

Low Energy Motion of H₂ on a Metallic Surface

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In recent theoretical studies of the H₂/Cu system using an embedding approach of a cluster model consisting of 22 Cu atoms, it has been shown that the chemisorption [1] and also the physisorption [2] of H₂ can be satisfactorily reproduced. A good test of the accuracy of the potential energy function in the physisorption domain is the comparison with ro-vibrational spectroscopic data obtained with EELS experiments [3]. The large rotational constant of H₂ associated with the anharmonic and anisotropic van der Waals potentials, 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).

Ro-vibrational energy levels of H₂ 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 theory: periodic (DFT) or cluster representation of the system (highly correlated wavefunction description). Highly correlated electronic calculations on the cluster model have been performed with the code MOLPRO using the MRCI or the coupled cluster CCSD(T) methods. The embedding method has been applied within the ONIOM approach. The periodic calculations have been performed with DFT approach with the code VASP and vdW-DF2 functional.

Two different formalisms are used to study the motion of the H₂ molecule considered as a rigid rotor: either a time-dependent dynamic approach or a variational approach using a time-independent Hamiltonian. The relative intensities of the transition lines have been obtained from the calculated dipole moment matrix elements and some widths have been deduced from the corrugation of the surface.

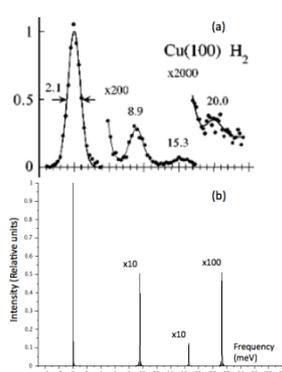


Figure 1: Calculated relative intensities of the ro-vibrational transitions

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References

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