High resolution molecular imaging, spectroscopy and manipulation

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I will try to identify and discuss the specificities of imaging molecules in the non-contact AFM mode and the factors that limit the resolution that can be reached in different cases.

A major difficulty in imaging molecules in nc-AFM stems from the relatively weak adsorption energies (especially on insulators) and weak diffusion barriers that they exhibit. The resolution is usually limited by the maximal force that the molecules can support without being laterally displaced or picked up by the tip. Imaging and manipulation are both sides of the same experiment.

The usual strategy that experimentalists employ to get the best resolution possible consists usually in increasing the tip-substrate interaction (by increasing the absolute value of the frequency detuning set value $|\Delta f|$ in the constant Δf mode or by reducing the tip-surface distance in the constant height mode) until "something" happens.

Beyond this crude approach, there are several ways to improve the imaging resolution:

- Optimizing the control parameters (feedback loops settings, oscillation amplitude, bias voltage,…)
- Adapting the system if possible (use another substrate or equip the molecule with grafting groups to enhance the adsorption energy)
- Modifying the tip

A major breakthrough was achieved with this last option by functionalizing the tip with small molecules (especially CO) [1]. Atomic and intra-molecular bond resolution is now routinely obtained on –generally- flat molecules at low temperature ($T<\approx 10K$) and with tuning forks, in the qPlus configuration. These experiment are performed at constant height.
This approach has still not been used at higher temperature, because these small molecules are not stable enough on the tip. But there are examples in the literature that display similar resolution with unintentionally functionalized tips, suggesting that the technique could be generalized.

After a brief historical introduction, the presentation will be organized around the two main and relatively distinct approaches that structure the literature:

- The imaging of molecules on bulk insulators -meaning that STM cannot be used- mainly with cantilevers and at room temperature.
- The imaging of molecules with functionalized tips and at low temperature, mainly with tuning forks and very often coupled to STM.

Afterwards, a few examples of lateral and vertical molecular manipulations will be presented and discussed.
Finally some perspectives on this domain will be given.

[1] L. Gross, F. Mohn, N. Moll and G. Meyer, Science **325**, 1110 (2009).