Spontaneous versus Stimulated Surface-Enhanced Raman Scattering of Liquid Water

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SI1 Data processing

1.1 Processing of spontaneous Raman spectra.

Raw data

![Raw spontaneous Raman spectra – pure water (black), AgNPs blue (blue) and AgNPs yellow (red) obtained with 514.5 nm Raman pump.](image)

Data processing for losses correction

Correction for reabsorption was made due to the relatively high absorption of AgNPs blue sample at excitation wavelength (514.5 nm) used in Raman measurements. The optical path between the cuvette surface and cuvette centre where the laser beam was focused and from which original scattering signal was from, was assumed to be 5 mm. Laser power and other experimental parameters used in the Raman measurements were the same for water and AgNPs samples. For calculation of reabsorption correction, transmittance values in visible spectral region for dispersions of silver nanoparticles and pure water were needed. Absorption measurements were carried out in QX cuvettes with an optical path 1 mm for AgNPs samples (water as a reference) and in with a 1 cm optical path for water (empty cuvette as a reference). Obtained absorption
results were recalculated to values of desired length of optical path (5 mm) and then to transmittance values. A schematic representation of the Raman measurement and descriptions for reabsorption correction calculations are presented in Figure S2.

\[ T_\lambda \] – transmittance of the sample for 5 mm optical path at excitation wavelength (514.5 nm);

\[ T_x f(x) \] – transmittance of the sample for 5 mm of optical path in spectral range of \( \nu_{\text{OH}} \) (590 – 648 nm);

\[ I_{\text{scat}}^x f(x) \] – intensity of scattered Raman signal;

\[ I_{\text{scat}}^{\text{cor}} f(x) \] – intensity of scattered Raman signal corrected by transmittance of the sample:

\[ I_{\text{scat}}^{\text{cor}} f(x) = \frac{I_{\text{scat}}^x f(x)}{T_\lambda \cdot T_x} \quad \text{(S1)} \]

This procedure can be justified with following derivation. The intensity of the Raman pump in the cuvette can be represented by:

\[ I_p(z) = I_0 e^{-\alpha_p z}, \quad \text{(S2)} \]

where \( I_0 \) is the intensity at the cuvette interface, \( \alpha_p \) is the absorption coefficient for the pump, \( z \) is the distance from the interface and the depletion due to Raman scattering has been neglected. The intensity of the signal is diminished by absorption (\( \alpha_S \)) on its way through half of the cuvette width (\( a/2 \)) to the side interface:

\[ I_s(z) = I_s^0(z) e^{-\alpha_S \frac{a}{2} z}, \quad \text{(S3)} \]

where \( I_s^0 \) is the intensity of scattered light in the centre of the cuvette:

\[ I_s^0(z) = g I_p(z), \quad \text{(S4)} \]

and \( g \) is the Raman gain. The average intensity measured by the detector is:
\[ \bar{I}_S = \frac{1}{a} \int_0^a dz \, g l_0 \, e^{-\alpha_p z} e^{-\alpha_S z} = \frac{1}{a} g l_0 \, e^{-\alpha_S z} \int_0^a dz \, e^{-\alpha_p z} = g l_0 \, e^{-\alpha_S z} \frac{1 - e^{-\alpha_p a}}{a \alpha_p}. \]  

(S5)

The right-hand most factor can be expanded into Taylor series to the second order:

\[ \frac{1 - e^{-\alpha_p a}}{a \alpha_p} \approx 1 - \frac{\alpha_p a}{2}. \]  

(S6)

For \( \alpha_p a \ll 1 \) (which is the case as the total absorption of the pump in the cuvette is 0.61 for AgNPs blue and much less for AgNPs yellow and pure water) this is equal to the expansion of:

\[ e^{-\alpha_p^2} \approx 1 - \frac{\alpha_p a}{2}, \]  

(S7)

therefore, we conclude with approximation:

\[ I_{scat}^x = \bar{I}_S \approx g l_0 \, e^{-\alpha_S z} \, e^{-\alpha_p a} = g l_0 T_x T_\lambda = I_{scat}^{cor} T_x T_\lambda, \]  

(S8)

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**Figure S3** - Spontaneous Raman spectra of pure water, AgNPs blue and AgNPs yellow after losses correction.
1.2 Processing of stimulated Raman spectra

The surface enhancement of the water signal in AgNPs blue was already observed in the raw SRS data (see comparison in Figure S5). To compare the “absolute” magnitude of surface enhancement the data were compared as Raman gain factor g (shown in Figure 3b in the Manuscript, for theoretical description see part SI3 of this SI). An alternative method for scaling the data was to normalize them to the reference peak (here: fused silica peak at 490 cm\(^{-1}\)) after background subtraction.
Comparison of raw SRS data obtained with different Raman pumps.

Figure S5 – Raw stimulated Raman spectra of pure water (black lines), AgNPs blue (blue lines) and AgNPs yellow (red lines) in the OH stretching range obtained with 515 nm pump (long dashed lines, Stokes shift registered), 715 nm (short dashed lines, anti-Stokes shift) and 755 nm (solid lines, anti-Stokes shift).
SRS spectra measured with 515 nm Raman pump after background subtraction. Here we show full SRS spectra in the wavenumber scale.

Figure S6 - Stimulated Raman spectra obtained with 515 nm pump after baseline subtraction; pure water (black lines), AgNPs blue (blue lines) and AgNPs yellow (red lines), for comparison - spectrum of the fused silica cuvette (green line), in the spectral range from 100 to 4100 cm⁻¹.
SRS spectra measured with 515 nm Raman pump normalized to the silica peak at 490 cm\(^{-1}\).

**Figure S7** - stimulated Raman spectra obtained with 515 nm pump after baseline subtraction, normalized to fused silica peak at 490 cm\(^{-1}\); pure water (black lines), AgNPs blue (blue lines) and AgNPs yellow (red lines) in the spectral range from 100 to 4200 cm\(^{-1}\).

### SI2 Influence of losses in Raman signal in stimulated Raman experiment

The evolution of the intensity of the Raman pump \(I_P\) and the signal \(I_S\) are described by following equations\(^{S1,2}\):

\[
\frac{dI_P(z)}{dz} = \mp g I_P(z) I_S(z) - \alpha_P I_P(z), \quad (S9)
\]

\[
\frac{dI_S(z)}{dz} = \pm g I_P(z) I_S(z) - \alpha_S I_S(z), \quad (S10)
\]

where, \(z \in [0, L]\) is the position within the sample of thickness \(L\), \(g\) is the stimulated Raman gain and \(\alpha_P/\alpha_S\) describe linear losses of pump and signal, respectively. The ‘+’ and ‘−’ signs correspond to Stokes and anti-Stokes scattering, respectively. It can be safely assumed that changes in the intensity of the pump due to scattering are small: \(gI_S \ll 1\), in such a case Eq. S9 becomes:
\[
\frac{dl_p(z)}{dz} = -\alpha_p l_p(z), \quad (S11)
\]

and has a solution:

\[
l_p(z) \approx l_p(0)e^{-\alpha_p z}, \quad (S12)
\]

After insertion of Eq. S12 into Eq. S10:

\[
\frac{dl_s(z)}{l_s(z)} = (\pm g l_p(0)e^{-\alpha_p z} - \alpha_s)dz, \quad (S13)
\]

which can be solved to obtain an expression for calculation of Raman gain with knowledge of losses input intensities and output intensity of the signal:

\[
g = \pm \frac{\alpha_p}{l_p(0)(1-e^{-\alpha_p z})} \left( \log \frac{l_s(L)}{l_s(0)} + \alpha_s L \right). \quad (S14)
\]

For the experimental scheme where intensity of the signal is measured, also in the absence of pump, the dependence of gain on the input signal intensity and signal losses can be removed. In the absence of Raman pump, the evolution of the signal beam intensity due to absorption is governed by equation:

\[
\frac{dl_s(z)}{dz} = -\alpha_s l_s(z), \quad (S15)
\]

with solution:

\[
l_s^0(L) = l_s^0(0)e^{-\alpha_s L}, \quad (S16)
\]

in such a case:

\[
g = \pm \frac{\alpha_p}{l_p(0)(1-e^{-\alpha_p z})} \log \frac{l_s(L)}{l_s^0(L)}. \quad (S17)
\]

For the \( \alpha_p = 0 \) case the Eq. S17 can be simplified to:

\[
g = \pm \frac{1}{l_p(0)} \log \frac{l_s(L)}{l_s^0(L)}. \quad (S18)
\]

This can be obtained by either solving Eq. S18 with constant \( l_p \) or by finding a \( \alpha_p \to 0 \) limit of Eq. S17.
Figure S8 - Stimulated Raman spectra presented as Raman g factor, before background subtraction, of pure water (black lines), AgNPs blue (blue lines) and AgNPs yellow (red lines) in the OH stretching range obtained with 515 nm pump (long dashed lines, Stokes shift registered), 715 nm (short dashed lines, anti-Stokes shift) and 755 nm (solid lines, anti-Stokes shift).
SI3 Geometrical model used to estimate a part of water molecules directly interacting with AgNPs surface

As all measurements were performed under the same conditions, all calculations, for simplicity, were done for 1 dm³ of the samples (water as well as AgNPs blue dispersion). The maximal number of water molecules interacting directly with AgNPs surface was estimated on the basis of size and shape of AgNPs, which was determined by TEM, and Ag concentration in the dispersion (17.96 µg/ml), which was determined by Flame Atomic Absorption Spectrometry. Based on TEM results, the shape of nanoparticles in AgNPs blue sample was assumed to be a prism with an average size of 34 nm in a sense of radial diameter (d=2R) of a circumscribed circle of a model
prism. It was also assumed that the water molecules are densely packed on the AgNPs surface in a hexagonal system. However, this assumption is out of physical sense, it allowed to calculate the maximal number of water molecules able to contact Ag surface directly. Considering the real system, obtained herein values are overestimated. The size of a single water molecule was assumed to be equal two van der Waals radii $r$ of water molecule – 0.17 nm.$^{3}$

The following procedure was applied to estimate number of water molecules interacting directly with AgNPs surface for AgNPs blue:

1. Calculation of an average surface $S_{AgNPs}$ of a single AgNPs:
   
   $$S_{AgNPs} = 2 \cdot \frac{1}{2} ah + 3 \cdot ad = 1190 \text{ nm}^2 \approx 1200 \text{ nm}^2,$$
   
   where: $a$ – side of triangle (29.4 nm), $h$ – height of triangle (25.5 nm), $d$ – thickness of the prism (5 nm).

2. Calculation of an average cross section surface $S_{H2O}$ of a single water molecule:
   
   $$S_{H2O} = \pi r^2 = 0.0907 \text{ nm}^2 \approx 0.09 \text{ nm}^2,$$
   
   where: $r$ – radius of water molecule (0.17 nm).
3. Calculation of number of water molecules $n_1$ that can cover the surface of single AgNP:

$$n_1 = \frac{s_{AgNPs}}{S_{H_2O}} \cdot f = 9866 \approx 9900,$$

where: $f$ - efficiency of space filling assumed to be equal 0.74, as it is the highest density that can be achieved by any arrangement of spheres, either regular or irregular.

4. Calculation of number of AgNPs:
   a. Calculation of volume $V$ of the single AgNP:
      $$V = \frac{1}{2}ah \cdot d = 1874 \text{ nm}^3 \approx 1900 \text{ nm}^3$$
   b. Calculation of mass $m_{AgNPs}$ of the single AgNP:
      $$m_{AgNPs} = V \delta = 1.966 \cdot 10^{-17} \text{ g} \approx 2 \cdot 10^{-17} \text{ g},$$
      where: $\delta$ is Ag density equal 10.49 g/cm$^3$
   c. Calculation of the total mass of Ag $M_{Ag}$ in 1 dm$^3$ of dispersion from FAAS results:
      $$C_{Ag} = 17.96 \text{ } \mu g/cm^3 \approx 0.018 \text{ g/dm}^3$$
      $$M_{Ag} = 0.018 \text{ g}$$
   d. Calculation of total number of AgNPs in 1 dm$^3$ $N_{AgNPs}$:
      $$N_{AgNPs} = \frac{M_{Ag}}{m_{AgNPs}} = 9.135 \cdot 10^{14} \approx 9 \cdot 10^{14},$$

5. Calculation of water molecules $N_{surf}$ that can cover all AgNPs

$$N_{surf} = N_{AgNPs} \cdot n_1 = 8.88 \cdot 10^{18} \approx 9 \cdot 10^{18}$$

6. Calculation of water molecules present in the dispersion (total number of water molecules in 1 dm$^3$, $C_{H_2O} = 55.51 \text{ mol/dm}^3$ – molar concentration of water:

$$N_{vol} = C_{H_2O} \cdot N_A = 3.34 \cdot 10^{25} \approx 3 \cdot 10^{25},$$

where $N_A$ is Avogadro number.

Therefore, only 1 water molecule per almost 10 million is able to interact with the AgNPs surface.

The above calculated number of water molecules that can cover all AgNPs in a 1 dm$^3$ dispersion was estimated based off the average size of AgNPs (34 nm). Taking into account the size distribution in this sample (34 ± 14 nm), analogous calculations were performed for systems where all AgNPs have the smallest (20 nm) or the largest possible size (48 nm). Results of calculations in both cases give values in the same order of magnitude as the one obtained for averaged size.
References:

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