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Role of the Substrate Field Inhomogeneities in Coherent Resonant Raman Scattering[†]

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The peculiar role of the substrate field on the nonlinear optical response of a molecular adsorbate experiencing a resonant Raman scattering process is analyzed. The description of the internal dynamics is done in terms of the renormalized normal mode coordinates that account for the conformational changes induced in the adsorbate by the substrate field. This analytical description, well-adapted to weak substrate fields, points out the underlying mechanisms that are responsible for the enhancement of the resonant Raman signal observed in some molecules. They involve elementary processes bringing additional intermediate vibrational states into play, depending on the nature of the field inhomogeneities. Also, according to the relative values of the unperturbed equilibrium positions of the modes, their displacements, and frequency changes due to the substrate field, enhancement as well as decrease of the signal can possibly be observed and are evaluated. Of course, for a strong substrate field, the number of intermediate vibrational levels participating in the Raman process becomes very large, and a complete numerical evaluation is required.

1. Introduction

Since the pionnering work of Fleischmann et al. performed using resonant Raman scattering on a pyridine molecule adsorbed on a silver surface and published in 1974,[1] spectroscopists have been confronted with the challenge of understanding why some molecules are so sensitive with respect to the presence of a metallic substrate while some others not. It is quite important to understand if it is just a casual fact or if there is any structural electronic and/or vibrational properties underlying this enhancement of the nonlinear optical response observed in resonant Raman scattering. Also, it is important to understand whether the substrate field can just enhance or eventually could inhibit the resonant Raman signal. Of course, while the first case is quite attractive, little attention is paid to the second one, which certainly frequently occurs.

Among the large varieties of spectroscopies accessible today to study molecular adsorbates, surface-enhanced Raman spectroscopy is a quite attractive method to investigate interactions and processes taking place between adsorbate molecules and their corresponding substrate surfaces. Furthermore, surface-enhanced Raman spectroscopy has been extensively used because of its low detection limit and high selectivity for adsorbates and has become a very powerful spectroscopic technique in a broad range of fields ranging from surface science to biophysics.[2−9]

This is why many works have been devoted to the determination of the enhancement processes. It is now well-established that the enhancement factor observed in surface-enhanced Raman spectroscopy depends on different factors including surface roughness,[6,10,11] surface material,[12−14] as well as the laser excitation frequency profile.[15] One type of enhancement, termed the electromagnetic enhancement and considered as the dominant contribution to the surface-enhanced Raman signal,[16] originates from the surface local electric field. Moreover, it has been shown, for the particular case of near metallic inhomogeneities, that the localized plasmon modes created by the resulting strong electromagnetic coupling between inhomogeneities are the main contribution to the enhanced signal.[17] Besides, there is another important source of enhancement termed the chemical enhancement mechanism, provided by a chemisorption process associated wit the photoinduced charge-transfer process between the adsorbate and the surface substrate. This mechanism, observed and described in the literature,[18] also participates efficiently in the resonant Raman scattering signal.

The recent experimental results published by Zuo and Jagodzinski[19] on pyridine offer the interesting opportunity of testing qualitatively as well as quantitatively the processes underlying the surface-enhanced resonant Raman scattering. In addition, since surface-enhanced resonant Raman spectra have been obtained simultaneously for pyridine adsorbed on the surfaces of different metals including cadmium, nickel, gold, iron, copper, and silver, it will be tempting in the future to test up to what extent a given process, the local substrate field effect for our purpose, could account simultaneously for these experimental observations. While our analytical work is not directed at explaining these experimental observations, it gives a description of the various processes taking place and contributing to the enhanced signal. To simulate quantitatively the previously mentioned experimental results, important numerical calculations are required.

It is the intent of the present work to analyze in terms of elementary processes how the internal dynamics of a molecule undergoing a resonant Raman scattering is altered by the presence of the field substrate. More specifically, the influence of the field on the resonant Raman intensity of a model vibrational normal mode is emphasized. Even if an analytical description is necessarily limited by the complexity of the calculation, it has the advantage of describing, at least for the first contributing terms, a comprehensive analysis of the various mechanisms underlying the modifications of the nonlinear optical response of the adsorbate. It is now well-established that the field substrate modifies the molecular charge distribution. These variations of the electronic charge are accounted for by

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the introduction of additional terms, the electronic partial charge and the electronic transition charge, coupling the various electronic configurations. In addition, because these interaction terms depend on the normal coordinates, a functional dependence that is a signature of the type of field inhomogeneity, additional contributions resulting from the coupling between vibrational states differing by ±1, ±2, ... quanta participate.

In section 2, we describe the dynamical process responsible for the resonant Raman process and competing with the hot luminescence.[20] In section 3, the role of the electric field induced by the local inhomogeneities of the field substrate is introduced. For the sake of simplicity, according to the Born−Oppenheimer procedure, we evaluate the vibrational structure, say, the displacements of the equilibrium positions and frequency changes of the adsorbate in the presence of the substrate field. Then, in section 4, the expression for the resonant Raman signal is obtained, emphasizing the peculiar role of the induced and permanent dipole moments. Finally, in section 5 some numerical simulations are performed to illustrate these results.

2. Formal Evaluation of the Coherent Resonance Raman Signal

The coherent resonant Raman effect is a third-order coherent process based on the interaction of a molecular system interacting with pump and probe laser fields. For our purpose, they will be termed $\vec{E}_p(\vec{\mathbf{r}},t)$ and $\vec{E}_t(\vec{\mathbf{r}},t)$, respectively, and are described by

$$\vec{E}_j(\vec{\mathbf{r}},t) = \vec{E}_j(-\omega_j)\, e^{iw_jt - i\vec{k}_j\cdot\vec{r}} + \vec{E}_j(\omega_j)\, e^{-iw_jt + i\vec{k}_j\cdot\vec{r}} \tag{2.1}$$

with $j = p$ or t. The molecular system itself, an adsorbate molecule on the substrate surface, is represented by its Hamiltonian **H,** which accounts for the molecule lying in the electrostatic field of the substrate. Its basic description will be required in the following for the evaluation of the coherent resonant Raman signal. As usual, the general dynamical evolution results from the Liouville equation

$$\frac{\partial\boldsymbol{\rho}(t)}{\partial t} = -\frac{i}{\hbar}[\mathbf{L} + \mathbf{L}_v(t)]\boldsymbol{\rho}(t) - \Gamma\boldsymbol{\rho}(t) \tag{2.2}$$

where $\boldsymbol{\rho}(t)$ is the density matrix of the adsorbate in presence of the substrate field, $\mathbf{L}_v(t)$ the interaction Liouvillian between the pump and probe laser beams and the adsorbate, and finally Γ, the damping operator, accounts for the relaxation and dephasing processes undergone by the molecule. The Liouvillian $\mathbf{L}_v(t)$ is associated with the dipolar interaction term described by

$$\mathbf{V}(t) = -\vec{\boldsymbol{\mu}}\cdot\vec{E}_j(\vec{r},t) \tag{2.3}$$

with $\vec{E}_{tot}(\vec{r},t) = \vec{E}_p(\vec{r},t) + \vec{E}_t(\vec{r},t)$ in the framework of the semiclassical description of the radiation−matter interaction. Using the rotating wave approximation and rejecting propagation effects, the interaction Hamiltonian can be expressed as

$$\mathbf{V}_{mn}(t) = -\vec{\boldsymbol{\mu}}_{mn}\cdot[\vec{E}_j(\omega_j)\, e^{-iw_jt + i\vec{k}_j\cdot\vec{r}}\mathcal{H}(E_m - E_m) + \vec{E}_j(-\omega_j)\, e^{iw_jt - i\vec{k}_j\cdot\vec{r}}\mathcal{H}(E_n - E_m)] \tag{2.4}$$

for a field $\vec{E}_j$ applied to the $m \rightleftarrows n$ transition. As usual, $\mathcal{H}(E)$ stands for the Heaviside function.

It is well-known that the coherent resonant Raman scattering is based on the third-order polarization contribution corresponding to

$$\vec{P}^{(3)}(\vec{r},t) = \mathrm{Tr}[\boldsymbol{\rho}^{(3)}(t)\vec{\boldsymbol{\mu}}] \tag{2.5}$$

and a general energy scheme appropriate to the description of the corresponding dynamics of the molecular adsorbate can be represented as shown in Figure 1.

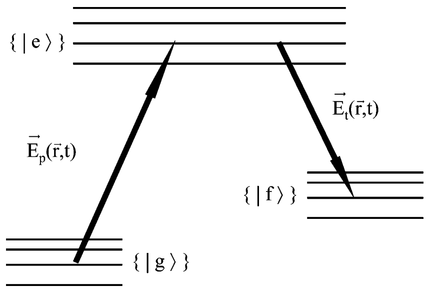

Figure 1. General scheme for coherent resonant Raman scattering.

TABLE 1: Description of the Various Pathways Entering in the Evaluation of the Matrix Elements of the Density Matrix $\boldsymbol{\rho}_{ef}^{(3)}(t)$ for an Initially Relaxed System and Narrow Spectral Laser Frequency Distributions

$\mathbf{G}(t-\tau_3)$	$\mathbf{L}_\nu(\tau_3)$	$\mathbf{G}(\tau_3-\tau_2)$	$\mathbf{L}_\nu(\tau_2)$	$\mathbf{G}(\tau_2-\tau_1)$	$\mathbf{L}_\nu(\tau_1)$	$\rho(t_0a)$
ef ef	*ef ee*	*ee ee*	*ee ge*	*ge ge*	*ge gg*	*gg*
ef ef	*ef ff*	*ff ee*	*ee ge*	*ge ge*	*ge gg*	*gg*
ef ef	*ef gf*	*gf gf*	*gf ge*	*ge ge*	*ge gg*	*gg*
ef ef	*ef ee*	*ee ee*	*ee eg*	*eg eg*	*eg gg*	*gg*
ef ef	*ef ff*	*ff ee*	*ee eg*	*eg eg*	*eg gg*	*gg*

The basic description involves, as the starting point, the evaluation of the density matrix of the molecular adsorbate. For the present purpose, the third-order contribution will be the main contribution to the polarization of interest in coherent resonant Raman scattering. From the usual perturbation expansion, the third-order term of the density matrix takes the form

$$\boldsymbol{\rho}^{(3)}(t) = \frac{i}{\hbar^3}\int_{t_0}^{t} d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1\, \mathbf{G}(t-\tau_3)\mathbf{L}_v(\tau_3) \times \mathbf{G}(\tau_3-\tau_2)\mathbf{L}_v(\tau_2)\mathbf{G}(\tau_2-\tau_1)\mathbf{L}_v(\tau_1)\boldsymbol{\rho}(t_0) \tag{2.6}$$

if, as usual, we assume that the molecular system is completely relaxed at the initial time t_0, leaving the adsorbate unchanged until the first excitation occurs. Also, the Liouvillian $\mathbf{L}_0'$ stands for the effective Liouvillian $\mathbf{L}_0' - i\hbar\Gamma$, and

$$\mathbf{G}(t) = e^{-(i/\hbar)\mathbf{L}_0't} \tag{2.7}$$

stands for the free evolution Liouvillian. For steady-state laser fields with narrow spectral frequency distributions, the various pathways contributing to the resonant Raman spectrum are given in Table 1.

Among these five contributions numbered from the top to the bottom, pathways 2 and 5 contribute to the hot luminescence, pathways 1 and 4 participate in stimulated emission, and finally the last one corresponding to pathway 3 is a purely coherent process. It is traditionnally termed the coherent resonance Raman scattering process.[20] It is just this contribution that we want to analyze in great detail here with respect to the influence of the substrate field. This particular interest is of course related to the large amount of work devoted to the understanding of the surface-enhanced resonant Raman scattering observed in adsorbate molecules with some substrate surface among gold, silver, and some other ones.[19] The evaluation of the different pathways requires the determination of the different matrix elements of the evolution Liouvillian $\mathbf{G}(t)$ given by the eq 2.7. Of course, the evolution of the coherences associated with the matrix elements $\langle\langle pq|\mathbf{G}(t)|pq\rangle\rangle\ \forall\ p \neq q$ is quite obvious because $\mathbf{G}(t)$ is diagonal in the coherence subspace $\{|pq\rangle\rangle\}\ \forall\ p \neq q$, so that

$$\langle\langle pq|\mathbf{G}(t)|pq\rangle\rangle = \mathrm{e}^{-iw_{pq}t-\Gamma_{pqpq}t} \tag{2.8}$$

However, to determine the evolution of the populations is more intricate because we must require the diagonalization of the free evolution Liouvillian in the Liouvillian population subspace. For adequate laser field frequencies and spectral widths, just one excited level $|e\rangle$ participates and gives the main contribution. Therefore, in the population subspace of interest, say, $|gg\rangle\rangle$, $|ee\rangle\rangle$, and $|ff\rangle\rangle$ for our purpose, the matrix elements of the zeroth-order evolution Liouvillian required for the evaluation of the coherent Raman signal can be evaluated as follows. Starting from the unperturbed Liouvillian equation

$$\frac{\partial\boldsymbol{\rho}^{(0)}(t)}{\partial t} = \left[-\frac{\mathrm{i}}{\hbar}\mathbf{L}_0 - \Gamma\right]\boldsymbol{\rho}^{(0)}(t) \tag{2.9}$$

we have by Laplace transformation

$$\bar{\boldsymbol{\rho}}^{(0)}(s) = \frac{1}{\frac{\mathrm{i}}{\hbar}\mathbf{L}_0 + \Gamma}\,\boldsymbol{\rho}^{(0)}(0) \quad \text{with} \quad \mathbf{M}(s) = s + \Gamma \tag{2.10}$$

Then, the inverse Laplace transform for the population in state $|n\rangle$ is given by the expression

$$\boldsymbol{\rho}_{nn}^{(0)}(t) = \frac{1}{2\pi\mathrm{i}}\int_{\epsilon-\mathrm{i}\infty}^{\epsilon+\mathrm{i}\infty} \mathrm{d}s\,\mathrm{e}^{st}\left\langle\left\langle nn\left|\frac{1}{\frac{\mathrm{i}}{\hbar}\mathbf{L}_0+\Gamma}\right|mm\right\rangle\right\rangle\boldsymbol{\rho}_{mm}^{(0)}(0) \tag{2.11}$$

In addition, if we assume negligible inverse relaxation processes, so that $\Gamma_{eegg} = \Gamma_{eeff} = 0$, and a stable ground configuration, implying that $\Gamma_{ffgg} = \Gamma_{gggg} = 0$, we obtain

$$\mathbf{M}(s) = \begin{pmatrix} s & \Gamma_{ggee} & \Gamma_{ggff} \\ 0 & s+\Gamma_{eeee} & 0 \\ 0 & \Gamma_{ffee} & s+\Gamma_{ffff} \end{pmatrix} \tag{2.12}$$

and subsequently

$$\mathbf{M}^{-1}(s) = \begin{pmatrix} \frac{1}{s} - & \frac{\Gamma_{ggee}s + \Gamma_{ggee}\Gamma_{ffff} - \Gamma_{ggff}\Gamma_{ffee}}{s(s+\Gamma_{eeee})(s+\Gamma_{ffff})} & -\frac{\Gamma_{ggff}}{s(s+\Gamma_{ffff})} \\ 0 & \frac{1}{s+\Gamma_{eeee}} & 0 \\ 0 & -\frac{\Gamma_{ffee}}{(s+\Gamma_{eeee})(s+\Gamma_{ffff})} & \frac{1}{s+\Gamma_{ffff}} \end{pmatrix} \tag{2.13}$$

This is all that we need to calculate the matrix elements of the evolution Liouvillian $G_{eeee}(\tau_3 - \tau_2)$ and $G_{ggee}(\tau_3 - \tau_2)$. Performing the time integration and using the time translation invariance, we obtain, from the identification with the definition

$$\rho_{jj}^{(0)}(t) = \mathbf{G}_{jjkk}(t-t')\boldsymbol{\rho}_{kk}^{(0)}(t') \tag{2.14}$$

the expression

$$G_{eeee}(\tau_3-\tau_2) = \mathrm{e}^{-\Gamma_{eeee}(\tau_3-\tau_2)}$$

$$G_{ffee}(\tau_3-\tau_2) = \frac{\Gamma_{ffee}}{\Gamma_{eeee}-\Gamma_{ffff}}[\mathrm{e}^{-\Gamma_{eeee}(\tau_3-\tau_2)} - \mathrm{e}^{-\Gamma_{ffff}(\tau_3-\tau_2)}] \tag{2.15}$$

Taking into account these previous evaluations, the density matrix can be readily evaluated, and we obtain

$$\boldsymbol{\rho}_{ef}^{(3)}(t) = \frac{\mathrm{i}}{\hbar^3}\vec{\boldsymbol{\mu}}_{ge}\cdot\vec{\mathrm{E}}_p(-\omega_p)\cdot\vec{\boldsymbol{\mu}}_{eg}\cdot\vec{\mathrm{E}}_p(\omega_p)\vec{\boldsymbol{\mu}}_{ef}\cdot\vec{\mathrm{E}}_t(\omega_t)\,\mathrm{e}^{-\mathrm{i}\omega_{ef}t-\Gamma_{efef}t} \times \sum_{n=1}^{7}K_n\left[\frac{\mathrm{e}^{(A_n+B_n+C_n)t}}{A_n(A_n+B_n)(A_n+B_n+C_n)} - \frac{\mathrm{e}^{(B_n+C_n)t}}{A_nB_n(B_n+C_n)} + \frac{\mathrm{e}^{C_nt}}{B_nC_n(A_n+B_n)} - \frac{1}{C_n(B_n+C_n)(A_n+B_n+C_n)}\right] \tag{2.16}$$

where the constants are given in Table 2 for the various contributions. Notice that pathways 2 and 5 in Table 1 give, each one, two contributions. In the long time limit, the density matrix element reduces to

$$\boldsymbol{\rho}_{ef}^{(3)}(t) = \frac{\mathrm{i}}{\hbar^3}\vec{\boldsymbol{\mu}}_{ge}\cdot\vec{\mathrm{E}}_p(-\omega_p)\cdot\vec{\boldsymbol{\mu}}_{eg}\cdot\vec{\mathrm{E}}_p(\omega_p)\vec{\boldsymbol{\mu}}_{ef}\cdot\vec{\mathrm{E}}_t(\omega_t) \times \sum_{n=1}^{7}\frac{K_n\,\mathrm{e}^{-i\omega_st}}{A_n(A_n+B_n)(A_n+B_n+C_n)} \tag{2.17}$$

Therefore, from the perturbational expansion of the polarization

$$\vec{\mathrm{P}}^{(3)}(\omega_t,t) = \vec{\mathrm{P}}^{(3)}(\omega_t)\,\mathrm{e}^{-\mathrm{i}\omega_tt} + \vec{\mathrm{P}}^{(3)}(-\omega_t)\,\mathrm{e}^{\mathrm{i}\omega_tt} \tag{2.18}$$

we can express the coherent resonant Raman signal as

$$I_{\mathrm{RRS}}(\omega_t) = -\frac{\omega_t^3}{2\pi^2c^3}\frac{\mathcal{T}[\vec{\mathrm{P}}^{(3)}(\omega_t)\cdot\vec{\mathrm{E}}_t(-\omega_t)]}{|\vec{\mathrm{E}}_t(\omega_t)|^2} \tag{2.19}$$

where the third-order polarization term $\vec{\mathrm{P}}^{(3)}(\omega_t)$ can be expressed as[20]

$$\vec{\mathrm{P}}^{(3)}(\omega_t) = \frac{\mathrm{i}}{\hbar^3}\vec{\boldsymbol{\mu}}_{ge}\cdot\vec{\mathrm{E}}_p(-\omega_p)\cdot\vec{\boldsymbol{\mu}}_{eg}\cdot\vec{\mathrm{E}}_p(\omega_p)\vec{\boldsymbol{\mu}}_{ef}\cdot\vec{\mathrm{E}}_t(\omega_t) \times \sum_{n=1}^{7}\frac{K_n}{A_n(A_n+B_n)(A_n+B_n+C_n)}\vec{\boldsymbol{\mu}}_{fe} \tag{2.20}$$

The various quantities A_n, B_n, and C_n as well as the matrix elements of the electric dipole moment depend on the energy level structure of the adsorbate molecule in the presence of the substrate electric field. This is why, in the next section, we will evaluate the modified electronic structure of the adsorbate as well as the vibrational frequencies of the modes perturbed by the substrate field and their corresponding Franck−Condon factors participating in the coherent resonant Raman scattering process.

3. Description of the Adsorbate in the Presence of the Substrate Field

The evaluation of the resonant Raman signal given by eq 2.19 requires the molecular eigenstates of the molecular adsorbate in the presence of the substrate field and their corresponding eigenenergies. It is the goal of the present section to evaluate these quantities as a function of the perturbation induced by the substrate electric field. In the following, we will note $\mathbf{H}(\mathbf{q},\mathbf{Q})$ the Hamiltonian of the perturbed molecular adsorbate. Since the electronic and vibrational structures of the

TABLE 2: Values of the Different Constants Participating in the Time Integration

n	K_n	A_n	B_n	C_n
1	-1	$i(\omega_{ge} + \omega_p) + \gamma_{gege}$	$-i(\omega_{ge} + \omega_p) - \gamma_{gege} + \gamma_{eeee}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{eeee}$
2	$\gamma_{ffee}/(\gamma_{eeee} - \gamma_{ffff})$	$i(\omega_{ge} + \omega_p) + \gamma_{gege}$	$-i(\omega_{ge} + \omega_p) - \gamma_{gege} + \gamma_{eeee}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{eeee}$
3	$-\gamma_{ffee}/(\gamma_{eeee} - \gamma_{ffff})$	$i(\omega_{ge} + \omega_p) + \gamma_{gege}$	$-i(\omega_{ge} + \omega_p) - \gamma_{gege} + \gamma_{ffff}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{fff}$
4	-1	$i(\omega_{ge} + \omega_p) + \gamma_{gege}$	$i(\omega_{gf} - \omega_{ge} - \omega_t) + \gamma_{gfgf} - \gamma_{gege}$	$i(\omega_{ef} - \omega_{gf} - \omega_p) + \gamma_{efef} - \gamma_{gfgf}$
5	-1	$i(\omega_{eg} - \omega_p) + \gamma_{egeg}$	$i(\omega_p - \omega_{eg}) + \gamma_{eeee} - \gamma_{egeg}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{eeee}$
6	$\gamma_{ffee}/(\gamma_{eeee} - \gamma_{ffff})$	$i(\omega_{eg} - \omega_p) + \gamma_{egeg}$	$i(\omega_p - \omega_{eg}) + \gamma_{eeee} - \gamma_{egeg}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{eeee}$
7	$-\gamma_{ffee}/(\gamma_{eeee} - \gamma_{ffff})$	$i(\omega_{eg} - \omega_p) + \gamma_{egeg}$	$i(\omega_p - \omega_{eg}) - \gamma_{egeg} + \gamma_{ffff}$	$i(\omega_{ef} - \omega_t) + \gamma_{efef} - \gamma_{ffff}$

perturbed molecular adsorbate deviate from that of the molecule in the gas phase due to the partial charge distribution created by the electrostatic field,[21−24] we have to solve the molecular eigenvalue problem

$$\mathbf{H}(\mathbf{q},\mathbf{Q})|\psi(\mathbf{q},\mathbf{Q})\rangle = E|\psi(\mathbf{q},\mathbf{Q})\rangle \tag{3.1}$$

where the total molecular adsorbate Hamiltonian given by

$$\mathbf{H}(\mathbf{q},\mathbf{Q}) = \mathbf{H}_0^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q}) + \sum_s \hat{c}_s(\mathbf{Q})\vartheta_s + \mathbf{T}(\mathbf{Q}) \tag{3.2}$$

is made of the Born−Oppenheimer molecular Hamiltonian $\mathbf{H}_0^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})$,[25] of the nuclear kinetic operator $\mathbf{T}(\mathbf{Q})$, and of the perturbation term $\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s$ resulting from the presence of the substrate electrostatic field responsible for the charge redistribution. Here, $\hat{c}_s(\mathbf{Q})$ stands for the effective charge operator on site s, and ϑ_s for the electrostatic potential acting on the effective charge.[26−29] Taking advantage of the adiabatic description of the Born−Oppenheimer molecular states,[25,30] the electronic eigenvalue problem of the model Hamiltonian $\mathbf{H}_{\mathrm{BO}} = \mathbf{T}(\mathbf{q}) + \mathbf{U}(\mathbf{q},\mathbf{Q})$ can be written as

$$[\mathbf{T}(\mathbf{q}) + \mathbf{U}(\mathbf{q},\mathbf{Q})]|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle = E_n^{(\mathrm{BO})}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle \tag{3.3}$$

where $\mathbf{T}(\mathbf{q})$ and $\mathbf{U}(\mathbf{q},\mathbf{Q})$ stand for the electronic kinetic operator and electron−electron and electron−nucleus interactions, respectively. If we introduce a perturbative treatment of the interaction induced by the substrate electrostatic field, then we have in the Born−Oppenheimer molecular basis set

$$[\mathbf{T}(\mathbf{q}) + \mathbf{U}(\mathbf{q},\mathbf{Q}) + \sum_s \hat{c}_s(\mathbf{Q})\vartheta_s]|\xi_n(\mathbf{q},\mathbf{Q})\rangle = \epsilon_n(\mathbf{Q})|\xi_n(\mathbf{q},\mathbf{Q})\rangle \tag{3.4}$$

Here, the electronic eigenenergies up to the second order can be expressed as

$$\begin{aligned}\epsilon_n(\mathbf{Q}) &= E_n^{(\mathrm{BO})}(\mathbf{Q}) + \epsilon_n^{(1)}(\mathbf{Q}) + \epsilon_n^{(2)}(\mathbf{Q}) + \cdots \\ &= E_n^{(\mathrm{BO})}(\mathbf{Q}) + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u + \cdots\end{aligned} \tag{3.5}$$

and, to first order, the eigenvectors take the form

$$|\xi_n(\mathbf{q},\mathbf{Q})\rangle = |\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_{m\neq n} \frac{\sum_s C_{mn}^{(s)}(\mathbf{Q})\vartheta_s}{E_n^{(\mathrm{BO})}(\mathbf{Q}) + E_m^{(\mathrm{BO})}(\mathbf{Q})} |\Phi_m^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \cdots \tag{3.6}$$

Also, we have introduced the notations

$$C_{nm}^{(s)}(\mathbf{Q}) = \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\hat{c}_s(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle$$

$$K_n^{(su)}(\mathbf{Q})\sum_{m\neq n} \frac{\langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\hat{c}_s(Q)|\Phi_m^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle\,\langle\Phi_m^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\hat{c}_u(Q)|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle}{E_n^{(\mathrm{BO})}(\mathbf{Q}) - E_m^{(\mathrm{BO})}(\mathbf{Q})} \tag{3.7}$$

which stand for either the electronic transition charge if $m \neq n$ or the electronic partial charge if $m = n$ and the charge response kernel, respectively. These expressions result straightforwardly from crude perturbative treatment. Notice that the evaluation of the electronic eigenfunctions and their corresponding energies do not require the Hamiltonian $\mathbf{T}(\mathbf{Q})$, which, of course, depends on the normal mode coordinates only.

At this stage, we are left with the evaluation of the vibrational eigenvalue problem. Taking into account the adiabatic approximation applied to the molecular adsorbate in the presence of the substrate electrostatic field, the molecular states can be expressed as

$$|\Psi_\nu(\mathbf{q},\mathbf{Q})\rangle = \sum_l |\xi_l(\mathbf{q},\mathbf{Q})\rangle|\chi_{l\nu}(\mathbf{Q})\rangle \tag{3.8}$$

where $|\xi_n(\mathbf{q},\mathbf{Q})\rangle$ stands for the electronic eigenstates defined by eq 3.4, and $|\chi_{n\nu}(\mathbf{Q})\rangle$ their corresponding vibrational states, which are solutions of the equation

$$\begin{aligned}&[\epsilon_n(\mathbf{Q}) - \epsilon_\nu + \mathbf{T}(\mathbf{Q}) + \langle\xi_n(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\xi_n(\mathbf{q},\mathbf{Q})\rangle]|\chi_{n\nu}(\mathbf{Q})\rangle \\ &\quad + \sum_{l\neq n}\left[\langle\xi_n(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\xi_l(\mathbf{q},\mathbf{Q})\rangle - \frac{\hbar^2}{M}\left(\left\langle\xi_n(\mathbf{q},\mathbf{Q})\left|\frac{\partial}{\partial\mathbf{Q}}\right|\xi_l(\mathbf{q},\mathbf{Q})\right\rangle\right)\frac{\partial}{\partial\mathbf{Q}}\right]|\chi_{l\nu}(\mathbf{Q})\rangle = 0\end{aligned} \tag{3.9}$$

It can be reduced to

$$[\mathbf{T}(\mathbf{Q}) + \mathbf{V}_{\mathrm{eff}}(\mathbf{Q}) - \epsilon_\nu]|\chi_{n\nu}(\mathbf{Q})\rangle = 0 \tag{3.10}$$

where, on account of the previous assumptions, the effective potential $\mathbf{V}_{\mathrm{eff}}(\mathbf{Q})$ corresponds to

$$\begin{aligned}\mathbf{V}_{\mathrm{eff}}(\mathbf{Q}) &= \epsilon_n(\mathbf{Q}) + \langle\xi_n(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\xi_n(\mathbf{q},\mathbf{Q})\rangle \\ &= E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\xi_n(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\xi_n(\mathbf{q},\mathbf{Q})\rangle \\ &\quad + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u + \cdots\end{aligned} \tag{3.11}$$

Notice that these assumptions are exactly the ones that validate the adiabatic description in the new basis states. They assume that the terms $\langle\xi_n(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\xi_l(\mathbf{q},\mathbf{Q})\rangle$ and $\langle\xi_n(\mathbf{q},\mathbf{Q})|\partial/\partial\mathbf{Q}|\xi_l(\mathbf{q},\mathbf{Q})\rangle\ \forall\ l,n$ can be neglected. These assumptions are similar to the ones usually introduced for the description of the Born−

Oppenheimer states but are now applied to the eigenstates $|\xi_l(\mathbf{q},\mathbf{Q})\rangle$. Therefore, a complete description, when necessary, will require the introduction of these residual coupling terms irrelevant for our purpose. Also, these results are valid as long as the partial charge interaction $\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s$ can be treated perturbatively. The vibrational equation of motion (eq 3.10) can be solved using the well-known procedure of the Born−Oppenheimer description, implying the small amplitude motion approximation. To this end, the perturbed vibrational wave functions will be described as harmonic oscillators characterized by new equilibrium positions $\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)}$ and frequencies Ω_n. Of course, these parameters can be related to their corresponding quantities $\mathbf{Q}_n^{(0)}$ and $\Omega_n^{(0)}$ for the unperturbed absorbate and are obtained from the relation

$$\frac{\partial}{\partial\mathbf{Q}}(E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle)_{Q=Q_n^{(0)}} = 0 \tag{3.12}$$

The eigenvalue vibrational problem can be expressed in the Born−Oppenheimer basis set. Retaining the diagonal contributions of $\mathbf{T}(\mathbf{Q})$ with respect to the electronic states, we obtain

$$[\mathbf{T}(\mathbf{Q}) + E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u - \epsilon_v]|\xi_{nv}(\mathbf{Q})\rangle = 0 \tag{3.13}$$

neglecting the term of higher order

$$\sum_{m\neq n}\langle\Phi_m^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_m^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle \times |\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s[E_n^{(\mathrm{BO})}(\mathbf{Q}) - E_m^{(\mathrm{BO})}(\mathbf{Q})]^{-1}|^2$$

For the perturbed adsorbate, the equilibrium position is defined by the condition $(\partial\nu(\mathbf{Q})/\partial\mathbf{Q})_{Q_n^{(0)}+Q_n^{(0)}} = 0$ where

$$\nu(\mathbf{Q}) = E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u \tag{3.14}$$

Therefore, if we develop the **Q**-dependence up to the first order, the previous condition gives

$$\delta\mathbf{Q}_n^{(0)} = -\left.\frac{\partial\nu(\mathbf{Q})}{\partial\mathbf{Q}}\right|_{Q=Q_n^{(0)}} \Big/ \left.\frac{\partial^2\nu(\mathbf{Q})}{\partial\mathbf{Q}^2}\right|_{Q=Q_n^{(0)}} \tag{3.15}$$

Then, using the definition of $\mathbf{Q}_n^{(0)}$ given by eq 3.12, we obtain the result

$$\delta\mathbf{Q}_n^{(0)} = -\left[\frac{\partial}{\partial\mathbf{Q}}(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0)}}\right] \times \left[\frac{\partial^2}{\partial\mathbf{Q}^2}(\mathbf{V}(\mathbf{Q}) - E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0)}}\right]^{-1} \tag{3.16}$$

which is the expression of the displacement of the equilibrium position of the oscillator induced by the substrate electrostatic field. If we introduce the expression of the unperturbed oscillator frequency given by

$$\Omega_n^{(0)} = \left[\frac{1}{M}\frac{\partial^2}{\partial\mathbf{Q}^2}(E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle)_{Q=Q_n^{(0)}}\right]^{1/2} \tag{3.17}$$

to lower orders, we can rewrite $\delta\mathbf{Q}_n^{(0)}$ as

$$\delta\mathbf{Q}_n^{(0)} = -\left[\frac{\partial}{\partial\mathbf{Q}}(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0)}}\right] \times \left[M\Omega_n^{(0)2} + \frac{\partial^2}{\partial Q^2}(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0)}}\right]^{-1} \tag{3.18}$$

Finally, we must evaluate the frequency change induced by the perturbating substrate electrostatic field. To this end, taking avantage of the **Q**-expansion of the effective potential **V**(**Q**) up to the second order, we can rewrite eq 3.13 in the form

$$\Bigg[\mathbf{T}(\mathbf{Q} - \mathbf{Q}_n^{(0,\mathrm{pert})}) + \frac{(\mathbf{Q} - \mathbf{Q}_n^{(0,\mathrm{pert})})^2}{2}\frac{\partial^2}{\partial\mathbf{Q}^2}(E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0,\mathrm{pert})}} - \epsilon_{nv} + E_n^{(\mathrm{BO})}(\mathbf{Q}_n^{(0,\mathrm{pert})}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q}_n^{(0,\mathrm{pert})})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q}_n^{(0,\mathrm{pert})})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q}_n^{(0,\mathrm{pert})})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q}_n^{(0,\mathrm{pert})})\vartheta_s\vartheta_u\Bigg] \times |\chi_{nv}^{(0)}(\mathbf{Q} - \mathbf{Q}_n^{(0,\mathrm{pert})})\rangle = 0 \tag{3.19}$$

using the notation $\mathbf{Q}_n^{(0,\mathrm{pert})} = \mathbf{Q}_n^{(0)} + \mathrm{d}\mathbf{Q}_n^{(0)}$ and remembering that the first derivative cancels at equilibrium. The corresponding eigenenergies and eigenfunctions of this renormalized harmonic oscillator are deduced straightforwardly as

$$\epsilon_{nv} = E_n^{(\mathrm{BO})}(\mathbf{Q}_n^{(0,\mathrm{pert})}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q}_n^{(0,\mathrm{pert})})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q}_n^{(0,\mathrm{pert})})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q}_n^{(0,\mathrm{pert})})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q}_n^{(0,\mathrm{pert})})\vartheta_s\vartheta_u + \left(v + \frac{1}{2}\right)\hbar\Omega_n$$

$$\chi_{nv}(\mathbf{Q} - \mathbf{Q}_n^{(0,\mathrm{pert})}) = \left[\left(\frac{1}{2^v v!}\right)\left(\frac{\hbar}{M\Omega_n}\right)^v\right]^{1/2} \times \left(\frac{\mathrm{M}\Omega_\mathrm{n}}{\pi\hbar}\right)^{1/4}\left[\frac{M\Omega_n}{\hbar}(\mathbf{Q} - \mathbf{Q}_n^{(0,\mathrm{pert})}) - \frac{\mathrm{d}}{\mathrm{d}\mathbf{Q}}\right]^v \mathrm{e}^{-(M\Omega_n/2\hbar)(\mathbf{Q}-\mathbf{Q}_n(0,\mathrm{pert}))^2} \tag{3.20}$$

Also, $\Omega_n^{(\mathrm{pert})}$ stands for the vibrational frequency of the perturbed harmonic oscillator. Its expression is straightforwardly obtained from eq 3.19 and can be written as

$$\Omega_n^{(\mathrm{pert})} = \left[\frac{1}{M}\frac{\partial^2}{\partial Q^2}(E_n^{(\mathrm{BO})}(\mathbf{Q}) + \langle\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\mathbf{T}(\mathbf{Q})|\Phi_n^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u)_{Q=Q_n^{(0,\mathrm{pert})}}\right]^{1/2} \tag{3.21}$$

Of course, corresponding eigenenergies and eigenfunctions of

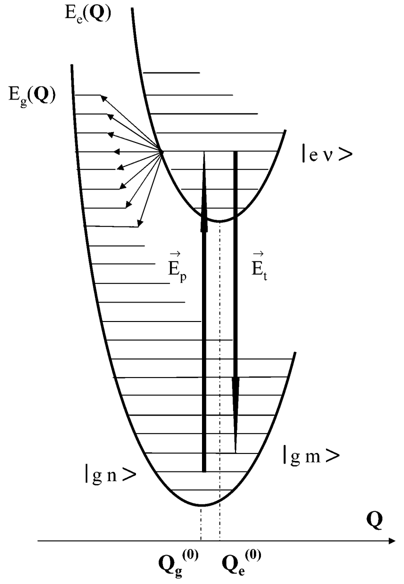

Figure 2. Energy scheme for resonant Raman scattering in the unperturbed molecular basis set. Notice that when using the perturbed states of the harmonic oscillator as a basis set which is not the case in our figure the couplings between the vibronic states disappear and the electronic configurations ξ_j become combinations of the unperturbed electronic ones.

the unperturbed harmonic oscillator are deduced straightforwardly by replacing equilibrium positions and frequencies using the transformations $\mathbf{Q}_n^{(0,\mathrm{pert})} \Rightarrow \mathbf{Q}_n^{(0)}$ and $\Omega_n \Rightarrow \Omega_n^{(0)}$. In addition, for a given mode, its frequency change and displacement of the equilibrium position induced by the electrostatic field are interdependent. This dependence is expressed by the relation

$$\delta\Omega_n \sim \frac{1}{2M\Omega_n^{(0)}}\frac{\partial^2}{\partial Q^2}\left[1+\delta\mathbf{Q}_n^{(0)}\frac{\partial}{\partial Q}\right](\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_s \hat{c}_s\,(Q)\vartheta_s|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \frac{\sum_{m\neq n}\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\,\langle\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_u \hat{c}_u(\mathbf{Q})\vartheta_u|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle}{E_n^{(BO)}(\mathbf{Q}) - E_m^{(BO)}(\mathbf{Q})_{Q=Q_n{}^{(0)}}} \qquad (3.22)$$

which is, to lower order, just the linearized relation between displacement and frequency change. Of course, to higher orders in $\mathbf{Q}$, which are required if the perturbing electrostatic field increases, this dependence becomes more intricate.

4. Contributions to the Resonant Raman Scattering

When the electronic and vibrational structures of the molecule adsorbed on the local inhomogeneity of the surface substrate and its local electric field are determined, we can evaluate the resonant Raman signal from the expression calculated previously and given by eq 2.19. For the present purpose, the level scheme of the unperturbed molecular adsorbate is represented in Figure 2, and the corresponding electronic eigenstates of the perturbed adsorbate take the form

$$|\xi_g(\mathbf{q},\mathbf{Q})\rangle = |\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_s \frac{C_{eg}^{(s)}(\mathbf{Q})\vartheta_s}{E_g^{(BO)}(\mathbf{Q}) - E_e^{(BO)}(\mathbf{Q})}|\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$$

$$|\xi_e(\mathbf{q},\mathbf{Q})\rangle = |\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_s \frac{C_{ge}^{(s)}(\mathbf{Q})\vartheta_s}{E_e^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \qquad (4.1)$$

As an example, we give the expression of the matrix element of the dipole moment required in our evaluation. For the perturbed adsorbate, we have

$$\begin{aligned}
\langle\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q})|\vec{\boldsymbol{\mu}}|\xi_g(\mathbf{q},\mathbf{Q})\chi_{gn}(\mathbf{Q})\rangle = {}& \langle\chi_{ev}(\mathbf{Q}-\mathbf{Q}_n^{(0,\mathrm{pert})},\boldsymbol{\Omega}_e^{(\mathrm{pert})})|\chi_{gn}(\mathbf{Q}-\mathbf{Q}_g^{(0,\mathrm{pert})},\boldsymbol{\Omega}_g^{(\mathrm{pert})})\rangle \\
&\times\langle\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\
&+\sum_s\frac{\langle\chi_{ev}(\mathbf{Q}-\mathbf{Q}_e^{(0,\mathrm{pert})},\boldsymbol{\Omega}_e^{(\mathrm{pert})})|C_{eg}^{(s)}(\mathbf{Q})\vartheta_s|\chi_{gn}(\mathbf{Q}-\mathbf{Q}_g^{(0,\mathrm{pert})},\boldsymbol{\Omega}_g^{(\mathrm{pert})})\rangle}{E_g^{(BO)}(\mathbf{Q})-E_e^{(BO)}(\mathbf{Q})} \\
&\times\langle\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\
&+\sum_u\frac{\langle\chi_{ev}(\mathbf{Q}-\mathbf{Q}_e^{(0,\mathrm{pert})},\boldsymbol{\Omega}_e^{(\mathrm{pert})})|C_{ge}^{(u)+}(\boldsymbol{Q})\vartheta_u^*|\chi_{gn}(\mathbf{Q}-\mathbf{Q}_g^{(0,\mathrm{pert})},\boldsymbol{\Omega}_g^{(\mathrm{pert})})\rangle}{E_e^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})} \\
&\times\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\
&+\sum_{s,u}\frac{\langle\chi_{ev}(\mathbf{Q}-\mathbf{Q}_e^{(0,\mathrm{pert})},\boldsymbol{\Omega}_e^{(\mathrm{pert})})|C_{ge}^{(u)+}(\mathbf{Q})\,C_{eg}^{(s)}(\mathbf{Q})\vartheta_u^*|\chi_{gn}(\mathbf{Q}-\mathbf{Q}_g^{(0,\mathrm{pert})},\boldsymbol{\Omega}_g^{(\mathrm{pert})})\rangle}{-[E_e^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\boldsymbol{Q})]^2} \\
&\times\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_e^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \qquad (4.2)
\end{aligned}$$

assuming the Condon approximation valid. Other matrix elements are evaluated similarly by the substitution

$$(e,v,g,n)\rightarrow(g,n,e,v) \quad \text{for} \quad \langle\xi_g(\mathbf{q},\mathbf{Q})\chi_{gn}(\mathbf{Q})|\vec{\boldsymbol{\mu}}|\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q})\rangle$$

$$(e,v,g,n)\rightarrow(e,v,g,m) \quad \text{for} \quad \langle\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q})|\vec{\boldsymbol{\mu}}|\xi_g(\mathbf{q},\mathbf{Q})\chi_{gm}(\mathbf{Q})\rangle$$

$$(e,v,g,n)\rightarrow(g,m,e,v) \quad \text{for} \quad \langle\xi_g(\mathbf{q},\mathbf{Q})\chi_{gm}(\mathbf{Q})|\vec{\boldsymbol{\mu}}|\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q})\rangle \qquad (4.3)$$

Therefore, we obtain for the zeroth-order contribution

$$[\vec{\boldsymbol{\mu}}_{gnev}\vec{\boldsymbol{\mu}}_{evgn}\vec{\boldsymbol{\mu}}_{evgm}]^{(0)} = |M^{(0)}N^{(0)}|^2 \qquad (4.4)$$

and for the first-order contribution

$$\begin{aligned}
[\vec{\boldsymbol{\mu}}_{gnev}\vec{\boldsymbol{\mu}}_{evgn}\vec{\boldsymbol{\mu}}_{evgm}]^{(1)} = {}& |M^{(0)}|^2[N^{(0)}(N_1^{(0)}+N_2^{(1)})^* \\
&+ N^{(0)*}(N_1^{(1)}+N_2^{(1)})] + |N^{(0)}|^2[M^{(0)}(M_1^{(1)}+M_2^{(1)})^* \\
&+ M^{(0)*}(M_1^{(1)}+M_2^{(1)})] \qquad (4.5)
\end{aligned}$$

where the various notations stand for

$$M^{(0)} = \langle \chi_{gn}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})|\chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})\rangle \times \langle \Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle$$

$$M_1^{(1)} = \sum_s \frac{\langle \chi_{gn}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})|C_{ge}^{(s)}(\mathbf{Q})\vartheta_s|\chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})\rangle}{E_e^{(\mathrm{BO})}(\mathbf{Q}) - E_g^{(\mathrm{BO})}(\mathbf{Q})} \times \langle \Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle$$

$$M_2^{(1)} = \sum_u \frac{\langle \chi_{gn}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})|C_{eg}^{(u)+}(\mathbf{Q})\vartheta_u^*|\chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})\rangle}{E_g^{(\mathrm{BO})}(\mathbf{Q}) - E_e^{(\mathrm{BO})}(\mathbf{Q})} \times \langle \Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle \quad (4.6)$$

and

$$N^{(0)} = \langle \chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})|\chi_{gm}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})\rangle \times \langle \Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle$$

$$N_1^{(1)} = \sum_s \frac{\langle \chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})|C_{eg}^{(s)}(\mathbf{Q})\vartheta_s|\chi_{gm}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})\rangle}{E_g^{(\mathrm{BO})}(\mathbf{Q}) - E_e^{(\mathrm{BO})}(\mathbf{Q})} \times \langle \Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_e^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle$$

$$N_2^{(1)} = \sum_u \frac{\langle \chi_{ev}(\mathbf{Q} - \mathbf{Q}_e^{(0,\mathrm{pert})},\Omega_e^{(\mathrm{pert})})|C_{ge}^{(u)+}(\mathbf{Q})\vartheta_u^*|\chi_{gm}(\mathbf{Q} - \mathbf{Q}_g^{(0,\mathrm{pert})},\Omega_g^{(\mathrm{pert})})\rangle}{E_e^{(\mathrm{BO})}(\mathbf{Q}) - E_g^{(\mathrm{BO})}(\mathbf{Q})} \times \langle \Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})|\vec{\boldsymbol{\mu}}|\Phi_g^{(\mathrm{BO})}(\mathbf{q},\mathbf{Q})\rangle \quad (4.7)$$

Therefore, the resonant Raman signal can now be expressed from eq 2.19 in terms of the zeroth- and first-order contributions as

$$I_{\mathrm{RRS}}(\omega_t) = -\frac{\omega_t^{\ 3}}{2\pi^2 c^3 |E_p|^2} \mathscr{T}\left[\frac{\mathrm{i}}{\hbar^3}\left|\langle \xi_g(\mathbf{q},\mathbf{Q})\chi_{gn}(\mathbf{Q})|\vec{\boldsymbol{\mu}}\cdot\vec{\epsilon}_p|\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q}\rangle \times \langle \xi_g(\mathbf{q},\mathbf{Q})\chi_{gm}(\boldsymbol{Q})|\vec{\boldsymbol{\mu}}\cdot\vec{\epsilon}_t|\xi_e(\mathbf{q},\mathbf{Q})\chi_{ev}(\mathbf{Q})\rangle\right|^2 \times \sum_{n=1}^{7} \frac{K_n}{A_n(A_n + B_n)(A_n + B_n + C_n)}\right. \quad (4.8)$$

This expression can still be expressed as

$$I_{\mathrm{RRS}}(\omega_t) = -\frac{\omega_t^{\ 3}}{2\pi^2\hbar^3 c^3|\vec{\mathrm{E}}_p(\omega_p)|^2}\Big\{|M^{(0)}N^{(0)}|^2 + [|M^{(0)}|^2[N^{(0)}(N_1^{(1)} + N_2^{(1)})^* + N^{(0)*}(N_1^{(1)} + N_2^{(1)})] + |N^{(0)}|^2[M^{(0)}(M_1^{(1)} + M_2^{(1)})^* + M^{(0)*}(M_1^{(1)} + M_2^{(1)})\}\sum_{n=1}^{7}\frac{K_n}{A_n(A_n + B_n)(A_n + B_n + C_n)} \quad (4.9)$$

where the quantities A_n, B_n, and C_n are now functions of the electronic and vibrational eigenenergies.

The inhomogeneities of the substrate field are accounted for by the dependence of the quantities $C_{jj'}^{(s)}(\mathbf{Q})$ on the normal coordinate. Of course, for a specific example, this dependence has to be modeled according to the particular structure of the surface where the adsorbate molecule is located. Such a description can be done by expanding $C_{jj'}^{(s)}(\mathbf{Q})$ in powers of the normal coordinate as

$$C_{jj'}^{(s)}(\mathbf{Q}) = \sum_{\lambda=0}^{\infty} \Lambda_{jj'\,(\lambda)}^{(s)}\mathbf{Q}^{\lambda} \quad (4.10)$$

Of course, for practical reasons, the contributions resulting from the various powers of $\mathbf{Q}$ required to reproduce the local inhomogeneity cannot always be evaluated explicitly. However, at least for small inhomogeneities, this approach has the great advantage of being quite informative to understand how the substrate field inhomogeneities affect the dynamical evolution and give a description in terms of the elementary vibrational processes that participate in the Raman signal.

In the next section, we will perform numerical simulations to analyze the influence of the electronic transition charge $C_{jj'}^{(s)}(\mathbf{Q})$ and electronic partial charge $C_{jj}^{(s)}(\mathbf{Q})$ on the resonant Raman signal.

5. Influence of the Field Inhomogeneity on the Raman Signal

To perform numerical simulations on the resonant Raman signal, we introduce a power expansion of the quantity $C_{jj'}^{(s)}(\mathbf{Q})$ in the form

$$C_{jj'}^{(s)}(\mathbf{Q}) = \Lambda_{jj'\,(0)}^{(s)} + \Lambda_{jj'\,(1)}^{(s)}\mathbf{Q} + \Lambda_{jj'\,(2)}^{(s)}\mathbf{Q}^2 + \cdots \quad (5.1)$$

However, here it has to be understood that while the various parameters $\Lambda_{jj'}^{(s)}$ must be chosen weak enough to satisfy the perturbation expansion used to calculate the electronic eigenenergies, their relative values can be quite different and do not satisfy any ordering associated with the magnitudes of λ. They depend on the structure of the inhomogeneity of the substrate field only.

To a lower order, the eigenenergies are obtained from eq 3.5. Using the expansion in eq 5.1 and the notation $\sum_s \langle \xi_e(\mathbf{q},\mathbf{Q})|C^{(s)}(\mathbf{Q})|\chi_{ev}(\mathbf{Q})\rangle\vartheta_s = \sum_s \Lambda_{ee(0)}^{(s)}\vartheta_s$, they can be expressed as

$$\epsilon_{ev} = E_e^{(\mathrm{BO})} + \sum_s \Lambda_{ee(0)}^{(s)}\vartheta_s + \hbar\Omega_e\left(v + \frac{1}{2}\right) \quad (5.2)$$

and analogous expressions are obtained for the other energy levels

$$\epsilon_{gn} = E_g^{(\mathrm{BO})} + \sum_s \Lambda_{gg(0)}^{(s)}\vartheta_s + \hbar\Omega_g\left(n + \frac{1}{2}\right)$$

$$\epsilon_{gm} = E_g^{(\mathrm{BO})} + \sum_s \Lambda_{gg(0)}^{(s)}\vartheta_s + \hbar\Omega_g\left(m + \frac{1}{2}\right) \quad (5.3)$$

Taking advantage of the expression for the resonant Raman signal given by eq 4.9 and the expansion of the perturbation induced by the substrate field in eq 4.10, the numerical simulations can be performed. To this end, we must introduce numerical values for the physical parameters. For our purpose, the frequency of the pump laser is $\omega_p = 11\,600$ cm^{-1}, and the Born−Oppenheimer electronic energies are fixed as $E_g^{(\mathrm{BO})} = 0$ cm^{-1} and $E_e^{(\mathrm{BO})} = 11\,000$ cm^{-1}. The vibrational frequencies are $\Omega_e = 450$ cm^{-1} for the excited configuration and $\Omega_g = 500$ cm^{-1} for the lower one. The vibronic levels participating in the Raman process are $n = 2$, $m = 4$, and $\nu = 2$. The relaxation and dephasing constants of the adsorbate correspond to $\Gamma_{evevevev} = 10$ cm^{-1}, $\Gamma_{gngngngn} = 0$ cm^{-1}, and $\Gamma_{gmgmgmgm} = 3$ cm^{-1} for the total decay rates. Besides, $\Gamma_{gngnevev} = -0.5\Gamma_{evevevev}$ and $\Gamma_{gmgmevev} = -0.5\Gamma_{evevevev}$ for the transition constants, and finally $\Gamma_{gnev} = 15$ cm^{-1}, $\Gamma_{gngm} = 10$ cm^{-1}, and $\Gamma_{gmev} = 15$ cm^{-1}

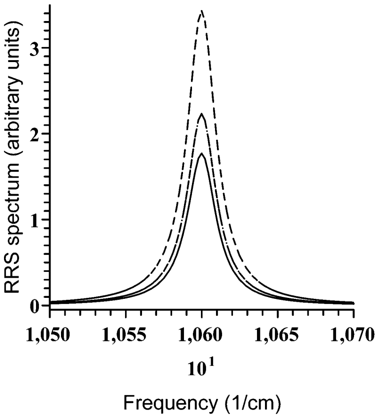

Figure 3. Frequency dependence of the resonant Raman spectrum corresponding to the zeroth-order contribution (solid line) with the parameters $\Theta_{ee}(0 \rightarrow 3) = \Theta_{gg}(0 \rightarrow 3) = \Theta_{eg}(0 \rightarrow 3) = 0$, to the homogeneous field case (dash−dotted line) with $\Theta_{ee}(0) = \Theta_{eg}(0) = 40\ \mathrm{cm}^{-1}$, $\Theta_{gg}(0) = 6\ \mathrm{cm}^{-1}$, all the other being equal to zero, and to the inhomogeneous field case (dashed line) with $\Theta_{ee}(0 \rightarrow 3) = 80\ \mathrm{cm}^{-1}$, $\Theta_{gg}(0 \rightarrow 3) = 10\ \mathrm{cm}^{-1}$, $\Theta_{eg}(0 \rightarrow 3) = 60\ \mathrm{cm}^{-1}$, respectively.

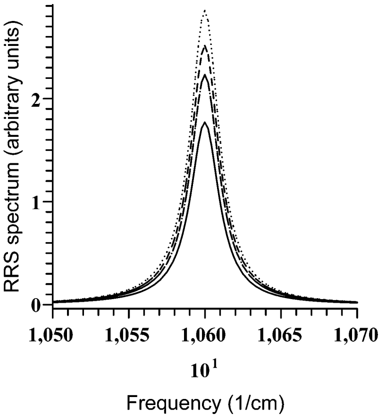

Figure 4. Frequency dependence of the resonant Raman spectrum in the case of a homogeneous substrate field for different electronic partial charges $\Theta_{ee}(0) = 40\ \mathrm{cm}^{-1}$ (dash−dotted line), $\Theta_{ee}(0) = 80\ \mathrm{cm}^{-1}$ (dashed line), and $\Theta_{ee}(0) = 120\ \mathrm{cm}^{-1}$ (dotted line). The other parameters are $\Theta_{gg}(0) = 6\ \mathrm{cm}^{-1}$, $\Theta_{eg}(0) = 40\ \mathrm{cm}^{-1}$, all the other ones being equal to zero. The solid line corresponds to the zeroth-order contribution.

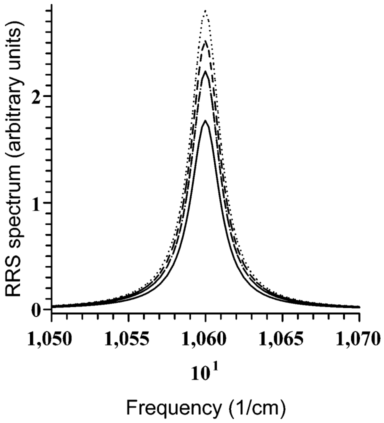

Figure 5. Same dependence as in Figure 4 except that here the case of different electronic transition charges is considered $\Theta_{eg}(0) = 40\ \mathrm{cm}^{-1}$ (dash−dotted line), $\Theta_{ee}(0) = 80\ \mathrm{cm}^{-1}$ (dashed line), and $\Theta_{ee}(0) = 120\ \mathrm{cm}^{-1}$ (dotted line) with $\Theta_{ee}(0) = 40\ \mathrm{cm}^{-1}$, all the other parameters being zero. Again, the solid line stands for the zeroth-order contribution.

for the pure dephasing constants. Also the equilibrium positions are $Q_e = 1.1$ and $Q_g = 1$, and the induced and permanent electronic dipole moments are respectively $\vec{\boldsymbol{\mu}}_{eg} = \vec{\boldsymbol{\mu}}_{ge} = 1$ and $\vec{\boldsymbol{\mu}}_{ee} = \vec{\boldsymbol{\mu}}_{gg} = 1$ with the additional constants $\hbar = 1$ and $M = 0.01$. In the following simulations, just one vibrational mode is involved. If required, many mode models can be developed along the same lines.

In Figure 3, we show various types of resonant Raman spectra of the adsorbate. It describes the spectrum of the resonant Raman signal involving the transition between the vibronic levels $|g,n = 2\rangle \rightarrow |e,\nu = 2\rangle$ and $|e,\nu = 2\rangle \rightarrow |g,m = 4\rangle$. The solid line stands for the zeroth-order contribution to the Raman spectrum, corresponding to the molecule in the absence of the substrate field. Then, the dash−dotted line describes the same spectrum when the molecular adsorbate is lying in a homogeneous substrate field. We note that the perturbation induced by the field enhances the Raman signal, first due to the increase of the Franck−Condon factors weighting the contribution of the induced dipole moments but also, when existing, because of the additional contributions of the permanent dipole moments. Notice that the contributions of these permanent dipole moments result from the perturbation induced by the substrate field. Finally, in the last curve associated with the presence of an inhomogeneous substrate field, we observe an additional increase specific to the inhomogeneity of the field. Of course, for different molecular or substrate field parameters, different variations could be observed. Now, we simulate the role played by specific physical parameters, and we begin with the case of a homogeneous substrate field. In Figures 4 and 5, we analyze the influence of the electronic partial charge $\Theta_{ee}(0)$ and of the electronic transition charge $\Theta_{eg}(0)$, respectively, for the case of a homogeneous substrate field. Here, because of the field homogeneity, there is no displacement nor frequency change of the vibrational structure, as can be seen from the expressions of $\delta \mathbf{Q}_n^{(0)}$ and $\delta \Omega_n$ given by eqs 3.18 and 3.22, respectively. Therefore, the variations of the electronic partial and transition charge will induce a modification of the magnitude of the resonance structure. In both cases, we note an enhancement of the resonance when electronic partial and transition charges increase by the same amount. This is confirmed in Figure 6, where the enhancement is represented as a function of $\Theta_{ee}(0)$ and $\Theta_{eg}(0)$. Of course, as expected, according to the sign of these parameters corresponding to the orientation of the substrate field, other types of variation could be found. What is more relevant is the high sensitivity of the nonlinear optical response of the adsorbate, here the resonant Raman signal, to the substrate field. Notice that the solid line stands for the variation of the electronic partial charge and the dashed line for the electronic transition charge. It is important to note that while these variations are almost linear stronger variations could be observed by increasing the values of the physical parameters, but this will require in turn higher order terms of the type $C_{mn}^{(s)}(\mathbf{Q})$ $C_{pq}^{(u)}(\mathbf{Q})$ or $K_n^{(su)}(\mathbf{Q})$, which have been rejected in the perturbational expansion. Since our interest lies more on the understanding of the processes taking place when the adsorbate lies on the substrate field, this approach gives interesting physical insights about the elementary processes taking place in such a system. For a more quantitative analysis, an evaluation of the electronic potential of the various configurations obtained by quantum chemical calculations[31] will be more convenient and need to be done for specific molecules.

Finally, we still have to discuss the influence of the electronic partial and transition charges when the substrate field is inhomogeneous. In this case, besides the conformational change of the adsorbate molecule resulting in a variation of the equilibrium positions of its normal coordinates, the internal dynamics of the adsorbate is strongly modified due to the

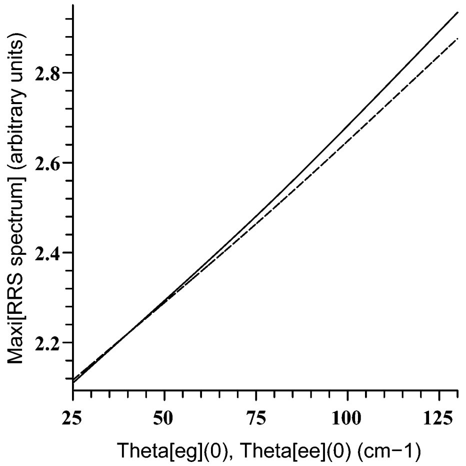

Figure 6. Enhancement of the resonant Raman scattering signal for a homogeneous substrate field by drawing the maxima of the Raman signal as a function of the electronic partial charges Θ_{ee} (solid line) and as a function of the electronic transition charges (dashed line). The values of the parameters are the same as in Figures 4 and 5, respectively.

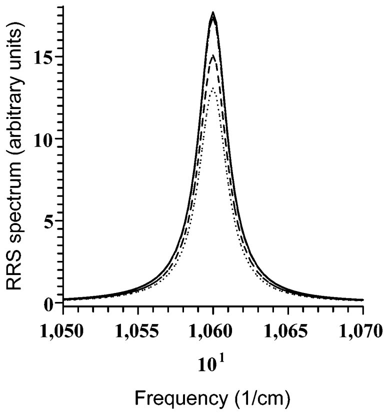

Figure 7. Frequency dependence of the resonant Raman signal for an inhomogeneous substrate field. The cases of different electronic partial charges $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = 40$ cm^{-1} (dash−dotted line), $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = 80$ cm^{-1} (dashed line), and $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = 120$ cm^{-1} (dotted line) are considered, with $\Theta_{gg}(0) = 6$ cm^{-1}, $\Theta_{eg}(0) = 40$ cm^{-1}, all other parameters being equal to zero. Again, the solid line stands for the zeroth-order contribution.

Q-dependence of the partial and transition charges. According to the type of field inhomogeneities, a broad range of terms of powers $\mathbf{Q}^n$ can participate. Then, instead of the simple Franck−Condon factors among the vibronic states $|m\rangle$, $|n\rangle$, and $|\nu\rangle$ participating in the resonant Raman process, the $\mathbf{Q}^n$ terms induce in the zeroth-order representation, as shown in Figure 2, transitions through intermediate vibrational states due to the couplings between vibrational states of the different electronic configurations. Here, because we have determined the vibrational structure of the molecular adsorbate in the presence of the substrate field, these transitions are accounted for. Then, as done previously for the homogeneous field case, we analyze successively the influence of the electronic partial and transition charges on the resonant Raman signal. In Figures 8 and 9 we exhibit the frequency dependence of the resonant Raman signal for different electronic transition charges. While in Figure 8 we note a decrease of the signal for increasing values of $\Theta_{ee}(i)$ $\forall\ i$, in Figure 9, obtained by changing the sign $\Theta_{ee}(i) \rightarrow -\Theta_{ee}(i)$ $\forall\ i$, we observe an opposite variation with an increase of the signal.

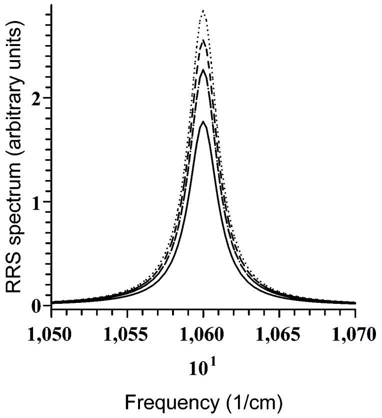

Figure 8. Same variations as in Figure 7 represented assuming electronic partial charges of opposite sign and keeping all other parameters identical. Then, $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = -40$ cm^{-1} (dash−dotted line), $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = -80$ cm^{-1} (dashed line), and $\Theta_{ee}(0) = \Theta_{ee}(1) = \Theta_{ee}(2) = \Theta_{ee}(3) = -120$ cm^{-1} (dotted line).

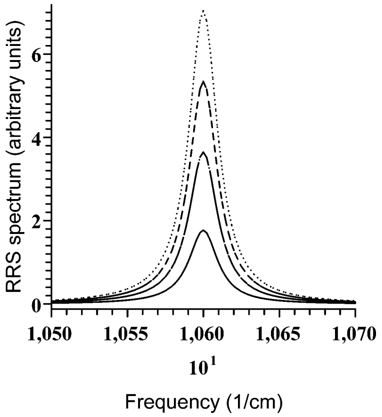

Figure 9. Frequency dependence of the resonant Raman signal for an inhomogeneous substrate field. The cases of different electronic transition charges $\Theta_{eg}(0) = \Theta_{eg}(1) = \Theta_{eg}(2) = \Theta_{eg}(3) = 40$ cm^{-1} (dash−dotted line), $\Theta_{eg}(0) = \Theta_{eg}(1) = \Theta_{eg}(2) = \Theta_{eg}(3) = 80$ cm^{-1} (dashed line), and $\Theta_{eg}(0) = \Theta_{eg}(1) = \Theta_{eg}(2) = \Theta_{eg}(3) = 120$ cm^{-1} (dotted line) are considered, with $\Theta_{gg}(0) = 6$ cm^{-1}, $\Theta_{ee}(0) = 40$ cm^{-1}, all other parameters being equal to zero. Again, the solid line stands for the zeroth-order contribution.

Then, in Figure 9, the influence of the electronic transition charge $\Theta_{pq}(i)$ is discussed. Here, we observe a more important amplification of the Raman signal than for $\Theta_{pp}(i)$. Comparison of these dependences is shown in Figure 10. The solid line corresponds to the variation of the maximum of the resonant Raman signal for increasing positive values of the electronic partial charge $\Theta_{ee}(i)$ $\forall\ i$, the dashed line is for the same variation with negative values of $\Theta_{ee}(i)$ $\forall\ i$, and finally the dotted line stands for the same variation as a function of the electronic transition charges $\Theta_{eg}(i)$ $\forall\ i$. Again, we can mention that the variations are almost linear because for the sake of simplicity, we have restricted the description to the first-order perturbation term for the electronic part and second order for the **Q**-expansion of $C_{mn}^{(s)}(\mathbf{Q})$. While the first approximation is perfectly valid because the electronic configurations keep their identity, the second one restricts the influence of the field inhomogeneity. However, it suffices for the moment to understand the internal dynamical processes that come into play due to the presence of the substrate field inhomogeneity.

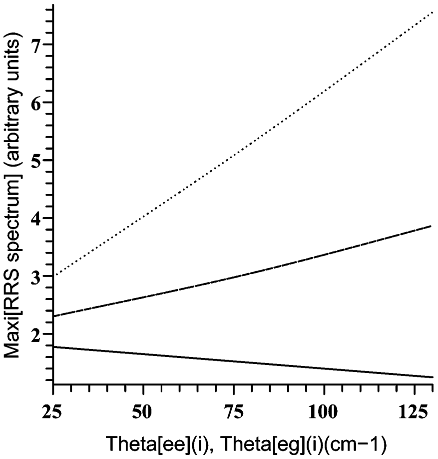

Figure 10. Enhancement of the resonant Raman scattering signal by drawing the maxima of the Raman signal as a function of the electronic partial charges Θ_{ee} (solid line for values taken from Figure 7 and dashed line for values taken from Figure 8) and as a function of the electronic transition charges (dotted line for values taken from Figure 9), respectively.

6. Conclusion

In the present paper, we have intended to shed light on some physical processes participating in the internal dynamics of an adsorbate lying in the electrostatic field of a metallic substrate surface. Two different situations are encountered depending on the nature of the surface field, which can be either homogeneous or inhomogeneous. While in the first case the resonant Raman signal is just weighted by the Franck−Condon factors, in the second case many vibrational intermediate states participate in the Raman process, and the spreading out over the intermediate vibrational states increases with the inhomogeneities of the substrate field. According to the unperturbed structure of the electronic configurations participating in the resonant Raman process and to the displacements and frequency changes induced by the substrate field, the Raman signal can be enhanced or reduced. In the case of a homogeneous substrate field, no displacement nor frequency change is observed, and according to the initial equilibrium positions of the modes in the electronic configurations, an enhancement of the signal can be observed that is mainly controlled by the Franck−Condon factors if we disregard small energy changes of the electronic energies resulting from coupling between the electronic potential surfaces. For the inhomogeneous case, the situation is more complex due to the dependence of the electronic partial and transition charges with the normal modes. This dependence introduces, besides the modifications of the Franck−Condon factors participating to the homogeneous case and still present here, additional pathways through intermediate vibrational levels whose extension is a signature of the type of field inhomogeneities. Of course, for analytical calculation constraints, only small inhomogeneities have been considered here. This is why the variations observed are limited to the nearly linear regime. Higher-order **Q**-dependence will lead to more important variations and consequently, for appropriate electronic surfaces, to stronger amplifications of the Raman signal. Such a situation will be more easily taken into account by evaluating numerically the electronic potential surfaces of the molecular adsorbate in the presence of the substrate field. This is currently under investigation.

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