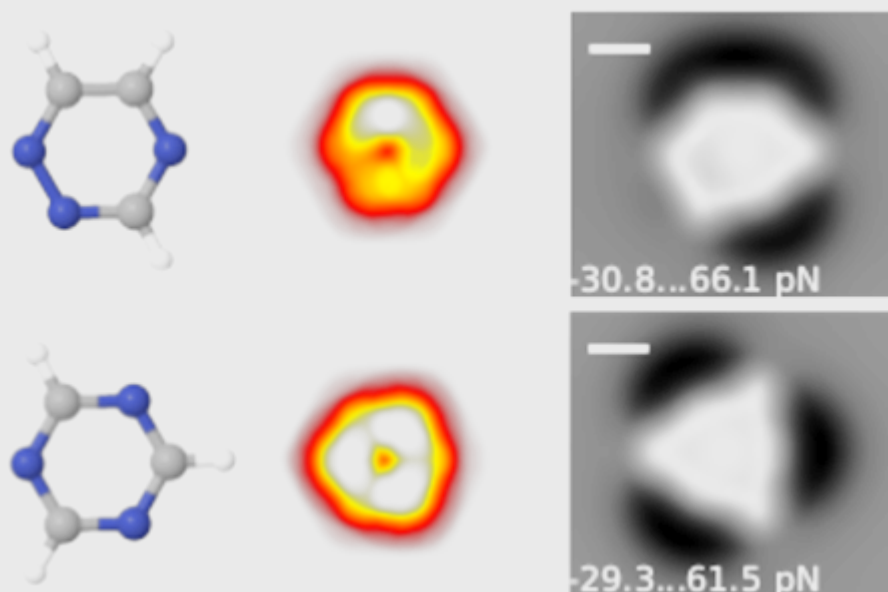


Molecular Identification and Bonding Information from High-resolution AFM



Article: published in [ACS Nano](#) by Pablo Pou and Ruben Perez, [IFIMAC](#) researchers and members of the Department of Theoretical Condensed Matter Physics.

High-resolution atomic force microscopy (HR-AFM) is able to image the internal structure of molecules, resolves features in the intermolecular regions of weakly bonded molecules, discriminates between bond orders in aromatic compounds, and has opened the door to following or even inducing on-surface chemical reactions. This revolution in molecular imaging has sparked a strong debate about the interpretation of the experiments and the development of new capabilities like chemical identification. Here, we introduce an efficient method to simulate HR-AFM images with CO probes. Our model explicitly takes into account the charge densities of the sample and the probe for the calculation of the short-range (SR) interaction and retains *ab initio* accuracy with only two parameters, that are essentially universal, independent of the number of chemical species and the complexity of the bonding topology. The application to molecular images shows a strong dependence on the stoichiometry and bonding configuration that precludes the chemical identification of individual atoms based on local force-distance curves. However, we have identified features in the 2D images and 3D force maps that reflect the highly anisotropic spatial decay of the molecular charge density and provide a way towards molecular identification. The model treats SR and electrostatics interactions on an equal footing and correctly pinpoints the Pauli repulsion as the underlying interaction responsible for the bond order discrimination in C60. Finally, we settle the controversy regarding the origin of the intermolecular features, discarding the effect of the charge redistribution associated with the H bonds, and linking them with the overlap of the wave functions of the atoms that constitute the bond. This overlap creates saddle regions in the potential energy landscape that are

sensed by the probe. [[Full article](#)]

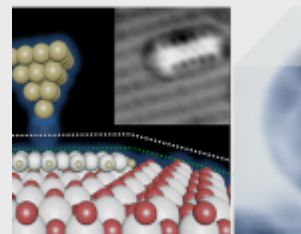
Submolecular AFM Imaging and Spectroscopy on Single Molecules Using KolibriSensor™ and Cantilevers

Title: Submolecular AFM Imaging and Spectroscopy on Single Molecules Using KolibriSensor™ and Cantilevers.

When: Monday, October 17, (2016), 12:00.

Place: Departamento de Física Teórica de la Materia Condensada, Facultad Ciencias, Module 5, Seminar Room (5th Floor).

Speaker: Tomoko K. Shimizu, Research Center for Advanced Measurement and Characterization National Institute for Materials Science (NIMS), Tsukuba, Japan.



Submolecular imaging using frequency-modulation (FM) atomic force microscopy (AFM) has recently been established as a stunning technique to reveal the chemical structure of unknown molecules, to characterize intra-molecular charge distributions, and to observe chemical transformations. So far, most of these feats were achieved on planar molecules using the so-called qPlus sensor, a specially designed quartz AFM sensor. The KolibriSensor, another type of quartz AFM sensor, is also expected to be capable of high-resolution imaging, but only very few experimental results have been reported to date.

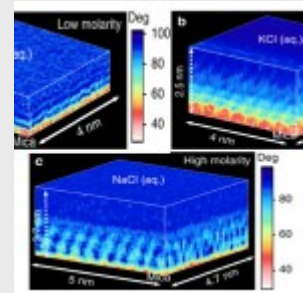
Here, we present submolecular resolution images and spectroscopic data on single molecules of a porphycene derivative [1] using small oscillation amplitudes with KolibriSensors. Force volume measurements with CO-functionalized probes [2] revealed features that may be related to the isomers of porphycene molecules. We also report a novel imaging method to achieve submolecular resolution on three-dimensional molecules and structures using a silicon (Si) cantilever-based AFM operated with large oscillation amplitudes. At variance with previous implementations, this method allowed us to simultaneously image both intra-molecular structures and the atomic arrangement of the substrate [3]. Force volume measurements over C60 molecules clarified the validity of our method to achieve submolecular resolution [3].

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Atomically Resolved Three-dimensional Structures of Electrolyte Aqueous Solutions Near a Solid Surface

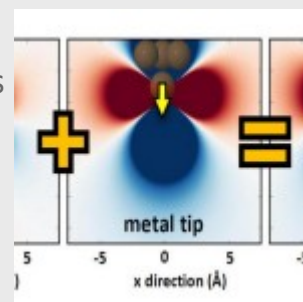
Article: published in [Nature Communications](#) by [Pedro Tarazona](#), Department of Theoretical Condensed Matter Physics and IFIMAC researcher.



In a collaboration with experimental and theoretical groups of the ICMM-CSIC and IFIMAC-UAM, this paper presents novel experimental results obtained with a three dimensional atomic force microscopy scanning (3D-AFM) taken within a salt-water solution near a mica surface. The atomic resolution of the 3D-AFM uncovers a crystal like structure within the liquid, which propagates from the mica, in structured layers, up to several nanometers. The theoretical analysis, based on a classical density functional description of the liquid mixture, provides the hints to understand a phenomenon which may be of relevance in a large variety of fields, from surface electrochemistry to molecular and cell biology. [\[Full article\]](#)

The Electric Field of CO Tips and Its Relevance for Atomic Force Microscopy

Article: published in [Nano Letters](#) by Michael Ellner, [Pablo Pou](#) and [Rubén Pérez](#), Department of Theoretical Condensed Matter Physics and IFIMAC researchers.



Frequency modulation atomic force microscopy (FM-AFM) has been recognized for

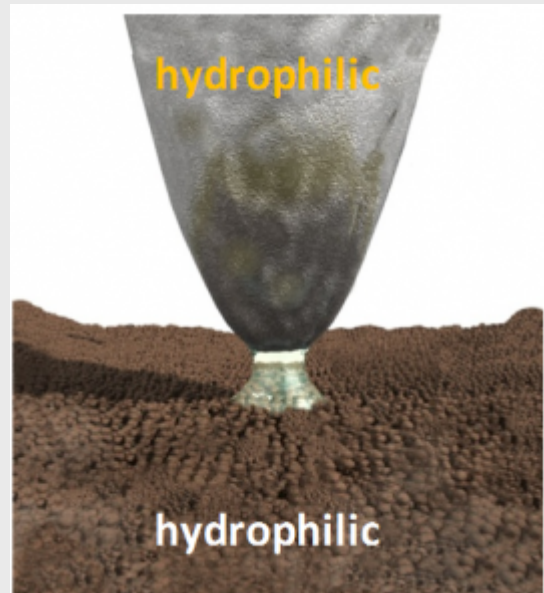
a long time as one of the best tools for materials characterization at the atomic scale. The use of metal tips decorated with CO molecules represented a significant step forward in this technique that paved the way for the visualization of the internal structures of molecules with unprecedented resolution. This high resolution has been explained in terms of the strong Pauli repulsion between the closed-shell molecule acting as the probe and the electronic charge of the molecule probed. In addition, the associated tilting of the CO molecule amplifies the spatial variations of the charge density on the sample.

Notwithstanding, experiments on polar and metallic systems show that electrostatic interactions are necessary to understand the complex contrast observed and its distance evolution. Attempts to describe those interactions in terms of a single electrostatic dipole replacing the tip have led to contradictory statements about its nature and strength.

Here, we solve this puzzle with a comprehensive experimental and theoretical characterization of the AFM contrast on Cl vacancies. Our model, based on density functional theory (DFT) calculations, reproduces the complex evolution of the contrast between both the Na cation and Cl anion sites, and the positively charged vacancy as a function of tip height, and highlights the key contribution of electrostatic interactions for tip-sample distances larger than 500 pm. For smaller separations, Pauli repulsion and the associated CO tilting start to dominate the contrast. The electrostatic field of the CO-metal tip can be represented by the superposition of the fields from the metal tip and the CO molecule. The long-range behavior is defined by the metal tip that contributes the field of a dipole with its positive pole at the apex. At short-range, the CO exhibits an opposite field that prevails. The interplay of these fields, with opposite sign in the near-field and rather different spatial extensions, explains the contrast evolution observed in our experiments and reconciles the apparently contradictory claims in the literature. [\[Full article\]](#)

[Structural flexibility mapping by bimodal atomic force microscopy in liquids](#)

Wednesday, 7th November 2012. 12:00-13:00



Elena Tomás Herruzo

(Instituto de Ciencia de Materiales de Madrid, CSIC)

ABSTRACT:

Bimodal atomic force microscopy is based on the simultaneous excitation of two eigenmodes of the cantilever. Bimodal AFM enables the simultaneous recording of several material properties and, at the same time, it also increases the sensitivity of the microscope.

Here, the excitation of two cantilever eigenmodes in dynamic force microscopy enables the separation between topography and flexibility mapping. We have measured variations of the elastic modulus in a single antibody pentamer of 10 MPa when the probe is moved from the end of the protein arm to the central protrusion. Bimodal dynamic force microscopy enables us to perform the measurements under very small repulsive loads (30–50 pN).

We also develop a model based on fractional calculus to express the frequency shift of the second eigenmode in terms of the fractional derivative of the interaction force. We show that this approximation is valid for situations in which the amplitude of the first mode is larger than the length of scale of the force, corresponding to the most common experimental case. The model allows the measurement of the effective elastic modulus and the contact radius on heterogeneous samples.

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