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Ro-vibrational spectroscopy in reduced dimensionality of physisorbed H₂ molecules on a metallic surface (Ag, Cu)

Eddy Bernard, Céline Houriez, Alexander O. Mitrushchenkov, Marie Guitou and Gilberte Chambaud

Laboratory MSME- University of Paris-Est Marne la Vallée, 77454 Champs sur Marne, FRANCE

Ro-vibrational energy levels of a H₂ molecule physisorbed on a metallic surface (Ag or Cu) Cu(100) are calculated, using a 5D or 2D potential energy function determined at different levels of approximation: periodic or cluster representation of the system, DFT or highly correlated wavefunction description.

In many studies, the metallic surface is described by a periodic 2D-representation, namely a slab representation and the electronic calculations are performed using Density Functional Theory (DFT) methods. The H₂ molecules are either bound to the surface or very close to it. Alternative studies have been performed modeling the surface as a metallic cluster. In the physisorption domain, the weak interaction is governed by van der Waals (vdW) forces and it is well known that standard exchange-correlation functionals provide a poor description of such dispersion interactions. However, recent studies have shown that sophisticated DFT approaches can give promising outcomes for such difficult cases and some data for physisorption energy can be used, as recently shown, to adjust new DFT functionals.

In recent theoretical studies on the H₂/Cu system [1] using an embedding approach of a cluster model consisting of 22 Cu atoms, it has been shown that the chemisorption of H₂ can be satisfactorily reproduced. On the contrary, the description of the physisorption domain is more delicate. A good test of the accuracy of the potential energy function in this domain is to compare the ro-vibrational spectroscopic data with EELS experiments [2]. The large rotational constant of H₂ associated with the anharmonic and anisotropic van der Waals potential, results in a coupling between the rotation of H₂ and the stretching along the physisorption well. Such data exist for H₂ on Cu(100) and on Ag(111).

Highly correlated electronic calculations on the cluster model have been performed with the 2012.1 version of the MOLPRO code [3] using the coupled cluster CCSD(T) method. The embedding method has been applied within the ONIOM approach. The periodic calculations have been performed with the VASP code [4] and various functionals.

In our calculations, the center of mass of the H_2 molecule has been moved on the surface (X and Y coordinates) in the periodic approach, otherwise it was kept on the Z axis on top of the central Cu atom and the interatomic distance H-H was kept at the equilibrium geometry of the H_2 molecule, 0.74 Å. The 2D potential energy cuts were obtained by varying only the Z distance and the θ angle between 0 and 90 degree.

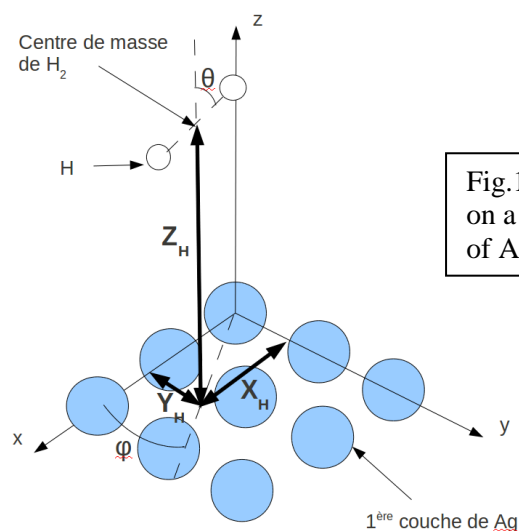


Fig.1: 5D coordinates of H_2 on a metallic (100) surface of Ag.

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