Dynamics of Dissociative Chemisorption: Cl_2/Si(111)-(2 × 1)

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We report the first simulation of a surface chemical reaction performed with the *ab initio* molecular dynamics approach. A set of trajectories with different initial conditions has been generated for single Cl_2 molecules impinging on the Si(111)-2×1 surface with incident translational energy of 1 eV. We observe a high probability of dissociation, triggered by active sites on the π-bonded chains, and accompanied by a large surface response and local rehybridization effects.

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Dissociation of molecules at semiconductor surfaces is an important process from both a scientific and technological point of view [1]. The underlying physics depends largely on the incident energy of impinging molecules. At lower incident energies ($\lesssim 2$ eV) the nature of the dissociation is believed to be mainly chemical while at high energies the dissociation is driven by direct momentum transfer to the atoms in the molecule [2]. Despite its technological importance to etching, chemical vapor deposition, and heterogeneous catalysis the chemically driven breakup of molecules is not very well understood. The reason is that a realistic model of a surface chemical reaction in this regime must start from a reliable description of the semiconductor surface and charge transfer processes between the surface and the molecule. This is a major difficulty for all approaches based on empirical interatomic potentials [3]. For that reason we have performed fully *ab initio* molecular dynamics (MD) simulations of a surface chemical reaction, employing state-of-the-art plane-wave pseudopotential techniques [4].

To date most understanding of dissociative chemisorption has relied on simplifications to the potential energy surfaces (PES) of the crash process or on assumptions on the topology of the surface by schematizing it as flat or modeling it by a jellium surface. The latter assumptions are clearly not valid for a corrugated reconstructed semiconductor surface. Most of the existing calculations either performed a full classical [5] or quantum [6] treatment of the dynamics but on an entirely empirical PES [5], or a model PES fitted to *ab initio* calculations [3], or a simplified *ab initio* [6] PES of low dimension, or they started from a realistic PES but disregarded the dynamics [7]. While these methods have provided significant insights into the process of dissociative chemisorption the underlying assumptions in all these approaches could bias the dynamics of dissociation and defeat the objective of determining how the outcome of surface collision depends on the position and orientation of the molecule on the surface, what triggers the dissociation, how the surface responds to dissociation, and whether dissociation occurs spontaneously as the molecule collides with the surface or whether it first sticks and breaks up later. These are the primary questions which our *ab initio* simulation addresses.

We have chosen to study Cl_2 on the π-bonded Si(111)-2×1 surface [8] first because of the availability of experimental results on dissociative adsorption of halogen molecules at semiconductor surfaces [9], and second because it is a convenient system for first-principles work. The convenience derives from the fact that Cl can be relatively easily treated with pseudopotentials, the vibrational frequencies are low enough to make quantum effects on atomic dynamics negligible, and unlike metal surfaces, the generation of electron-hole pairs upon molecular collision is absent. In addition the bonding and electronic structure of Cl overlayers on Si(111) have been studied experimentally [10] and theoretically [11] and are relatively well understood. Our choice of fairly high incident translational energies (1 eV) of impinging molecules is motivated by a high value of the initial sticking coefficient s_0 for related systems [12] and by a relative insensitivity of s_0 to surface reconstruction at higher incident energies [13]. Our *ab initio* simulation provides details of the dynamics of initial stages of the surface chemical reaction which are presently inaccessible to experiments. Hence our simulations represent an augmentation of real experiments and point the way to simulations of larger technological relevance such as F_2 or O_2/Si(111)-7×7.

The main results of our MD simulation are as follows. We observe (1) sticking and dissociation in each case, suggesting a sticking coefficient close to unity in this regime, (2) both spontaneous breakup of Cl_2 molecules upon collision with the surface as well as sticking of Cl_2 in a short-lived precursor state followed by molecular decomposition, the mode depending on molecular orientation, (3) the onset of dissociation is triggered by stretching the molecular bond due to the interaction with "active sites" on the π-bonded chains, and (4) the molecular dissociation is accompanied by a large surface response and rehybridization effects.

All the calculations described below have been performed using massively parallel computation [14]. Our procedure consists of generating a set of trajectories for single Cl_2 molecules impinging on Si(111)-2×1 [8]. At the beginning of each trajectory the centroid of the Cl_2 molecule was located 2.8 or 4.8 Å above the π-bonded

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chain, depending on the position in the surface unit cell. The initial horizontal position and the molecular orientation relative to the surface for our five simulations are described in Table I. These positions were chosen to sample most of the important surface sites and molecular orientations within our limited statistics. For simplicity, in all cases the incident translational energy of the Cl_2 molecule was chosen to be 1 eV with small vibrational and no rotational excitation.

We have used a repeated slab geometry with four double layers and an almost square $2\sqrt{3}\times 3$ surface unit cell with horizontal dimensions 11.5 Å×13.3 Å. This cell is large enough to eliminate spurious image interactions. The slabs are separated by a vacuum region of 14.3 Å. We impose inversion symmetry on the slab. All 96 silicon atoms and the chlorine atoms are allowed to move. The silicon slab is initially in its equilibrium configuration, with the constituent atoms at rest. In the electronic structure part of the simulation we used the local density approximation (LDA) of density functional theory with Perdew and Zunger's parametrization of the exchange and correlation energy [15]. We have optimized the Cl pseudopotential using the technique of Rappe *et al.* [16] and for Si we use a Kerker pseudopotential [17]. We obtain converged results with these potentials at an energy cutoff of 10 Ry. The pseudopotentials were applied in the Kleinman-Bylander form [18] using the real-space projection technique [19]. The electronic states were expanded at the Γ point of the Brillouin zone. We quenched the Kohn-Sham orbitals at each MD step with a precision of 5×10^{-6} eV/atom using the band-by-band conjugate gradients minimization [20] combined with the extrapolation technique for the electronic wave functions [21]. We allow for reoccupation of the electronic states and level crossings, which is important for a correct description of the weakening of the molecular bond due to charge transfer processes from the surface to the molecular antibonding orbitals. The classical equations of motion for the ions have been integrated using the Verlet algorithm [22] with a step length of $\Delta t = 20$ a.u. (~ 0.48 fs). We follow each trajectory for between 200 and 400 fs which is enough elapsed time to permit the collision with the surface to occur and to classify the outcome.

With the *ab initio* approach used in our study the only remaining approximations are the LDA and the assumption of classical adiabatic dynamics. We expect the last approximation to play a minor role in the processes studied here. We have checked the effect of the LDA error on our simulation by studying the formation energy of silicon tetrachloride: $Si + 2Cl_2 \rightarrow SiCl_4$. Using the same parameters as in our simulation we find that the calculated energy differs from the experimental value ($\Delta E_{\text{exp}} = -7.29$ eV) [23] by less than 4%, thus indicating a realistic description of the energetics. The main limitation in our simulation derives from poor statistics.

TABLE I. Horizontal position and orientation of the molecule relative to the surface. *CH* denotes π-bonded chain, *V* valley between two π-bonded chains, and *H* a hole underneath a sixfold ring extending from the chain to the valley. *P* denotes an orientation of the molecule parallel to the surface; *N* denotes a position along the normal. ⊥ (∥) denotes position of the molecule perpendicular (parallel) to the π-bonded chain.

	Trajectory No. 1	2	3	4	5
Orientation	*CH-P* ⊥	*V-P* ⊥	*V-P* ∥	*H-N*	*CH-N*

We now turn to the analysis of our results. Figure 1 shows a ball-and-stick model of the atomic configurations at the beginning of the simulation, after collision of the molecule with the surface, and at the end of each trajectory.

The first two trajectories represent two extreme choices of initial conditions. In the former the molecule strikes the surface in a region of high electronic density generated by the unsatisfied Si bonds in the π-bonded chains. In the latter the molecule is directed towards the region of low electronic density in the valley. However, in both cases the Cl_2 molecule spontaneously dissociates upon collision with the surface, the outcome being dichlorination with both atoms of the impinging Cl_2 bonded to the substrate. In response the π-bonded chains deform appreciably and locally rehybridize towards sp^3 bonding, lifting the silicon atoms above the π-bonded chain. It is evident that the π-bonded chains play a critical role in both dissociation processes and in the first trajectory the motion of the silicon atom is crucial in capturing the second chlorine. Interestingly, dissociation occurs also in trajectory No. 3, where the molecular axis is parallel to the π-bonded chains and the molecule-chain interaction is much less direct.

The dynamical scenario in the cases where the molecular axis is oriented along the surface normal (trajectories No. 4 and No. 5) initially involves monochlorination. The Cl_2 molecule remains in a precursor state with the other Cl atom weakly bonded to the chemisorbed Cl and bond length stretched by ~50%. The initial conditions for trajectory No. 4 were chosen to determine whether the Cl_2 molecule could penetrate into the subsurface region since the hole underneath the sixfold ring is intuitively the most natural entrance channel. Interestingly, the Cl_2 molecule does not show any tendency to penetrate the subsurface region and is instead displaced laterally towards the π-bonded chain. This demonstrates that even at rather high incident energies parts of the surface unit cell are inaccessible to the molecule. In this geometry the energy gained from formation of the Si-Cl bond is largely deposited in the substrate. At longer times the molecule tilts parallel to the π-bonded chains in trajectory No. 5 and across the valley towards the neighboring π-bonded chain in trajectory No. 4. In both cases the length of the molecular bond increases as the molecule tilts. In trajectory No. 5 this clearly results in dissociation, with the

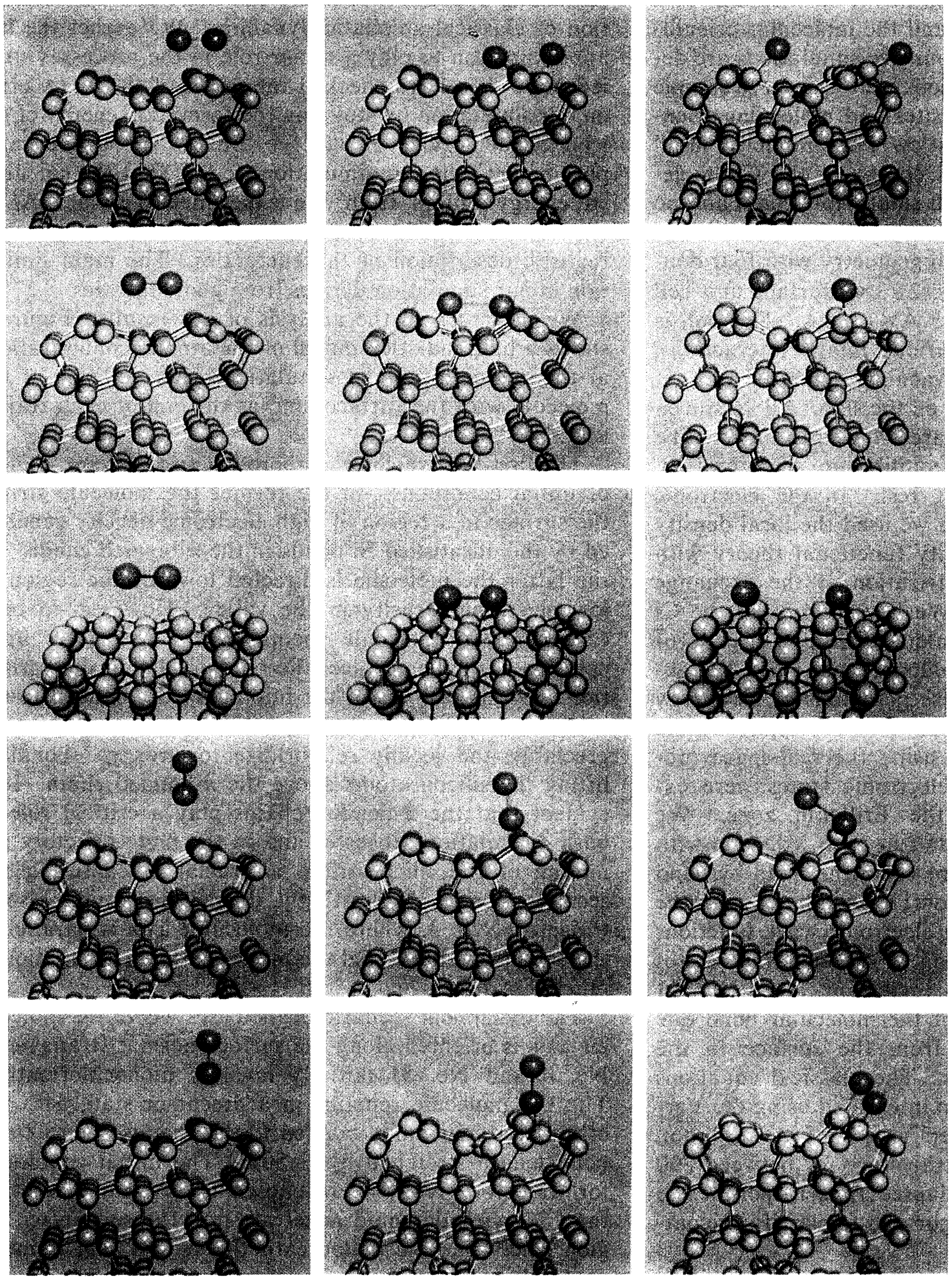

FIG. 1. Ball-and-stick model of chlorination of the Si(111)-2×1 surface for the five trajectories (cf. Table I). Left, middle, and right panels show the initial configurations, the configurations after collision with the surface, and at the end of each trajectory, respectively. In trajectory No. 3 the slab is rotated by 90°. Note the large local deformations of the π-bonded chains and the tendency to increase sp^3 bonding in the reaction product.

final reaction product again being dichlorination of the surface. An interesting feature in this simulation is that a local defect, which changes the buckling of the π chain and the topology of the bonding in the silicon substrate, is created by the collision. Full dissociation was not completed in trajectory No. 4 on the time scale of our simulation. The probable outcome, however, is dichlorination by further stretching the Cl_2 bond on approaching the dangling bonds on the neighboring π-bonded chain.

The previous analysis is based primarily on distances between atoms. It is of interest to study the breakup of the molecular bond and the creation of chemical bonding to the substrate. This is done for one of the trajectories in Fig. 2, which shows the isovalue surfaces of self-consistent valence electronic charge density. Breaking of the molecular bond and rebonding to the surface is clearly visible. A more detailed analysis of the electronic properties will be presented elsewhere [24].

In conclusion, we have presented the first fully *ab initio* MD simulation of molecular dissociation of Cl_2 on Si(111)-2×1. A set of trajectories has been generated starting from different initial conditions and at transla-

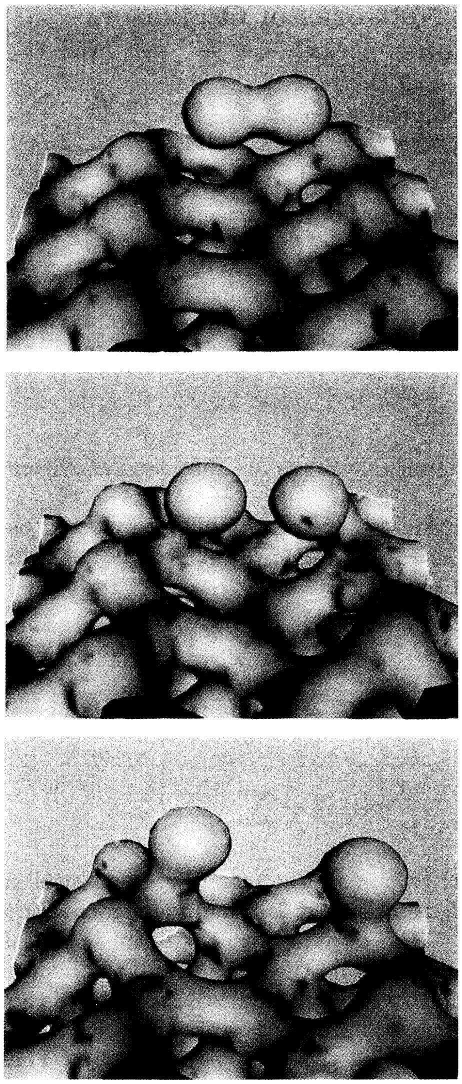

FIG. 2. Isovalue surfaces of the valence electronic charge density corresponding to the configurations of trajectory No. 2 shown in Fig. 1.

tional energies of 1 eV. We find sticking and dissociation in all the cases studied. The Cl_2 molecules either breakup upon collision with the surface or remain sticking in a short-lived molecular state followed by dissociation at a later time. The "active sites" on the π chains are found to play an important role in triggering the decomposition process. Large surface response and local surface rehybridization effects accompany the molecular dissociation. Overcoming the major limitation of the present approach, that of limited statistics, will be possible using larger parallel computers.

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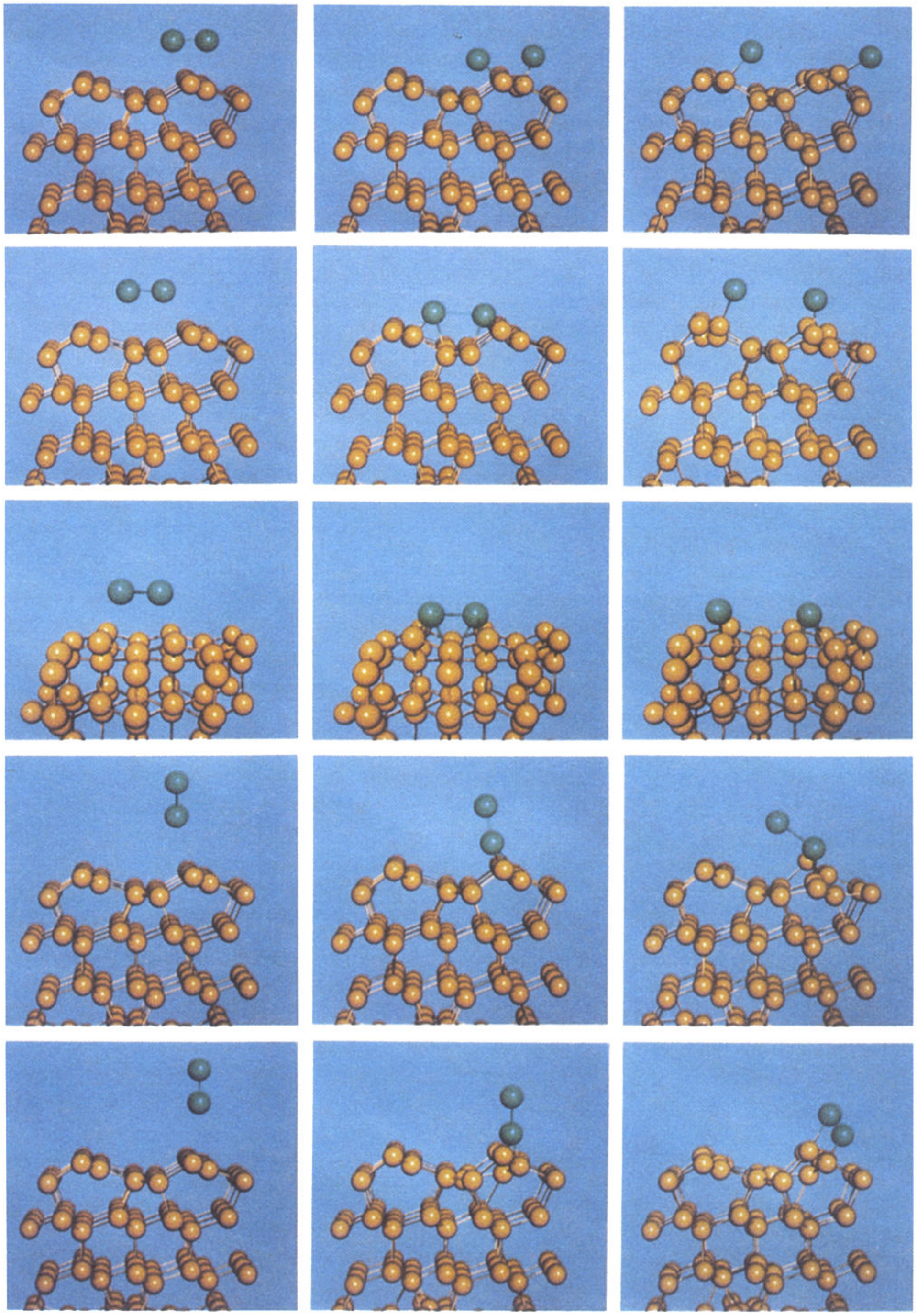

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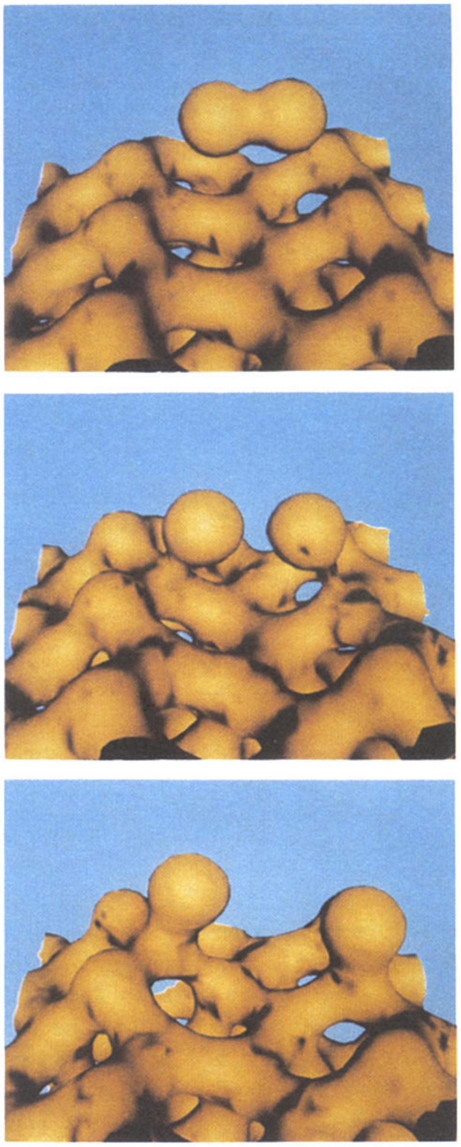

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