Thermal recombination reactions on metal surfaces: Transition state theory with dynamical corrections.

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In order to accurately describe atomic scale motion associated with chemical reactions that are relevant to many important industrial processes, the experimentally evidenced non-adiabaticity in gas-surface interactions must be included. Furthermore, to fully characterise the influence of Born-Oppenheimer approximation [1] (BOA) failure on reactions is essential to develope the next generation of predictive theory of surface chemistry. A model systems for which appears likely that electronic coupling can influence reactivity are H_2 recombinative desorption on the Au(111) and Cu(111) surfaces. This systems have a late barrier for dissociation located close to the surface and with large internuclear distance [2]. Such characteristics, as well as current measurements by metal-insulator-metal (MIM) junctions when H atoms interact with Au [3], indicate that electronic excitations might be relevant in the recombination rate constants.

Transition state theory (TST) is undoubtedly the most successful and widely employed theoretical approach for studying reaction rates involving species that undergo reaction at or near thermal-equilibrium conditions. To go beyond the BOA, non-adiabaticity is introduced within the dynamic factor that corrects the TST constant rate. An accurate description of the electronic excitations is accomplished with the recently developed ab-initio molecular dynamics with electronic friction (AIMDEF) method [4]. This method is based on the local density electronic friction (LDFA) [5] method, which was recently shown to successfully model translational energy loss measurements for H colliding with Au(111) [6].

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