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## Surface $S_N2$ reaction mechanisms of $H_2O$ on the Chlorinated Si(100) surface

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The surface adsorption of  $H_2O$  on the chlorinated Si(100) surface has been studied with MP2 as well as multi-reference MP2 theories. Two kinetically highly accessible reaction pathways have been found. They are composed of five fundamental processes as shown below: (1) the chlorine adsorption on both ends of Si dimer with large exothermicity, (2)  $S_N2$  reaction of  $H_2O$  on the chlorinated Si surface, (3) the *intra*-dimer condensation reaction, (4) the *secondary*  $S_N2$  reaction of  $H_2O$ , (5) the over-saturated  $S_N2$  reaction of  $H_2O$ . It is shown that the overall surface adsorption of  $H_2O$  on the chlorinated Si surface has a relatively small reaction barrier of 23.9 kcal/mol, in accord with experiment, while the *intra*-dimer condensation reaction has a large reaction barrier of 53.2 kcal/mol.  $S_N2$  transition state structures commonly has 4-membered ring, in which the O-H and the Si-Cl bond activations occur simultaneously, which would not usually happen in solution chemistry. During the reaction processes, many weak hydrogen bonding species were identified. The reaction pathways based on these mechanisms illustrate that the surface adsorptions are mainly determined by the nucleophilicity of incoming oxygen atom.