Supporting information: The effect of STM parameters on tip-enhanced Raman spectra

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1 Dependence of TERS intensity on STM parameters

In figure S1 we present the integrated intensity of the 245 cm^{-1} (A) and 997 cm^{-1} (B) bands as a function of I_t for constant values of bias voltage in Ar (0.02 V green, 0.04 V dark blue, 0.1 V purple) and water (0.04 V, light blue) and the integrated intensity of the 245 cm^{-1} (C) and 997 cm^{-1} (D) bands as a function of E_b for constant values of tunelling current in Ar (0.3 nA orange, 0.8 nA red, 1.3 nA black) and water (1.3 nA, light blue).

In Ar, the absolute TERS intensity of the 245 cm^{-1} peak increases linearly with I_t, while in water the intensity remains almost unchanged (figure S1 A). The slopes obtained by linear fits, indicating the rate of growth, are 20 $\pm$ 3, 23 $\pm$ 3 and 31 $\pm$ 4 counts/nA at 0.1, 0.04 and 0.02 V respectively in Ar, and 0.4 $\pm$ 2 at 0.04 V in water. This band is covered in liquid by a far-field feature that hinders the fitting procedure, being a possible cause for the large difference in trend (note that the liquid results in figure S1 A are multiplied by a factor of 5 to facilitate the comparison, much weaker intensities were detected in liquid).

The total intensity increase in the current range scanned are 70 %, 107 % and 131 % in Ar at 0.02 V, 0.04 V and 0.1 V respectively and only 23 % in water. The 997 cm^{-1} peak (figure S1B) increases linearly with I_t in Ar and water with slopes of 14 $\pm$ 3, 13 $\pm$ 4 and 26 $\pm$ 3 counts/nA at 0.1, 0.04 and 0.02 V respectively in Ar, and 10 $\pm$ 6 at 0.04 V in water. The slower growth of this peak with current leads to slightly lower absolute intensity gains: 81 %, 57 % and 73 % in Ar at 0.02 V, 0.04 V and 0.1 V respectively and 76 % in water. These results are summarized in table S1.

As discussed in the main text, the constant value of E_b applied while varying the current has an influence on the absolute TERS intensity. For higher voltages (0.1 V, purple) the overall intensity

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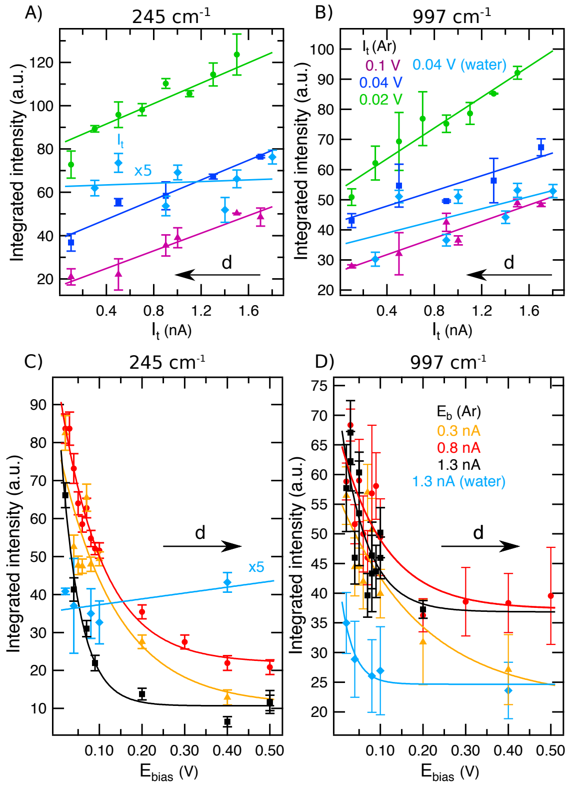

Figure S 1: A: Integrated intensity of the 245 cm^{-1} mode (B: 997 cm^{-1}) as a function of I$_t$ at constant E$_b$ values of 0.02 V (green), 0.04 V (dark blue), 0.1 V (purple) in Ar and 0.04 V in water (light blue). C: Integrated intensity of the 245 cm^{-1} mode (D: 997 cm^{-1}) as a function of E$_b$ at constant I$_t$ values of 0.3 nA (orange), 0.8 nA (red), 1.3 nA (black) in Ar and 1.3 nA in water (light blue). Normalized to the same power and integration time. Averaged results from spectra taken in scans up and down are presented with standard deviation as error. Solid lines represent linear fittings (A and B) and exponential fittings (C and D) of the experimental data points.

detected is smaller than for lower values (0.02 V, green) in agreement with the expected tip retraction at high E$_b$. Additionally the rate of growth of both bands (slopes in the fittings) are higher at 0.02 V, by 31 % (245 cm^{-1}) and 50 % (997 cm^{-1}).

When comparing the two peaks analysed, we observe that the slopes and percentage of signal gain are higher for the Au-S mode, that is thus more affected by the current ramp. Note that this hypothesis does not hold in the case of liquid experiments where a slope close to zero is obtained for the 245 cm^{-1} peak. The results of the 997 cm^{-1} peak show a very similar trend between Ar and water results, being the mode more intense in the liquid spectra where the low wavenumber region is affected by a broad far-field contribution (figure 1 main manuscript). In view of this, we assume that the intensity results of the 245 cm^{-1} mode in water are possibly affected by the fitting procedure and conclude that the effect of ramping I$_t$ in the TERS intensity is similar in Ar and water, with average values of intensity gain (taking into account both bands and different values of E$_b$ applied) of 87% in Ar and 76 % in water (we discarded in water the results obtained from the 245 cm^{-1} band).

Table S 1: Results of linear fittings to the I_{TERS} vs I_t data points of figures S1 A and B

E_b/V	slope/counts·nA^{-1}		Increase I_{TERS}/%	
	245 cm^{-1}	997 cm^{-1}	245 cm^{-1}	997 cm^{-1}
0.1	20 ± 3	14 ± 3	131	73
0.04	23 ± 3	13 ± 4	107	57
0.02	31 ± 4	26 ± 3	70	81
0.04 (water)	0.4 ± 2	10 ± 6	23	76

The integrated intensity as a function of E_b shown in figure S1 C and D shows very different behavior than the results obtained when ramping I_t. It is obvious from the figures that the trend of I_{TERS} upon bias increase deviates from the linearity obtained when tuning the tunneling current (figure S1 A and B). In Ar, the intensity decrease of the 245 cm^{-1} peak can be modelled with an exponential decay function for all values of constant I_t. In contrast, the water results show an initial decrease in the range 0.02-0.1 V and the band intensity grows again at 0.5 V. As discussed, the fitting of this band is not straightforward due to a broad far-field feature in the low-wavenumber region, and therefore the results are not as reliable as for the 997 cm^{-1}. The band intensity of the 997 peak shows an exponential dependence with E_b in Ar and liquid experiments.

When decreasing the bias, the absolute intensity of the 245 cm^{-1} is increased by 478 %, 300 % and 539 % at I_t values of 1.3, 0.8 and 0.3 nA, respectively in Ar and 28 % in liquid. I $_{ters}$ of the 997 cm^{-1} mode shows a weaker dependence on E_b. The absolute intensity of this mode rises by 80 %, 73 % and 108 % at I_t values of 1.3, 0.8 and 0.3 nA in Ar, respectively and 47 % in water at 1.3 nA. In average considering the results of both bands at different values of constant tunneling, I_{TERS} rises by 263 % when increasing the bias in Ar and 38 % in liquid. The results are summarized in table S2

Table S 2: Absolute intensity increase of the Raman bands obtained when decreasing the bias value from 0.5 V up to 0.02 V. *Note that this value is calculated considering the initial decrease from 0.02 V to 0.1 V.

I_t/nA	Increase I_{TERS}/%	
	245 cm^{-1}	997 cm^{-1}
0.3	539	108
0.8	300	73
1.3	478	80
1.3 (water)	28*	47

In view of these results, it is obvious that the value of E_b applied in a TERS experiment is much more likely to influence the nearfield enhancement and thus the intensity detected than the tunelling current in the ranges explored in these experiments.

1.1 Raman shifts

In figure S2 we present the Raman shift of the 245 cm^{-1} mode as a function of I_t (A) for constant values of bias voltage in Ar (0.02 V green, 0.04 V dark blue, 0.1 V purple) and water (0.04 V, light blue), and as a function of E_b (B) for constant values of tunelling current in Ar (0.3 nA orange, 0.8 nA red, 1.3 nA black) and water (1.3 nA, light blue). C and D show the equivalent shifts for the 997 cm^{-1} peak.

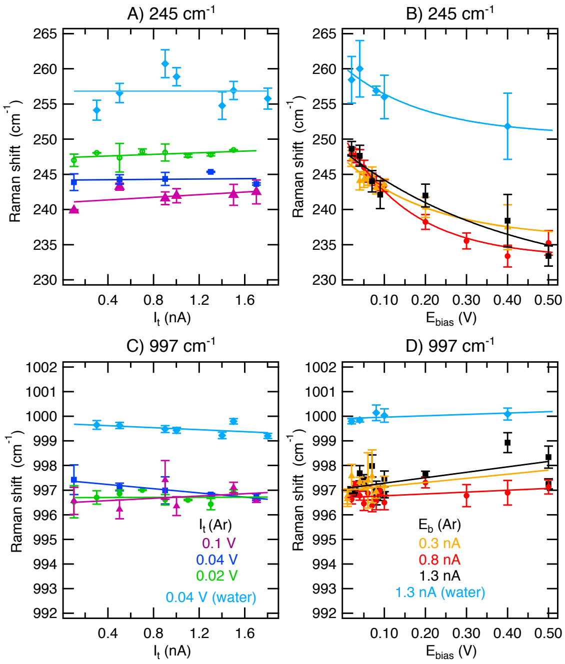

Figure S 2: Raman shift of the 245 cm^{-1} as a function of I_t (A) for constant values of bias voltage in Ar (0.02 V green, 0.04 V dark blue, 0.1 V purple) and water (0.04 V, light blue), and as a function of E_b (B) for constant values of tunelling current in Ar (0.3 nA orange, 0.8 nA red, 1.3 nA black) and water (1.3 nA, light blue). C and D show the equivalent shifts for the 997 cm^{-1} band. Averaged results from spectra taken in scans up and down are presented with standard deviation as error. Solid lines represent linear fittings (A, C and D) and exponential fittings (B) of the experimental data points.

Tuning the current does not drastically affect the position of the bands at 245 cm^{-1} (A) and 997 cm^{-1} (C). The curves can be fitted to linear functions with slopes close to zero (table S3). The largest shift is experienced by the 245 cm^{-1} mode at 0.1 V, however the shift is as small as 1 cm^{-1} through the whole current range scanned. Such small variations in peak positions while ramping I_t, together with the fact that the intensity changes discussed in the main manuscript follow a relation as expected solely from a gap distance change, indicate that no chemical interaction is occuring while ramping the tunneling current. Ramping the bias voltage results in similar linear dependence of the position of the 997 cm^{-1} band (fitting results are included in table S3), while it induces shifts in the 245 cm^{-1} Au-S mode. This shift is discussed in the main manuscript.

Table S 3: Results of linear fittings to the Raman shift vs I_t data points of figures S2 A and C, and to the Raman shift vs E_b data points of figure S2 D.

E_b/V	slope/$cm^{-1} \cdot nA^{-1}$	
	245 cm^{-1}	997 cm^{-1}
0.1	0.9 ± 0.9	0.2 ± 0.3
0.04	0.1 ± 0.6	-0.4 ± 0.04
0.02	0.6 ± 0.3	0.01 ± 0.1
0.04 (water)	0.01 ± 1	-0.2 ± 0.2
I_t/V	slope/$cm^{-1} \cdot V^{-1}$	
	245 cm^{-1}	997 cm^{-1}
0.3	n.a.	1.7 ± 0.8
0.8	n.a.	0.7 ± 0.5
1.3	n.a.	2.2 ± 0.8
1.3 (water)	n.a.	0.6 ± 0.5