Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Gas Molecules Sandwiched in Hydration Layers at Graphite/Water Interfaces

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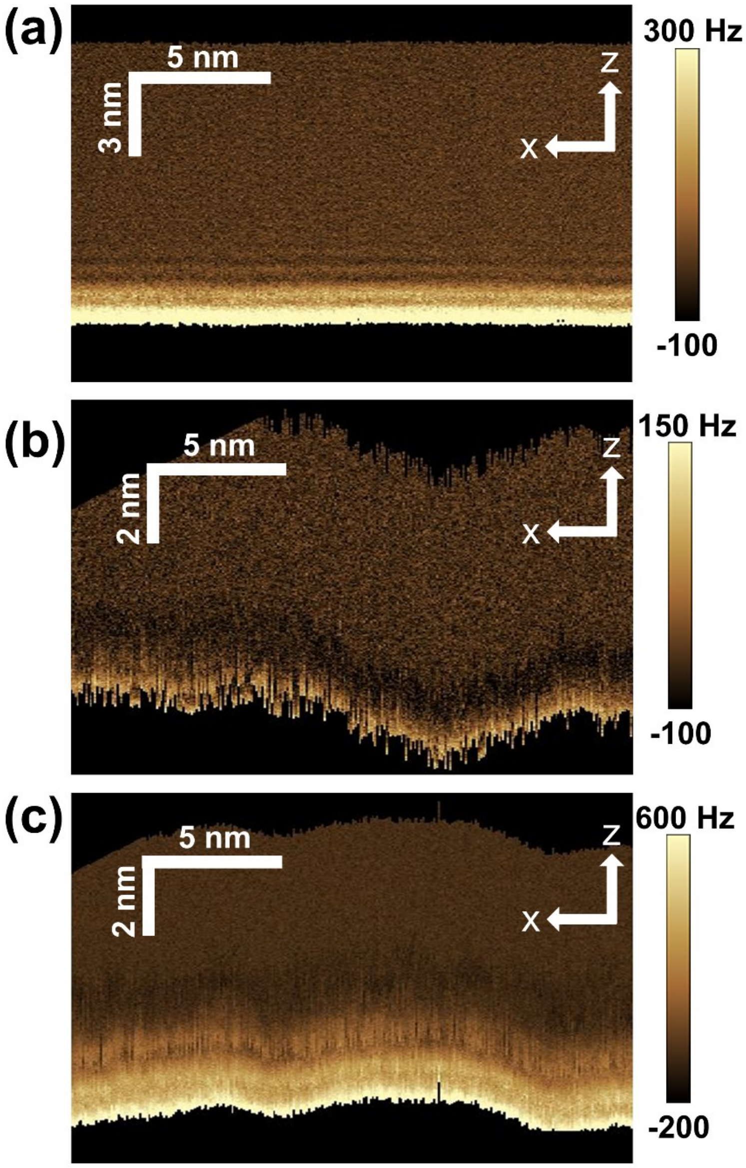
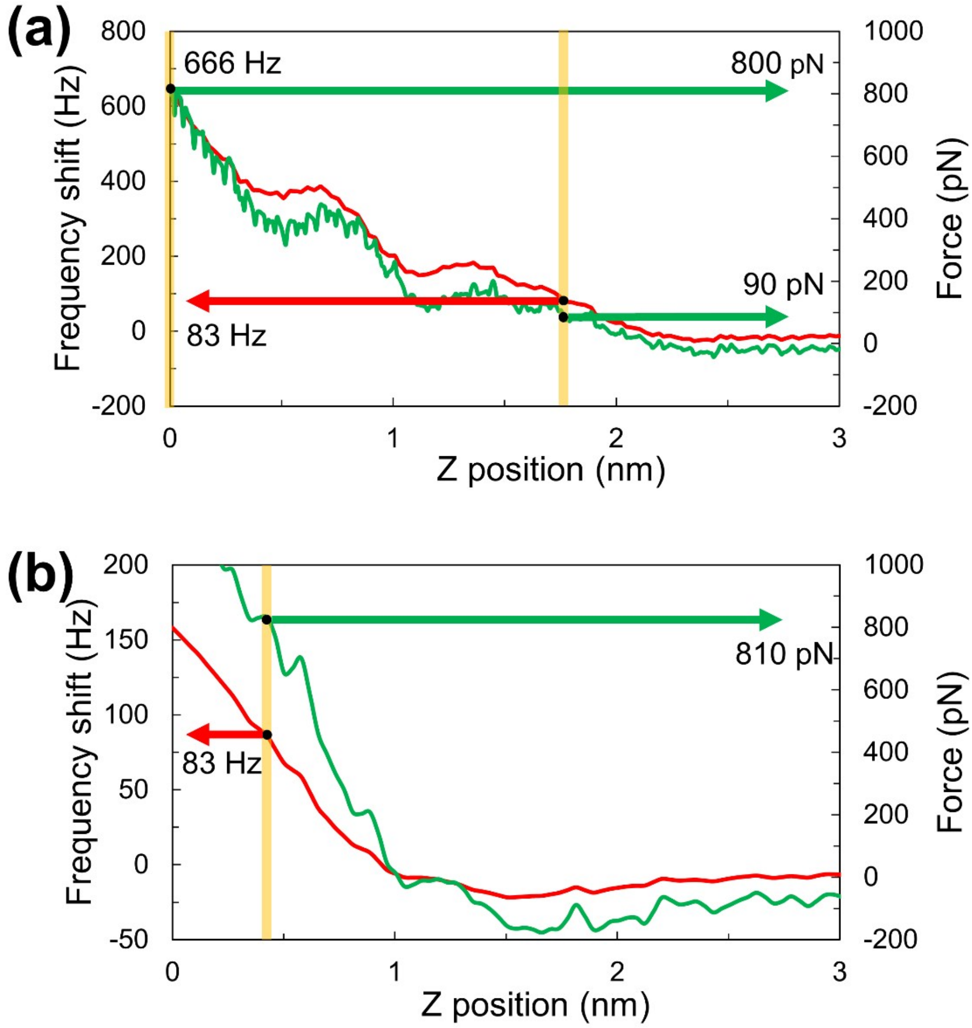


Supplementary Figure 1. Two-dimensional frequency-shift maps during retraction. (a) on the bare HOPG surface, (b) on the adsorbed gas layers, and (c) when penetrating the adsorbed gas layers.

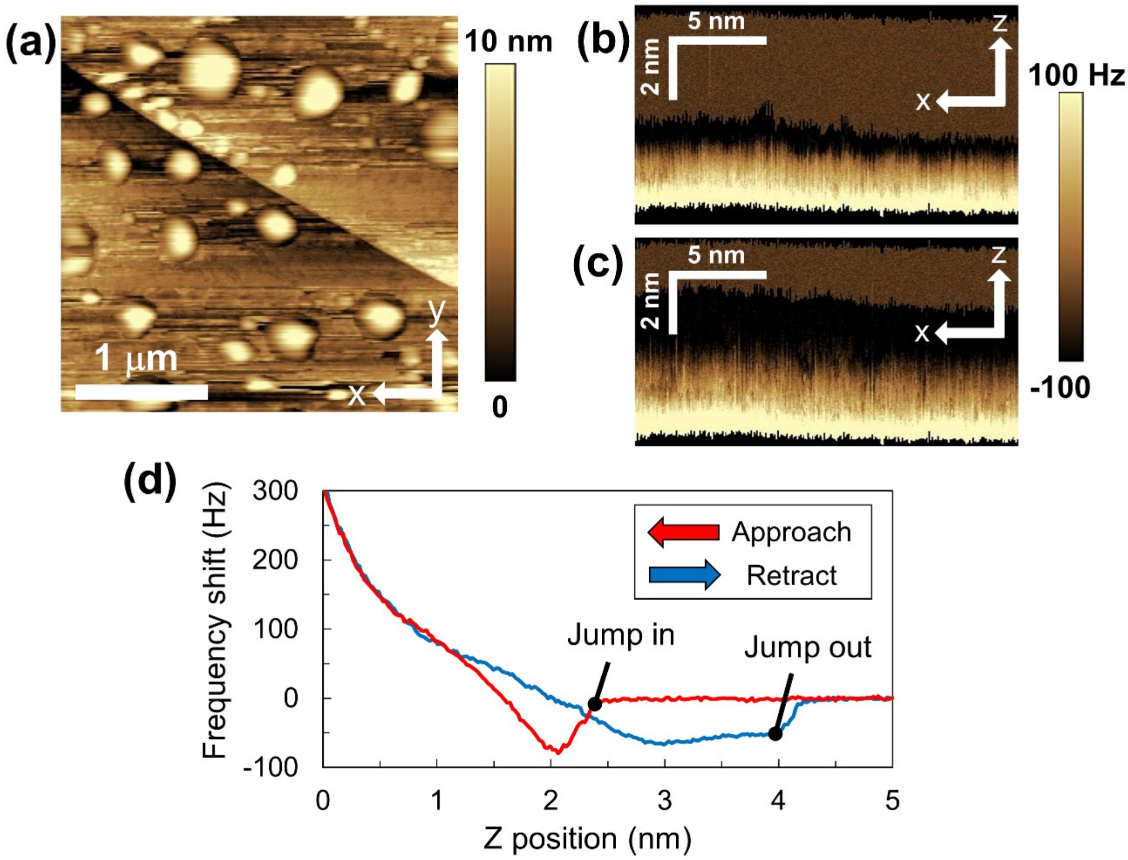


Supplementary Figure 2. Averaged frequency shift–distance curves (red lines) and the corresponding force curves (green lines) translated by Sader's formula[1] with amplitudes of (a) 0.8 nm and (b) 4.0 nm. The black dots indicate the preset values of the frequency shifts (+83 Hz and +666 Hz) and the corresponding load force. In (a), the load forces of 90 and 800 pN correspond to frequency shifts of +83 and +666 Hz; the same load forces were used in Fig. 2(a–d) and Fig. 3(b,c) in the main article, respectively. In (b), the load force of 810 pN corresponds to a frequency shift of +83 Hz; this load force was used in Fig. 3(a).

Supplementary note 1

A height image at the HOPG/pure water interface after the solvent-exchange process is shown in Fig. S3(a). Many spherical cap-shaped nanobubbles with base diameters of less than 500 nm were observed. We previously reported that the shape of surface nanobubbles becomes distorted when measured with a hydrophobic tip[2], which is consistent with the result of Fig. S3(a). Figure S3(b, c) shows the 2D frequency-shift maps in the area where no nanobubbles exist at the same interface. There is a clear difference between the approach and retraction, especially in the range where the frequency is negatively shifted. The frequency shift–distance curves, which are extracted from Fig. S3(b,c) are shown in Fig. S3(d). A periodic structure was not observed, but clear hysteresis appeared between the approach and retraction.

During approach, a jump-in of the frequency shift was observed at Z = 2.4 nm. This occurred because the hydrophobic tip dries when it comes into contact with the gas phase, resulting in the formation of a three-phase contact line on the tip surface (i.e. the interfacial gas phase was locally protruded). The negative frequency shift reached a maximum at a Z position of 2.0 nm and then gradually decreased, eventually becoming positive. This is because the three-phase contact line was pinned on the AFM tip surface; thus, the applied force to the tip changed from attractive to repulsive by reversing the direction of the gas/liquid interface (i.e. the gas phase is locally depressed). In the retraction, the attractive force continued up to 4.0 nm. This is because strong pinning at the tip surface induced a large deformation of the gas/liquid interface. Finally, the frequency shift suddenly became zero because of depinning (jump-out) of the interface. These results are in good agreement with the experimental[2] and simulation results[3] of the force curve obtained on nanobubbles on a hydrophobic surface. From these results, we can conclude that not only the surface nanobubbles, but also the adsorbed gas layers, exist at the HOPG/pure water interface. It is difficult to determine the hydration structure with adsorbed gas layers by the hydrophobic tip because the force derived from the gas/liquid surface tension works predominantly on the tip surface.



Supplementary Figure 3. Analysis of the HOPG/pure water interface with nanoscopic gas phases obtained with the hydrophobic AFM tip. (a) Height image (3 μm × 3 μm). (b,c) 2D frequency-shift maps in the approach and retraction, respectively. (d) Averaged frequency shift–distance curves.

Supplementary Reference

1. Sader, J. E. & Jarvis, S. P. Accurate formulas for interaction force and energy in frequency modulation force spectroscopy. *Appl. Phys. Lett.* **84**, 1801–1803 (2004).
2. Teshima, H., Takahashi, K., Takata, Y. & Nishiyama, T. Wettability of AFM tip influences the profile of interfacial nanobubbles. *J. Appl. Phys.* **123**, 054303 (2018).
3. Guo, Z., Liu, Y., Xiao, Q., Schönherr, H. & Zhang, X. Modeling the Interaction between AFM Tips and Pinned Surface Nanobubbles. *Langmuir* **32**, 751–758 (2016).