Electronic Supporting Information (ESI)

In Situ SERS detection of dissolved nitrate on hydrated gold substrates

Timo Küster and Geoffrey D. Bothun*

Department of Chemical Engineering, University of Rhode Island, 2 East Alumni Ave, Kingston, RI, 02881 USA

Corresponding author: gbothun@uri.edu, +1-401-874-9518

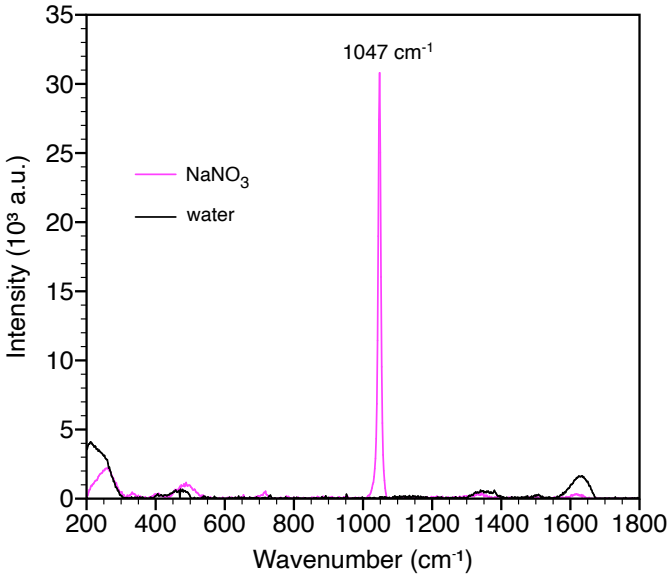

Figure S1. Raman spectra of 0.25 M $NaNO_3$ measured at room temperature with integration time of 20 s and at a laser power of 100 mW. The peak corresponding to symmetric stretching (ν_1) was identified at 1047 cm^{-1} in agreement with William and Begun[1] for 1 M $NaNO_3$ at 25 °C.

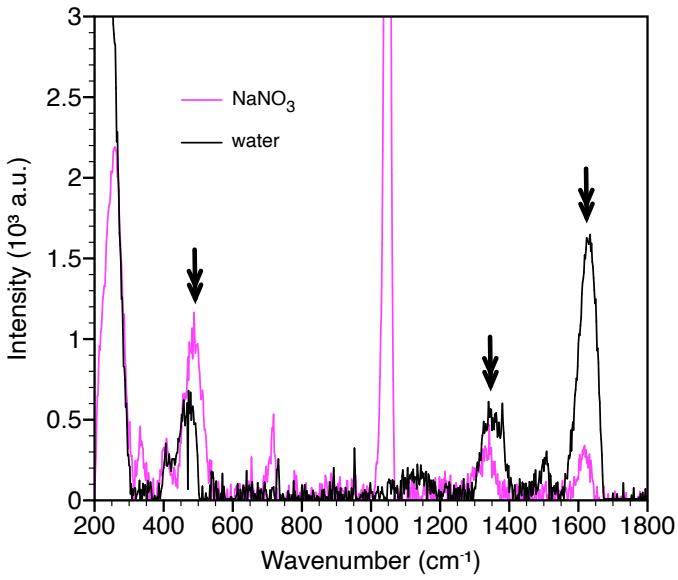

Figure S2. Magnified Raman spectra shown in Figure S1. The peak at 480 cm^{-1} with a shoulder peak near 520 cm^{-1} reflect a mixture of amorphous and crystalline silicon, respectively, from the glass cuvette. The peak at 1615 cm^{-1} is assigned to water bending. An additional unassigned peak is observed near 1330 cm^{-1} in both spectra.

Calculations

Table S1: Fitting parameters derived for Langmuir adsorption model. K represents the Langmuir constant and I_{sat} is the intensity at the saturation concentration. The subscripts indicate the wavenumbers at which the data was evaluated.

Processing method	**K_{1079} (nM^{-1})**	**$I_{sat,\ 1079}$**	**R^2_{1079}**	**K_{1332} (nM^{-1})**	**$I_{sat,\ 1332}$**	**R^2_{1332}**
Baselined	0.0105	672.3	0.74	0.0106	1194.7	0.81
SNV	0.0071	0.4369	0.94	0.0072	0.7829	0.93
Si normalization (baselined)	0.0045	1.0530	0.81	0.0047	1.8537	0.84
Si normalization (SNV)	0.0057	0.9591	0.82	0.0059	1.705	0.85

The limit of detection was calculated for the SNV normalized data by calculating the intensity at the LOD (equation 5 in manuscript)

$I_b = \underline{I_b} + 3 \cdot \sigma_b = 0.0500 + 3 * 0.0289 = 0.1367$

and substituting I with I_b in the rearranged Langmuir equation (equation 6 in manuscript) to obtain the limit of detection concentration.

$$C = \frac{I}{I_{sat} \cdot K - I \cdot K} = \frac{0.1367}{0.4369 \cdot 0.0071\ nM^{-1} - 0.1367 \cdot 0.0071\ nM^{-1}} = 64.1\ nM$$

References

1 W. L. Marshall and G. M. Begun, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 1963–1978.