Supporting information

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

Figure S2: A) Curves of $\kappa$ as a function of excitation energy for different resonance energies from the single model resonance of ref. 1 (a fixed $\Gamma=500 \text{ cm}^{-1}$ was used). B) values for $(\text{IAS/IS})_{\text{model}} = \kappa*0.28$ (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 $\kappa$-values were obtained from (a) at 633 nm excitation wavelength (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 $\kappa$-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