Spectroscopy of physisorbed molecules

Gilberte Chambaud, E. Bernard, C. Houriez, A. Mitrushchenkov, Marie
Guitou

HAL Id: hal-01081752

https://hal-upec-upem.archives-ouvertes.fr/hal-01081752

Submitted on 10 Nov 2014

SPECTROSCOPY OF PHYSISORBED MOLECULES

Eddy Bernard, Céline Houriez, Alexander Mitrushchenkov, Marie Guitou and <u>Gilberte Chambaud</u>

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

Ro-vibrational energy levels of H_2 molecules physisorbed on a metallic surface (Ag (111) or 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 the physisorption domain, the weak interactions between the H_2 molecules and the metallic surface are 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 H_2/Cu system [1] using an embedding approach of a cluster model consisting of 22 Cu atoms, it has been shown that the chemisorption of H_2 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 the comparison with ro-vibrational spectroscopic data with EELS experiments [2]. The large rotational constant of H_2 associated with the anharmonic and anisotropic van der Waals potentials, results in a coupling between the rotation of H_2 and the stretching along the physisorption well. Such data exist for H_2 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 using the coupled cluster CCSD(T) method. The embedding method has been applied within the ONIOM approach. The periodic calculations have been performed with DFT approach within the VASP code and various functionals.

In our calculations, the center of mass of the H_2 molecule has been moved on the surface in the periodic approach, otherwise it was kept on the Z axis on top of the central Cu/Ag 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. The 5D potential energy cutes include the X and Y coordinates on the surface and the φ angle (helicopter rotation of H_2 parallel to the surface).
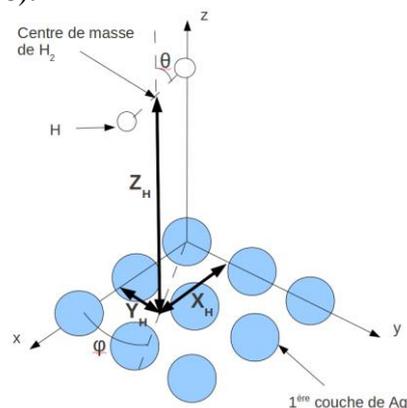
REFERENCES

1. F. Göltl, C. Houriez, M. Guitou, G. Chambaud and Ph. Sautet, J. Phys. Chem. C, 118, 5374-5382 (2014)
2. K. Svensson, J. Bellman, A. Hellman and S. Andersson, Phys. Rev. B **71**, 245402 (2005)