The role of lattice reconstruction in gas-surface reactions

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In modeling the reactions that take place on metal and other surfaces, the substrate is generally treated either as rigid, or the lattice atoms are allowed to vibrate harmonically about their equilibrium positions. We consider several systems where the lattice can reconstruct in the presence of the adsorbates, significantly modifying the reactivity. One example is the dissociative adsorption of methane on Ni(111). Density Functional Theory (DFT) was used to examine the energetics of dissociation, which takes place directly over a Ni atom. We find that at the transition state, this Ni atom would prefer to pucker out of the surface by a few tenths of an Angstrom, which lowers the barrier by a few tenths of an eV. To determine if the heavy metal atom actually has time to reconstruct during this high-energy reaction, we implement high dimensional fully quantum scattering calculations. We find that the lattice has time to at least partially reconstruct, significantly increasing the reactivity relative to a static lattice. Increasing the temperature of the lattice is also shown to strongly increase reactivity, particularly at lower incident energies. The reactions of H atoms with graphite (0001) have also been explored. In order for an H atom to chemisorb onto a graphite terrace, the bonding carbon atom must pucker out of the surface plane by 0.36 Angstroms. While first shown by DFT, this has since been confirmed experimentally. This reconstruction dominates the energetics and dynamics of chemisorption. Moreover, the chemisorption of one H atom significantly modifies the energetics of subsequent H chemisorption at the neighboring sites, all involving various types of lattice reconstructions. This lattice puckering is shown to also play a role in the Eley Rideal abstraction of chemisorbed H atoms by gas phase H atoms, to form highly excited molecular hydrogen.