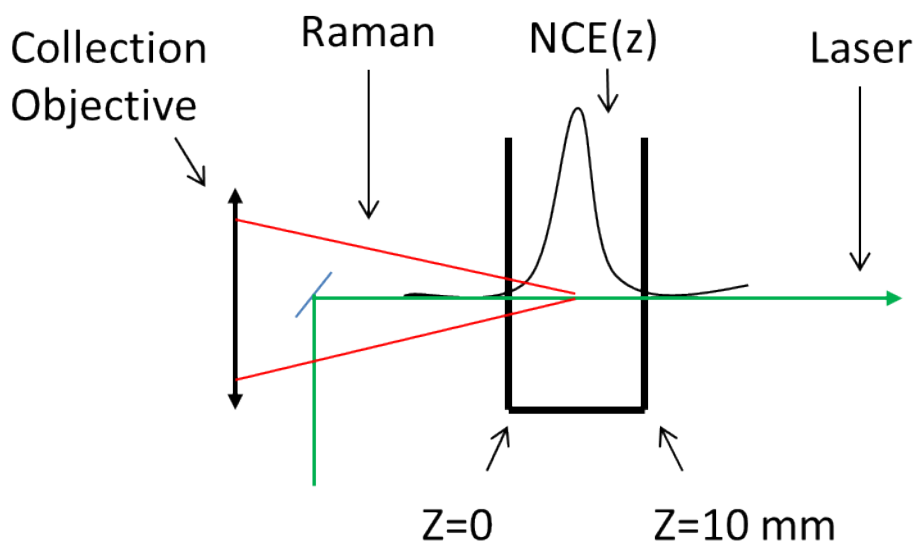# NUMERICAL CORRECTION FOR SELF-ABSORPTION

A simplified sketch of the experimental situation is the following:

A laser beam (green line) enters the cuvette containing the sample, but since the solution is not transparent both the laser beam and the generated Raman scattering (red line) will be partly absorbed along their own paths. The Raman signal is collected in back-scattering and the normalized axial collection efficiency (NCE) of the instrument depends on z: NCE is maximum approximately at the center of the cuvette, where the focus of the laser and of the objective are located.

Let's consider an expression for the Raman signal emitted by a transparent sample:

$$P_{Raman} = \sigma\, C_V \int\limits_{\rho=0}^{\rho=+\infty} 2\pi\rho \int\limits_{z=0}^{z=+L} I(\rho,z)\, \eta(\rho,z)\, d\rho\, dz$$

(01)

Where σ is the differential Raman cross section of the molecules, C_V is the volumetric density of molecules in the sample, z and ρ are polar coordinates that identify the laser propagation direction and the distance from the axis. $I(\rho,z)$ is the laser intensity and $\eta(\rho,z)$ the collection

efficiency. z=0 corresponds to the first face of the cuvette hit by the laser and L is its thickness.

Let's introduce the effect of attenuation of the signal due to the absorption of the laser beam and of the Raman scattering:

$$P_{Raman}^{Self\,Abs} = \sigma\, C_V \int_{\rho=0}^{\rho=+\infty} 2\pi\rho \int_{z=0}^{z=+L} I(z)\, 10^{-\left(Ext(\lambda_L) + Ext(\lambda_R)\right)z}\, \eta(\rho,z)\, d\rho\, dz$$

(02)

Where $Ext(\lambda_L)$ and $Ext(\lambda_R)$ are the extinction at the laser and Raman wavelengths respectively. In the formula above it is implicitly assumed that the laser beam and the Raman scattering travel the same distance (for a 1 cm thick cuvette and a collection objective with f#=1.2 this approximation is valid within 10%); moreover the dependence of $I(\rho,z)$ on ρ has been neglected and therefore $I(z)$ represents a radially averaged intensity.

Expression 02 can be recast in terms of normalized axial collection efficiency, a parameter that can be experimentally measured by recording the Raman signal of a Silicon slab as a function of the z position and normalizing the curve at the maximum.
Formula 01, for a slab of silicon can be rewritten as:

$$P_{Raman\,Si}(z) = \delta_P C_{Si} \sigma_{Si} \int_{\rho=0}^{\rho=+\infty} 2\pi\rho I(z)\eta(\rho,z)d\rho$$

(03)

Where δ_P is the penetration depth and C_{Si} is the volumetric density of atoms in Silicon. $I(z)$ in this case is radially averaged (like in Formula 02) and also averaged with respect to the penetration in the sample (this approximation holds since silicon is an opaque sample and δ_P is much smaller than the z range we explore). $P_{Raman\,Si}(z)$ is a bell-shaped curve with maximum at z_0 corresponding to the laser and the objective focus.
We define the normalized collection efficiency $NCE(z)$ as:

$$\frac{P_{Raman\,Si}(z)}{P_{Raman\,Si}(z_0)} = \frac{\delta_P C_{Si}\sigma_{Si}\displaystyle\int_{\rho=0}^{\rho=+\infty} 2\pi\rho I(z)\eta(\rho,z)d\rho}{\delta_P C_{Si}\sigma_{Si}\displaystyle\int_{\rho=0}^{\rho=+\infty} 2\pi\rho I(z_0)\eta(\rho,z_0)d\rho} = \frac{\displaystyle\int_{\rho=0}^{\rho=+\infty} 2\pi\rho I(z)\eta(\rho,z)d\rho}{KI(z_0)} = NCE(z)$$

(05)

$$K = \int_{\rho=0}^{\rho=+\infty} 2\pi\rho\eta(\rho,z_0)d\rho$$

Expression 03 can be rewritten in terms of $NCE(z)$ in the following way:

$$P_{Raman}^{Self\,Abs} = KI(z_0)\sigma\,C_V \int_{z=0}^{z=+L} 10^{-\left(Ext(\lambda_L)+Ext(\lambda_R)\right)z} NCE(z)dz$$

(06)

The ratio between the Raman without and with self-absorption correction (R) is the factor that must be used to correct the experimental values:

$$R = \frac{P_{Raman}}{P_{Raman}^{Self\,Abs}} = \frac{\displaystyle\int_{z=0}^{z=+L} NCE(z)dz}{\displaystyle\int_{z=0}^{z=+L} 10^{-\left(Ext(\lambda_L)+Ext(\lambda_R)\right)z} NCE(z)dz}$$

(07)

Considering that the reference and the sample share the same axial efficiency because the two cuvettes are placed at the same position, and that the reference is transparent in the 568-800 nm region, EF turns out to be:

$$EF_{corrected} = EF_{experimental}R$$

(08)

In order to work out the value of R, the knowledge of $NCE(z)$, $Ext(\lambda_L)$ and $Ext(\lambda_R)$ is required.

The extinction spectrum has been fitted to have an analytical expression for $Ext(\lambda_L)$ and $Ext(\lambda_R)$ (Figure 1). The black line represent the extinction experimental fit, the green lines are the three Lorenzian curves used in the fit and the red line their summation.
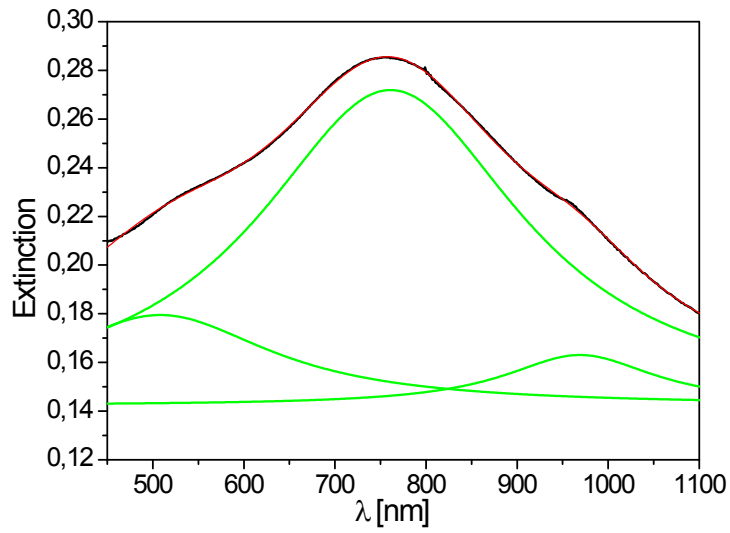
Figure 1

In Figure 2 it is reported a typical example of NCE (black dots) and the fit with a Lorenzian curve (red line).
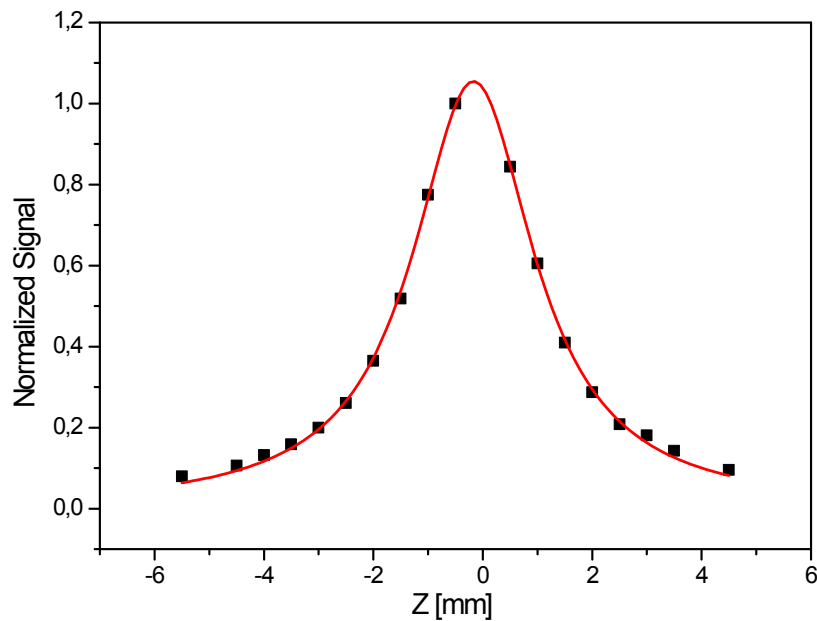

Figure 2

The Lorenzian curve used has the following formula:

$$y = \frac{2A}{\pi} \frac{w}{4(z - z_1)^2 + w^2}$$

Where A is the Area, w the full width at half maximum (FHWM). The trace have been centered at $z_1 \sim 0$. The values are reported in Table 1

Table 1

w [mm]	2,7
A [mm]	4,48

The parameters reported here are typical values for NCE both with the visible and with the NIR excitation, in fact repeated measurements of NCE at all wavelengths under similar experimental configuration showed that w can vary in the range 2-3.4 mm. Moreover, also the estimation of z_0 is susceptible of some error, since once the maximum of NCE is identified by scanning the Silicon slab, replacing the silicon with the solution in cuvette does not guarantee that the focus is located right at the center of the cell. So we went through a brief study of the effect of these parameters on the correction factor R.

We show in Figure 3 how R changes as a function of w, keeping the parameters in Table 1 constant and setting $z_0 = 5$ mm: the black line is the extinction spectrum and the colored lines represent the value of R calculated for w = 2,3,4 mm (from top to bottom respectively). Clearly w has only a minor effect on the correction.
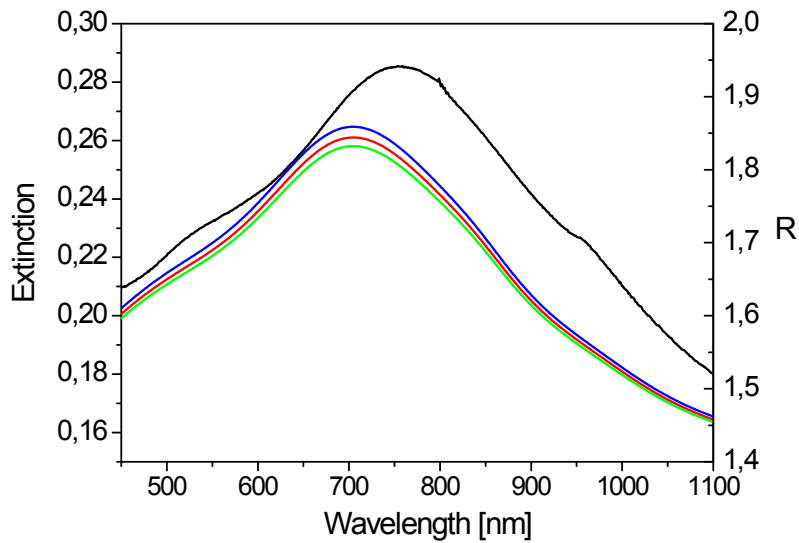
Figure 3

In Figure 4 it is shown what happens to R when z_0 is varied around the center of the cuvette: the black line represent the extinction spectrum and the colored lines the value of R at z_0=3,4,5,6,7 mm (from bottom to top respectively). The other parameters are those in Table 1. Therefore z_0 can somewhat alter the absolute value of the correction, but not so much its spectral shape.
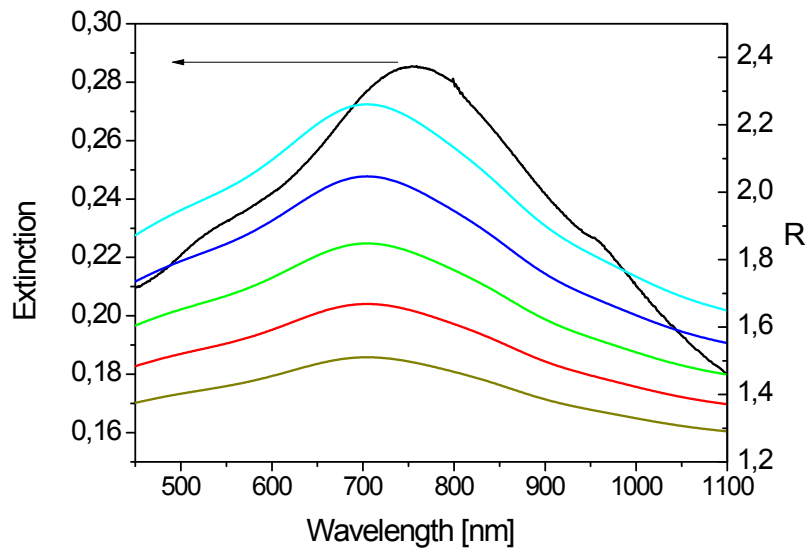

Figure 4

Finally the experimental values of EF have been corrected calculating R at all wavelengths with the input parameters of Table 1 and z_0=5 mm.

In Figure 5 the experimental data (black points) and the self-absorption corrected data (red points) are shown along with the correction factor R (solid black line). The effect of the correction is limited to a slight increase in the absolute value, with only a minor effect on the shape of the EF profile.
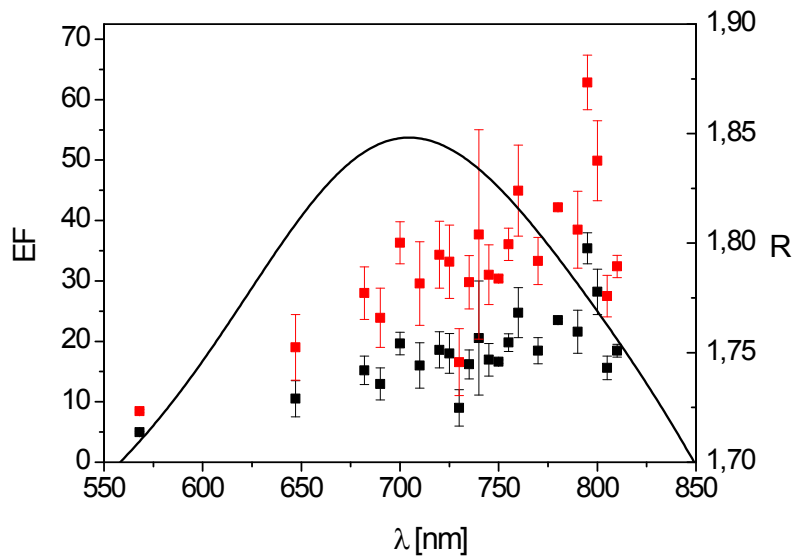

Figure 5

ESTIMATION OF THE MEAN VALUES AND THE ERROR BARS OF EF

At every excitation wavelength, two "limit" baselines were drawn for the 1595 cm^{-1} peak of NAFTA6 in acetone, providing a lower ($^{NAFTA6}min$) and a higher ($^{NAFTA6}max$) estimate of the area. The same procedure was adopted for NAFTA6@NC, providing NAFTA6@NC$_{min}$ and NAFTA6@NC$_{max}$.

I_{Raman} and I_{SERS} were worked out as:

$$I_{Raman} = \frac{1}{2}(NAFTA6_{min} + NAFTA6_{max})$$

$$I_{SERS} = \frac{1}{2}(NAFTA6@NC_{min} + NAFTA6@NC_{max})$$

- At the wavelengths where the EF measurements were measured only once, EF is calculated inserting I_{Raman} and I_{SERS} in equation 5 in the main text. The error bars were calculated as

$$ErB = \frac{1}{2}\left(\frac{NAFTA6@NC_{min}}{NAFTA6_{max}} - \frac{NAFTA6@NC_{max}}{NAFTA6_{min}}\right)$$

   Finally

$$EF = \frac{C_{NAFTA6}}{C_{NAFTA6@NC}} \frac{I_{SERS}}{I_{Raman}} \pm ErB$$

- At the wavelengths where the EF measurements were repeated more times, the best value of EF was estimated as the average of the single values and the error bars as the semi-dispersion between the highest and lowest value in the group of measurements.
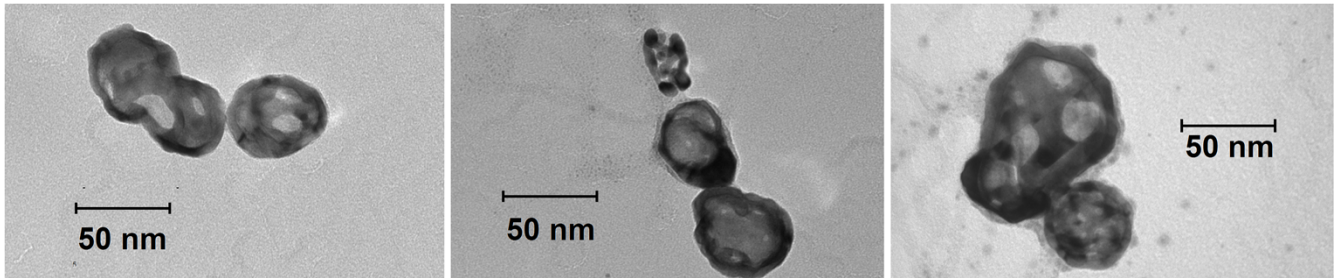
ADDITIONAL TEM IMAGES

Figure 6: Additional TEM Images showing some dimers and trimers of NCs on the TEM grid.