The origin of STM-contrast anomalies of n-alkanes on graphite

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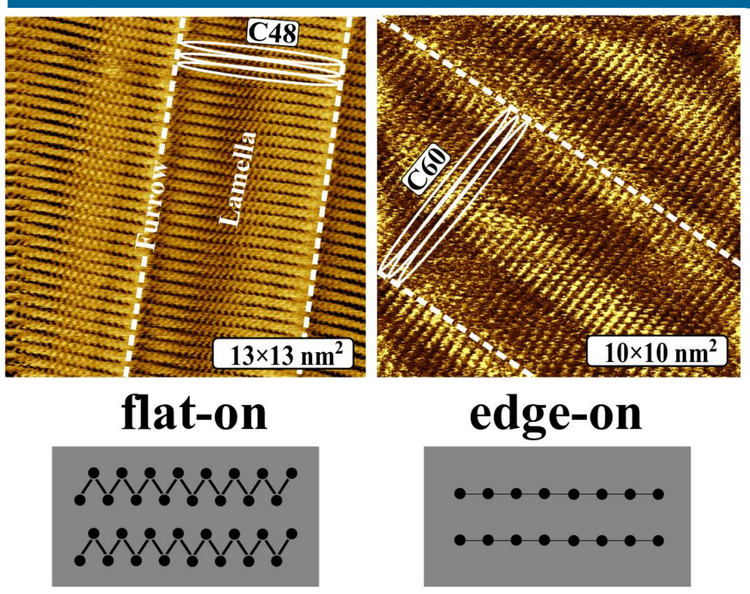
Herein, we experimentally demonstrate how misfit between n-alkane molecule (T_{alk} = 2.51 Å) and graphite (T_{gr} = 2.46 Å) as well as current-voltage parameters of STM drastically influence on STM-patterns. We directly visualize a deviation of molecule's brightness from already proposed. Through analysis of these patterns we find that each molecule undergoes deformations to fit a close-packing of entire monolayer. A direct consequence of such deformations is a sharp change of brightness of terminal CH_3- and pre-terminal CH_2-groups and modulation of brightness of CH_2-groups along molecule's skeleton. In order to explain high brightness of some parts of skeleton we consider tunneling electrons as de Broglie standing waves, which establishes between monolayer and STM-tip.

Introduction



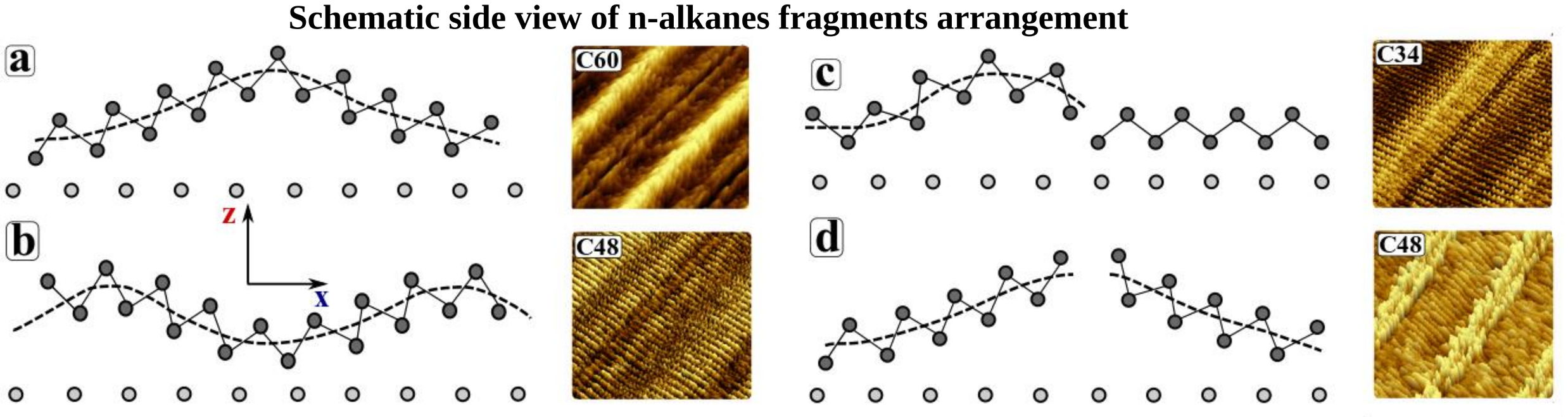
Monolayers of n-alkanes (C_nH_{2n+2}, hereafter C_n) on graphite demonstrate a lamella-furrow structure with molecules perpendicular to furrows.

These molecules adsorb in all-trans configurations with carbon skeleton plane parallel (*flat-on*) and perpendicular (*edge-on*) to the surface. For such arrangements current from lamellae is higher than the one from furrows forming a striped bright–dark STM-pattern in which across lamellae are rows of uniform bright spots (CH_2-groups).

However, a spring-like behavior of n-alkane leads to appearance of dynamically-living STM-brightness that does not correspond to all-trans flat-on and/or edge-on configurations.

I. Deformations of molecules' skeletons

Schematic side view of n-alkanes fragments arrangement

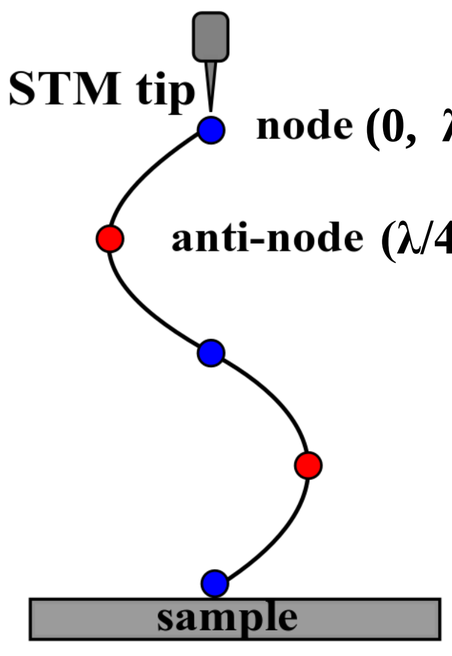


Bending **(a-b)** and fragment's rotation **(c)** of skeleton as well as combination of both within a single molecule **(d)**.

CH_2-units demonstrate monotonous modulation of brightness along alkyl chains **(a-b)**. A chain fragment (several CH_2-units) could rotate around one of the valence –C-C– bond inducing abrupt rising of its z-coordinate **(c)**. For instance, pre-terminal CH_2- and terminal CH_3-groups show significantly increased brightness **(d)**.

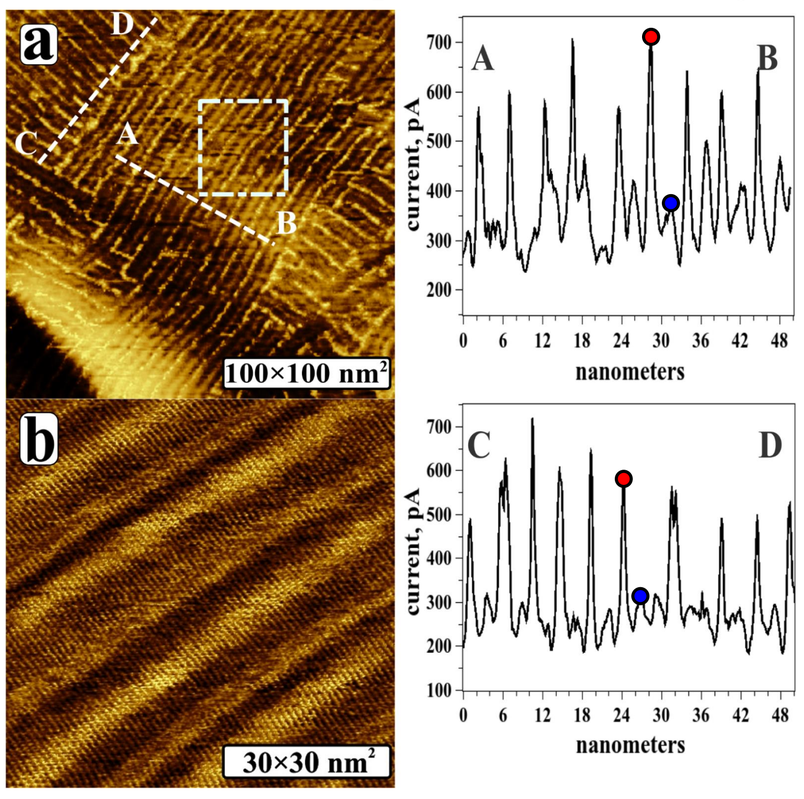
II. Abnormal brightness of terminal units

Model of standing waves between STM-tip and sample



!When z-coordinate of the tip, which keeps over the CH_2/CH_3-unit, coincides with the coordinate of anti-node the unit in STM-image appears to be much more brighter**!**

STM current map of $C_{60}H_{122}$ monolayer



The significantly increased brightness of terminal units is recognizable for $C_{60}H_{122}$ molecules in **(a)**.

Cross sections reveals absence of furrows and amplification of tunneling current amplitude at the ends of molecules.

Cross sections from different domains show that the amplification does not depend on the orientation of molecules relative to graphite surface.

The packing in **(a)**, was stable during ~1 hour. After changing the current setpoint It the brightness of terminal units changed immediately **(b)**.

Conclusions

A deformation of a molecule due to an elastic nature of alkyl skeleton produces the difference in z-coordinate (tip-sample distance) of CH_2/CH_3-units along alkyl chains of a molecule. Such difference leads to an amplification of the tunneling current from the units closest to the tip. This amplification as a possible detection of anti-nodes of de Broglie waves coming from raised up CH_2/CH_3-units. In turn, a setpoint current, likewise other scanning parameter, determines a tip-sample distance as well and, thus, the STM-contrast.

Another general result – the wavelength shift between node and anti-node does not point out the accurate value of rising of alkyl unit above the skeleton. This value may be distorted via CH_2/CH_3-wave-functions overlapping.Thus, further studies in this direction is required.