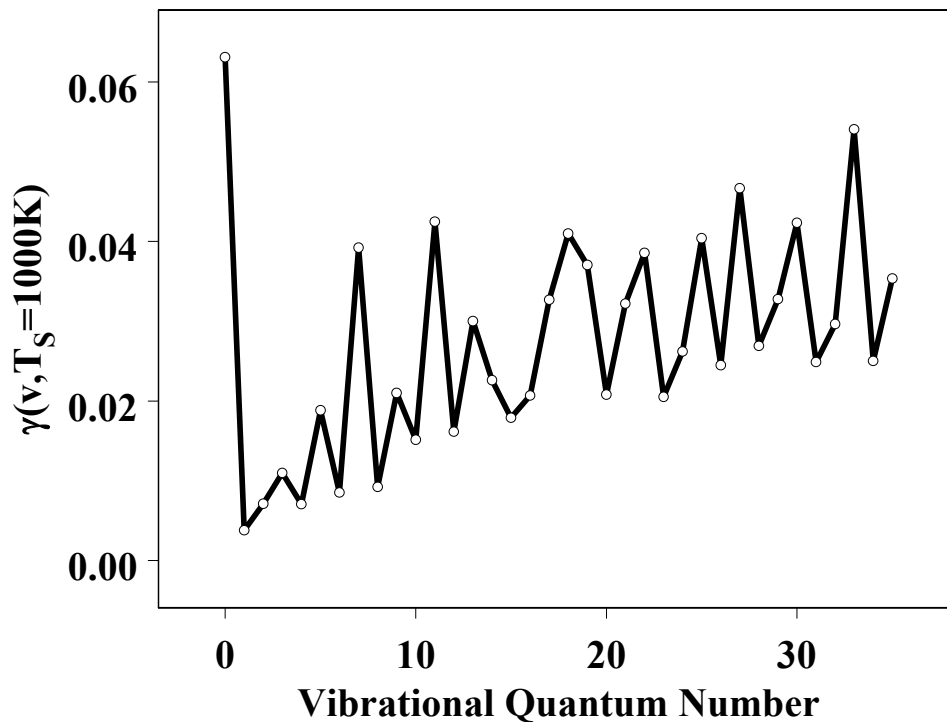
Fig.15: The vibrational spectral distribution of the recombination coefficient γ for O₂(v)
formed in the reaction: O + O$_{ad}$ *silica ---> O$_2$(v,j) + silica is reported as
a function of the vibrational quantum number v. T$_S$=1000K.

The energy transferred to the surface in the recombination processes is generally claimed to be among the primary sources of the surface damage. Molecular dynamics simulations for O (and N) recombination on silica surfaces have shown that this energy is only a small fraction of the total energy delivered in the reaction, so that the energy accommodation coefficient β should be less than one (contrary to what is generally assumed in kinetic modelling calculations, i.e β=1). Indeed, the overall energy transferred to the substrate is the result of a complex mechanism and it is due to the concurrence of various surface processes. The adsorption processes can play an important role since the energy exchanged with the surface can be quite large. In Fig. 16 a typical adsorption collision:

O + O$_{ad}$ + silica ------->   [O$_2$]$_{ad}$ + silica-------> O + O$_{ad}$ + silica/β-cristobalite   Ts=1000K
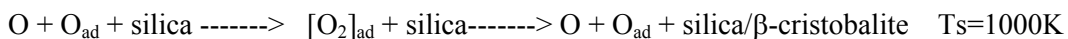
is reported together with the corresponding energy transferred to the silica substrate.
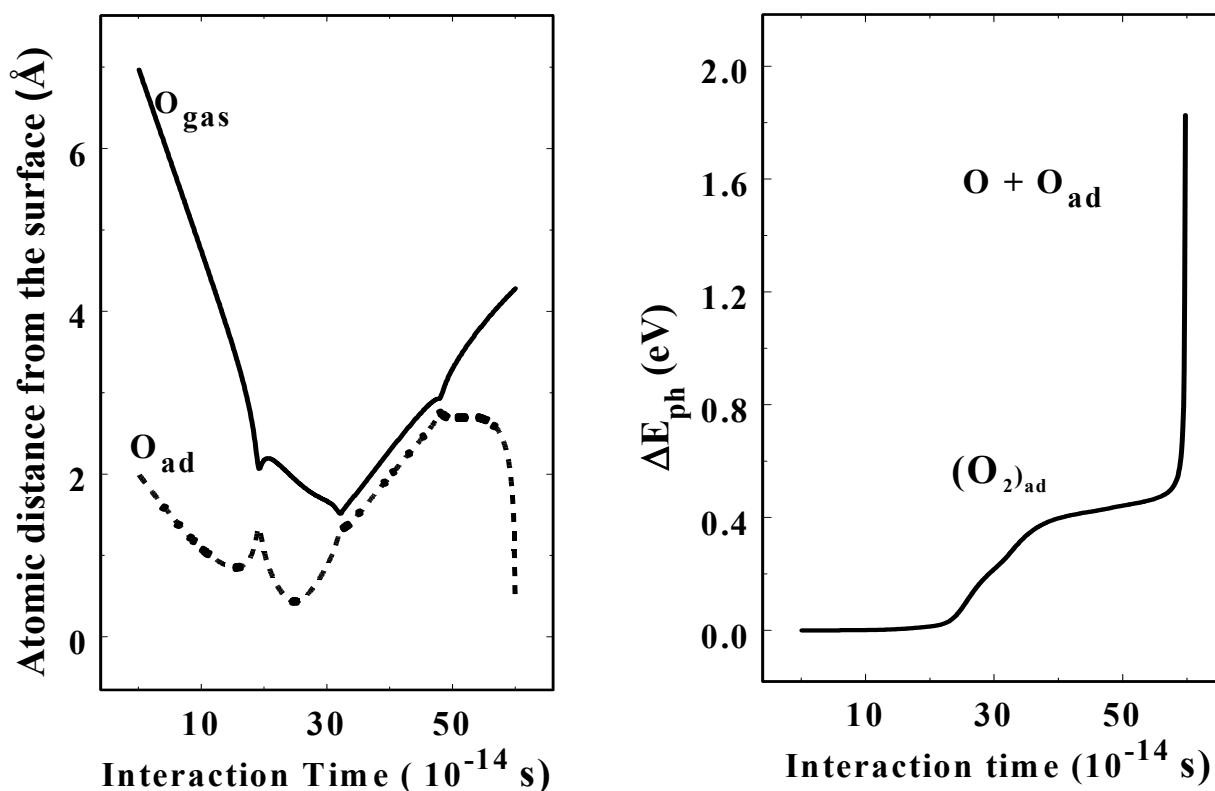
Fig. 16: A typical collision for the adsorption process: O + O$_{ad}$ + silica --->[O$_2$]$_{ad}$ + silica--->
O + O$_{ad}$ + silica/β-cristobalite is reported together with the corresponding energy
transferred to the silica substrate. a) the z coordinate of the two oxygen atoms
is reported as a function of the collisional time. b) the corresponding
energy transferred to the silica surface is shown. T$_S$=1000K.

FINAL REMARKS

The development and applications of the semiclassical approach to the molecule-surface dynamics have made possible MD simulations of elementary surface processes involving oxygen and nitrogen atoms over silica model surfaces relevant to the TPS system. In the simulations various important behaviours of the surface substrate, such as the phonon structure, the surface polymorphic modifications, the site and the intrinsic surface temperature effect can be incorporate and their impact on the surface catalytic activity studied at a very elementary level. Collisional data, such as the global and the vibrational state selected recombination coefficient γ, the energy distributions in the product states, the energy flow pathways and the energy released to the surface in the recombination reaction as well as in the adsorption/desorption processes can be determined. The accuracy of the calculated coefficients mostly relies on the accuracy of the interaction potential assumed in the dynamics, rather than to the approximations made in the collisional model. As a matter of fact, the determination of a reasonable PES for these complex heterogeneous systems is the most critical problem to solve. MD simulations have some limitations, among the others: i) the surface processes can be followed in the short time scale (few picoseconds). ii)the surface inserted in the simulations is, in general, a flat perfect crystal surface, iii) the dynamics occurs on an adiabatic potential surface so that surface processes involving electronically excited states are not explored. Though the inclusion of these effects add more complexity and computational time requirements, the importance of MD calculations for the catalytic systems candidate for the future TPS systems will become more evident in the next future.

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