A theoretical-computational approach to highlight the role of long-range interactions in the energy exchanges at surfaces: the case of nitrogen molecules on tungsten.

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The long-range anisotropic interactions affect the evolution of microscopic elementary processes occurring under a variety of conditions. In particular, they determine all basic features of the precursor state (the adduct formed by collisions of reagents) that further evolves towards the product final states of fundamental chemical/physical processes occurring in gaseous and condensed phases, as well as at the gaseous-solid/liquid inter-phases [1,2]. However, the role of such interactions is often not described at the required level of detail. The long-range forces play a primary role in the interaction of molecules with a surface, therefore, only an accurate description of the latter permits to properly account for all basic details of molecular scattering by surface, especially under thermal and sub-thermal conditions where the role of weak long range forces is exalted [3]. Recently, we have proven that the Improved Lennard Jones (ILJ) potential function, formulated in Ref. [4] for the interaction in the gas phase, is also suitable for an accurate and detailed description of the processes taking place at the gas-surface interface, providing better results in comparison with those from Density Functional Theory (DFT) functionals corrected for long-range interactions [3]. Over time we have developed a well-tested theoretical-computational approach to study the dynamics of elementary processes, promoted by gas-surface collision events. Such an approach exploits Molecular Dynamics (MD) calculations based on a chemical state-to-state semiclassical collisional method (see for instance Refs. [5,6] and references therein).

In this framework, we have undertaken the study of nitrogen molecules, taken in well-defined initial roto-vibrational states (j_i, v_i), interacting with a tungsten surface. The interest in this topic arises from the fact that nitrogen impinging on this surface is considered a prototype case useful to understand and explain the processes occurring on other metal surfaces of interest in nitrogen industrial processes, the ammonia synthesis *in primis*. Lately, MD calculations have been performed by us adopting a new Potential Energy Surface (PES), in which long-range interactions are suitably characterized through the ILJ function. Accordingly, for the sticking probability of nitrogen molecules on W(001), we were able to provide results further improving the already good comparison, recently obtained with calculations performed using interactions from DFT method corrected for long-range van der Waals contributions, with the experimental data [6].

In this contribution, the results obtained for the inelastic scattering of nitrogen molecules on two different tungsten surface planes (001) and (110) are presented and discussed with respect to process probability, roto-vibrational accommodation coefficients, final roto-vibrational distributions, reaction energetics and reaction mechanism. The final target is to highlight the role of long-range forces in the energy exchanges at the surface. In Figure 1 the scattering probability of $N_2(0;0)$ from W(001) is reported as a function of molecule collision energy (E_{coll}). It appears that the probability of molecular

inelastic scattering is an activated process that rises steeply to a nearly constant value of 0.7 independently of collision energy.
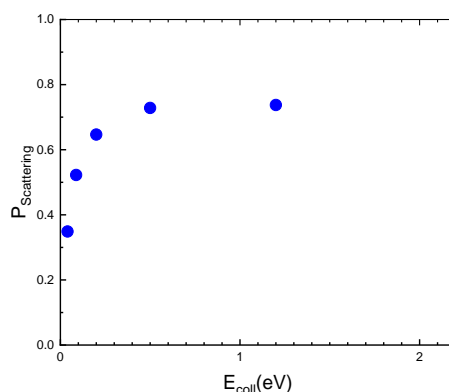

Fig. 1: Inelastic scattering probability for $N_2(0;0)$ from W(001). The surface temperature is 300K.

Molecules scattered from W(001) are rotationally excited and this excitation, from a preliminary investigation of the reaction mechanism, can be attributed to the energy exchange mechanisms that are activated when the molecule approaches the surface due to the formation of a precursor state stabilized by long-range forces. As an example, in Figure 2 the final rotational distribution of $N_2(0;0)$ colliding with E_{coll}=0.088eV on the surface is displayed.
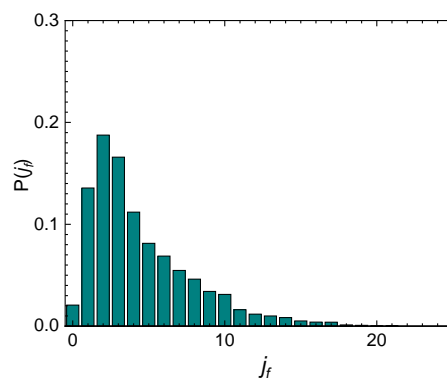

Fig. 2: Final rotational distribution for $N_2(0;0)$ colliding W(001) with E_{coll}=0.088eV. The surface temperature is 300K.

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