56c Accelerated Molecular Dynamics Simulation of Thermal Desorption

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Thermal desorption has been the focus of much research in surface science. Much recent emphasis has been placed on categorizing the desorption of alkanes from a variety of surfaces including graphite [1], gold [2], platinum [3], and magnesium oxide [4]. Alkanes represent prototypical large molecules with many degrees of freedom. It is not clear how these degrees of freedom affect the desorption energetics. Experimentally, temperature programmed desorption (TPD) is a powerful tool to characterize desorption parameters such as the binding energy and the prefactor. Although different surfaces exhibit similar binding energies for alkane desorption, the prefactors have been observed to vary over many orders of magnitude for different surfaces. The origins of these variations are currently unclear. Studies also conflict on the functionality of the prefactor with chain length. Experiments on gold [2] and graphite [1] show a prefactor that is constant with chain length, although the values differ by six orders of magnitude. Experiments on magnesium oxide [4] and simulations on gold [5] show a prefactor that increases with increasing chain length. The increase in prefactor on magnesium oxide is validated through a rigid-rotor statistical mechanical argument. To probe these issues, we have developed an all-atom model to simulate alkane desorption. The entire simulation is run within the framework of transition state theory (TST) to obtain rate constants. Accelerated MD through the use of umbrella sampling extends the time scale of the simulation so that desorption events can occur. Our work shows that the prefactor increases with increasing chain length for small alkane molecules desorbing from graphite. It has a value greater than that of alkanes desorbing from gold, consistent with the slightly higher binding energy on graphite. We predict that the prefactor will become constant as the chain length increases and the molecule can no longer be treated as a rigid rotor and internal degrees of freedom must be taken into account. Coverage is varied to examine the effect of environment on desorption parameters.

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