Characterization of an oxalic acid layer on *Cu(111)*.

M. N. Faraggi[1], M. Trelka[2], *C.* Isvoranu[3], C. Martí-Gastaldo[4], E. Coronado[4], J. Schnadt[3], J. M. Gallego[5,6] , R. Otero[2,5], R. Miranda[2,5] and A. Arnau[1,7]

[1] *Donostia International Physics Center (DIPC), P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain.*
[2] *Dpto. de Física de la Materia Condensada, Universidad Autónoma de Madrid, Cantonblanco, 28049-Madrid, Spain.*
[3] *Dpto. of Synchrotron Radiation Research, Lund University, Box 117, S-22100 Lund, Sweden.*
[4] *Instituto de Ciencia Molecular (ICMol) 46980, Paterna, Spain.*
[5] *Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, 28049-Madrid, Spain.*
[6] *Instituto de Ciencia de Materiales de Madrid - CSIC, Cantoblanco, 28049-Madrid, Spain.*
[7] *Departamento de Física de Materiales, Facultad de Química UPV/EHU and Centro de Física de Materiales CFM-MPC, Centro Mixto (CSIC-UPV/EHU), San Sebastián, Spain.*

In this work, we present a combined experimental and theoretical study of the geometric and electronic structure of the self-assembled monolayer nanostructure formed by deposition of oxalic acid ($C_2O_4H_2$) (Fig. 1(a)) on a *Cu(111)* surface. Both scanning tunneling microscopy (STM) and photoemission (XPS) techniques are used to characterize the nanostructure formed before and after thermal annealing. First principles density functional theory (DFT) calculations permit to perform an energetic analysis that helps in understanding several questions that remain unclear in the experiment, like the role of the deprotonation of the carboxylic group of the molecules or the possibility of forming coordination bonds with *Cu* adatoms upon adsorption.

Based on DFT calculations through VASP [1, 2] code we obtain the binding energy for different monomers configurations. Energetic results point out to a strong preference of the molecule to be absorbed after deprotonation (confirmed by XPS measurements) and bonding with cooper adatoms. This allows us to propose a double deprotonated molecule with two cooper adatoms as candidate to understand the STM topographical images (Fig. 1 b)). Making use of a Bader charge analysis and induced charge density we analyze the chemical environment of the proposed structure. The combined study with experimental data unveils the coexistence of different moieties of the oxalic acid -produced by dissociative processes- that depend on the coverage level. Going further and taking into account the molecular crystal structures [3] we propose a plausible geometry description for the oxalic acid monolayer, which includes *Cu* adatoms on the *Cu(111)* surface and deprotonation of the molecule, given place to the simulated STM image, shown in Fig.1 c).

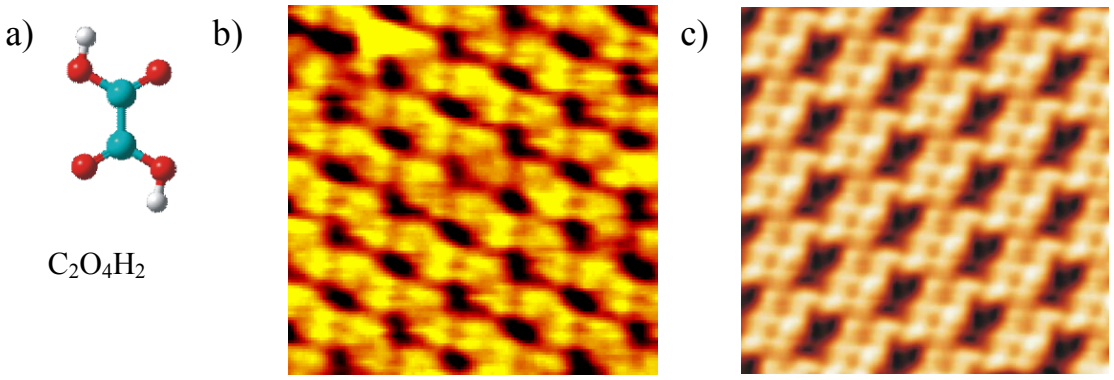

Figure 1: a) Acid oxalic molecule, STM images (7x7 nm) b) experimental and c) simulation [4].

References

[1] G. Kresse, J. Hafner, Phys. Rev. B **49** (20), 14251, 1994.

[2] G. Kresse, J. Furthmuller, Phys. Rev. B **54** (16), 11169, 1996.

[3] I. Nobeli, and S. L. Price, J. Phys. Chem. A **103**, 6448 (1999).

[4] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, Rev. Sci. Instrum. 78 013705 (2007).