Imaging Noncovalent Bonds; Overinterpretation Criticized by Simulations

Ali Sadeghi
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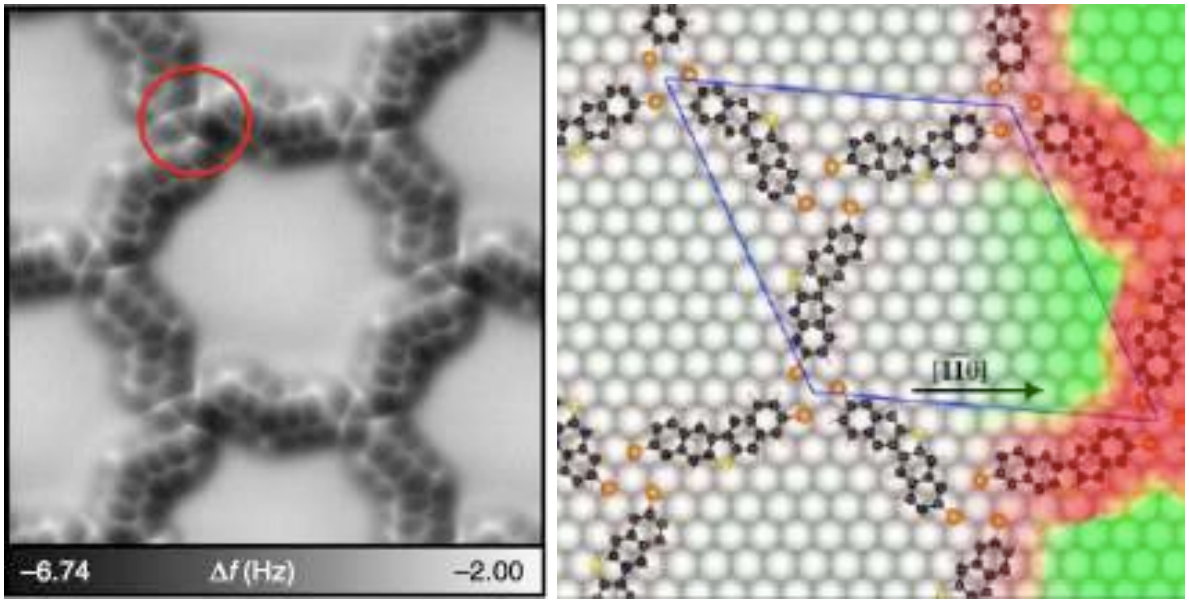


Modeling & Fabrication of Nanostructures made of 2D Materials, July 2019, Tehran

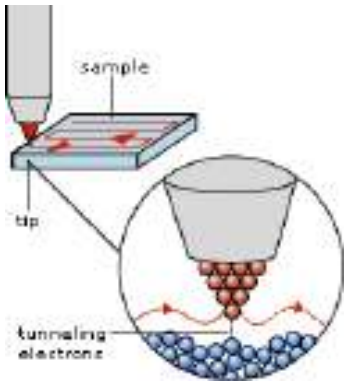
Outline

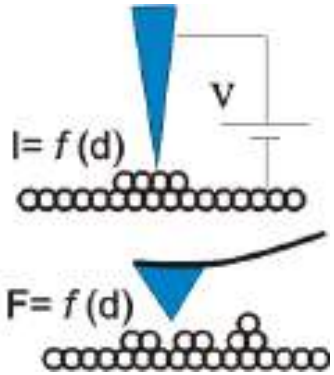
"The Lab on a Tip"

- Surface physicists need **imaging surfaces with atomic resolution** to investigate local electric properties, topography, charge distribution, ...
- The tool of the choice: Scanning Probe Microscopy (SPM)
  A large family: numerous variants
- sensor = probe tip with atomically sharp apex

$$\text{signal} = \begin{cases} \text{current } I = f(x, y; d): & \text{STM (1981)} \Rightarrow \text{Nobel prize (1986)} \\ \text{force } F = f(x, y; d): & \text{AFM (1986)} \Rightarrow \text{non-conducting samples} \\ \text{capacitance } C = f(x, y; d) & \\ \dots & \end{cases}$$

- Manipulation



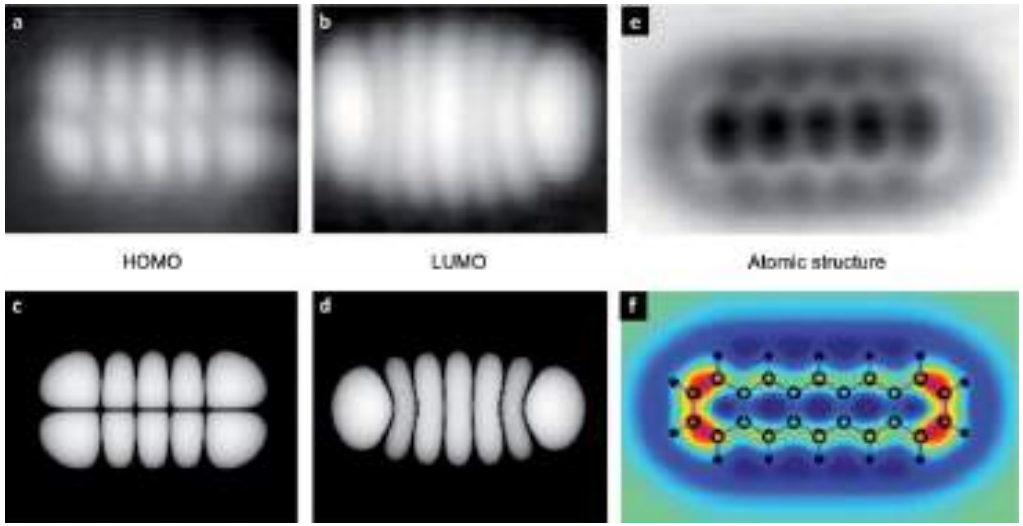


www.tcd.ie (Henger's webpage)

What is really imaged at atomic scale?

- **STM = Orbital Imaging:** Tersoff-Hamann $I(\mathbf{r}) \propto \sum_{E_f - eV_{\text{tip}}}^{E_f} |\Psi_i(\mathbf{r})|^2$

  Measuring the **Local Density Of electronic States** (LDOS) at position **r**,
  $\Rightarrow$ No direct connection to the chemical structure!
- **AFM = Electron Density Imaging:** **due to Pauli repulsion**
  Sensing the force on the tip-apex by **total electronic density** at position **r**,
  $\Rightarrow$ More directly related to chemical structure

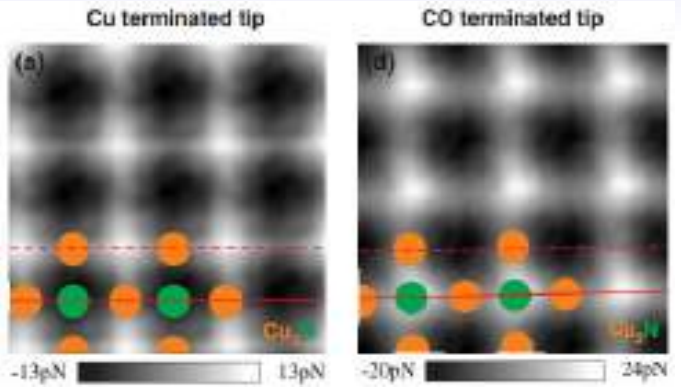


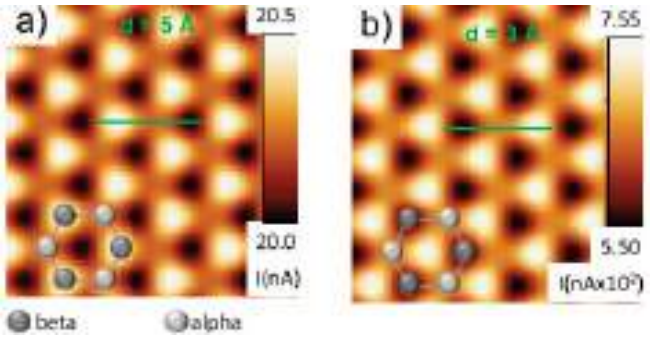
J. Repp et al. PRL (2005); L. Gross, Nature Chem. (2011)

Not so Easy to Explain Imaging Mechanism

CO Tip Functionalization Inverts Atomic Force Microscopy Contrast via Short-Range Electrostatic Forces

M. Schneiderbauer et al. PRL (2014)



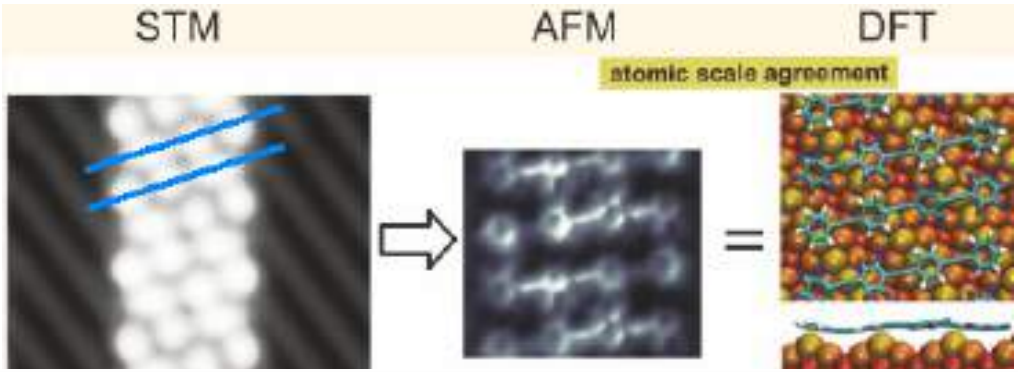


Forces and currents in carbon nanostructures: are we imaging atoms?

M. Ondracek et al. PRL (2011)

Obtaining Detailed Structural Information about Supramolecular Systems on Surfaces

S. Kawai, AS, *et al., ACS Nano (2013)*



Imaging Noncovalent Bonds; Overinterpretation Criticized by Simulations

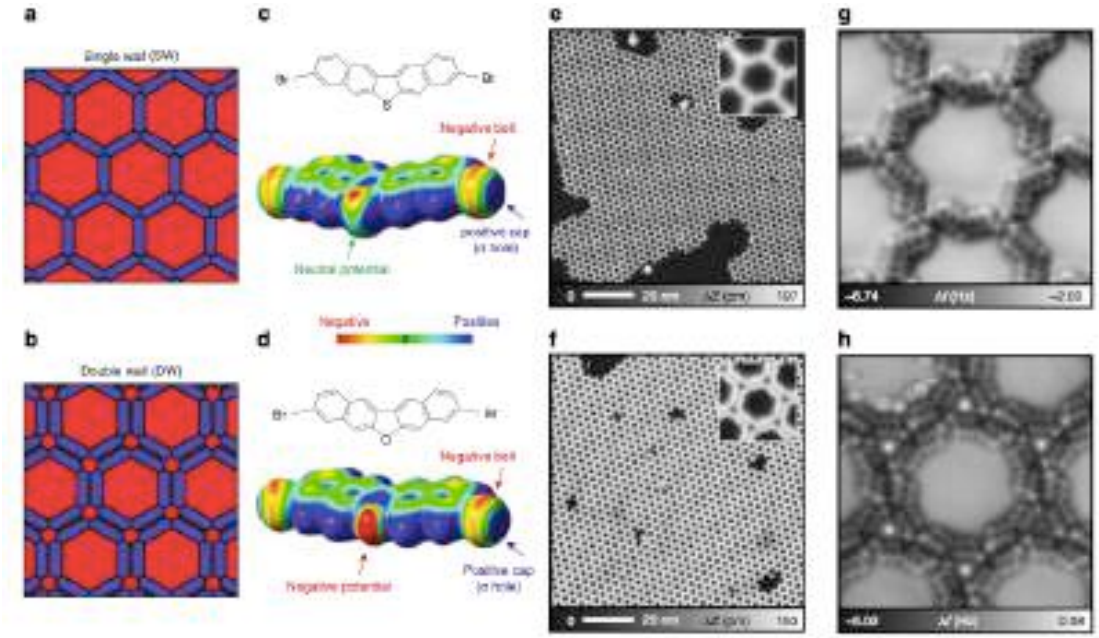
Not so Easy to Explain Imaging Mechanism

- Experiment:
  - How can we accurately detect the signal?
  - How can we enhance the resolution?
  - Can we develop imaging methods based on new mechanisms?
  - ...
- Theory:
  - How to interpret the image as a signature of **local interactions**?
    $\Rightarrow$ *atomistic calculations are required on an atomic scale.*
  - *How to translate tip-sample* **local interactions** *to surface properties?*

The common practice:

Experimental-Theoretical-Computational Joint

I Piquero-Zulaica, J. Lobo-Checa, AS, Z. M. Abd El-Fattah, C. Mitsui, T. Okamoto, R. Pawlak, T. Meier, A. Arnau, J. Enrique Ortega, J. Takeya, S. Goedecker, E. Meyer, and S. Kawai, Nature Commun. 8, 787 (2017)



Outline

Intermolecular Bonds

WIKIPEDIA
The Free Encyclopedia

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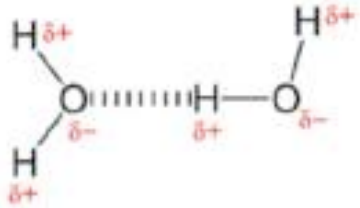
Featured content

Non-covalent interactions

From Wikipedia, the free encyclopedia

A **non-covalent interaction** differs from a covalent bond in that it does not involve the sharing of electrons, but rather involves more dispersed variations of electromagnetic interactions between molecules or within a molecule.[1]

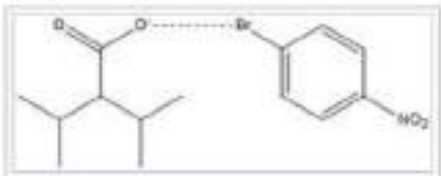
Hydrogen bonding [edit]



A hydrogen bond (H-bond), is a specific type of interaction that involves dipole-dipole attraction between a partially positive hydrogen atom and a highly electronegative, partially negative oxygen, nitrogen, sulfur, or fluorine atom (not covalently bound to said hydrogen atom). It is not a covalent bond, but instead is classified as a strong non-covalent interaction. It is responsible for why water is a liquid at room temperature and not a gas (given water's low molecular weight). Most commonly, the strength of hydrogen bonds lies between 0 - 4 kcal/mol, but can sometimes be as strong as 40 kcal/mol[1]

Halogen bonding [edit]

Halogen bonding is a type of non-covalent interaction which does not involve the formation nor breaking of actual bonds, but rather is similar to the dipole-dipole interaction known as hydrogen bonding. In halogen bonding, a halogen atom acts as an electrophile, or electron-seeking

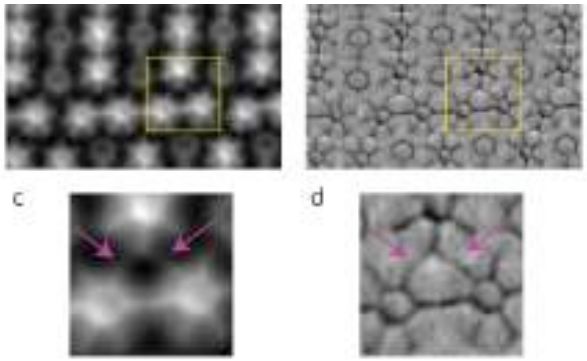


Imaging Intermolecular Bonds

Extended Halogen Bonding between Fully Fluorinated Aromatic Molecules

Shigeki Kawai,[*,†,‡] Ali Sadeghi,[†,§] Feng Xu,[⊥] Lifen Peng,[⊥] Akihiro Orita,[⊥] Junzo Otera,[⊥] Stefan Goedecker,[†] and Ernst Meyer[†]

[†]Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland, [‡]PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan, [§]Department of Physics, Shahid Beheshti University, Evin, 19839 Tehran, Iran, and [⊥]Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan



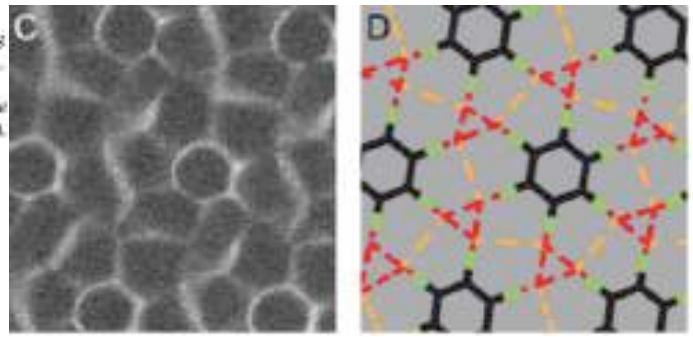
Science

REPORTS

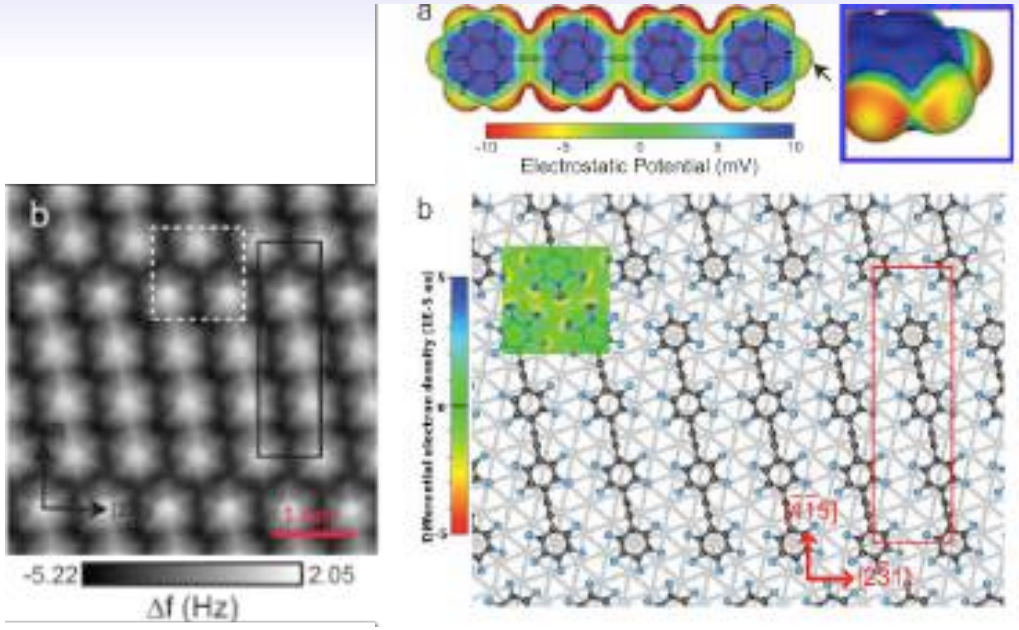
Cite as: Z. Han *et al.*, *Science* 10.1126/science.aai8625 (2017).

Imaging the halogen bond in self-assembled halogenbenzenes on silver

Zhumin Han,[1] Gregory Czap,[1] Chi-lun Chiang,[1] Chen Xu,[1] Peter J. Wagner,[1] Xinyuan Wei,[1,3] Yanxing Zhang,[1,3] Ruqian Wu,[1,2]* W. Ho[1,4]*



Extended X-Bonding

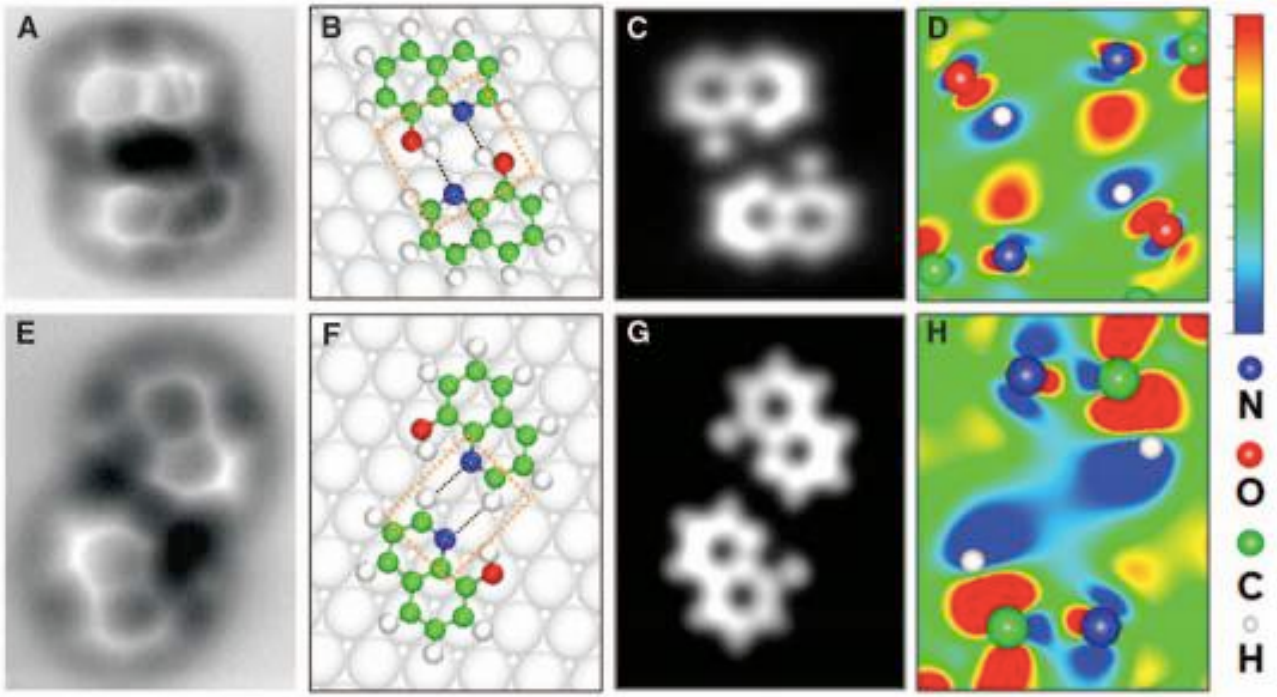


- Experiment:
  - Directional self-assembly despite F-F repulsion
  - High contrast inter-molecular bonds (X-bonds) in filtered AFM images
- DFT calculations:
  - No conventional σ-hole in case of F atoms
  - vdW attraction + directional ES repulsion
  - No electron accumulation on X-bonds

S. Kawai, AS, et al. ACS Nano, 9 (2015)

Imaging H-Bonding

Fig. 3. AFM measurements and DFT calculations of 8-hq dimers on Cu(111). Constant-height frequency shift image of the O-H···N dimer (**A**) and the N···H-Ph dimer (Ph, phenyl) (**E**) and their corresponding DFT-calculated structure models (**B** and **F**), electron density maps (**C** and **G**), and charge difference maps (**D** and **H**). Imaging parameters: $V = 0$ V, $A = 100$ pm, $\Delta z = +50$ pm (A), $\Delta z = +10$ pm (E). Image size: (A) 1.6 by 1.6 nm; (E) 1.5 by 2.0 nm. The dashed frames in (B) and (F) indicate the calculation regions in (D) and (H).

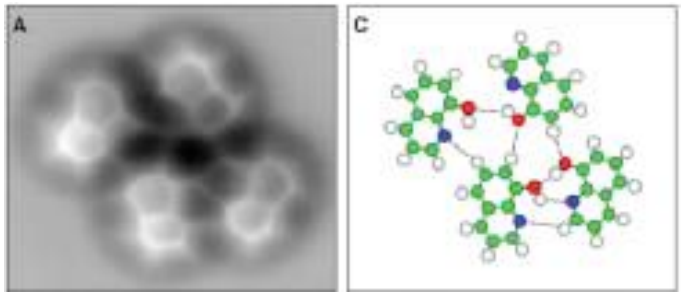


J. Zhang, et al. Science, 342 (2013)

Imaging H-Bonding

Claiming:

- Real-space visualization of the formation of H-bonding in 8-hq molecular assemblies on a Cu(111) substrate, using AFM



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Volume 92 Issue 46 | p. 8 | News of The Week
Issue Date: November 17, 2014 | Web Date: November 14, 2014

Hydrogen Bond Images From AFM Questioned

Microscopy: "Bonds" may be artifact of tip flexibility

By Jyllian Kemsley

Purported hydrogen bond interactions appearing in atomic force microscopy (AFM) images may be an experimental artifact.

AFM images published last year by a team led by Xiaohui Qiu and Zhihai Cheng of China's National Center for Nanoscience &

Outline

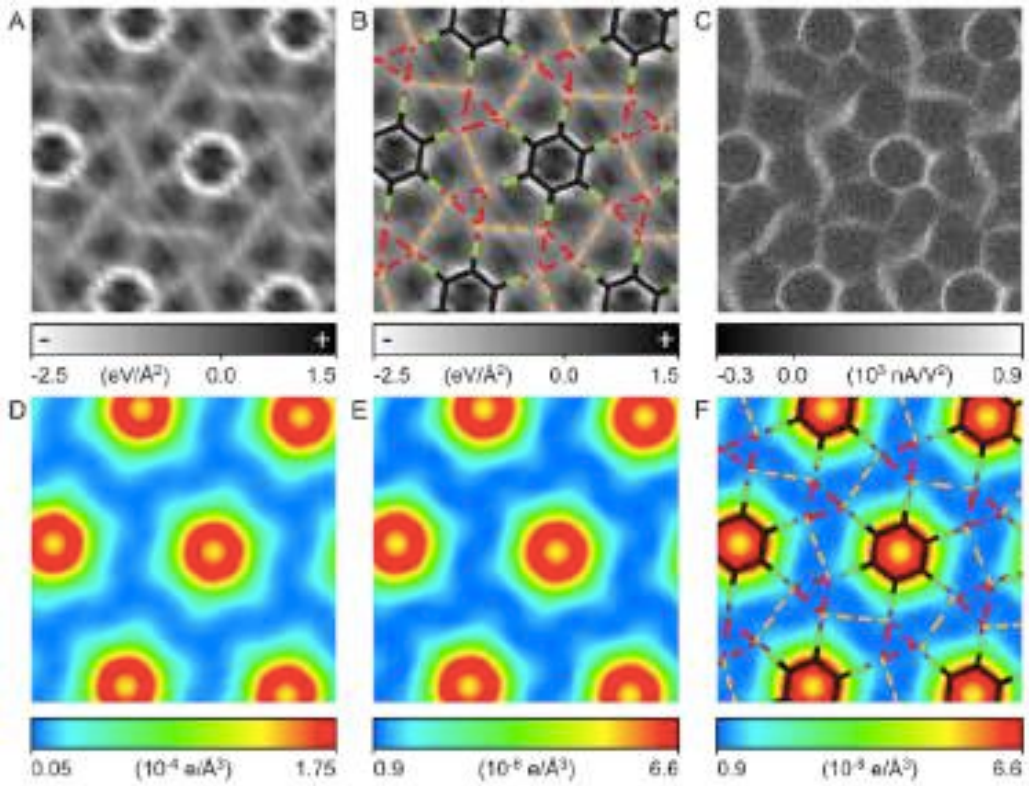
Halogen Bond Imaging Explanation

Science REPORTS

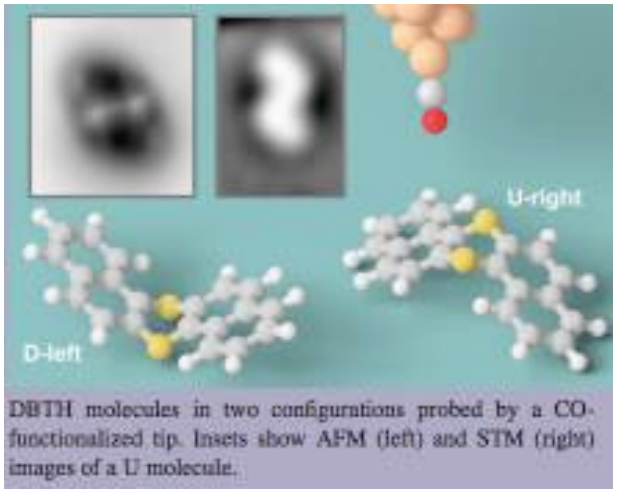
Cite as: Z. Han et al., Science 10.1126/science.aai8625 (2017).

Imaging the halogen bond in self-assembled halogenbenzenes on silver

Zhumin Han,[1] Gregory Czap,[1] Chi-lun Chiang,[1] Chen Xu,[1] Peter J. Wagner,[1] Xinyuan Wei,[1,3] Yanxing Zhang,[1,3] Ruqian Wu,[1,2]* W. Ho[1,4]*

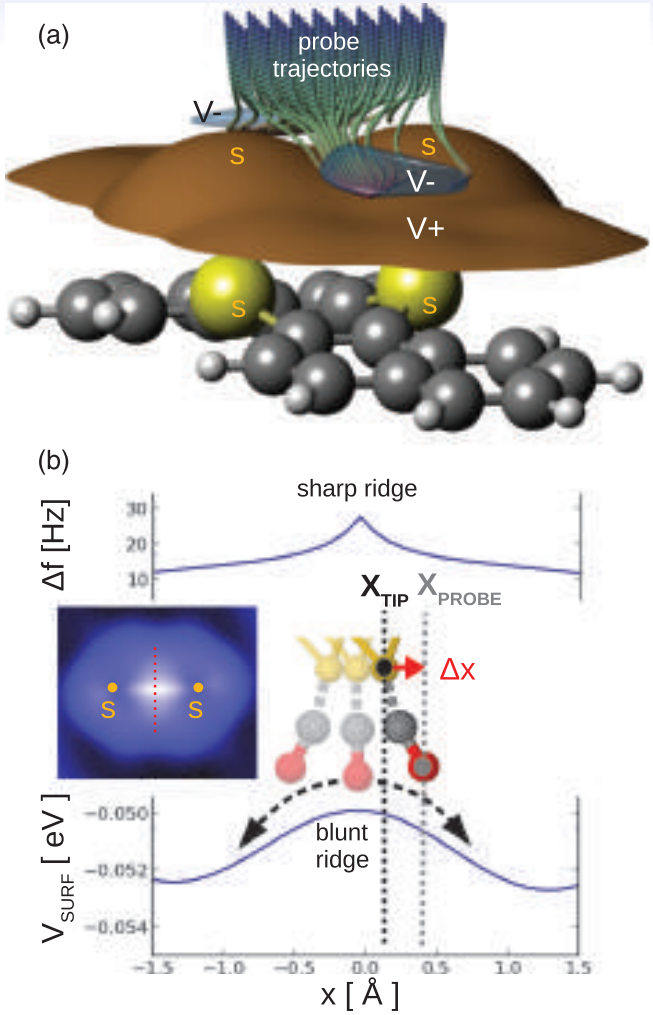


AFM Contrast with no Chemical Bonds!



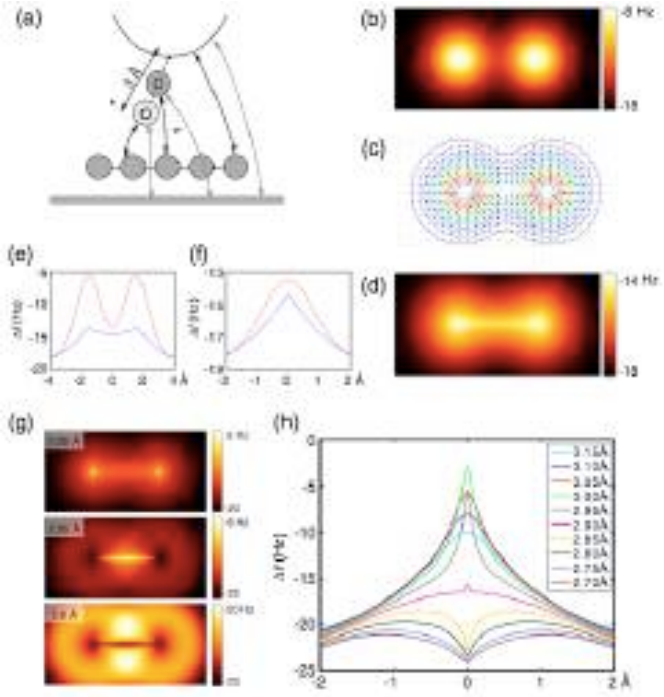
High-resolution STM & AFM of stereochemically resolved dibenzo[a,h]thianthrene molecules, Pavlicek et al, Phys. Status Solidi B (2013)

- Experiment: Ridges not necessarily correlates with chemical bonds
- Simulation: Sharp structural resolution, in AFM & STM, is due to **strong lateral relaxations of the tip apex particle**



Mechanism of high-resolution STM/AFM imaging with functionalized tips, Hapala and Jelinek, Phys. Rev. B 90

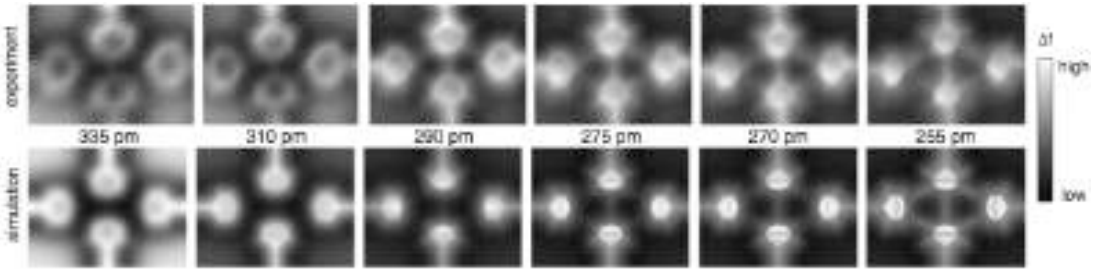
AFM Contrast with no Chemical Bonds!



PRL 113, 186102 (2014) PHYSICAL REVIEW LETTERS week ending 31 OCTOBER 2014

Intermolecular Contrast in Atomic Force Microscopy Images without Intermolecular Bonds

Sampsa K. Hämäläinen,[1] Nadine van der Heijden,[2] Joost van der Lit,[2] Stephan den Hartog,[2] Peter Liljeroth,[1,*] and Ingmar Swart[2,†]



Summary

Imaging non-covalent bonds

- We Know that
  - AFM experiment with CO-functionalized tips: H-bonds. X-bonds, ...
  - Theory: no electron accumulation + lateral relaxation of apex particle
  - $\Rightarrow$ different from real imaging of chemical bonds
- Still

Thank you for your attention!