Surface Diffusion Rates of Adsorbates from Molecular Quantum Dynamics Calculations

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The formula proposed by van Hove in 1954 [1] for the dynamical structure factor (DSF) related to particle scattering at mobile adsorbates has recently been extended to the case when the adsobates' excited states have finite lifetimes due to relaxation phenomena [2].

The new formula is evaluated quantum mechanically using wave functions, energies and lifetimes of vibrational states obtained for H/Pd(111) from first principle calculations. The results are capable of capturing qualitative features of diffusion rates measured for similar systems [3], as well as with recently measured values for this system, if one assumes that the total rate obtained from the DSF is the sum of a diffusion and a friction rate.

In this talk, we show that quantum effects such as tunneling and resonances might be important for the diffusion of adsorbates even at room temperature.

[1] L. van Hove, Phys. Rev. 95, 249–262 (1954).

[2] T. Firmino, R. Marquardt, F. Gatti, W. Dong, J. Phys. Chem. Lett. 5 4270-4274 (2014).

[3] A. P. Jardine, G. Alexandrowicz, H. Hedgeland, W. Allison, J. Ellis, Phys. Chem. Chem. Phys. 11 3355-3374 (2009).