# Supporting Information (SI)
# Dynamics of $N_2$ sticking on W(100): The decisive role of van der Waals interactions

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In Fig. S1 we show a representation of the $N_2$ molecule over the surface unit cell for several configurations of interest. On the left panel and on top right panel we show the configurations described in Table 1, which lie in the minimum energy path to dissociation. On the bottom right panel we show the lowest energy configuration for the non-dissociated molecule. It corresponds to the molecule placed in the hollow site with $\theta=90°$, $\phi=45°$, Z=1.28Å and r=1.31Å. This configuration is not present in the minimum energy path to dissociation. It is worth noting that this configuration and the configuration (a) from Fig. S1 correspond to potential minima in six dimensions, while the other two configurations depicted here are 2D-minima.
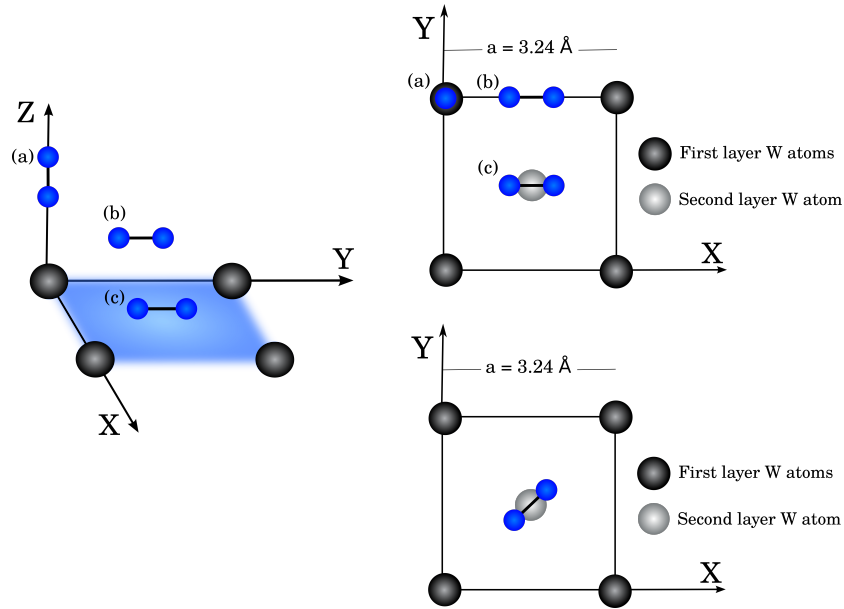


Figure S1: Left panel: Representation of the different positions of the $N_2$ molecule over the surface unit cell in the three configurations of Table 1. (a) Molecule positioned in the top site at a distance of Z=2.68Å from the surface and with an internuclear distance of r=1.13Å. (b) Molecule located over the bridge site with Z=1.82Å and r=1.20Å. (c) Molecule over the hollow site with Z=1.04Å and r=1.43Å. On the right hand side we show the top view of the selected positions (upper panel) and the lowest energy configuration for the non-dissociated molecule (bottom panel).

The additional figure presented here is aimed to show the full curve for the probability of $N_2$ molecules to reach a distance of Z=2.5Å from the W surface as a function of initial collision energy for the PW91-PES and the vdW-DF2-PES. In Fig. S2 we show that at this distance from the surface a deep minimum at around $E_i \simeq 40$meV is present with the PW91-PES, and when van der Waals forces are included, nitrogen molecules experience smaller barriers in the entrance channels allowing the majority of them to approach the surface (>90% at the minimum). This phenomenon is a direct cause of the non-monotonic behavior that the full sticking probabilty ($S_0$) shows in this low regime of energies.
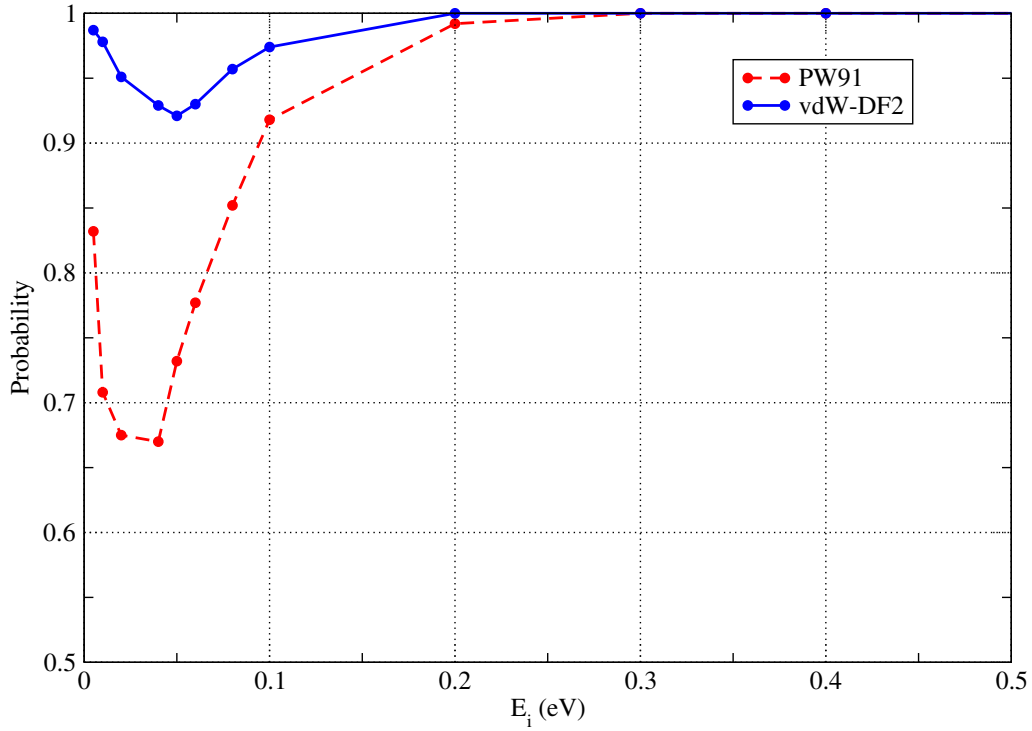


Figure S2: Probability for 10 000 trajectories to reach a distance of Z=2.5Å from the surface as a function of the initial kinetic energy under normal incidence for the PW91-PES (red circles) and the vdW-DF2-PES (blue circles).