



HAL
open science

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

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

► To cite this version:

Gilberte Chambaud, Alexander Mitrushchenkov, C. Houriez, Marie Guitou, E. Bernard. Ro-vibrational spectroscopy in reduced dimensionality of physisorbed H₂ molecules on a metallic surface (Ag, Cu). Workshop HeSSSMe 2014, Pilar de Lara Castells, Oct 2014, Madrid, Spain. hal-01081746

HAL Id: hal-01081746

<https://hal.science/hal-01081746v1>

Submitted on 10 Nov 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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 H₂ 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 H₂ 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.

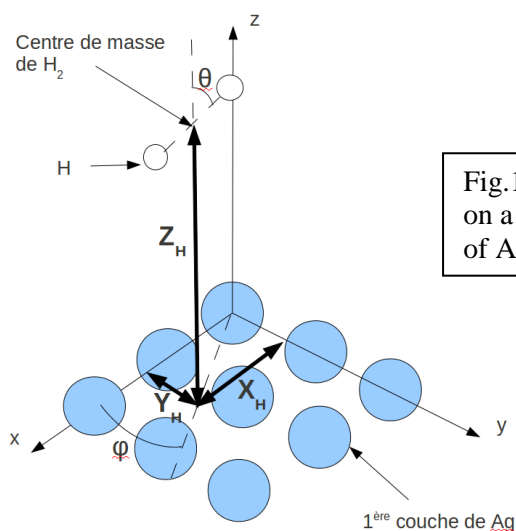


Fig.1: 5D coordinates of H₂ on a metallic (100) surface of Ag.

Acknowledgments: The authors thank the ANR-2010-BLAN-720 DYQUMA for financial support of one of us (CH)

References :

1. F. Göttl, 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)
3. MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang
4. Kresse G. Hafner J., *Phys. Rev. B* **48**, 13115 (1993); Kresse G., Furthmüller J., *Comput. Mat. Sci.* **6**, 15 (1996)