Supporting information for

Junction plasmon driven population inversion of molecular vibrations: a ps-SERS study

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Vibrational populations and enhancement.

In normal spontaneous Raman (SR), the scattering rate:

$$R_{SR} = I\sigma \tag{S1}$$

is given by the differential cross section:

$$\frac{d\sigma}{d\Omega} = \frac{16\pi^4}{\lambda_s^3\lambda_i}\langle \hat{e}_s \cdot \alpha_{si} \cdot \hat{e}_i \rangle^2 \tag{S2}$$

integrated over the experimental solid angle Ω of detection. The λ_s^3 term recognizes the spontaneous nature of the process, with photons scattered into the vacuum density of states. The total rate is given by summing the matrix element over all initial and final matter and field states. For a two-level system, the population ratio N_1/N_0 can be obtained from the AS and S scattering rates (intensities) by taking into account the associated vacuum density of states:

$$\frac{N_1}{N_0} = \frac{I_{AS}}{I_S}\left(\frac{\lambda_{AS}}{\lambda_S}\right)^3 \tag{S3}$$

A quartic correction is used on many recent works,[1-5] perhaps borrowed either from older literature where energy meters are used in detection instead of photon count rates. Equation S3 is the appropriate form for most modern Raman instrumentation, i.e. counting devices.

In SERS, it is useful to separate enhancement factors $\beta_{i,s}$ of the incident field and the scattering rate:

$$R_{SERS} = \left(\beta_i^2 I_i\right)\left(\beta_s^2 \sigma_s\right) = I_L \sigma_s^* \tag{S4}$$

The incident field is enhanced by the ratio of local and applied fields, $\beta_i = E_L/E_0$. The scattering is enhanced by the density of states in the local cavity of the nantenna rather than the vacuum, as recognized by Purcell[6]:

$$\beta_s^2 = F = \frac{3}{4\pi^2}\frac{\lambda_s^3 Q}{V} \tag{S5}$$

Q is the quality factor and V is the mode volume of the cavity. Plasmonic nantennas are leaky due to both ohmic and radiative damping. Based on extinction resonances (see Fig. 1 or 2), Q ~ 7. The cavity volume is principally geometric, although its estimates greatly vary from pico- to nano-volume.[7, 8] Clearly, the orientation and location of the molecule relative to the cavity, which is not known, determines the coupling. An estimate that seems operative based on observed enhancement factors, would be the product of the junction gap and surface area occupied by the plasmon, $V = 4\pi r^2 g$ (with gap g = 1 nm, nanosphere radius = 50 nm, 5.8×10^3 , which leads to partitioning of the observed overall enhancement factor, $\beta_i^2\beta_s^2 = 10^8$ into $\beta_i = 130$ and $\beta_s = 75$). Even if we assume Q/V to be independent of wavelength, since the cavity will have to ultimately re-emit into the far field, (S3) is restored. Thus, in the limit of leaky cavities, (S3) remains valid in SERS. In the limit of bright cavities, the ratios may be determined by the plasmonic resonances, but in a nontrivial way. Not all modes couple to the junction, not all junction modes couple to the molecule, and dark modes do not couple to the far-field. As such, it is difficult to connect dark field spectra with the expected enhancement factors and their wavelength dependence.[9] One is often forced to resort to theory to explain experimental observations.

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