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Supplementary Information for:

Impact of the Plasmonic Near- and Far-Field Resonance-Energy Shift on the Enhancement of Infrared Vibrational Signals

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Enhancement Correction for Different Antenna Lengths

For the comparison of enhanced vibrational signals obtained from nanoantennas with different lengths, one has to consider the antennas' different near-field intensities. For example, vibrational signals obtained from shorter antennas with smaller near-field intensity have to be scaled up to enable a comparison with longer ones featuring higher near-field intensities (see Figure S1).

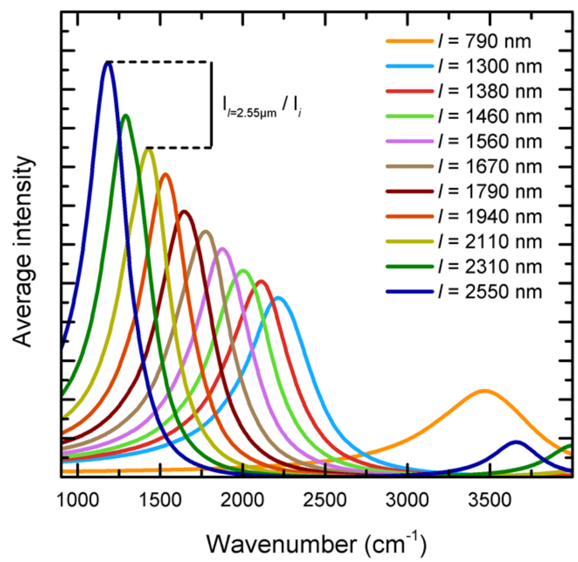

Figure S1. FDTD simulations: Average near-field intensity in a half circular arc (see Figure S2) at the tips of gold nanoantennas with various lengths on a substrate with a refractive index of $n = 1.43$ (CaF_2), plotted versus frequency. The ratio $I_{l=2.55\mu m}/I_i$ is determined by reading out the intensity peak values as indicated by the dashed lines.

In our analysis, this is taken into account by multiplication of the area-corrected vibrational signal enhancement $\frac{S}{S_{ref}} \cdot \frac{G_{Ant}}{G_{SEIRA}}$ with the ratio I_{max}/I_i between the intensity of the longest antenna $I_{max} = I_{l=2.55\mu m}$ and each antenna I_i, obtained from FDTD simulations, which are described below. In order to determine the ratio between the near-field peak intensities of nanoantennas of different lengths, we calculated the average intensity within a half circular arc normalized to a simulation with no nanoantenna involved. As depicted in the near-field intensity distribution plot in Figure S2, the width of the half circular arc located at the antenna hotspot at the tip was chosen to 5 nm, such, that it matches the thickness of the evaporated 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) probe layer under the assumption of a homogeneous coverage. The intensity was recorded for the plasmon resonance frequency.

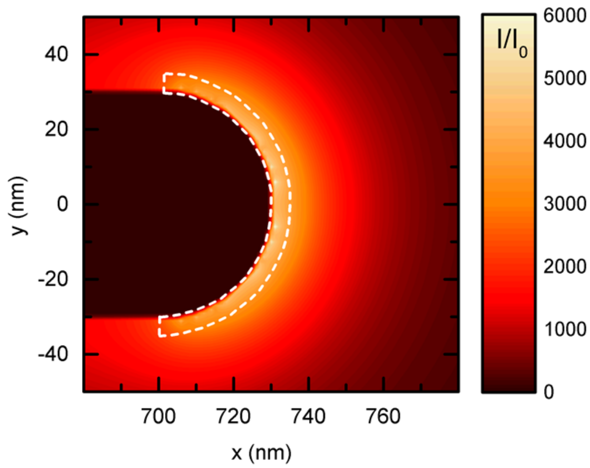

Figure S2. FDTD simulation: Spatial distribution of the near-field intensity I at the plasmonic resonance in the tip region of a gold nanoantenna with a length of $l = 1.46\ \mu m$ on a substrate with a refractive index of $n = 1.43$ (CaF_2). The near-field intensity I is normalized to a simulation of the bare substrate (I_0). The dashed line indicates the half circular arc used for intensity averaging.

Figure S1 shows the obtained spatially averaged spectral near-field distributions for nanoantennas of different lengths following the above mentioned approach. Obviously, the near-field intensity decreases with decreasing length of the nanoantennas. The peak values I_i of the simulated intensity spectra used for the correction factor $I_{l=2.55\mu m}/I_i$ are read out as indicated in Figure S1. The above described correction is only meaningful for the assumption of similar spectral behavior of the near-field for each antenna length. For tuning ratios around 1 this is valid, for large tuning factors the near-field intensity is influenced by other effects, for example the excitation of higher order modes.

Finite-Difference Time-Domain Simulations

The calculations were performed using the commercial software FDTD Solutions v8.5.3, Lumerical Solutions, Inc. with a dielectric function for gold fitted with a 10 coefficient model to optical data for gold taken from Palik[1] and a constant refractive index of $n = 1.43$ for the CaF_2 substrate. As boundary conditions, perfectly matched layers (PMLs) were used. The simulation region was set cubic with an edge length of at least twice the wavelength. The TFSF method was used combined with a mesh subgridding of $5\,\mathrm{nm} \times 5\,\mathrm{nm} \times 5\,\mathrm{nm}$ over the whole antenna and $1\,\mathrm{nm} \times 1\,\mathrm{nm} \times 1\,\mathrm{nm}$ at the tip regions. The default gridding in the remaining simulation region was set to auto non-uniform meshing with an accuracy of 5. Light was injected using a plane wave source polarized parallel to the long antenna axis with a spectral range from $800\,\mathrm{cm}^{-1}$ to $5000\,\mathrm{cm}^{-1}$. Electromagnetic field intensities were recorded using a 2D frequency domain power monitor parallel to the substrate at half-height of the antenna and a spectral resolution of $3.5\,\mathrm{cm}^{-1}$. For more details see Ref. 2. The simulations were carried out on the high-performance computing cluster bwGRiD (http://www.bw-grid.de), member of the German D-Grid initiative, funded by the Ministry for Education and Research and the Ministry for Science, Research and Arts Baden-Wuerttemberg.

References

1 E. Palik, *Handbook of Optical Constants of Solids*, Elsevier Science, 1985.

2 C. Huck, F. Neubrech, J. Vogt, A. Toma, D. Gerbert, J. Katzmann, T. Härtling and A. Pucci, *ACS Nano*, 2014, **8**, 4908–4914.