Strength of the $\Delta \omega$ and $\Delta \gamma$ signals

In $e$-EFM the tunneling rate affects the strength of the cantilever dissipation and frequency shift signals. One can obtain the cantilever resonance frequency shift and dissipation induced by the periodic tunneling process: $^1$

$$\Delta \omega \propto \frac{\omega \Gamma^2}{\omega^2 + \Gamma^2}$$  \hspace{1cm} (1)

$$\Delta \gamma = \Delta \left( \frac{1}{Q} \right) \omega \propto \frac{\omega^2 \Gamma^2}{\omega^2 + \Gamma^2}$$  \hspace{1cm} (2)

where $\omega = 2\pi f$. $\Delta \left( \frac{1}{Q} \right)$ denotes the energy dissipation per one oscillation cycle, while $\Delta \gamma$ the energy dissipation per unit time. In $e$-EFM the ratio of the two signals is related to the tunneling rate, $\Gamma$:

$$\Gamma = -2 \omega \frac{\Delta \omega}{\Delta \gamma}$$  \hspace{1cm} (3)

$^1$To whom correspondence should be addressed
Simultaneous optimization of $\sum_{i=1}^{3} \Delta \gamma_i (\gamma_i^0, V_i^0, \alpha_i)$

Table S1 shows the parameters $\gamma_i^0$, $V_i^0$, and $\alpha_i$ obtained from a simultaneous fit of $\sum_{i=1}^{3} \Delta \gamma_i (\gamma_i^0, V_i^0, \alpha_i)$ to the dissipation data shown in Figure 3e. The addition energy is derived using averaged pairs of $\alpha$ parameters, for example for peaks 1 and 2 $E_{\text{add}}$ is calculated as follows:

$$E_{\text{add}} = e^{\alpha_1 + \alpha_2} \Delta_{12}$$  \hspace{1cm} (4)

This gives four $E_{\text{add}}$ values within 110-164 meV recorded for two peaks and both scan directions (forward and backward), which is represented by $E_{\text{add}} = (137 \pm 27)$ meV.

Table S1: Parameters $\gamma_i^0$, $V_i^0$, and $\alpha_i$ obtained during a simultaneous fit of $\sum_{i=1}^{3} \Delta \gamma_i (\gamma_i^0, V_i^0, \alpha_i)$ to the dissipation data shown in Figure 3e.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Forward</th>
<th>Backward</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.030</td>
<td>0.025</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.039</td>
<td>0.042</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>0.054</td>
<td>0.045</td>
</tr>
<tr>
<td>$\gamma_1^0$ (Hz)</td>
<td>61</td>
<td>68</td>
</tr>
<tr>
<td>$\gamma_2^0$ (Hz)</td>
<td>119</td>
<td>127</td>
</tr>
<tr>
<td>$\gamma_3^0$ (Hz)</td>
<td>285</td>
<td>312</td>
</tr>
<tr>
<td>$V_1^0$ (V)</td>
<td>3.35</td>
<td>3.19</td>
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<tr>
<td>$V_2^0$ (V)</td>
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<td>6.70</td>
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<tr>
<td>$V_3^0$ (V)</td>
<td>10.27</td>
<td>10.14</td>
</tr>
<tr>
<td>$\Delta_{12}$ (V)</td>
<td>3.62</td>
<td>3.30</td>
</tr>
<tr>
<td>$\Delta_{23}$ (V)</td>
<td>3.53</td>
<td>3.44</td>
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<tr>
<td>Offset (Hz)</td>
<td>$-12$</td>
<td>$-20$</td>
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</table>

Tunneling rates

Figure S1 shows the frequency shift $\Delta f$ versus the bias voltage $V_B$ measured over the upper nanoparticle simultaneously with the dissipation $\Delta \gamma$ shown in Figure 3e (backward direction). To show frequency shift features originating from the tunneling process, a large parabolic background
arising from the capacitive force between the tip and the sample has been subtracted. Compared to $\Delta \gamma$, the $\Delta f$ signal is noisier because of the noise in the background signal. Nevertheless, it is possible to identify three peaks coinciding with the dissipation features observed in Figure 3e. Peaks 1-3 have amplitudes of approximately: $\Delta f = 22$, 27, and 200 Hz, respectively. Using Equation 3 and the parameters $\gamma^0_i$ from Table S1 this gives the estimation of the tunneling rates $\frac{\Gamma_i}{2\pi} = 1163$, 764, and 2304 kHz, which are within one order of magnitude of the resonance frequency of the cantilever (approximately 286 kHz).

![Graph](image)

Figure S1: The frequency shift $\Delta f$ versus the bias voltage $V_B$ measured over the upper nanoparticle simultaneously with the dissipation $\Delta \gamma$ that is shown in Figure 3e (backward direction). A large parabolic background arising from the capacitive force between the tip and the sample has been subtracted. The dashed lines indicate the position of peaks in the $\gamma$-$V_B$ spectrum. The solid line represents expected theoretical shape of the peaks given by the parameters obtained from the $\gamma$-$V_B$ spectrum and using a formula equivalent to Equation 1 in the main article.

### Finite element electrostatic simulation

To calculate the charge distribution and capacitances in COMSOL a built-in physics-controlled mesh generator is used to partition a 2D axisymmetric model. The mesh is further refined by increasing the distribution of elements near the nanoparticle and the tip apex. In this way the local element size varies from 0.35 to 2 nm with the highest density around the nanoparticle. All
experiments are assumed to occur in vacuum and the relative dielectric constant of NaCl is taken to be 5.9. The capacitances are calculated using the capacitance matrix formalism.$^2$

**Dependence of capacitances** $C_{\Sigma}$, $C_{BE}$, $C_{TIP}$ and $C_{ENV}$ on the tip-sample distance.

Table S2 shows the values of capacitances $C_{\Sigma}$, $C_{BE}$, $C_{TIP}$ and $C_{ENV}$ calculated for different tip-sample distances in the geometry shown in Figure 4a. Even with a large range of the change in the tip-sample distance, the major contribution to the total capacitance $C_{\Sigma}$ originates from the mutual capacitance to the back electrode $C_{BE}$. This capacitance increases only $\approx 2\%$ when the distance is reduced from 10 nm to 6 nm. At the same time, the $\alpha$ parameter changes from 0.071018 to 0.038408.

Table S2: Capacitances $C_{\Sigma}$, $C_{BE}$, $C_{TIP}$ and $C_{ENV}$ for different tip-sample separation in the geometry shown in Figure 4a.

<table>
<thead>
<tr>
<th>Tip-sample distance (nm)</th>
<th>$C_{\Sigma}$ (aF)</th>
<th>$C_{BE}$ (aF)</th>
<th>$C_{TIP}$ (aF)</th>
<th>$C_{ENV}$ (aF)</th>
<th>$\alpha$</th>
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<tbody>
<tr>
<td>6</td>
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<td>0.092715</td>
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<td>0.081686</td>
<td>0.000222</td>
<td>0.038408</td>
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**References**
