Calibrating atomic-scale force sensors installed at the tip apex of a scanning tunneling microscope

G. Kichin, C. Wagner, F. S. Tautz, and R. Temirov[*]

Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany and
Jülich Aachen Research Alliance (JARA)–Fundamentals of Future Information Technology, 52425 Jülich, Germany

Scanning tunneling microscopy (STM) tips decorated with either a single carbon monoxide molecule or a single xenon atom are characterized by simultaneous force and conductance measurements using a combined low-temperature noncontact atomic force and scanning tunneling microscope (NC-AFM/STM). It is shown that in both cases the particle decorating the tip simultaneously performs the function of an atomic-scale force sensor and transducer which couples the short-range force acting on the tip to the tunneling conductance of the junction. On the basis of the experimental data, two distinct coupling regimes are identified; in one of them the force sensor-transducer function is calibrated quantitatively.

Almost thirty years after its invention, the technique of scanning tunneling microscopy (STM) still experiences many exciting developments. One of them—the recently reported scanning tunneling hydrogen microscopy (STHM)—extends the imaging capabilities of low-temperature STM by filling the junction with molecular hydrogen (H_2).[1] As has been revealed in the latest experiments, the structural resolution produced in STHM experiments is *generically* induced by STM tips decorated with either single molecules (H_2, D_2, CO, CH_4) or atoms (Xe).[2] In an attempt to identify the mechanism that induces the STHM resolution, it has been proposed that the particle decorating the STM tip functions as a combined "force sensor" and "signal transducer."[3] The possibility to use the STM tip as a microscopic force sensor provides interesting opportunities both for high-resolution imaging and spectroscopy. However, before these opportunities can be fully exploited, it is necessary to develop a quantitative model describing the STHM imaging mechanism. Here we make an important step in this direction, presenting simultaneous force and conductance measurements on the basis of which the sensor-transducer function of the decorated STM tips is quantitatively calibrated.

For the purpose of calibrating the microscopic sensor-transducer comprised of a single particle adsorbed at the STM tip apex, we set up an experiment in which a known force is applied to the tip and the response of the junction conductance is measured. To obtain the correct calibration it is necessary to separate the effect of the force applied to the sensor from all other factors influencing the conductance. Therefore the force cannot be tuned by simply changing the tip-surface distance, because in that case the tunneling current mostly follows the changes of the local density of states (LDOS). Instead we use the recent results of Gross *et al.*,[4] who have shown that the force acting on the tip can be tuned in the pN range by positioning the tip at a *constant distance* from the surface, at different locations above the backbone of a planar organic adsorbate. Using a single 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecule residing in a monolayer film adsorbed on the Au(111) surface, we tune the force acting on the tip by moving the tip at constant height above the PTCDA by a mere 1.4 Å from the middle of its central carbon ring [indicated by the blue circle in Fig. 1(a)] to the location above

the nearest carbon atom [red circle in Fig. 1(a)]. Since the LDOS does not vary appreciably between these two locations (see below), any variation of the differential tunneling conductance $\Delta dI/dV(z) = dI/dV_{atom}(z) - dI/dV_{ring}(z)$ must be induced by a change of the force $\Delta F(z) = F_{atom}(z) - F_{ring}(z)$ acting on the tip.

For the measurements, all of which have been conducted using a CREATEC low-temperature ultra-high vacuum qPlus[5] NC-AFM/STM, we first prepared an atomically clean Au(111) surface following the standard recipe of repeated sputtering and annealing cycles. A submonolayer film of PTCDA molecules was deposited at room temperature onto the prepared surface using a home-built Knudsen cell. A qPlus sensor with a glued $15\,\mu$m thick PtIr wire was obtained from CREATEC and a $300\,\mu$m long tip was prepared by cutting the PtIr wire with a focused ion beam. Finally, the tip was crashed numerous times into the Au(111) substrate at 5 K to cover the tip apex with substrate atoms. The preparation resulted in a qPlus oscillation frequency of $f_0 = 30.3$ kHz. During the measurements, the amplitude of the sensor's oscillation was kept constant at ≈ 0.2 Å.[6] Experiments were carried out at 5 K.

Scanning the tip of the oscillating qPlus sensor over the PTCDA molecule in the constant height mode, sequences of simultaneous frequency shift (Δf) and conductance (dI/dV) images were recorded at various tip-surface distances.[7] Three different types of tips were used: (i) a clean Au tip, (ii) an Au tip decorated with a single CO molecule (CO tip), and (iii) an Au tip decorated with a single Xe atom (Xe tip).[2] Evaluating Δf and dI/dV at the two locations [indicated with the colored circles in Fig. 1(a)] of each image in the z sequence, we extract pairs of force $\left[F_{atom}(z),F_{ring}(z)\right]$ and conductance $\left[dI/dV_{atom}(z),dI/dV_{ring}(z)\right]$ spectra.[8]

The image sequence made with the Au tip shows featureless contrast of PTCDA in both detection channels [cf. Fig. 1(a)]. Therefore, as Fig. 1(b) shows, $F_{atom}(z) = F_{ring}(z)$ and $dI/dV_{atom}(z) = dI/dV_{ring}(z)$. The second equality confirms that the LDOS of PTCDA, evaluated at the energy $E_F + eV$ defined by the applied tunneling bias V, exhibits no variation between the two chosen locations. According to the $F(z)$ spectra in Fig. 1(b), the Au tip is very reactive and experiences a strong attraction towards the surface.[10] The chemical nature of this attraction becomes apparent at $z = 3$ Å,
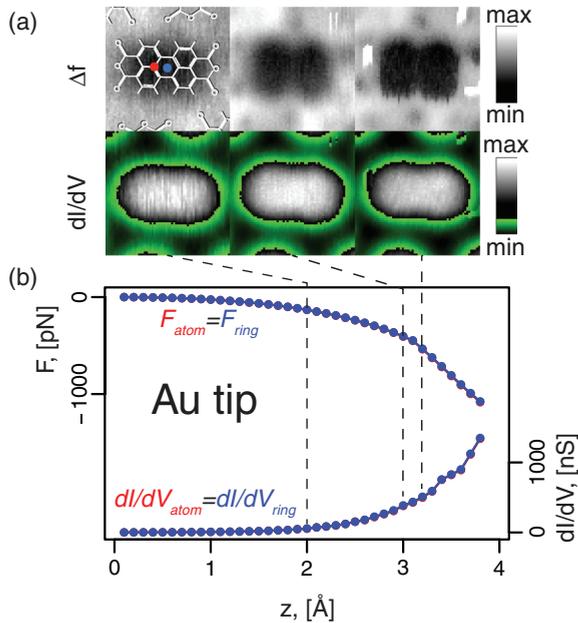
FIG. 1. (Color) (a) $64 \times 64\,pixel$, $13 \times 13\,\text{Å}^2$ constant height Δf (top) and dI/dV (bottom) images selected from the image sequence measured above the PTCDA molecule adsorbed on Au(111) with the clean Au tip. Tunneling bias: $V = -12\,\text{mV}$. The chemical structure formula of PTCDA is shown, red and blue circles mark the positions at which $F(z)$ and $dI/dV(z)$ were evaluated. The used color scales are shown next to the respective groups of images. The two-color scale was used for better representation of the large dynamic range in the dI/dV images. For the Δf images in the left, middle, and right panels the ($\Delta f_{\min}$, $\Delta f_{\max}$) of the corresponding scales are ($-26\,\text{Hz}$, $-23\,\text{Hz}$), ($-45\,\text{Hz}$, $-32\,\text{Hz}$), and ($-85\,\text{Hz}$, $-50\,\text{Hz}$). For the dI/dV images the ($dI/dV_{\min}$, $dI/dV_{\max}$) of the corresponding scales are (10 nS, 77 nS), (50 nS, 416 nS), and (66 nS, 562 nS). (b) $F(z)$ (top) and $dI/dV(z)$ (bottom) spectra extracted from the image series shown in Fig. 1(a)[8]. The blue spectra were obtained above the center of the carbon ring [blue circle in Fig. 1(a)]; the red spectra, at the carbon atom [red circle in Fig. 1(a)]. Note that in the case of the clean Au tip the red and the blue spectra coincide. The F scale is defined such that a negative (positive) value corresponds to an attractive (repulsive) force. For the definition of the z scale see Ref. 7. The dashed lines mark the z values at which the images from Fig. 1(a) were measured.

where the Δf images show local interaction of the tip with the corner oxygens of PTCDA. Upon further approach, this interaction destabilizes the junction, flipping the oxygen up [see the spikes of Δf in Fig. 1(a)] to form a chemical bond with the tip.[11]

Contrary to the Au tip, the CO tip resolves the internal molecular structure of PTCDA in both the Δf and dI/dV channels [cf. Fig. 2(a)]. The appearance of molecular structure resolution in the Δf image measured at $z = 2\,\text{Å}$ indicates that at this distance the tip encounters the short-range Pauli repulsion acting on it from PTCDA.[3,4,12] Indeed, the extracted $F(z)$ spectra shown in the upper panel of Fig. 2(b) confirm that upon tip approach, the repulsion above the atom increases faster than above the ring. Therefore, the value of $\Delta F(z)$ is *tuned* by changing the tip-surface distance and thus can be used to characterize the conductance response $\Delta dI/dV$. Upon tip

approach, in the range of distances $z \lesssim 2.3\,\text{Å}$, the value of $\Delta F(z)$ is positive and keeps increasing as the tip approaches the surface. At the same time the $dI/dV(z)$ curves in the lower panel of Fig. 2(b) show that the value of $\Delta dI/dV(z)$ is negative and keeps decreasing. This is direct evidence for the sensor-transducer function of the CO tip that couples ΔF and $\Delta dI/dV$. Qualitatively the coupling in this range of tip-surface distances is such that *the junction conductance drops as the force pressing on the tip increases.*

Although $\Delta F(z)$ is tuned by changing the tip-surface distance, there is an upper boundary to the value of $\Delta F(z)$ which can be achieved. As becomes apparent from Fig. 2(b), at smaller tip-surface distances ($z \gtrsim 2.3\,\text{Å}$) the tip-surface interaction becomes dominated by an attractive force that inverts the contrast in the Δf images and turns $\Delta F(z)$ to negative values.[13,14] Interestingly, the contrast in the dI/dV images shows a rather weak response to changes in the tip-surface interactions. This implies that at shorter tip-surface distances the coupling between $\Delta F(z)$ and $\Delta dI/dV$ has a different character (see below).

Turning to the images recorded with the Xe tip, we first of all register that its resolution of the molecular structure is worse if compared to the CO tip [cf. Fig. 2(c)]. Only very close to the surface ($z = 3.1\,\text{Å}$) can the characteristic pattern of the PTCDA backbone be discerned by visual inspection. The reason for the poorer image resolution is two-fold: First, as becomes apparent from the extracted $F(z)$ spectra shown in the upper panel of Fig. 2(d), the Xe tip is more reactive than the CO tip; as a result, both the $\Delta F(z)$ and $\Delta dI/dV(z)$ signals come on top of a high background that makes their detection more difficult. Second, it has been observed that in comparison to the CO tip, the quality of the Xe-tip images is more sensitive to the increase of the qPlus oscillation amplitude. This could be caused by the softer tip-Xe bond and therefore stronger displacements of the Xe atom induced by the tip oscillations. Despite all the factors compromising the quality of the Xe-tip images, the extracted $F(z)$ and $dI/dV(z)$ spectra show that, similar to the CO tip, $\Delta dI/dV(z)$ and $\Delta F(z)$ are coupled.

For a quantitative analysis of the observed coupling, we plot in Fig. 3 $\Delta dI/dV(z)$ vs $\Delta F(z)$ for both types of tips. For each type we show two spectra, acquired in different experimental runs, to demonstrate the reproducibility of the measurement. As Fig. 3 shows, upon initial approach all tips reproducibly follow a regime in which the coupling between $\Delta F(z)$ and $\Delta dI/dV$ is *linear*: $\Delta dI/dV(z) = \alpha \Delta F(z)$. Evaluating the coupling constants α, we find that $\alpha_{\text{Xe}} \approx -2000\,\text{S/N}$ while $\alpha_{\text{CO}} \approx -200\,\text{S/N}$. Although the coupling has different strengths for CO and Xe tips, qualitatively it follows the same rule: *The conductance of the junction decreases linearly with the increase of the force pressing on the tip.* Most importantly, comparing the data collected with different tips in different experimental runs, we find that the obtained coupling constants are solely defined by the type of particle decorating the tip, but not by the tip itself. Therefore, we conclude that α_{CO} and α_{Xe} uniquely calibrate the linear regime of the CO- and Xe-based force sensors-transducers.

As the tip is moved closer to the surface, the linear coupling regime breaks down for both types of tips. Figure 3 suggests that the tip-surface distance at which this happens is defined
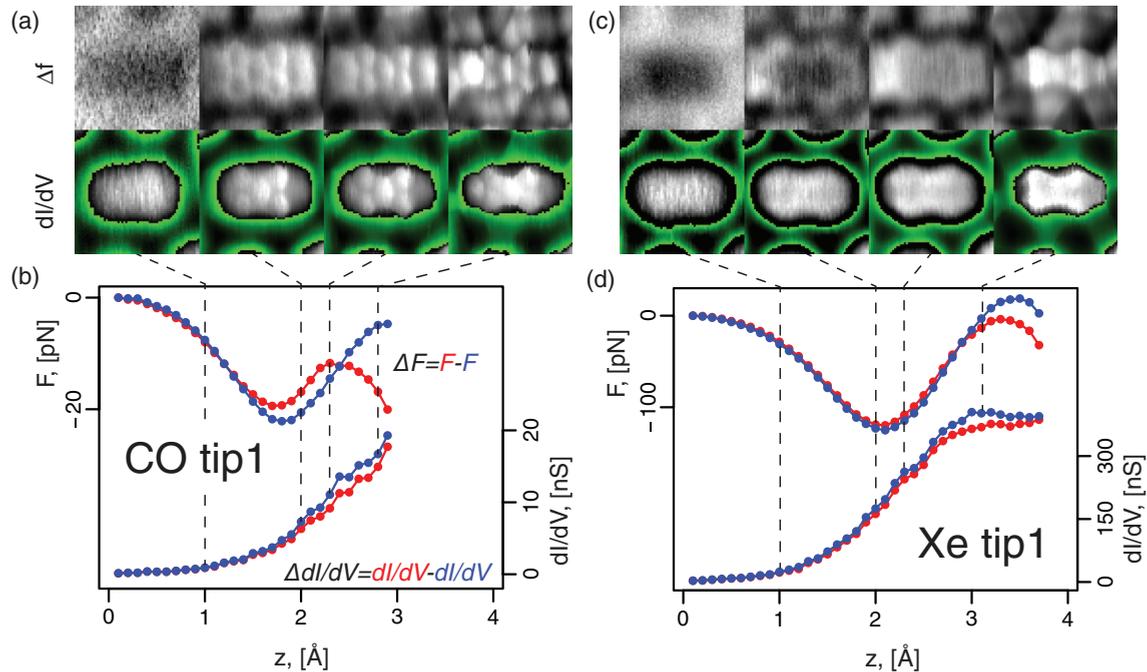
FIG. 2. (Color) In (a) and (c), 64×64 $pixel$, 13×13 Å constant height Δf (top) and dI/dV (bottom) images selected from the image sequences measured above the PTCDA molecule adsorbed on Au(111) with the (a) CO and (c) Xe tips are shown. Tunneling bias: $V = -12$ mV. For the Δf images the (Δf_{min}, Δf_{max}) of the used color scales are (from left to right) (-11 Hz, -7 Hz), (-13 Hz, 9 Hz), (-12 Hz, 17 Hz), (-14 Hz, 30 Hz) for CO; and (-6 Hz, -4 Hz), (-11 Hz, -7 Hz), (-11Hz, 2 Hz), (-6 Hz, 20 Hz) for Xe images. (dI/dV_{min}, dI/dV_{max}) from left to right are (0.1 nS, 2 nS), (2 nS, 21 nS), (2 nS, 29 nS), (4 nS, 42 nS) for CO; and (2 nS, 15 nS), (7 nS, 109 nS), (9 nS, 176 nS), (19 nS, 374 nS) for Xe. In (b) and (d), $F(z)$ (top) and $dI/dV(z)$ (bottom) spectra extracted from the series of images measured with the (b) CO and (d) Xe tips are displayed.[8] The color coding of the spectra is the same as in Fig. 1(b). The F scale is defined similarly to Fig. 1(b). For the definition of the z scale, see Ref. 7. The dashed lines mark the z values at which the images from (a) and (c) were measured.

by the type of particle decorating the tip. Comparing the critical distance values obtained from Fig. 3 with the $F(z)$
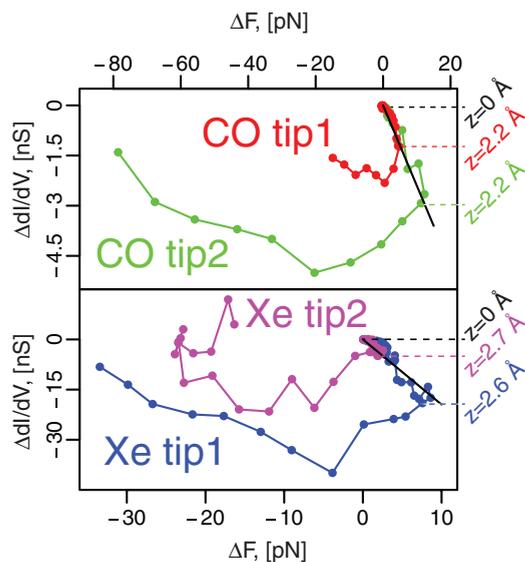
FIG. 3. (Color) Conductance response $\Delta dI/dV$ vs the applied force $\Delta F(z)$. The upper (lower) panel shows spectra measured with two different CO (Xe) tips. The regime in which the response of conductance is linear is indicated by the black fitted lines. The distance at which each tip starts to deviate from the linear response regime is marked on the right.

and $dI/dV(z)$ spectra from Figs. 2(b) and 2(d), we find that the linear coupling regime breaks down when the appearing attractive force that was mentioned above starts dominating the interactions in the junction. Note that in this range a coupling between $\Delta dI/dV(z)$ and $\Delta F(z)$ is still present. However, as follows from Fig. 3, it has a complicated form and is also strongly tip dependent.

We anticipate that the conclusions obtained here for CO and Xe should also be applicable to other particles (H_2, D_2, or CH_4) that are known to yield a very similar STHM resolution.[1–3] Accordingly, each of these particles, when placed at the tip apex, should produce a similar coupling between force and conductance as observed here, thus performing the function of a force sensor-transducer. The coupling is expected to follow two distinct regimes: In the linear regime, which is realized at larger tip-surface distances, the decrease of the junction conductance is proportional to the increase of the force pressing on the tip. Therefore, the linear regime is fully defined by a single proportionality constant that may vary between the different types of particles, but should not depend strongly on the microscopic tip structure. Moreover, the similarity of STHM images obtained with the different particles, together with the fact that their bonding to the tip has rather different character (chemical vs van der Waals), suggests that the physical mechanism behind the linear coupling regime and the STHM resolution of molecular structures must have a universal character that is largely independent of the details of the tip's or particle's atomic structure.

In light of the above conclusions we analyze the existing models that attempt to describe the STHM imaging. The model of Martinez *et al.*[15] ascribes the STHM contrast to the modified character of the outermost tip orbitals, caused by the chemical adsorption of a single hydrogen atom produced by the dissociation of H_2 on the Au tip apex at low temperatures. The model thus relies on the *specific details* of the chemical interaction between H_2 and Au and has no obvious explanation for the coupling between force and conductance reported here. In contrast, the model proposed in our earlier publication[3] starts with the general notion that any particle adsorbed on the tip also interacts with the surface; changes of the particle-surface interaction that occur during scanning influence the position of the particle with respect to the tip. Therefore, the particle's position contains information about its various interactions with the surface. If the position of the particle affects the electron tunneling in the junction, the force acting on the particle becomes coupled to the conductance. The character of this coupling will be defined by the physical mechanism through which the particle's position affects the electron tunneling.

At present, there are two mechanisms that explain how the displacement of the particle on the tip affects the tunneling. According to one of them, the particle changes the tip's density of states via the Pauli repulsion acting between the tip and the particle.[3] Another model, proposed recently by van der Maas *et al.*,[16] states that the particle adsorbed at the tip elastically scatters tunneling electrons, with the scattering cross section depending on the tip-particle distance. In qualitative agreement with our observations made in the linear coupling regime, both models predict that the increase of the force pressing on the tip will lower the junction conductance. Hence, for further discrimination between these two models, quantitative simulations are necessary.

Finally, we briefly address the regime of nonlinear coupling. Although in this regime the precise coupling between $\Delta F(z)$ and $\Delta dI/dV(z)$ is tip dependent (see above), it is still true that qualitatively similar behaviors are found for all tips which we have investigated (Fig. 3). At the same time, it is interesting to note that the z range in which the nonlinear coupling is found coincides with the z range in which we previously observed the STHM imaging of hydrogen bonds between adjacent molecules.[2,17] This image contrast can also be seen in the rightmost images in Figs. 2(a) and 2(c), respectively, in both the Δf and the dI/dV channels. We can thus conclude that hydrogen bonds exert a specific force on the sensor particle and that whatever the mechanism that produces the nonlinear coupling, this mechanism also transduces this force into the conductance channel.

*Corresponding author: r.temirov@fz-juelich.de

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[7] The absolute distance between the tip and the surface is not known from the experiment. Instead, we use a relative tip-surface distance scale z. The value of z is defined as the distance by which the tip is approached from its stabilization point towards the surface prior to the respective constant height scan. Although the tip was always stabilized at the same lateral location, the actual tip-surface distance is expected to vary between the different tips. Therefore, the absolute values of the z scales in Figs. 1(b), 2(b), and 2(d) are not directly comparable.

[8] $F(z)$ spectra were extracted from the sequences of Δf images by first extracting the $\Delta f(z)$ spectra and then calculating the integral $\int_0^z \frac{2k_0}{f_0}\Delta f(z)dz$ over the measured range of distances.[5] k_0 was taken to be equal to 1800 N/m (Ref. 9).

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[13] Note that the contrast inversion in the Δf channel occurs at smaller z if compared to $F(z)$. This is to be expected since $F(z) \propto \int \Delta f(z)\,dz$ (Ref. 8).

[14] As the appearing attractive force shows, the tip-surface interaction cannot be described with a simple two-particle Lennard-Jones type potential. This behavior is not surprising, since the considered junction has more degrees of freedom (e.g., the translational degrees of freedom of the particle adsorbed at the apex), changes of which will influence the interactions in the junction.

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