

Non-reactive interaction of molecules with a surface: cluster or periodic approach?

Gilberte Chambaud

► **To cite this version:**

Gilberte Chambaud. Non-reactive interaction of molecules with a surface: cluster or periodic approach?. International Symposium on CO2 capture, Majdi Hochlaf, Sep 2013, Champs sur Marne, France. hal-01081750

HAL Id: hal-01081750

<https://hal-upec-upem.archives-ouvertes.fr/hal-01081750>

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.

Non-reactive interaction of molecules with a surface: cluster or periodic approach?

Gilberte Chambaud

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

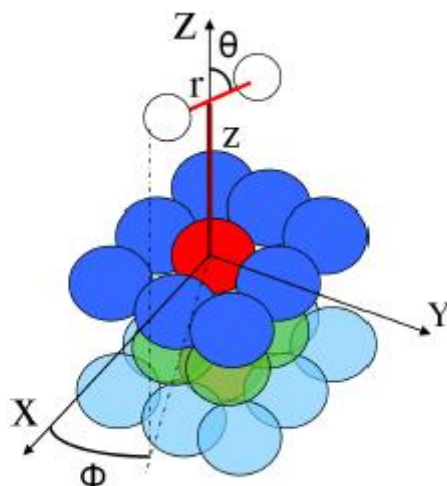
The non-reactive interactions of molecules with a metallic or ionic surface are subjects of numerous studies particularly for their importance in capture and release of molecules processes, in polarization of surfaces and also in energy transfers.

In such studies one has specifically to deal with long range interactions. With the usual periodic codes (VASP or Crystal), the surface is described by a periodic 2D-representation, namely a slab representation and the calculations are performed using Density Functional Theory (DFT) methods. In the physisorption domain, the weak interaction is governed by van der Waals (vdW) forces and it is well known that so far standard exchange-correlation functionals provide a poor description of such dispersion interactions [1] even though recent studies have shown that sophisticated DFT approaches can give promising outcomes for such difficult cases.

Alternative studies have been performed, modeling the metallic surface by a cluster as in recent theoretical calculations on the H₂/Cu or H₂/Ag systems using a cluster model consisting of 22 Cu or Ag atoms [Fig.1]. It has been shown that the chemisorption and physisorption of H₂ layers can be satisfactorily reproduced by highly correlated electronic wavefunctions (MRCI or CCSD(T) methods using MOLPRO[2]). Such pure ab initio methods are very efficient, they can provide reliable local properties (as for example rotational spectroscopy of the physisorbed molecule[3]) but they are missing delocalization effects, they are expensive and cannot be used for large systems.

In order to compensate the deficiencies of both, cluster and periodic approaches, the 22 atoms cluster has been included in a periodic frame, using the embedded method. This ansatz is shown to be helpful for short range interactions but cannot improve significantly the long range ones.

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



References :

1. G. Cilpa, J. Colin, F. Labat, C. Adamo and G. Chambaud, *Theor. Chem. Acc.*, **131**, 3,1189 (2012)
2. MOLPRO, version 2012.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see <http://www.molpro.net>.
3. C. Houriez, A.O. Mitrushchenkov, M. Guitou and G. Chambaud, *Surface Sci.* (in press)