https://doi.org/10.1017/S1551929521000705 Published online by Cambridge University Press

Surface Potential Imaging of $F_{14}H_{20}$ Molecules via Sideband Kelvin Probe Force Microscopy

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Abstract: Sideband Kelvin probe force microscopy (KPFM) uses the intermodulation of an electrostatic drive force and a mechanical drive force to upconvert the electrostatic frequency to the first flexural resonance, where the high-quality factor of the resonance yields a more sensitive measurement. The sideband KPFM signal is calculated using a local interaction between the tip apex and the sample, rather than a total interaction between the cantilever and the sample, improving the spatial resolution over other technique variations. This paper covers the sideband KPFM details, including trade-offs and imaging of semi-fluorinated alkanes, such as $F_{14}H_{20}$, and self-assembled molecular nanostructures.

Keywords: atomic force microscopy, sideband Kelvin probe force microscopy, molecular nanostructure, topography, surface potential, semi-fluorinated alkanes $F_{14}H_{20}$

Introduction

From materials science to biological research, scientists have adopted Kelvin probe force microscopy (KPFM) to measure surface potential and work functions. KPFM follows the electrostatic force microscopy (EFM) operation principle. It measures a contact potential difference (CPD) and determines the sample's work function using DC bias feedback. However, conventional off-resonance KPFM produces low spatial resolution and low signal-to-noise ratios due to long-range crosstalk caused by the interaction between the sample and the total body of the cantilever. Sideband KPFM has an unparalleled spatial resolution and centers on the local interaction between the tip apex and sample, making it useful for analyzing grain boundaries, semiconductor junctions, photovoltaics materials, and even molecular structures [1–3].

KPFM operates by measuring the CPD. CPD is an electrostatic potential that exists between samples of two dissimilar, electrically connected materials. Considering atomic force microscopy (AFM), the AFM tip and sample are two different materials. Each of the materials has a specific conduction band and a separate work function. The work function of a material is the amount of energy required to move an electron to infinity from the surface of a given solid [2].

If the tip and the sample are electrically connected, the electrical connection will induce a natural flow of electrons and will create a potential difference between the two materials (Figure 1). This potential difference is measurable by applying the theoretical formula of contact potential difference:

$$CPD = \frac{\varphi_{sample} - \varphi_{tip}}{e} \quad (1)$$

where φ_{tip} and φ_{sample} are the work function of the sample and tip, respectively, and e corresponds to the electronic charge. Obtaining the work function of the material is possible by multiplying the surface potential of the materials by a single electron charge.

Equation (1) can be explained using the Kelvin probe method, which relies on detecting the electric field of the materials composing the AFM tip and sample. By modifying the voltage CPD, the electric field varies. Thereby, when applying an external bias (V_{DC}) of the same magnitude to the AFM tip but in the opposite direction, the surface charge of the contact area is nullified. Once there are no electrostatic forces, the work function difference has the same value as the applied voltage CPD; consequently, the work function of the sample can be calculated if the work function of the tip is known (Equation (2)) [3].

$$\varphi_s = e \cdot V_{CPD} + \varphi_t \quad (2)$$

Off-Resonance KPFM

When considering the AFM tip and the sample as a capacitor, analyzing the electrostatic forces between them is straightforward, as the amount of energy can be calculated with the difference in voltage and the capacitance. KPFM uses two frequencies to acquire topography and surface potential simultaneously. The standard procedure for KPFM consists of using two lock-in amplifiers (Figure 2A). The first lock-in amplifier modulates the frequency used to oscillate the cantilever at its mechanical resonant frequency, using a piezoelectric material to obtain a topography image. The second lock-in amplifier regulates the frequency, generally at 17 kHz, to measure the surface potential. This technique is denoted "off-resonance KPFM," as we can theoretically choose any resonance frequency as long as it does not match the cantilever's mechanical resonance [2]. Additionally, off-resonance KPFM obtains surface potential information by measuring the total interaction of the complete cantilever with the sample, limiting its spatial resolution.

Sideband KPFM

Sideband KPFM is a technique that exploits the intermodulation of an electrostatic drive force and a mechanical drive force to upconvert the electrostatic frequency to the first flexural resonance, where the high Q "quality factor" yields a more sensitive measurement [3]. Additionally, the sideband KPFM signal is calculated by using a local interaction between the tip apex and the sample rather than a total interaction between the cantilever and the sample, improving the spatial resolution over off-resonance KPFM. Local interaction allows the system to measure the surface potential of localized features with high resolution, due to the reduced interaction with other parts of the cantilever. The reason for the substantial reduction of the interaction, induced by the cantilever and the tip, is the downward distance dependence of the lever and cone forces on the experimentally important range [1].

The electrical driving frequencies of sideband KPFM appear at the sidebands of the mechanical oscillation of the cantilever (Figure 3), reducing the long-range crosstalk [3].

 doi:10.1017/S1551929521000705

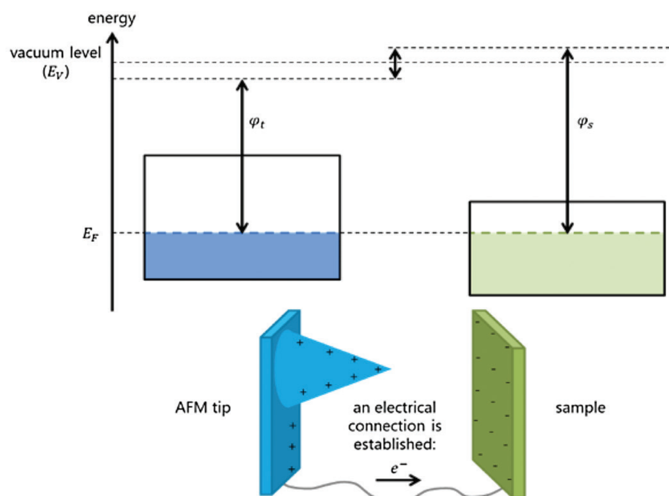

Figure 1: Contact potential difference between an AFM tip and sample.

The sideband frequencies of the mechanical oscillation and the local interaction of the tip apex allow sideband KPFM to accurately measure the surface potential with an increased resolution compared to off-resonance KPFM.

When performing sideband KPFM, instead of using a frequency of 17 kHz, the KPFM mode works with the sideband's frequencies, usually 1–5 kHz off from the cantilever's mechanical resonance. This method uses two lock-in amplifiers (Figure 2B) to lock on the sideband frequencies. Figure 2B shows that the second lock-in amplifier modulates the left sideband, while the third modulates the right sideband. The surface potential is obtained by averaging the DC voltage feedback from both sideband frequencies [1].

Electrostatic Force Microscopy (EFM) Amplitude Sensitivity

The KPFM signal-to-noise ratio reflects the magnitude of the electrostatic interaction, or EFM amplitude sensitivity. The higher the EFM amplitude sensitivity, the higher the KPFM signal-to-noise ratio response can be. The EFM amplitude sensitivity can be defined as ΔEFM amplitude / Δ tip bias. When the cantilever's resonance frequency equals the electrical driving frequency, the EFM amplitude can be defined as:

$$X = \frac{\delta_c}{\delta_z}(V_{CPD} + V_{DC})\frac{V_{AC}Q}{k} \qquad (3)$$

where X is the amplitude of the cantilever displacement, Q is the cantilever's Q factor, and k is the spring constant of the cantilever. Thereby, the EFM amplitude is directly proportional to the V_{AC} and inversely proportional to the cantilever's spring constant. Another factor that affects the EFM amplitude sensitivity is the laser displacement on the photo detector (Δa) [4]. It is defined as:

$$\Delta a = 3\frac{L_x}{L_C}\Delta Z \qquad (4)$$

Figure 2: Sideband KPFM feedback loop: a) off-resonance KPFM loop; b) sideband KPFM loop.

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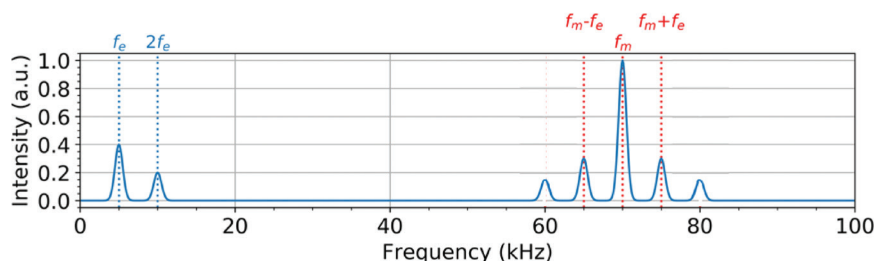

Figure 3: Fourier transform of the vertical deflection comparing off-resonance KPFM versus sideband KPFM.

where L_x is the distance between the tip and the cantilever, L_c the cantilever's length, and ΔZ the displacement of the cantilever oscillation. Therefore, the longer the cantilever, the smaller the displacement. The EFM amplitude sensitivity, thus the KPFM signal sensitivity, increases when the cantilever has a short length and/or a small spring constant [4].

Eicosylperfluorotetradecane $F_{14}H_{20}$

KPFM not only measures the CPD on metals or semiconductors, but it can also measure the surface potential of organic or soft samples like the self-assembled molecules of some alkanes. Eicosylperfluorotetradecane, $F(CF_2)_{14}(CH_2)20H$, or its abbreviated form $F_{14}H_{20}$, is a semifluorinated alkane with a perfluorinated chain segment. It consists of two incompatible subunits that segregate into distinct domains. The mismatch in the cross section between the perfluoro and the perhydro alkyl tail result in distinctive superstructure formations (Figure 4). The mechanism describing how these compounds order in specific polymorphism is not yet fully understood. The investigation of semifluorinated alkanes, such as $F_{14}H_{20}$, contributes to self-assembly knowledge [5]. $F_{14}H_{20}$ nanomolecular structures have dipole orientation, rendering considerable surface potential of 0.8V, and thus is suited for studying the assembly of molecules and their electronic properties on the nanoscale using KPFM [6].

Methods

In this study, a Park NX10 AFM system, equipped with SmartScan™ software, was used to measure the local contact potential difference and topography of $F_{14}H_{20}$ molecular structures. The study shows a comparison between sideband KPFM and conventional off-resonance KPFM image resolution. For the sideband KPFM experiments, lock-in amplifiers were used to send a 3 kHz AC signal to the cantilever, while the standard technique used a 17 kHz AC signal. SmartScan automatically selected the phase and amplitude of the resonances. For these experiments, the average signal of both sidebands was recorded. Two different types of conductive cantilevers, NSC14/Cr-Au and NSC36-C/Cr-Au, were used to analyze the correlation between EFM amplitude sensitivity, the cantilever's length, and the spring constant. NSC14/Cr-Au and NSC36-C/Cr-Au were 125 and 130 μm long and had a spring constant of 5 and 0.6 N/m, respectively.

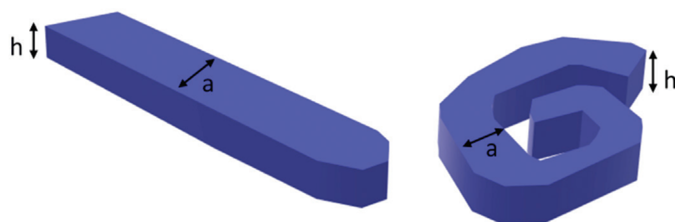

Figure 4: Schematic pictures of the ribbon and the spiral morphology for $F_{14}H_{20}$.

Results and Discussion

Figure 5 shows a surface potential comparison between sideband and conventional off-KPFM images obtained with a NSC36-C/Cr-Au cantilever. The sideband KPFM measurement of the $F_{14}H_{20}$ aggregates shows a surface potential contrast of 600–650 mV between the fluorinated parts of the molecules and the substrate, along with a clear lateral resolution where even the in-between space of the aggregates can be distinguished (Figures 5a and 5b). Images of the conventional off-resonance KPFM measurements show that the technique successfully measures the potential difference of the aggregates and the substrate; however, the potential difference gives a value of 300 mV (Figures 5c and 5d). The spatial resolution is not as well defined. The improvement

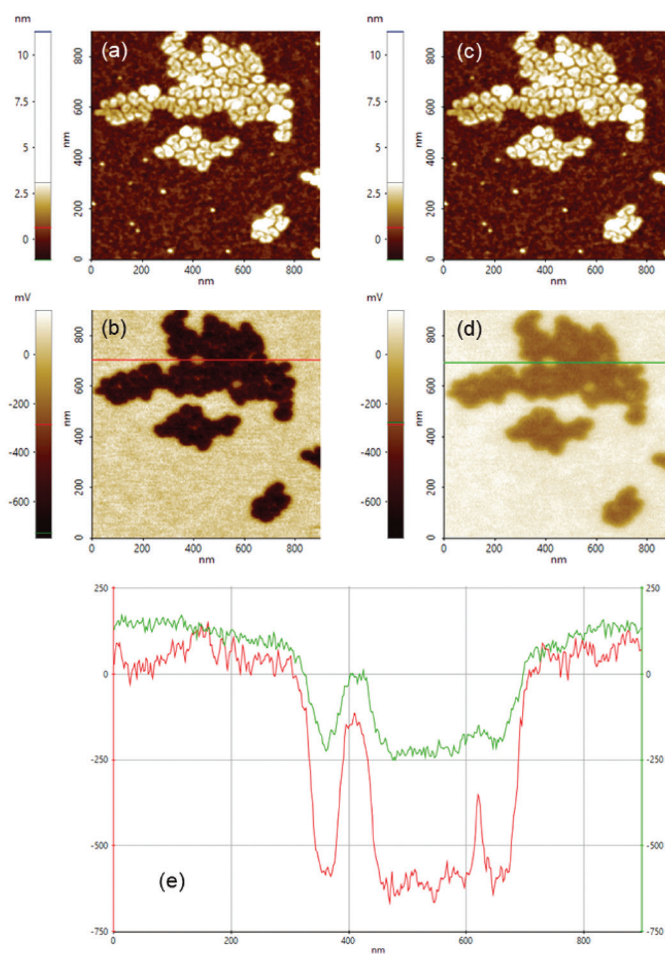

Figure 5: Sideband and off-resonance comparison: (a) sideband topography image; (b) sideband surface potential image; (c) off-resonance topography image; (d) off-resonance surface potential image; (e) line profiles taken along the red line in (b) and along the green line in (d).

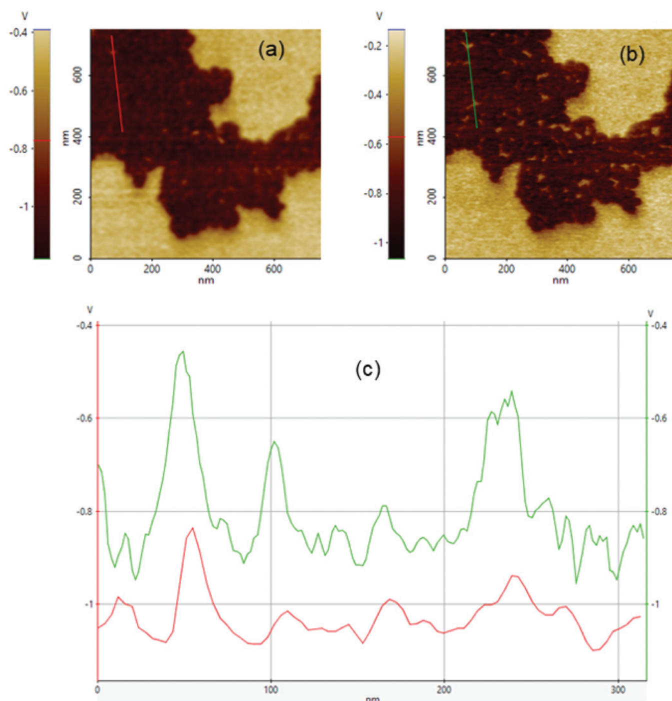

Figure 6: Surface potential difference of $F_{14}H_{20}$ via sideband KPFM: (a) surface potential imaged with probe NSC14/Cr-Au; (b) surface potential imaged with probe NSC36C/Cr-Au; (c) line profiles taken along red line in (a) and green line in (b).

of resolution when using the sideband mode relies on the local interaction between the tip apex and sample. The topography images indicate that the $F_{14}H_{20}$ aggregates of this sample form an incomplete spiral superstructure (Figure 5). These incomplete spirals tend to form more compacted superstructures, reducing the in-between spaces of the aggregates [5].

Figure 6 shows the results of the correlation between the spring constant of the cantilever and KPFM signal-to-noise ratio sensitivity. Cantilever NSC14/Cr-Au (Figure 6a) shows a lower sensitivity for the surface potential changes than cantilever NSC36-C/Cr-Au (Figure 6b). Line profiles taken from images shown in Figures 6a and 6b demonstrate that using either type of cantilever tip allows sideband KPFM to detect small changes in the surface potential, even between the $F_{14}H_{20}$ superstructures. The fact that NSC36-C/Cr-Au shows a higher KPFM signal sensitivity, and has a spring constant that is almost ten times smaller than NSC14/Cr-Au, indicates a correlation between the spring constant of the probe and the sensitivity. Equation 4 establishes that the length of the cantilever is also crucial for EFM amplitude sensitivity; both cantilevers have almost the same length, so the correlation between cantilever length and EFM sensitivity is not analyzed. Further experiments are needed to investigate the correlation between the cantilever's length, the EFM amplitude, and the KPFM signal sensitivity.

Summary

In this study, sideband KPFM on a Park NX10 atomic force microscope was used to image $F_{14}H_{20}$ molecular structures. This study validates sideband KPFM as a technique that measures the surface potential with higher sensitivity and spatial resolution when compared to the conventional off-resonance KPFM techniques. The results suggest a correlation between KPFM signal sensitivity and the cantilever spring constant, and that a lower spring constant of the cantilever yields higher sensitivity than stiffer cantilevers. Further study is necessary to understand the correlation between KPFM signal sensitivity and cantilever length.

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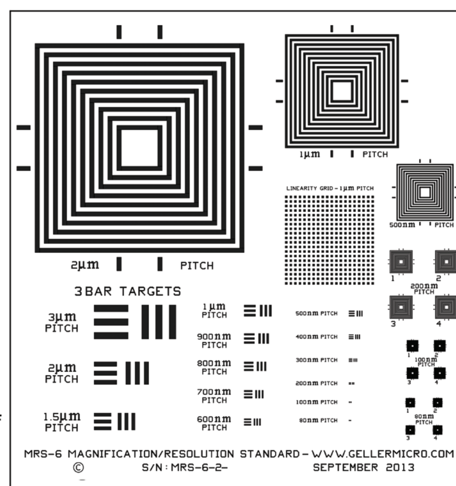

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