VISUALISING THE ORBITALS OF AN ADSORBED MOLECULE

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Recent experiments [1, 2] have shown that visualising the frontier orbitals of an adsorbed molecule by Scanning Tunneling microscopy (STM) was possible. These results were obtained by interposing between the molecule and the metallic substrate an ultrathin insulating layer (NaCl/Cu(111) in [1], Al_2O_3/NiAl(110) in [2]). The role of this layer is to electronically decouple the molecule from the substrate while still allowing the transport of a weak tunneling current across the system. The molecule keeps then an electronic structure very close to that of the isolated, free molecule. The situation is fundamentally different when the molecule is directly adsorbed on the metal: the molecular levels are then broadened, shifted, and coupled due to the interaction with the metal. Image calculations show that a large number of molecular orbitals contribute to the STM images, even if in some cases an internal structure similar to that expected for a molecular orbital is discernible.

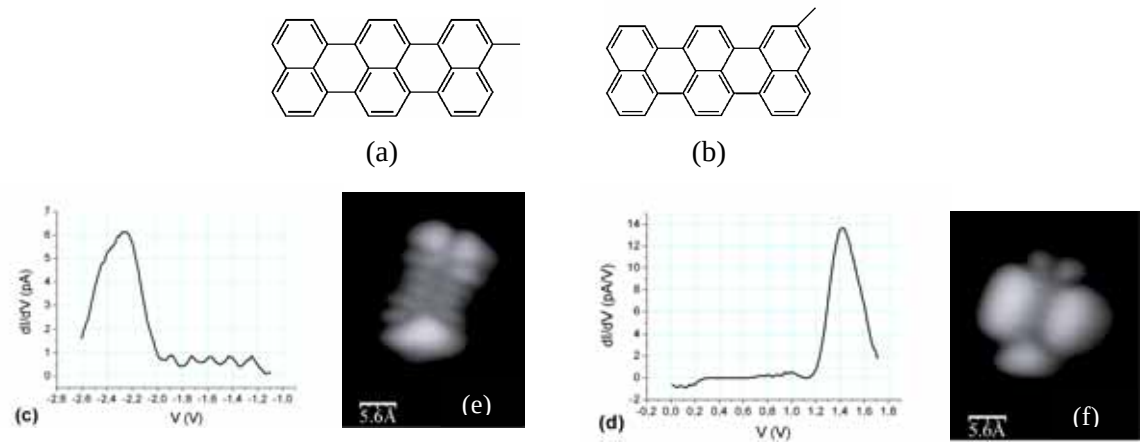

Figure 1: *(a) methylterrylene (MeT) isomers 1 and 2 (c) and (d) Spectra dI/dV (V) above the centre of MET (iso1) adsorbed on NaCl/Cu(111) and STM image (e) Vt=-2,3 V and (f) Vt=1,4 V. It=1pA.*

These considerations will be illustrated by a study of the adsorption of two isomers of methylterrylene (figure 1a et b) by low-temperature STM (4.7K). The molecules were deposited either directly on the metal or on a NaCl bi-layer adsorbed on Cu(111). On NaCl, the dI/dV(V) spectrum acquired above the centre of the molecule displays two strong resonances near -2.3 V and +1.4 V (figure 1c and d). The images obtained near these energies display well defined characteristic patterns (figure 1e and f) which are very similar to the spatial distribution of the electronic probability density calculated for the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the free molecule. In contrast, the images and the spectra obtained when the molecule is directly adsorbed on the metal do not exhibit particular patterns. The experimental images will be compared to images calculated using the EH-ESQC method [3]. In particular, it will be shown that the image displayed in figure 1e (resp. 1f) results from the exclusive contribution of the HOMO (resp. LUMO).

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[3] P. Sautet and C. Joachim, *Chem Phys. Lett.* **185**, 23 (1991)