Dissociation and Vibrational Deactivation of H_2 and D_2 on Metallic Surfaces: a Theoretical Survey

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Dissociative chemisorption of roto-vibrationally excited H_2 molecules:

$H_2(v,j)$ + wall ------> H + H + wall

hydrogen atom recombination at the wall:

H + H + wall -----> $H_2(v,j)$ + wall

vibrational excitation/de-excitations in molecule-surface (wall) collisions:

$H_2(v,j)$ + wall ----> $H_2(v',j')$ + wall

these are elementary processes of great importance in the classical field of chemical catalysis as well as in the field of non-equilibrium reaction kinetics, including plasma/wall processes, chemical vapour deposition, nuclear reactors.

The direct observation of such processes in real physical situations is not very easy, and this explains why the rate coefficients relevant to heterogeneous processes, typically the recombination coefficient γ, the dissociation probability of vibrationally excited H_2 molecules and the accommodation coefficient β, are very poorly known. On the contrary, the state-to-state rate constants for a large number of molecular processes involving $H_2(v)$ in the gas phase are known to a high degree of accuracy [1].

In the last few years the dissociative chemisorption of H_2 and D_2 on metallic surfaces has been extensively studied both experimentally and theoretically. Aim of the present paper is to report on a detailed molecular dynamics study on catalytic interactions of H_2/D_2 in a specific roto-vibrational state on single crystal Cu surfaces.

In contrast to transition metals, where the surface processes have very low energetic barriers, the dissociation of H_2 and D_2 on Cu is rather slow, and this is consistent with the existence of high activation barriers. The interesting aspect of such interactions is therefore that the corresponding rate coefficients depend critically on the vibrational (and rotational) state of the molecule approaching the surface. These and other aspects of the $H_2(v,j)/Cu$ interactions, usually not considered in the kinetic modelling of non-equilibrium plasma processes, will be presented and discussed on the basis of recent molecular dynamics studies [2]. In particular, the dissociation probabilities for H_2 in a specific vibrational state, together with the recombination coefficient γ and the vibrational distribution of the desorbing H_2 molecules, will be given for a specific translational temperature of the particles impinging the surface at a given surface temperature.

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