

## Surface chemistry from first-principles: dissociative chemisorption of $\text{Cl}_2$ on Al(111)

Nicola Marzari and Roberto Car  
*Chemistry Department, Princeton University NJ*

Ab-initio molecular dynamics simulations are a useful tool to study the energetics and thermodynamics of comparatively large systems, while retaining the accuracy of a full quantum-mechanical treatment. Recent algorithmic advances allow us to extend this approach to metallic systems, at a computational cost comparable to that of semiconductors or insulators. We report here the first study of a chemical reaction at a metal surface performed with full ab-initio molecular-dynamics simulations at finite temperature. The trajectories of  $\text{Cl}_2$  molecules impinging on a thermalized Al(111) surface have been studied using a  $11.5 \times 11.5 \times 30 \text{ \AA}$  supercell containing an Al(111) slab with 8 layers of 16 atoms, separated by  $\sim 14 \text{ \AA}$  of vacuum. The trajectories have been followed for up to 2 ps each, and different initial conditions for the orientation of the molecule and the point of first impact have been probed. The highly exothermic reaction leads in all cases to dissociative chemisorption. The energy released is often transferred directly into kinetic energy of the adsorbed species, leading to a large translational motion of the isolated Cl atoms on the surface (“cannonball” dissociation). The transferral of charge and the filling of bonding or antibonding orbitals can be followed during the simulations, highlighting the interplay of chemical and kinetic effects. The latter are enhanced by aluminum and chlorine having comparable atomic masses. At variance with the commonly-assumed model of fcc-hollow adsorption for halogens on metals, we find that on aluminum the on-top site is favored as a rest position for the chlorine adatoms.