

## Supplementary materials

### A high-resolution model for non-contact atomic force microscopy with a flexible molecule on the tip apex

Chun-Sheng Guo,<sup>a,\*</sup> Michel A Van Hove,<sup>b</sup> Xinguo Ren,<sup>c,d</sup> Yong Zhao<sup>a,e</sup>

<sup>a</sup>Key Laboratory of Advanced Technology of Materials (Ministry of Education), Superconductivity and New Energy R&D Center, Mail Stop 165#, Southwest Jiaotong University, Chengdu 610031, Sichuan, China

<sup>b</sup>Institute of Computational and Theoretical Studies and Department of Physics, Hong Kong Baptist University, Hong Kong, China

<sup>c</sup>Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei 230026, Anhui, China

<sup>d</sup>Synergistic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei, 230026, Anhui, China

<sup>e</sup>School of Materials Science and Engineering, University of New South Wales, Sydney, 2052 NSW, Australia

#### 1. Vertical force patterns have the same contrast as frequency shift images

To obtain atomic resolution by NC-AFM with a CO molecule-functionalized tip (FMT), it is necessary to operate in a regime where the contrast is mainly determined by Pauli repulsion approximately described by  $e^{-\lambda(Z-a)}$ , where  $\lambda$  and  $a$  are constants,  $\lambda > 0$  and  $a > Z$ , for heights  $Z$  below where the repulsion minimum is found, as shown in Fig. S1 below 3.6 Å.

Approximately, for two different sites, the contrast of vertical interaction force is:  $C_F \propto e^{-\lambda_1(Z-a_1)} - e^{-\lambda_2(Z-a_2)}$ . If site (1) is greater in brightness than site (2), then  $C_F \propto e^{-\lambda_1(Z-a_1)} - e^{-\lambda_2(Z-a_2)} > 0$ , where  $a_1 \approx a_2 > Z$ , which implies  $\lambda_1 > \lambda_2$ .

Consequently, the contrast of the frequency shift is:

$$C_{\Delta f} \propto \lambda_1 e^{-\lambda_1(Z-a_1)} - \lambda_2 e^{-\lambda_2(Z-a_2)} = \lambda_1 \left[ e^{-\lambda_1(Z-a_1)} - \frac{\lambda_2}{\lambda_1} e^{-\lambda_2(Z-a_2)} \right] > 0, \text{ because } \lambda_2 / \lambda_1 < 1.$$

This means that the contrast in frequency shift for two different sites is the same as for the corresponding vertical force. Consequently, we can directly use the interaction

force  $F_z^{tilt}$  patterns to simulate the AFM frequency shift images. Actually, it has already been noted in several reports that vertical force and frequency shift show similar features.<sup>1-4</sup>

Using the interaction force pattern in the place of the AFM frequency shift image saves much calculation time.

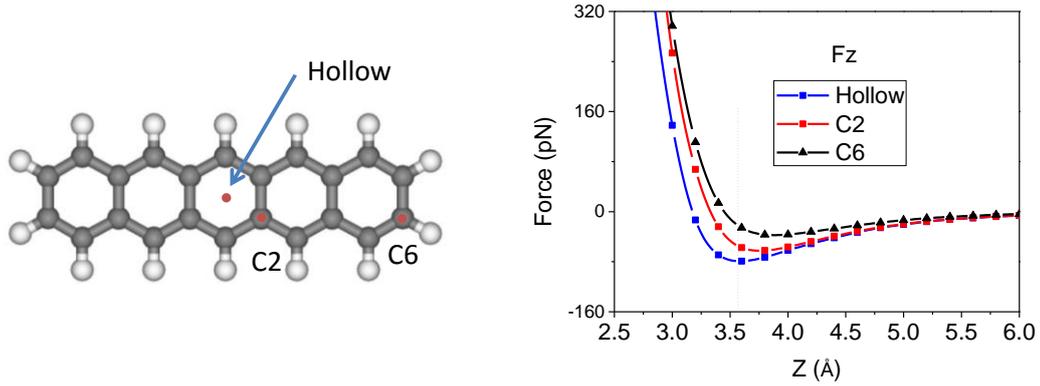


Fig. S1. Chemical structure of pentacene (left panel) and line profile of vertical force at different positions above pentacene (right panel). The red points on the molecule mark the three sampled positions used in the right panel.  $Z$  is  $H_{scan}$ , the distance from O in the CO tip to the sample surface. Reasonable force maps are always obtained below 3.6 Å in our simulations.

## 2. Calculation of the frequency shift with $F_z^{tilt}$

We use a simple numerical derivative to calculate the frequency map, namely

$$\Delta f(Z) \approx -\frac{f_0}{2k_0} \frac{F_z^{tilt}(Z+dZ) - F_z^{tilt}(Z)}{dZ}$$

If we use two different values of the scanning height,  $H_{scan}$  ( $Z$  in the formula), with a small interval, the result is unacceptably noisy, as shown in Fig. S2a. Therefore we calculated for pentacene with five sets of  $F_z^{tilt}$  and then the frequency shift is

obtained by differentiating the  $F_z^{tilt}$  profile to reduce noise. For example, map shown in Fig. S2b is obtained with  $F_z^{tilt}$  for  $H_{scan}$  values of 3.71 vs. 3.70 Å.

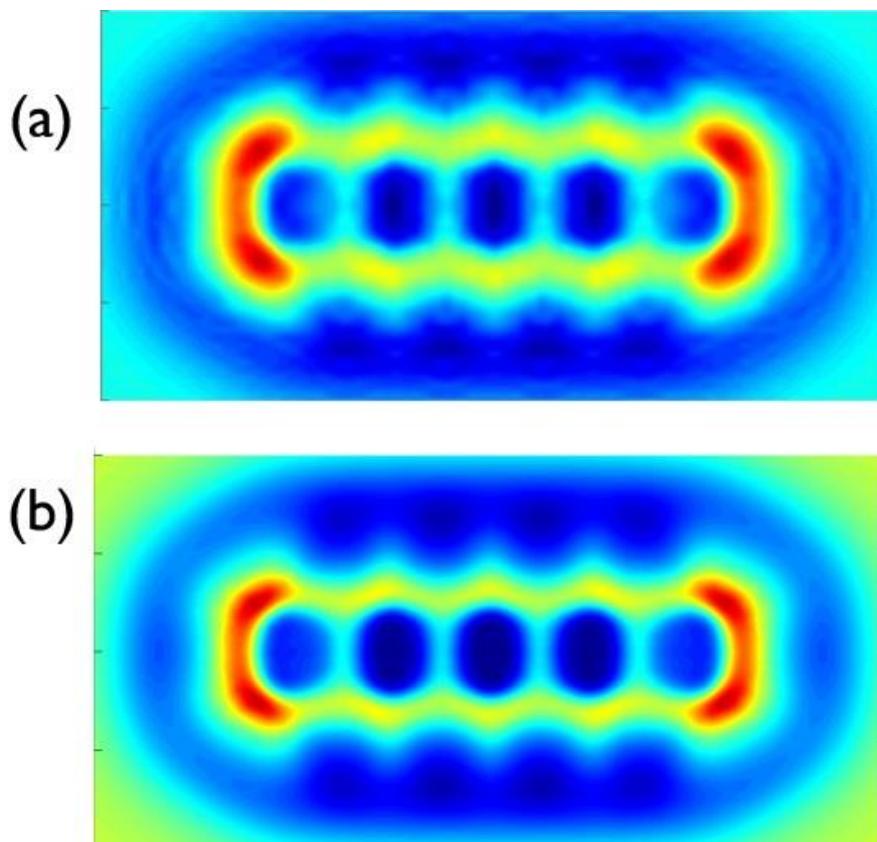


Fig. S2. Frequency shift map (a) obtained as the change of  $F_z^{tilt}$  for  $H_{scan}$  values of 3.70 vs. 3.75 Å, and (b) calculated by differentiation of  $F_z^{tilt}$  which is obtained for tip heights ranging from  $H_{scan} = 3.675$  Å to 3.75 Å with a vertical spacing of 0.025 Å, as mentioned in the main article. Fig. S2b is the same as Fig. 2b in the main article, where it is reproduced in gray.

### 3. Electron density within planes above a pentacene molecule

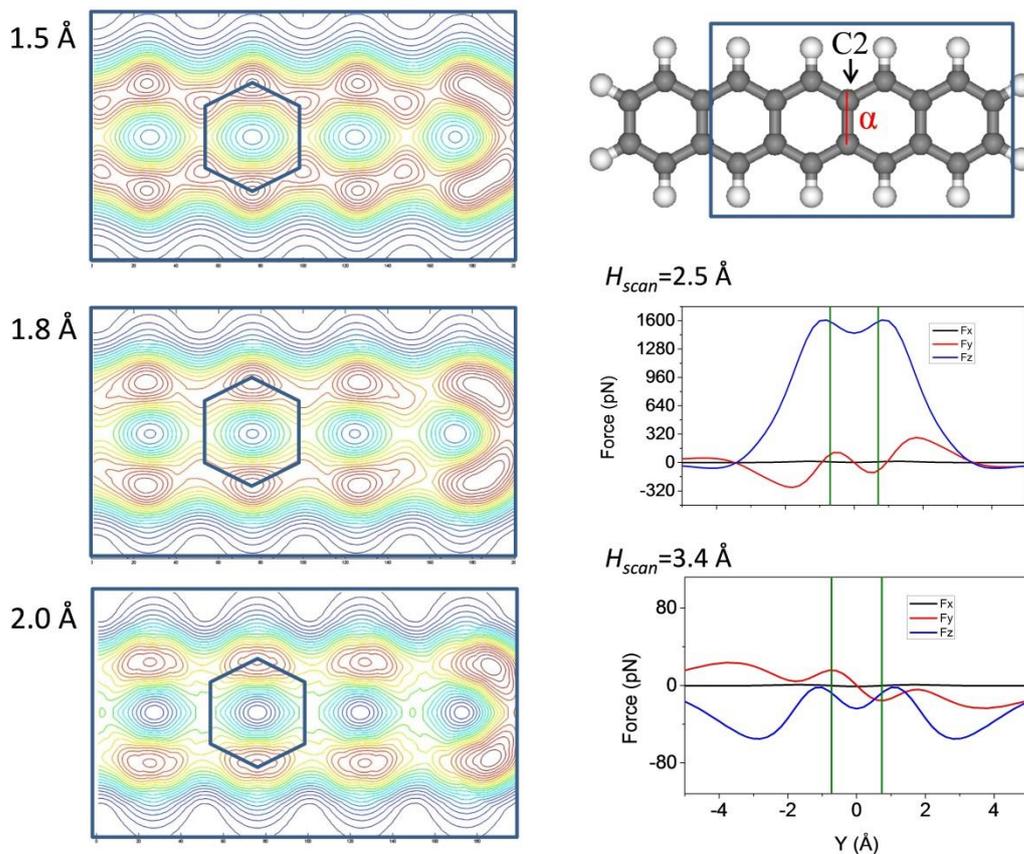


Fig. S3. Left panels: Electron density contours of a pentacene molecule located 1.5 Å, 1.8 Å and 2.0 Å above its molecular plane. The box size is 10.0 by 6.0 Å<sup>2</sup>, and the hexagons denote the central C<sub>6</sub> positions. Right panels: at top, chemical structure of pentacene with  $\alpha$ -bond marked in red, C2 atom and a box denoted for the area of electron density shown in left panels; below, two line profiles of the vertical force  $F_z$  and lateral forces  $F_x$  and  $F_y$  along the  $\alpha$ -bond at  $H_{scan}=2.5 \text{ \AA}$  and 3.4 Å, where the  $F_z$  maxima are about 0.2 Å and 0.35 Å outside the C2 position, respectively. The vertical green lines link the positions of C atoms

As shown in Fig. S3, the maxima of the electron density of a pentacene molecule in the region of overlap between the CO and pentacene can be displaced laterally from the projections of the nuclear positions. The maximum electron density along a C-C bridge is shifted outwards from the carbon (e.g. C2) atomic-position in planes above

the pentacene molecule. For example, it located at about 0.1, 0.25 and 0.35 Å away from the carbon (C2) within the 1.5, 1.8 and 2.0 Å plane, respectively. We can see that both the electron density maxima and the force  $F_z$  maxima move progressively away from the projected positions of the nuclei, as height increases, but the locations of the two kinds of maxima are not the same at a given height. Consequently, we conjecture that it is not just a single layer of electrons at the height of  $H_{scan}$  that contributes to the vertical force  $F_z$ ; rather, the repulsive force that the tip feels should be considered as an integrated effect arising from the electrons in a region of certain thickness below the tip.

## References

- (1) Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy. *Science* **2009**, *325*, 1110-1114.
- (2) Gross, L.; Mohn, F.; Moll, N.; Schuler, B.; Criado, A.; Guitian, E.; Pena, D.; Gourdon, A.; Meyer, G. Bond-Order Discrimination by Atomic Force Microscopy. *Science* **2012**, *337*, 1326-1329.
- (3) Moll, N.; Gross, L.; Mohn, F.; Curioni, A.; Meyer, G. The Mechanisms Underlying the Enhanced Resolution of Atomic Force Microscopy with Functionalized Tips. *New Journal of Physics* **2010**, *12*, 125020.
- (4) Moll, N.; Gross, L.; Mohn, F.; Curioni, A.; Meyer, G. A Simple Model of Molecular Imaging with Noncontact Atomic Force Microscopy. *New Journal of Physics* **2012**, *14*, 083023.