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**Supporting Information for**

# Molecules in the mirror: How SERS backgrounds arise from the

# quantum method of images

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**Full derivation of equation (5):**

   The probability amplitude for making a Raman transition from the electronic ground-state and vibrational state, $v$ to the electronic ground-state and vibrational state, $v'$ is proportional to the molecular tensor[1]

$$\alpha_{ij}^{0v',0v} = \langle \chi_{0v'} | \sum_r \left( \frac{\mu_i^{0r}\mu_j^{r0}}{E_{r0}-\hbar\omega} + \frac{\mu_j^{0r}\mu_i^{r0}}{E_{r0}+\hbar\omega} \right) | \chi_{0v} \rangle \tag{1}$$

where $|\chi_{0v}\rangle$ is the electronic ground-state and vibrational state, $v'$, $E_{r0}$ is the energy difference between the vibrational ground state and the virtual state $r$, $\mu^{0r}$ is the dipole matrix element between the vibrational ground state and $r$, while $i$ denotes the polarization of the emitted Raman $E$ field, $j$ denotes the polarization of the incident $E$ field and $\omega$ is the frequency of the exciting radiation. The first term in the summand contains the near-resonant denominator, $E_{r0} - \hbar\omega$, and so we can omit the second far smaller non-resonant term to give

$$\alpha_{ij}^{0v',0v} = \langle \chi_{0v'} | \sum_r \frac{\mu_i^{0r}\mu_j^{r0}}{E_{r0}-\hbar\omega} | \chi_{0v} \rangle \quad . \tag{2}$$

   The spectrum of the emitted Raman line is given by the Fourier transform of the temporal correlation function for this transition amplitude:

$$\alpha_{ij}^{0v',0v*}(t)\alpha_{ij}^{0v',0v}(0) = \langle \chi_{0v} | e^{i\hat{H}t/\hbar} \sum_r \frac{\mu_i^{0r}\mu_j^{r0}}{E_{r0}-\hbar\omega} e^{-i\hat{H}t/\hbar} | \chi_{0v'} \rangle \langle \chi_{0v'} | \sum_r \frac{\mu_i^{0r}\mu_j^{r0}}{E_{r0}-\hbar\omega} | \chi_{0v} \rangle, \tag{3}$$

where $\hat{H}$ is the molecular Hamiltonian. This procedure is the analogue of that for an absorption or emission spectrum in which the spectrum is the Fourier transform of the temporal correlation function for the transition matrix element.[2] For the Stokes line, when a transition in the real molecule is made from the vibrational ground state, $|\chi_{00}\rangle$ to a vibrational excited state, $|\chi_{0v'}\rangle$ there will be an energy difference compared to $|\chi_{00}\rangle$ of $E_{v'} = \hbar\omega_{v'}$ as well as a characteristic linewidth, $\gamma_{v'}$. We can derive this by including the coupling of the state to the broad continuum of available decay modes using standard techniques from quantum optics.[2] It suffices for our purposes, however, to replace the real vibrational energy by the effective complex energy $\hbar(\omega_{v'} - i\pi\gamma_{v'})$, so that the amplitude for remaining in the state $|\chi_{0v'}\rangle$ after time $t$ is

$e^{-i\omega_{v'}t-\pi\gamma_{v'}t}$. Substituting this into our temporal correlation function and evaluating the Fourier transform gives the spectrum

$$S(\Omega) = \frac{\gamma_{v'}}{\left(\Omega-\omega_{v'}\right)^2+\pi^2\gamma_{v'}^2} \tag{4}$$

where we have chosen the constant of proportionality to give a normalized spectrum.

The image molecule will also contribute and therefore equation (1) will be supplemented by a second molecular tensor for the image molecule:

$$\alpha_{ij}^{Image\ 0v',0v}(\omega) = \langle\chi_{0v'}|\sum_r \frac{\mu_i'^{0r}\mu_j'^{r0}}{E_{r0}-\hbar\omega}|\chi_{0v}\rangle$$

$$= \left|\frac{\varepsilon_2(\omega)-\varepsilon_1(\omega)}{\varepsilon_2(\omega)+\varepsilon_1(\omega)}\right|^2 \langle\chi_{0v'}|\sum_r \frac{\tilde{\mu}_i^{0r}\tilde{\mu}_j^{r0}}{E_{r0}-\hbar\omega}|\chi_{0v}\rangle. \tag{5}$$

The vibrational line for the image molecule will have a linewidth, $\Gamma_{v'}$, which is typically very much larger than that for the associated line in the molecule itself. This is because of the resistive damping of the currents, associated with the image, in the metal surface. The image contribution to the spectrum is obtained as above from the temporal correlation function. Combining the two contributions to the spectrum we find

$$S(\Omega) = \frac{\gamma_{v'}}{\left(\Omega-\omega_{v'}\right)^2+\pi^2\gamma_{v'}^2} + \left|\frac{\varepsilon_2(\omega)-\varepsilon_1(\omega)}{\varepsilon_2(\omega)+\varepsilon_1(\omega)}\right|^4 \frac{\Gamma_{v'}}{(\Omega-\omega_{v'})^2+\pi^2\Gamma_{v'}^2}. \tag{6}$$

There is no interference in the spectrum between Raman light emitted by the molecule and its image. This is because we could, at least in principle, examine the molecule immediately following the emission and determine its vibrational state. If it has made the transition to the state $|\chi_{0v'}\rangle$ then we would know that the light came from the molecule. If it has not then we would know that light came from its image. The existence, even in principle, of such "which path" information suffices to remove the possibility of any interference.

1    Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics: An Introduction to Radiation-Molecule Interactions*; Academic Press: London, 1998.

2    Barnett, S. M.; Radmore, P. M. *Methods in Theoretical Quantum Optics*; Clarendon Press: Oxford, 1997.