USING DIFFRACTION TO STUDY THE HYDROGEN DISSOCIATION DYNAMICS AT SURFACES: EXPERIMENT AND THEORY

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The dissociative chemisorption of molecules on solid surfaces is the basic step in many surface chemical reactions. Owing to its simplicity, special interest has been devoted to the scattering dynamics of hydrogen on metal surfaces since it can be considered as the first step towards an understanding of the dynamics of more complex systems. The possibility of carrying out six-dimensional dynamical calculations [1-3] has renewed the interest in diffraction studies with H_2/D_2 molecular beams. The diffraction of H_2 and D_2 molecular beams is in principle quite similar to the case of He, the major difference being the possibility of rotational-state transitions in the case of molecular scattering [4]. This leads to the appearance of additional diffraction peaks in the angular distributions, which are called rotationally inelastic diffraction (RID) peaks.

Here were report on a combined experimental and theoretical study performed on Pd(111) and NiAl(110), which are prototypes of surfaces with a low and a high dissociation barrier, respectively. The H_2 diffraction experiments have been performed with the apparatus recently transferred from the Freie Universitaet Berlin to the Surface Science Lab at the UAM. In this experimental set up the angular distribution of the scattered H_2 molecules is analyzed with a quadrupole mass spectrometer mounted on a two-axis goniometer. This allows rotations of 200º in the scattering plane (defined by the incident beam direction and the normal to the surface) as well as ±15º away from the scattering plane for a fixed incident angle. Elastic in-plane and out-of-plane diffraction were observed over the incident energy range 75-157 meV in both systems. For H_2/Pd(111), the most conspicuous feature observed in the diffraction spectra is the large intensity scattered out-of-plane [5]. For D_2/NiAl(110), RID peaks were also observed. The absolute $0 \Rightarrow 2$ transition probability was found to increase from 10 to 20 % in the energy range investigated, whereas the one corresponding to the $2 \Rightarrow 0$ transition remained constant at 10 % [6].

To understand these findings, we have calculated the potential energy surface (PES) for both systems using Density Functional Theory (DFT) at the level of the GGA and using the slab/supercell approach. A continuous representantion of the 6D PES was obtained by interpolation using the Corrugation Reducing Procedure, whose high accuracy has been proved for several systems. The computed PES accounts for the adsorption energy threshold and vibrational enhancement effect observed in previous experiments. We compare classical trajectory dynamical calculations based on this PES with the results of our diffraction experiments. Our analysis suggests that out-of-plane diffraction is the dominant diffraction pattern for non-activated systems. This is the consequence of a dynamical effect associated with grazing incidence and not of a purely "static" one such as surface corrugation [5]. On activated systems, although in-plane diffraction is the dominant diffraction channel, out-of-plane diffraction may also occur at higher incident energies.

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