PCCP - Electronic Supplementary Information

Image molecular dipoles in Surface Enhanced Raman Scattering

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In this Electronic Supplementary Information we will give more details on the derivation of the charge density induced by a dipole oscillating dynamically $P(t) = P_0 \cos \omega t$, in a metal surface situated at a distance d. It is assumed that the dipole orientation is parallel to the metal surface.

All fields oscillate with the frequency ω. The Maxwell equations may be written in this case:

$$\text{curl}\,\boldsymbol{E} = -\,i\omega\boldsymbol{B}, \qquad \text{curl}\,\boldsymbol{B} = \mu_0\boldsymbol{j} + \in_0 \mu_0\, i\omega\, \boldsymbol{E}$$

Together with the continuity equation $\text{div}\,\boldsymbol{j} + \partial\rho/\partial t = 0$ and with $\boldsymbol{j} = \sigma\boldsymbol{E}$, s being the complex conductivity given by eq. (11), main text, everything combines into:

$$\Delta\boldsymbol{E} - \frac{1}{\in_0}\nabla\rho = \frac{ik}{c\tau_0}\boldsymbol{E} - k^2\boldsymbol{E} \qquad \text{(ESI-1)}$$

In the optical regime, $\tau_0 = \in_0/\sigma_0 \sim 10^{-18}$ s, $\omega \sim 10^{16}$ s^{-1}, $k = \omega/c \sim 3 \times 10^7$ m^{-1}, therefore the first term on the right hand side is dominant.

The gradient of the charge density is negligible from the continuity equation combined with Ohm's law, far away from the plasma frequency. It follows a simple equation:

$$\Delta\boldsymbol{E} = \frac{ik}{c\tau_0}\boldsymbol{E} \equiv \kappa^2\boldsymbol{E} \qquad \text{(ESI-2)}$$

where κ is chosen such as to represent a damping wave for increasing z values ($z = 0$ is the metal surface, z > 0 idicates regions inside the metal). A good choice is:

$$\kappa = -\kappa_0 - i\kappa_0 \qquad \text{with} \qquad \kappa_0 = \left(\frac{k}{2c\tau_0}\right)^{1/2} = \frac{1}{c}\left(\frac{\omega\sigma}{2\in_0}\right)^{1/2} \qquad \text{(ESI-3)}$$

The penetration and oscillating character of the field inside the metal is now straightforward. One can now write down the field $\boldsymbol{E}_{\text{ext.}}$ produced by a charge q situated at a distance d ($z = -d$) from the metal surface:

z < 0:

$$E_{\text{ext.},x} = \frac{qx}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}}$$
$$E_{\text{ext.},y} = \frac{qy}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}}$$
$$E_{\text{ext.},z} = \frac{q(z+d))}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}}$$

z $\geq$ 0:

$$E_{\text{ext.},x} = \frac{qx\exp(\kappa z)}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}}$$
$$E_{\text{ext.},y} = \frac{qy\exp(\kappa z)}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}} \qquad \text{(ESI-4)}$$
$$E_{\text{ext.},z} = \frac{qd\exp(\kappa z)}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{3/2}}$$

Now it is easy to compute the divergence of this external field:

$$\mathrm{div}\boldsymbol{E}_{\mathrm{ext.}} = \frac{q\exp(\kappa z)\left\{(x^2+y^2)(\kappa d-1)+d^2(\kappa d+2)\right\}}{4\pi\in_0\left\{x^2+y^2+(z+d)^2\right\}^{5/2}} \tag{ESI-5}$$

We apply the same algorithm as defined by eq. (12), main text:

$$\sigma(\omega)\mathrm{div}\left(\boldsymbol{E}_{\mathrm{ext.}}+\boldsymbol{E}_{\mathrm{ind.}}\right)=\sigma(\omega)\mathrm{div}\boldsymbol{E}_{\mathrm{ext.}}+\frac{\sigma(\omega)}{\in_0}\rho_{\mathrm{ind.}}=\mathrm{div}\,\boldsymbol{j}=-i\frac{\partial\rho_{\mathrm{ind.}}}{\partial t}=-i\omega\rho_{\mathrm{ind.}} \tag{ESI-6}$$

From (ESI-5) and (ESI-6) one can easiliy derive $\rho_{\mathrm{ind.}}(x, y, z)$ for a charge q. Note that it is complex in this case.

$$\rho_{\mathrm{ind.}}\left(1-\frac{\omega^2}{\omega_p^{\;2}}+i\omega\tau_0\right)=\frac{q}{4\pi}\exp(\kappa z)\frac{(x^2+y^2)(\kappa_0 d+i\kappa_0 d+1)+d^2(\kappa_0 d+i\kappa_0 d-2)}{(x^2+y^2+d^2)^{5/2}} \quad \text{(ESI-6)}$$

For one dipole, one derives directly the approximation corresponding to the last equality of eq. (10) by Taylor development:

$$\rho_{\mathrm{dip.}}\left(1-\frac{\omega^2}{\omega_p^{\;2}}+i\omega\tau_0\right)=\frac{q\delta_0}{4\pi}\exp(\kappa z)\frac{\partial}{\partial x}\left\{\frac{(x^2+y^2)(\kappa_0 d+i\kappa_0 d+1)+d^2(\kappa_0 d+i\kappa_0 d-2)}{(x^2+y^2+d^2)^{5/2}}\right\} \tag{ESI-7}$$

Now, $q\delta_0 = P = P_0 \exp(i\omega t)$, the oscillating dipole moment. Combining everything, after some algebra one obtains:

$$\rho_{\mathrm{dip.}}=\frac{P_0}{4\pi}\mathrm{Re}\left\{\frac{\exp(\kappa z+i\omega t)x\left[d^2(12-\kappa d)-(x^2+y^2)(3+5\kappa d)\right]}{\left(1-\frac{\omega^2}{\omega_p^{\;2}}+i\omega\tau_0\right)(x^2+y^2+d^2)^{7/2}}\right\} \tag{ESI-8}$$

One evaluates this charge density in the plane of the metal ($z = 0$). By separating the real part of eq. (ESI-8), one obtains four terms, two of them oscillating like cos ωt and two like sin ωt. Keeping just the former two terms, which oscillate in phase with the molecular dipole, the dynamical charge density, eq. (14) from the main text, is obtained.