Unusual reactivity at silicon from surface constraints

Lisa Pecher, Ralf Tonner*

Philipps-Universität Marburg, Fachbereich Chemie, 35032 Marburg, Germany, E-Mail: tonner@chemie.uni-marburg.de

Silicon is one of the most important elements in material science and its low-index surfaces are widely used substrates, e.g. for transistor technology. Recently, increasing research efforts are made toward functionalizing the surface with organic and inorganic adsorbates. Intriguingly, the constraints imposed on the silicon atoms as being part of a solid surface create arrangements that are hard to achieve in molecular chemistry and lead to surprising reactivity. One prominent example is the buckled silicon dimer at the reconstructed Si(001) surface (Fig. 1) which barely has molecular analogues.[1] We explored the impact of this unusual arrangement on the chemical reactions at this surface, which has been termed a "molecular reagent" in the past,[2] with computational methods. This leads to a (re-)discovery of molecular chemistry concepts like S_N2 reactions.[3] Surprisingly, not only the surface dimer is reactive but also saturated subsurface atoms (Si_{sub}) can play a key role in the observed surface chemistry which will be explained with molecular orbital analysis.[4]

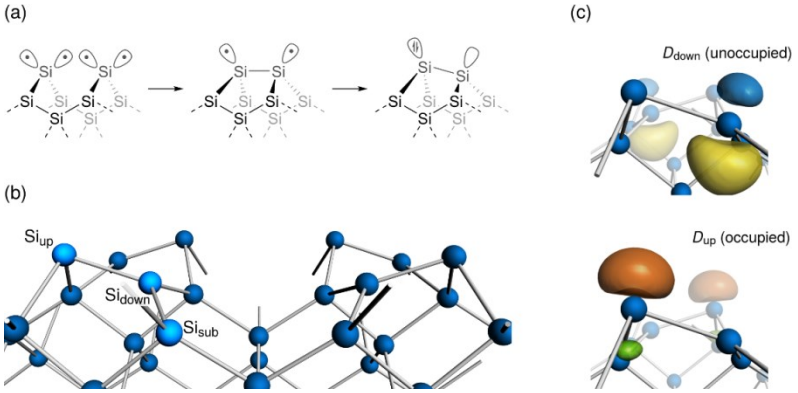

Figure 1. (a) Schematic depiction of the Si(001) surface reconstruction process. Dots indicate unpaired electrons. (b) Structure of Si(001) in the most stable reconstruction, c(4 × 2), with nomenclature used subsequently. (c) Crystal orbitals of a Si(001) slab.

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