Discerning the origins of the amplitude fluctuations in dynamic Raman NanoSpectroscopy

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Assignment of Raman lines

Table 1: BT indicates *Benzene Thiol*; this molecule is chemisorbed dissociatively onto gold NPs and SERS spectra are related to benzenethiolate which is the species bound to gold via its sulfur atom (from ref [17]).*Citrate species* indicate either adsorbated citrate (I) or its main oxydation product namely, acetone dicarboxylic acid (II) (from ref [15]). s, m, w indicate relative intensities as strong, medium and weak, respectively

SERS Spectra from Fig.2c and Fig.4(Q) Raman shift (cm^{-1})	Relative Intensity	Possible species assignment
1700	m	*Citrate species*(II)
1620	m	*Citrate species*(II)
1580/1560	m	*Citrate species*(I+II)
1540	s	**BT**
1485	m-w	**BT**
1450	m-w	*Citrate species*(I+II)
1410	m-w	Citratespecies (II)
1350	m-w	*Citrate species*(I+II)
1300	m	*Citrate species*(I+II)
1250	m-w	*Citrate species*(I+II)
1200	m	*Citrate species*(I+II)
1130	m-w	*Citrate species*(I+II)
1095	m-s	**BT**
1020	m-w	**BT**
992	m-s	**BT**
950	m-s	*Citrate species*(I+II)

Statistical treatment of spectra

The probability density functions $p_{\nu}(A_{\nu})$ of the photon rates A_{ν} were estimated experimentally for each wavenumber ν. Histograms were built using a bin number n defined by the root of the number N of acquired spectra and bin sizes ΔA_{ν} obtained by the intervals between the minimum $A_{min,\nu}$ and the maximum $A_{max,\nu}$ of the photon rates.

$$n_{=}\sqrt{N} \tag{1}$$

$$\Delta A_\nu = \frac{A_{max,\nu} - A_{min,\nu}}{n} \tag{2}$$

$p_\nu(A_\nu)$ are defined by the number of events $n_\nu(A_\nu)$ having its photon rate A_ν comprised in the interval between A_ν and $A_\nu + \Delta A_\nu$ and divided by n and ΔA_ν.

$$p_\nu(A_\nu) = \frac{n_\nu(A_\nu)}{\Delta A_\nu n} \tag{3}$$

Hence, the integral of $p_\nu(A_\nu)$ over the entire range of photon rates A_ν is equal to one. The variance $\sigma_\nu^2(A_\nu)$ is used to describe how far $A_\nu(i)$ lies from the mean $\langle A_\nu \rangle$

$$\langle A_\nu \rangle = \sum_{i=1}^{n} p_\nu(i) A_\nu(i) \tag{4}$$

$$\sigma_\nu^2 = \sum_{i=1}^{n} p_\nu(i)(A_\nu(i) - \langle A_\nu \rangle)^2 \tag{5}$$

The relative standard deviation *RSD* was used to express the chance occurence of the Raman line.

$$RSD_\nu = \frac{\sigma_\nu}{\langle A_\nu \rangle} \tag{6}$$

Log Logistic distribution

The log logistic distribution is similar in shape to the log-normal distribution (geometric Brownian motion) but is used to describe heavier tails. The log-logistic distribution, sometimes known as the Fisk distribution, is encountered in a variety of fields (economy, biology, physics) to analyse life time data. The log-logistic distribution was applied successfully to describe a process that is the product of a number of variables of small amplitude, namely we attempt to describe the process as a coupling between the substrate properties (EM field or electron tunnelling) and the molecular Raman scattering. The two-parameters log logistic distribution is described by its theoretical power density function $p_{theo,\nu}(A_\nu)$.

$$p_{theo,v}(A_v) = \frac{\frac{\beta}{\alpha}(\frac{A_v}{\alpha})^{\beta-1}}{(1+(\frac{A_v}{\alpha})^{\beta})^2} \tag{7}$$

and its cumulative density function $F_{theo,v}(A_v)$

$$F_{theo,v}(A_v) = \sum_{j=1}^{A_v} p_{theo,v}(j)\Delta A_v = \frac{1}{(1+\frac{A_v}{\alpha})^{-\beta}} \tag{8}$$

α is a scale parameter that corresponds to the median of the distribution (i.e. the value of A_v having $F(A_v)$=0.5). Note that the median is less sensitive to the extreme values compared to the mean. α_v is obtained by the following relations :

$$\alpha_v = \frac{\sin b}{b}\langle A_v \rangle \tag{9}$$

where b is obtained by solving the equation :

$$RSD_v^2 = \frac{2b}{\sin 2b} - \frac{b^2}{\sin b} \tag{10}$$

The shape parameter β_v can be deduced from b

$$\beta_v = \frac{\pi}{b} \tag{11}$$

When β_v is high, α_v tends to $\langle I_v \rangle$. Note that α_v tends to the infinity when β_v approaches the value of 2.