Supporting information

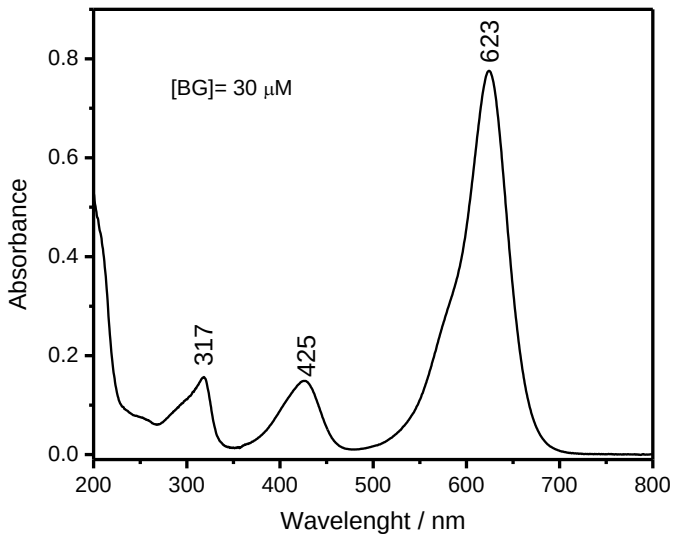

Figure S1: UV-Vis absorption spectrum of a 30 μM BG aqueous solution.

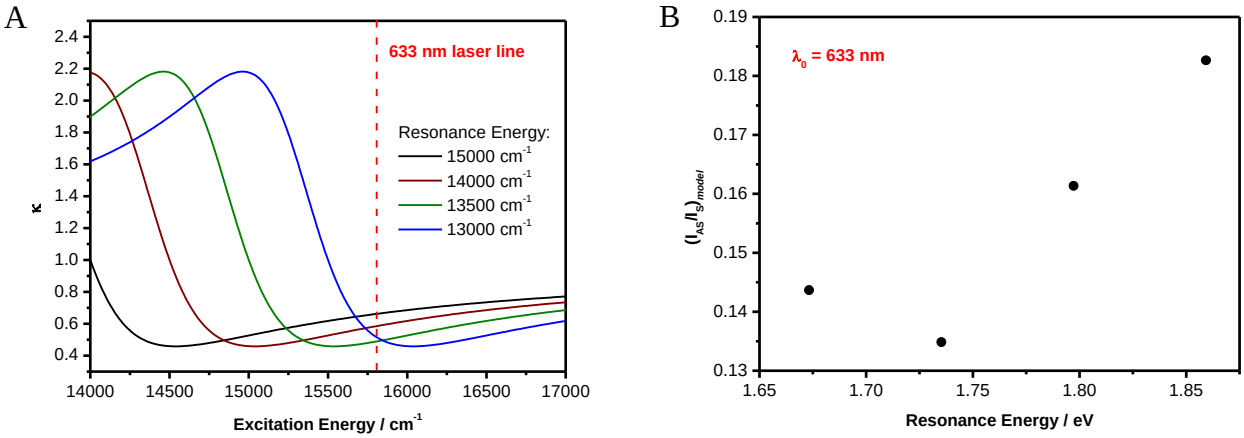

Figure S2: A) Curves of κ as a function of excitation energy for different resonance energies from the single model resonance of ref. 1 (a fixed Γ=500 cm^{-1} was used). B) values for $(IAS/IS)_{model}$ = κ*0.28 (where 0.28 is the expected thermal anti-Stokes/ Stokes ratio for the ~220 cm^{-1} mode of BG calculated from equation (1) in the main manuscript). These κ-values were obtained from (a) at 633 nm excitation wavelenght (marked in (a) as a red dashed line). Notice that the potential variation shown in (b) is in good agreement with the experimental data (Figure 2 in the main manuscript).

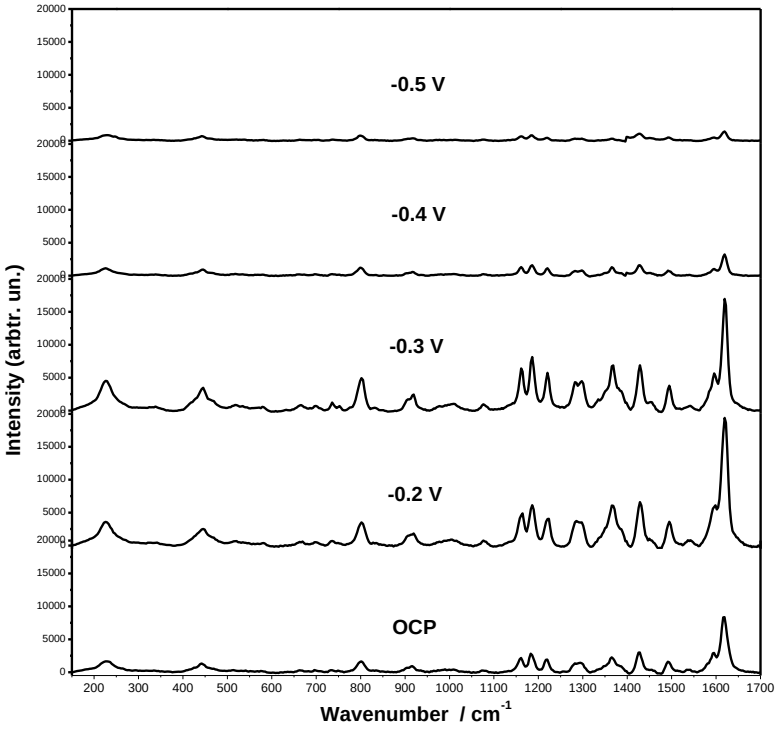

Figure S3: Average SERRS spectra of BG (5 μM) for different applied potentials as indicated in the figure.

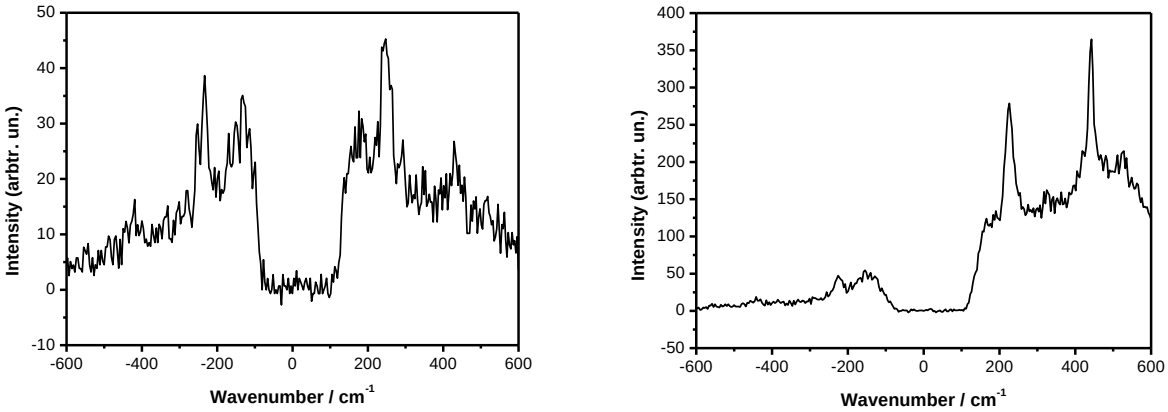

Figure S4: "Single-molecule" spectra from the data set with anti-Stokes enhanced (A) and Stokes enhanced scattering (B).

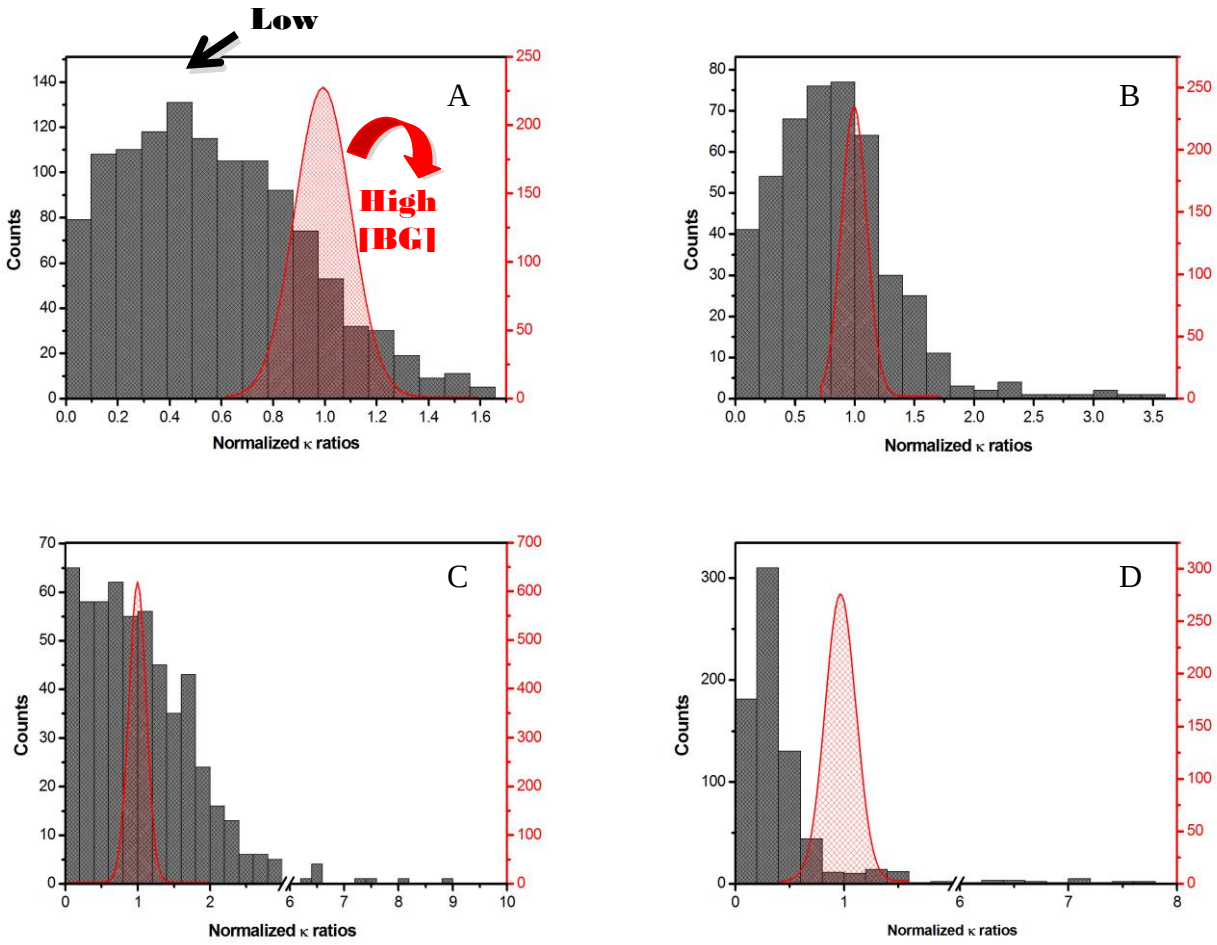

Figure S5: Histograms of κ-values for BG adsorbed on a roughened silver electrode (grey bars). [BG] = 20 nM, 0.1 M KBr. A) -0.1 V, B) -0.2 V, C) –0.3 V and D) -0.4 V . The shaded gaussian (in red) in each graph is a distribution in the average SERRS conditions (as in Figure 1).

Reference

1- A. G. Brolo, A. C. Sanderson, A. P. Smith, *Phys. Rev. B*, 2004, **69**, 045424.