# Hydrogen dissociation on aluminum cluster interacting with carbon surfaces by first principle calculations

Francesca Costanzo, Marc C. van Hemert and Geert-Jan Kroes

*Faculty of Science, Leiden Institute of Chemistry, Theoretical Chemistry*

*Einsteinweg 55, 2333 CC Leiden*

Dissociation of $H_2$ on bare $Al_n$ clusters (n=2,4,6) has recently been studied theoretically [1], where transition states, reaction paths, and the effect of the two low spin states of $Al_n$ have been considered. Comparison of theory with experimental results agrees regarding the high reactivity of the $Al_6$ cluster.

Moreover theoretical studies of the dissociation of $H_2$ on carbon materials such as graphene[2] and single and double walled nanotubes[3] have recently demonstrated the catalytic effect of these carbon surfaces on the dissociation of the hydrogen molecule.

From these encouraging results, we aim to study the combined effect that $Al_n$ clusters (n=2,4,6) and carbon surfaces such as coronene (C) and graphene (G) have on the dissociation energy of the hydrogen molecule.

We studied the interaction of $H_2$ with $Al_n$ (n=2,4,6) clusters on the G and C surfaces using Density Functional Theory. To study physisorbed states we account for vdW interactions in DFT using the methods of Langreth and Grimme [4,5]. Various $H_2$ physisorbed configurations on the $Al_n$ cluster on C and G surfaces were considered.

The analysis of the interaction of $Al_n$ cluster on G show that the presence of Carbon atoms promotes the dissociation of $H_2$ over the small $Al_n$ clusters with n=2 and 4. Results of $Al_n$ on C show that coronene stabilizes the $Al_n$ clusters in the singlet state. This result turns out quite interesting considering that the bare $Al_2$ and $Al_4$ clusters, without carbon materials, are more stable in the triplet state and the dissociation of $H_2$ molecule has eventually to follow a triplet pathway on these systems.

Reaction paths, leading from the physisorbed state to the dissociated chemisorbed state for $Al_n$ clusters interacting with both C and G have been studied by Nudged Elastic Band (NEB) [6] calculations.

Our study demonstrates the catalytic effect that combining carbon surfaces and $Al_n$ clusters has on the dissociation of Hydrogen molecule. The case of the $H_2$ on $Al_4$ on C turns out to be a particularly interesting system since dissociate the hydrogen molecule barrierless. The electrostatic energy, charge transfer and molecular orbital analysis explain the observed phenomena.

References:

[1] I. Pino, G. J. Kroes, M. C. van Hemert *J. Chem. Phys.*, **133**, 184304 (2010)

[2] F. Costanzo, P.L. Silvestrelli and F. Ancilotto, *J. Chem. Theory Comput.*, 8, 1288 (2012)

[3] F. Costanzo, P.L. Silvestrelli, R. Scipioni, F. Ancilotto, *Phys. Rev B. submitted.*

[4] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, B.I. Lundqvist, *Phys. Rev. Lett.*, ***92,*** 246401 (2004)

[5] S. Grimme, *J. Comput. Chem.* ,***27,*** 1787 (2006)

[6] G. Henkelman, H. Jónsson, *J. Chem. Phys.*, **113**, 9978 (2000).