Tracking Molecular Conformations of Stearic Acid in Surface-Adsorbed Monolayers

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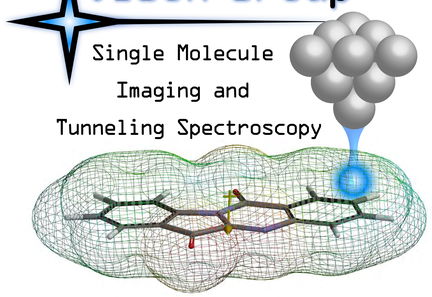
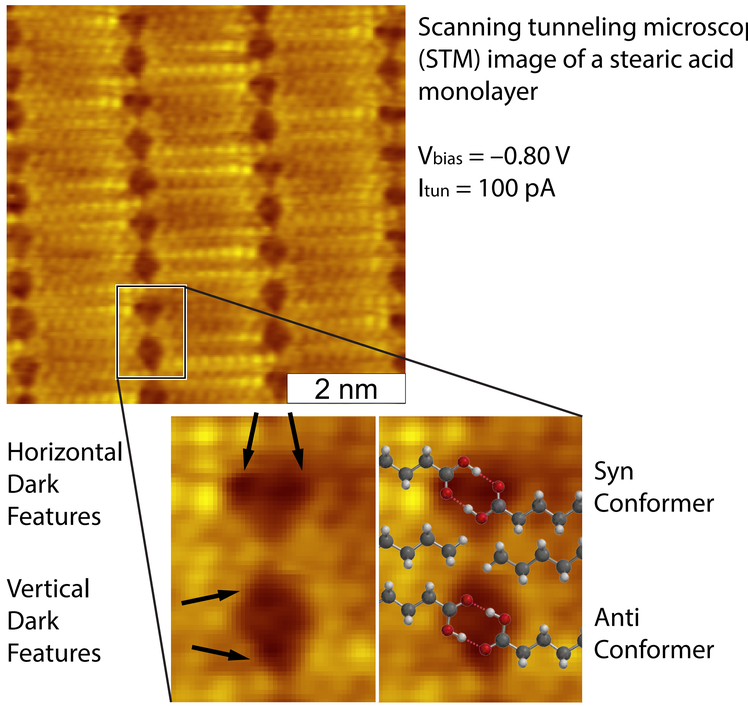


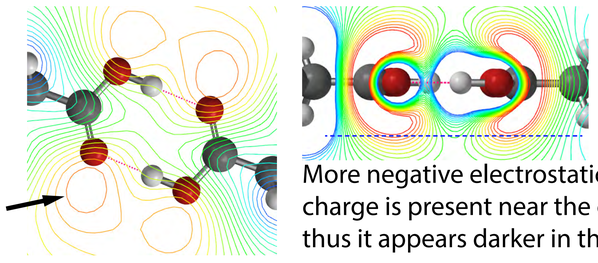
INTRODUCTION

Stearic acid was observed to adsorb onto highly-oriented pyrolytic graphite (HOPG) in 2 different conformations.



Scanning tunneling microscopy (STM) image of a stearic acid monolayer

V_{bias} = –0.80 V
I_{tun} = 100 pA

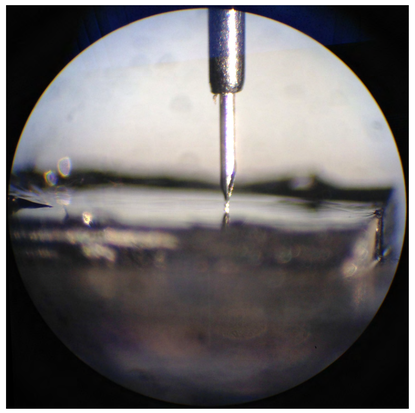


More negative electrostatic charge is present near the carbonyl, thus it appears darker in the image.

- Gas-phase DFT shows the syn conformer is favored by 13.5 kJ/mol.
- Would result in a ~99:1 ratio at thermal equilibrium @298 K.
- STM image above shows ~2:1 ratio.
- Suggests a large barrier to rotation.

The purpose of this investigation is to track conformations over time to see if interconversion can be observed.

EXPERIMENTAL



A drop of solution of stearic acid in 1-phenyloctane was placed onto the HOPG surface.

The STM tip is immersed directly in the stearic acid solution to image the monolayer at the solution-HOPG interface.

- STM was used to observe stearic acid adsorbed onto the HOPG surface.
- Images were collected under low drift ambient conditions.
- Images were collected in constant current mode with a sample bias of +0.80 V and a setpoint of 100 pA.
- Surface was imaged, and features (conformers) were tracked for ~2 hours.

RESULTS

Conformers were identified by the shape of the carboxyl ring in the STM image.

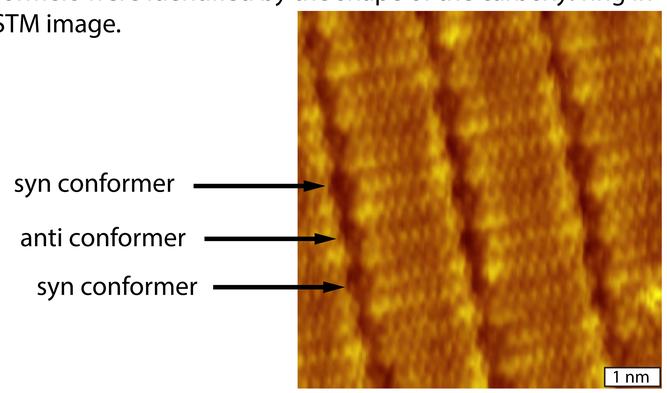
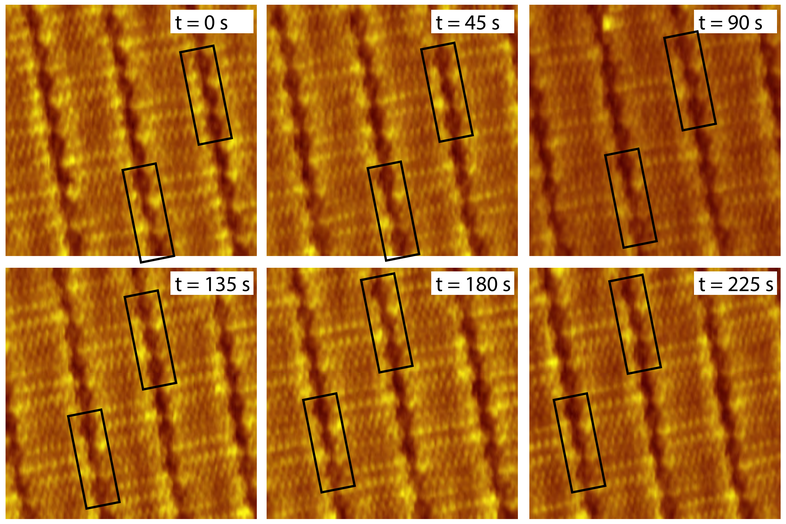


Image size: 7 nm by 7 nm
V_{bias} = +0.80 V; I_{tun} = 100 pA

Individual conformers were then tracked over time to observe whether or not they interconverted from anti to syn or vice-versa.

The following images show examples of molecules tracked during time-lapse STM imaging.



Of eleven conformer groups tracked in the experiment, there were no clear changes of conformation.

CONCLUSIONS

- Molecular conformations do not frequently interconvert.
- This suggests a high energy barrier to rotation.
- Adsorption mechanism must allow for either conformer to be present upon formation of the monolayer.

ACKNOWLEDGMENTS

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X. Guo, F. Marriucci, N. Price, E.L. Stewart, J.C. Baum, J.A. Olson, *J. Phys Chem. C*, **2015**, *119*, 24804–24811.