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Spectroscopy of H₂ physisorbed on a Cu(100) surface

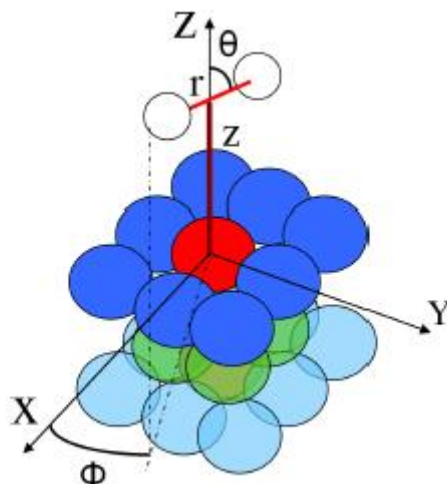
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Rotation and vibration energy levels of a H₂ molecule physisorbed on a Cu(100) surface are calculated, using a 2D potential energy function determined with high level electronic calculations and a cluster model to represent the Cu surface.

In most of the previous studies, the metallic surface is described by a periodic 2D-representation, namely a slab representation, the calculations are performed using Density Functional Theory (DFT) methods and 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 a cluster model consisting of 13 Cu atoms, it has been shown that the chemisorption and physisorption of H₂ layers can be satisfactorily reproduced by highly correlated electronic wavefunctions. On the contrary, there is no unique functional that can provide reliable data for close and long distance of the H₂ molecule from the metallic surface. Therefore the present study, which is concerned with spectroscopy, requires accurate data and thus we used highly correlated wavefunctions and a cluster approach, Fig. 1.

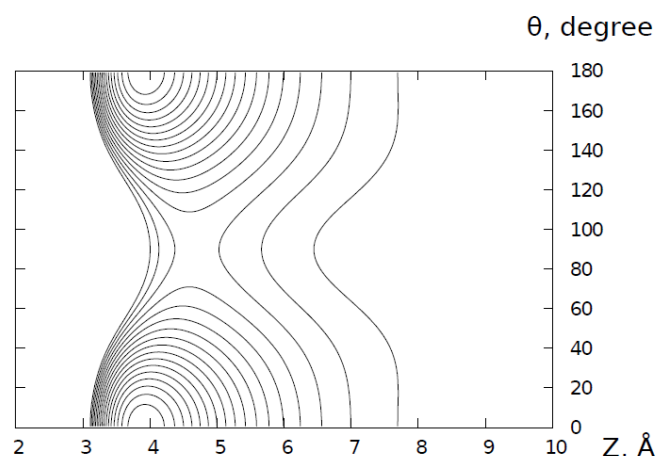
Fig.1 Representation of the H₂ Cu(22) cluster system.



The electronic calculations have been performed with the 2012.1 version of the MOLPRO code [2] using the coupled cluster CCSD(T) method. In all calculations the center of mass of the H₂ molecule has been kept on the Z axis on top of the central Cu atom and the interatomic distance H-H has been kept at the equilibrium geometry of the H₂ molecule, 0.74Å. The 2D potential energy cuts, were obtained by varying the Z distance and the θ angle (for values: 0, 45 and 90 degree)

The large rotational constant of H_2 associated with the anharmonic and anisotropic van der Waals potential – Fig.2, results in a strong coupling between the rotation of H_2 and the stretching along the physisorption well.

Fig. 2: Plot of the 2D physisorption potential. The contour lines are distant by 20 cm^{-1}



The following assumptions are made: first, we consider only vertical (Z) motion of the H_2 center-of-mass. Thus, we neglect the potential dependence on X and Y , as well as corresponding kinetic energy. We have checked that in the physisorption domain, the potential is practically independent on φ , varying by less than 1 cm^{-1} allowing to neglect the potential dependence on φ , assuring that m is a good quantum number. Then, the rigid rotor approximation is used for the H_2 molecule, and neglecting internal kinetic energy term. This is justified by the fact that the H_2 vibrational excitation energy is much bigger than the energy interval investigated here.

The calculated energy levels are assigned with three quantum numbers, (v,j,m) , v for the vdW stretching, j for the rotation associated to θ and m for φ . Calculated transitions are compared in the following table with existing experimental data[3].

Transition	calculation	Experiment
$(0,0,0) \rightarrow (0,2,1)$	44	44
$(0,0,0) \rightarrow (1,2,1)$	51	52
$(0,0,0) \rightarrow (2,2,1)$	56	58

The comparison between our *ab initio* calculations and experimental results of transition energies, given here shows a rather good agreement confirming the reliability of our approach.

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