What rules the reactivity of thermal N_2 molecules on W surfaces?

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The knowledge at atomic scale of the electronic properties and dynamical processes that rule gas–surface reactivity is crucial to understand and control key processes as oxidation, corrosion, hydrogen storage and heterogenous catalysis, among others. In the past, the theoretical analysis of surface reactivity was limited by the difficulty to provide a reliable description of all the variables involved in this kind of processes. The recent development of theoretical methods, based on ab initio calculations of the multidimensional potential energy surface, allows now a quite accurate description of the molecule–surface interaction. This achievement has contributed to get new insight into the field: assumptions that were conventionally accepted are currently questioned in view of the results obtained with more refined calculations. Our recent study on the dissociation of N_2 molecules on the W(110) surface is a good example of it [1, 2].

Early studies based on work function measurements and flash desorption spectroscopy showed that N_2 on W has the largest crystallographic anisotropies as regards adsorption yields and sticking coefficients [3, 4]. Later measurements of the initial sticking coefficient S_0 as a function of the N_2 initial kinetic energy E_i showed that, while dissociation is considerable for vanishingly small beam energy on the W(100) surface [5], it is roughly two orders of magnitude smaller at T=800K on the W(110) face [6]. This remarkable difference in reactivity has been conventionally attributed to the non-activated and activated characters of the two processes respectively. It has been shown [7] that the high reactivity on the (100) surface is indeed associated with the fact that the N_2/W(100) system is non activated, i.e., there exist paths leading to dissociation without any energy barrier. On the (110) surface of W, however, the dissociation probability is of the order of a few 10^{-3} for beam energies below 300 meV, it increases rather quickly towards 0.2 until 1 eV, and goes on rising more smoothly until a value of 0.3 for an energy of 2.5 eV [6]. This behavior is usually considered as typical of that of an activated system, i.e., no path leads to dissociation without overcoming a barrier.

Using density functional theory to calculate the six dimensional potential energy surface and classical dynamics, we show that the large difference in reactive behavior between the (100) and (110) faces at low energies is entirely determined by the shape of the potential energy surface far from the surface (above 3 Å) [1, 2]. The explanation therefore lies neither on the geometry and energy of the final state (2 N atoms on the surface) nor on the presence or absence of an intermediate well in which the molecule could be temporarily trapped. Such a well exists for both the (110) and (100) faces. The crucial point is that only for the latter the well is accessible to low-energy molecules. We also show that there are non-activated paths to dissociation in the interaction of N_2 with W(110) surfaces. Nevertheless, the value of the sticking coefficient S_0 at low impact energies E_i is very small. This result contradicts the standard along which dissociation probabilities that increase with the incident kinetic energy are the result of a direct activated process. Furthermore, it contravenes the common assumption that intermediate states (such as dynamic trapping in our case) and non-activated paths always result in large values of the sticking coefficient at very low energies.

Finally, we will also investigate a new open question under discussion, the validity of the adiabatic approximation in the description of thermal molecules interacting with surfaces. Most of the theoretical studies that analyze gas–surface reactivity are based on such an approximation, that neglects energy dissipation effects. Here, we present a model to include the contribution of electron–hole excitations to the molecular dynamics and analyze under which conditions this energy dissipation channel can be relevant.

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