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Contributions of the substrate electric field to the molecular adsorbate optical nonlinearities

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The nonlinear optical response of an adsorbate, whose structure is altered by the inhomogeneous electrostatic field of the substrate, has been evaluated with a particular emphasis on the sum-frequency generation process. In the limiting case of an homogeneous electrostatic field, besides the contributions associated with the induced dipole moments, we have additional contributions which only exist if the adsorbed molecule has permanent dipole moments. Also, the Franck-Condon factors of the unperturbed molecule weight the internal couplings induced by the electrostatic field. For the more general inhomogeneous electrostatic field case, while the main observations remain valid, the Franck-Condon factors are modified by the molecular structure changes induced by the electrostatic field. In addition, we have a strong redistribution of the vibronic couplings resulting from the analytical **Q** dependence of the partial charge distribution which is a signature of the field inhomogeneities.

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I. INTRODUCTION

The interaction of molecules with their surroundings is a recurrent problem which occurs in a large number of fields ranging from single-molecule nanomanipulation like DNA [1] to forming artificial structures directly from atoms or molecules [2–4]. Of special interest for interfacial materials science is the incorporation of biomolecules into well-defined layered structures, which provides interesting models for biological membranes. They can be used for studying specific interactions and may be convenient tools for designing artificial systems with biological functions such as sensors [5–8]. While a lot of experimental data informative about structure distorsions have been obtained from traditional Raman spectroscopies, it is now well established that nonlinear spectroscopies, and more specifically infrared-visible sum-frequency generation spectroscopy, are currently used to study vibrational dynamics to understand the properties, as well as the structure of adsorbed molecules on surface and interfaces [9–14]. Informations as diverse as vibrational frequencies, bond lengths, local chemical surrounding of adsorbed molecules, or their orientations can be determined. Also, two-dimensional vibrational spectroscopy has been developed recently by using infrared-visible spectroscopy suitable to study the coupling between vibrational modes at surfaces [15] and has been applied to the study of lateral interactions between adsorbed molecules [16]. In view of these high experimental performances, there is a need for more detailed theoretical descriptions of the dynamics occurring on adsorbed systems.

When a molecule is bounded to a substrate surface, its partial charge density is altered by the substrate electrostatic field which induces a distorsion of the molecular electronic structure. This deviation of the partial charge distribution has been modelized [17,18] and accounts for the electronic polarization and partial charge redistribution [19–21]. Because of the molecular electronic distorsions taking place in the adsorbed molecule, the molecular vibrational structure is changed and, consequently, the resulting electron density of the molecule is not anymore in equilibrium with the instantaneous molecular structure, implying a structural transformation of the molecule to reach new equilibrium positions. As a consequence, the electronic potential surface and the subsequent vibrational properties are changed accordingly [22,23].

From previous *ab initio* vibrational analysis of *trans*- and *cis*-*N*-methylacetamide, energies, geometries, and force constants have been calculated for two hydrogen bonded molecules, one at the N—H group and the other at the C═O group [24–27]. In addition, other calculations on *N*-methylacetamide solvated by water molecules [28,29], exhibited changes in bond lengths and bond angles, as well as vibrational frequency shifts of the normal modes depending on the number of surrounding water molecules. All these observations strongly suggest interrelations between electronic and molecular structure distorsions, and motivated their modelization [30–32]. Besides, it has to be mentioned that while the charge response kernel expression has been obtained by Morita and Kato using a coupled-perturbed Hartree-Fock equation which explicitly includes the field [33,34], Cho got it from a sum over states [21] and relates the partial charge and charge response kernel to the static molecular polarizability, which strongly depends on the molecular structure.

In the present work, we emphasize the role played by the substrate electrostatic field on the nonlinear optical response associated to a sum-frequency generation process. In Sec. II, we overview the general equations for electronic and vibrational motions in the framework of the adiabatic Born-

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Oppenheimer approximation. In the usual Born-Oppenheimer description, the partial charge term just gives renormalized Born-Oppenheimer states and the transition charge terms induce coupling between these vibronic molecular states. Then, in Sec. III, we establish the electronic and vibrational equations of motion in terms of the diagonalized vibronic molecular states at the depend of an effective potential which is a function of the normal mode coordinates and involves the interaction Hamiltonian of the electrostatic field. From this equation, we can solve the vibrational eigenvalue problem in terms of the unperturbed one. This enables the determination of the new equilibrium positions and frequency shifts induced by the inhomogeneous electrostatic field. Finally, in Sec. IV, we describe the sum-frequency process taking place in the adsorbed molecule submitted to the electrostatic field substrate. Numerical simulations are done in Sec. V. In the limiting case of an homogeneous electrostatic field which is first examined, they show that besides additional contributions to the zeroth-order optical susceptibility which are generated by the homogeneous electrostatic field on the induced dipole moments, we have supplementary contributions which only exist if the adsorbed molecule has permanent dipoles moment in its excited states. For the more general inhomogeneous electrostatic field case, previous additional contributions exist, but the dynamics underlying these contributions are much more involved because of the **Q** dependence of the partial charge distribution which modifies the couplings between the various vibronic structures. It is interesting to note that the permanent dipole moments can affect quite differently the sum-frequency optical susceptibility according to the structure of the substrate surface electrostatic field. While for an homogeneous field we obtain a decrease of the nonlinear response, the presence of inhomogeneities in the substrate electrostatic field enhances the sum-frequency susceptibility.

II. DESCRIPTION OF THE ADSORBATE PERTURBED BY THE SUBSTRATE ELECTROSTATIC FIELD

The time-dependent Schrödinger equation driving the evolution of the molecular adsorbate perturbed by the electrostatic field of the substrate and undergoing the excitation induced by two laser beams can be described, in the framework of the semiclassical description, by the Hamiltonian

$$\mathcal{H}(\mathbf{q},\mathbf{Q},t) = H(\mathbf{q},\mathbf{Q}) - \boldsymbol{\mu}\cdot\mathbf{E}(\mathbf{r},t), \qquad (2.1)$$

where $H(\mathbf{q},\mathbf{Q})$ stands for the molecular Hamiltonian in presence of the substrate, $\boldsymbol{\mu}$ is the dipole moment of the adsorbate, and $\mathbf{E}(\mathbf{r},t)$ the total laser field. Once the eigenvalue problem of the molecular Hamiltonian is solved, the optical nonlinearities can be evaluated right the way using the well-known methods of the nonlinear optics [9]. Here, since the electronic structure of the molecular adsorbate deviates from that of the molecule in gas-phase due to the partial charge distribution created by the electrostatic field, we have to solve the eigenvalue problem

$$H(\mathbf{q},\mathbf{Q})|\Psi(\mathbf{q},\mathbf{Q})\rangle = E|\Psi(\mathbf{q},\mathbf{Q})\rangle, \qquad (2.2)$$

where the molecular adsorbate Hamiltonian $H(\mathbf{q},\mathbf{Q}) = H_0(\mathbf{q},\mathbf{Q}) + \Sigma_s \hat{c}_s(\mathbf{Q})\vartheta_s$ is made of the molecular Hamiltonian $H_0(\mathbf{q},\mathbf{Q})$ and the perturbation $\Sigma_s \hat{c}_s(\mathbf{Q})\vartheta_s$ resulting from the presence of the substrate electrostatic field. As usual, $H_0(\mathbf{q},\mathbf{Q})$ involves electronic, nuclear, and mixed contributions:

$$H_0(\mathbf{q},\mathbf{Q}) = T(\mathbf{q}) + T(\mathbf{Q}) + U(\mathbf{q},\mathbf{Q}) + V(\mathbf{Q}), \qquad (2.3)$$

with $T(\mathbf{q})$ and $T(\mathbf{Q})$ the electronic and nuclear kinetic operators, $U(\mathbf{q},\mathbf{Q})$ the electron-electron and electron-nucleus potential energy operator, and $V(\mathbf{Q})$ the corresponding nucleus-nucleus potential energy operator. Finally, $\hat{c}_s(\mathbf{Q})$ stands for the effective charge operator on site s and ϑ_s the electrostatic potential acting on the effective charge. Taking advantage of the adiabatic description of the Born-Oppenheimer (BO) molecular states [35,36], from the electronic eigenvalue problem of the model Hamiltonian $H_{BO} = T(\mathbf{q}) + U(\mathbf{q},\mathbf{Q})$ written as

$$[T(\mathbf{q}) + U(\mathbf{q},\mathbf{Q})]|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle = E_n^{(BO)}(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle, \qquad (2.4)$$

the eigenvectors of $H(\mathbf{q},\mathbf{Q})$ can be developed into the form

$$|\Psi_i(\mathbf{q},\mathbf{Q})\rangle = \sum_n |\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle. \qquad (2.5)$$

If we introduce a perturbative treatment of the interaction induced by the substrate electrostatic field, we get in the BO molecular basis set of states defined by

$$\left[T(\mathbf{q}) + U(\mathbf{q},\mathbf{Q}) + \sum_s \hat{c}_s(\mathbf{Q})\vartheta_s\right]|\xi_n(\mathbf{q},\mathbf{Q})\rangle = \mathcal{E}_n(\mathbf{Q})|\xi_n(\mathbf{q},\mathbf{Q})\rangle, \qquad (2.6)$$

where the electronic eigenenergies up to the second order are expressed as

$$\begin{aligned}\mathcal{E}_n(\mathbf{Q}) &= E_n^{(BO)}(\mathbf{Q}) + \mathcal{E}_n^{(1)}(\mathbf{Q}) + \mathcal{E}_n^{(2)}(\mathbf{Q}) + \cdots \\ &= E_n^{(BO)}(\mathbf{Q}) + \sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s \\ &\quad + \sum_{s,u} K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u + \cdots \end{aligned} \qquad (2.7)$$

and the eigenvectors to first order take the form

$$|\xi_n(\mathbf{q},\mathbf{Q})\rangle = |\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_{m\neq n} \frac{\sum_s C_{mn}^{(s)}(\mathbf{Q})\vartheta_s}{E_n^{(BO)}(\mathbf{Q}) - E_m^{(BO)}(\mathbf{Q})} \times |\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \cdots . \qquad (2.8)$$

These expressions result straightforwardly from crude perturbative treatment. Notice that the evaluation of the electronic wave function and their corresponding energies do not require the Hamiltonians $T(\mathbf{Q})$ and $V(\mathbf{Q})$, which depend on the normal mode coordinates only. They will be introduced in the following for the evaluation of the vibrational eigenvalue problem. Also, we have introduced the notations

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

$$K_n^{(su)}(\mathbf{Q}) = \sum_{m\neq n} \frac{\langle \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|\hat{c}_s(\mathbf{Q})|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})|\hat{c}_u(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle}{E_n^{(BO)}(\mathbf{Q}) - E_m^{(BO)}(\mathbf{Q})}, \tag{2.9}$$

which stand either for the electronic transition charge if $m \neq n$ or for the electronic partial charge if $m=n$ and the charge response kernel, respectively.

We come now to a detailed description of the vibrational structure still based on the BO molecular states. The formal solution of the total molecular Hamiltonian $H(\mathbf{q},\mathbf{Q})$ in Eq. (2.2) is given by

$$\left[T(\mathbf{q}) + U(\mathbf{q},\mathbf{Q}) + \sum_s \hat{c}_s(\mathbf{Q})\vartheta_s + T(\mathbf{Q}) + V(\mathbf{Q})\right] \times \sum_n |\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle = \mathcal{E}_i \sum_n |\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle. \tag{2.10}$$

From the eigenvalue problem of $T(\mathbf{q})+U(\mathbf{q},\mathbf{Q})$ expressed by Eq. (2.4) and the scalar product obtained by projecting this previous equation on the molecular BO zeroth-order electronic state $|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$, the previous equation becomes

$$[E_p^{(BO)}(\mathbf{Q}) - \mathcal{E}_i]\rangle|\theta_{pi}(\mathbf{Q})\rangle + \sum_n \sum_s C_{pn}^{(s)}(\mathbf{Q})\vartheta_s|\theta_{ni}(\mathbf{Q})\rangle + \sum_n \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q}) + V(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle = 0. \tag{2.11}$$

According to details given in Appendix A, the eigenvalue problem of the adsorbed molecule undergoing the electrostatic field of the substrate given in Eq. (2.11) reduces to

$$\left[E_p^{(BO)}(\mathbf{Q}) - \mathcal{E}_i + \sum_s C_{pp}^{(s)}(\mathbf{Q})\vartheta_s + V(\mathbf{Q}) + T(\mathbf{Q}) + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right]|\theta_{pi}(\mathbf{Q})\rangle + \sum_{n\neq p}\left[\sum_s C_{pn}^{(s)}(\mathbf{Q})\vartheta_s + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle - \frac{h^2}{M}\left(\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\frac{\partial}{\partial \mathbf{Q}}|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)\frac{\partial}{\partial \mathbf{Q}}\right] \times |\theta_{ni}(\mathbf{Q})\rangle = 0. \tag{2.12}$$

For the sake of convenience, only one normal mode has been accounted for here. Otherwise, a sum over the normal modes has to be introduced.

In the past decades, it has been established in the studies of nonradiative molecular transitions [37,38] that vibrational states associated with different electronic states are coupled through the interaction terms $T(\mathbf{Q})$ and $\partial/\partial\mathbf{Q}$. Here, due to the presence of the electrostatic field substrate, an additional coupling term induced by the charge operator $\hat{c}_s(\mathbf{Q})$ appears and is proportional to the electrostatic field substrate. Therefore, a polarizable molecule undergoing such a field will have its vibrational states relative to different electronic configurations coupled in the same way as $T(\mathbf{Q})$ and $\partial/\partial\mathbf{Q}$ proceed for internal conversion process. In order to solve the vibrational equation of the molecular adsorbate in presence of the electrostatic field which can be inhomogeneous, we take advantage of the adiabatic approximation usually introduced to express the molecular state in electronic and vibrational parts. If we neglect the nondiagonal couplings in Eq. (2.12)—say, $\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$ $\forall p, n\neq p$ and $\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|(\partial/\partial\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$ $\forall p,n$, which are the specific assumptions of the adiabatic BO description—the resulting BO eigenstates provide a convenient representation. In this basis, these residual terms will be responsible for internal conversion. When the substrate electrostatic field is acting on the adsorbate molecule, to preserve this adiabatic representation, we must neglect the term $\Sigma_s C_{pn}^{(s)}(\mathbf{Q})\vartheta_s$, which we will introduce as an additional residual coupling later. The resulting adiabatic molecular states take the form

$$|\Psi_{pi}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle = |\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{pi}(\mathbf{Q})\rangle. \tag{2.13}$$

Therefore, the vibrational equation of motion can be expressed as

$$[T(\mathbf{Q}) + V_{eff}^{(BO)}(\mathbf{Q}) - \mathcal{E}_i]|\theta_{pi}(\mathbf{Q})\rangle = 0, \tag{2.14}$$

where the effective potential $V_{eff}^{(BO)}(\mathbf{Q})$ stands for

$$V_{eff}^{(BO)}(\mathbf{Q}) = V(\mathbf{Q}) + E_p^{(BO)}(\mathbf{Q}) + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_s C_{pp}^{(s)}(\mathbf{Q})\vartheta_s. \tag{2.15}$$

As mentioned by Cho [30], we note that the perturbation induced by the electrostatic field of the substrate surface modifies the electronic potential surface driving the nuclear motion of the molecule. Consequently, there is a modification of the equilibrium positions and vibrational frequencies of the normal modes with respect to the ones of the isolated molecule. For the sake of simplicity, they will be evaluated in the next section on a different representation built from the molecular eigenstates of the adsorbate and electrostatic field Hamiltonian.

III. EVALUATION OF THE SECOND-ORDER OPTICAL SUSCEPTIBILITY

Among the theoretical approaches devoted to second-order optical molecular susceptibilities [9,39,40], the Liouvillian formalism [14,41] is of particular interest to describe the dynamical evolution of the adsorbed molecule located in the electrostatic field of the substrate. For the sake of simplicity, we introduce the various Liouvillians L, L_0, and L_{BO} corresponding to the Hamiltonians H, H_0, and H_{BO}, respectively. Also, L_V stands for the interaction between the adsorbed molecule and the two laser beams, say

$$L_V = [-\boldsymbol{\mu} \cdot \mathbf{E}(\mathbf{r},t),]$$

$$\text{if } \mathbf{E}(\mathbf{r},t) = \sum_{f=1}^{2} [\mathbf{E}_f^{\star} e^{i\omega_f t - i\mathbf{k}_f \cdot \mathbf{r}} + \mathbf{E}_f e^{-i\omega_f t + i\mathbf{k}_f \cdot \mathbf{r}}], \quad (3.1)$$

where the star symbol stands for the complex conjugate quantity. Therefore, the dynamical equation takes the form

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}[L + L_V(t)]\rho(t) - \Gamma\rho(t), \qquad (3.2)$$

where Γ stands for the damping operator accounting for the radiative and nonradiative Markovian processes occurring in the molecular adsorbate. Quite often, the nonradiative contributions to Γ arise from the interaction terms $\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}) \rangle$ and $\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q}) | (\partial/\partial\mathbf{Q}) \times | \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}) \rangle$. If we define the transformation $\rho(t) = e^{-(i/\hbar)L' t}\rho^{(I)}(t)$ with the usual notation $L' = L - i\hbar\Gamma$, the dynamical equation (3.2) becomes

$$\frac{\partial \rho^{(I)}(t)}{\partial t} = -\frac{i}{\hbar} L_V^{(I)}(t)\rho^{(I)}(t), \qquad (3.3)$$

with the additional notation

$$L_V^{(I)}(t) = e^{(i/\hbar)L' t} L_V(t) e^{-(i/\hbar)L' t}. \qquad (3.4)$$

The second-order perturbation term, pertinent to the description of second-harmonic generation and sum-frequency generation, results straightforwardly from Eq. (3.3) and can be written as

$$\rho^{(I)(2)}(t) = -\frac{1}{\hbar^2}\int_{t_i}^{t} d\tau_2 \int_{t_i}^{\tau_2} d\tau_1 \, L_V^{(I)}(\tau_2) L_V^{(I)}(\tau_1)\rho(t_i), \qquad (3.5)$$

because, at the initial time t_i, the density matrix is diagonal. Of course, the definition of the initial density matrix must account for the influence of the electrostatic field of the substrate surface. Therefore, from the adiabatic approximation, $\rho(t_i)$ will be expressed in terms of the molecular eigenstates

$$|\Psi_\nu(\mathbf{q},\mathbf{Q})\rangle = \sum_l |\xi_l(\mathbf{q},\mathbf{Q})\rangle |\chi_{l\nu}(\mathbf{Q})\rangle, \qquad (3.6)$$

where $|\xi_n(\mathbf{q},\mathbf{Q})\rangle$ stands for the electronic eigenstates defined by Eq. (2.6) and $|\chi_{n\nu}(\mathbf{Q})\rangle$ their corresponding vibrational states, which are solutions of the equation

$$\begin{aligned}
&[\mathcal{E}_n(\mathbf{Q}) - \mathcal{E}_\nu + V(\mathbf{Q}) + T(\mathbf{Q}) + \langle \xi_n(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \xi_n(\mathbf{q},\mathbf{Q}) \rangle] \\
&\quad \times |\chi_{n\nu}(\mathbf{Q})\rangle + \sum_{l \neq n} \Bigg[\langle \xi_n(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \xi_l(\mathbf{q},\mathbf{Q}) \rangle \\
&\quad - \frac{\hbar^2}{M}\left(\langle \xi_n(\mathbf{q},\mathbf{Q}) | \frac{\partial}{\partial \mathbf{Q}} | \xi_l(\mathbf{q},\mathbf{Q}) \rangle \right) \frac{\partial}{\partial \mathbf{Q}} \Bigg] |\chi_{l\nu}(\mathbf{Q})\rangle = 0,
\end{aligned} \qquad (3.7)$$

and reduces to

$$[T(\mathbf{Q}) + V_{eff}(\mathbf{Q}) - \mathcal{E}_\nu] |\chi_{n\nu}(\mathbf{Q})\rangle = 0, \qquad (3.8)$$

where, according to the assumptions which validate the adiabatic description of this new basis states, the terms $\langle \xi_n(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \xi_l(\mathbf{q},\mathbf{Q}) \rangle \ \forall \, l, n \neq l$ and $\langle \xi_n(\mathbf{q},\mathbf{Q}) | (\partial/\partial\mathbf{Q}) | \xi_l(\mathbf{q},\mathbf{Q}) \rangle \ \forall \, l, n$ have been neglected. These assumptions are similar to the ones introduced previously for the electronic BO states, but are now applied to the eigenstates $|\xi_l(\mathbf{q},\mathbf{Q})\rangle$. A complete description will require the introduction of the residual coupling terms previously rejected. Here the effective potential $V_{eff}(\mathbf{Q})$ corresponds to

$$\begin{aligned}
V_{eff}(\mathbf{Q}) &= \mathcal{E}_n(\mathbf{Q}) + V(\mathbf{Q}) + \langle \xi_n(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \xi_n(\mathbf{q},\mathbf{Q}) \rangle \\
&= V(\mathbf{Q}) + E_n^{(BO)}(\mathbf{Q}) + \langle \xi_n(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \xi_n(\mathbf{q},\mathbf{Q}) \rangle \\
&\quad + \sum_s C_{nn}^{(s)}(\mathbf{Q}) \vartheta_s + \sum_{s,u} K_n^{(su)}(\mathbf{Q}) \vartheta_s \vartheta_u + \cdots
\end{aligned} \qquad (3.9)$$

as long as the partial charge interaction $\Sigma_s \hat{c}_s(\mathbf{Q}) \vartheta_s$ can be treated perturbatively. To solve the vibrational equation of motion (3.8), we use the well-known small-amplitude motion approximation. Then vibrational solutions can be expressed in terms of harmonic oscillator wave functions whose parameters like equilibrium position $\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)}$ and frequency Ω_n will be related to the corresponding parameters $\mathbf{Q}_n^{(0)}$ and $\Omega_n^{(0)}$ of the unperturbed oscillator. Notice that while the electrostatic field substrate cancels, the equilibrium condition is given by

$$\begin{aligned}
&\frac{\partial}{\partial \mathbf{Q}}[V(\mathbf{Q}) + E_n^{(BO)}(\mathbf{Q}) \\
&\quad + \langle \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}) | T(\mathbf{Q}) | \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}) \rangle]_{\mathbf{Q}=\mathbf{Q}_n^{(0)}} = 0.
\end{aligned} \qquad (3.10)$$

If we express the vibrational equation of motion (3.8) in the BO basis set, we get

$$\Biggl[T(\mathbf{Q})+\Biggl\{V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\sum_{m\neq n}\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\frac{\sum_s C_{mn}^{(s)}(\mathbf{Q})\vartheta_s}{E_n^{(BO)}(\mathbf{Q})-E_m^{(BO)}(\mathbf{Q})}$$
$$+\sum_{m\neq n}\langle\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\frac{\sum_s C_{mn}^{(s)^+}(\mathbf{Q})\vartheta_s^\star}{E_n^{(BO)}(\mathbf{Q})-E_m^{(BO)}(\mathbf{Q})}+\sum_{p\neq n}\sum_{q\neq n}\langle\Phi_q^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$$
$$\times\frac{\sum_s C_{pn}^{(s)}(\mathbf{Q})\vartheta_s}{E_n^{(BO)}(\mathbf{Q})-E_p^{(BO)}(\mathbf{Q})}\frac{\sum_u C_{nq}^{(u)^+}(\mathbf{Q})\vartheta_u^\star}{E_n^{(BO)}(\mathbf{Q})-E_q^{(BO)}(\mathbf{Q})}+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Biggr\}\Biggr]|\xi_{n\nu}(\mathbf{Q})\rangle=\mathcal{E}_\nu|\xi_{n\nu}(\mathbf{Q})\rangle, \tag{3.11}$$

where the perturbational expansions (2.7) and (2.8) have been used. Owing to the adiabatic approximation, we just retain the diagonal contributions of $T(\mathbf{Q})$ with respect to the electronic states, so that

$$\Biggl[T(\mathbf{Q})+\Biggl\{V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$$
$$+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Biggr\}\Biggr]|\xi_{n\nu}(\mathbf{Q})\rangle$$
$$=\mathcal{E}_\nu|\xi_{n\nu}(\mathbf{Q})\rangle, \tag{3.12}$$

if the third-order diagonal term

$$\sum_{m\neq n}\langle\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\left|\frac{\sum_s C_{mn}^{(s)}(\mathbf{Q})\vartheta_s}{E_n^{(BO)}(\mathbf{Q})-E_m^{(BO)}(\mathbf{Q})}\right|^2 \tag{3.13}$$

is neglected. In presence of the substrate surface electrostatic field, the equilibrium position is defined by the condition

$$\left.\frac{\partial\mathcal{V}(\mathbf{Q})}{\partial\mathbf{Q}}\right|_{\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)}}=0, \tag{3.14}$$

where

$$\mathcal{V}(\mathbf{Q})=V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$$
$$+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u. \tag{3.15}$$

Therefore, if we develop the $\mathbf{Q}$ dependence up to first order, the condition (3.16) gives

$$\delta\mathbf{Q}_n^{(0)}=-\frac{\left.\frac{\partial\mathcal{V}(\mathbf{Q})}{\partial\mathbf{Q}}\right|_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}}{\left.\frac{\partial^2\mathcal{V}(\mathbf{Q})}{\partial\mathbf{Q}^2}\right|_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}} \tag{3.16}$$

or, more explicitly, on account of the definition of $\mathbf{Q}_n^{(0)}$ given by Eq. (3.10),

$$\delta\mathbf{Q}_n^{(0)}=-\left[\frac{\partial}{\partial\mathbf{Q}}\left(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\right)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\right]$$
$$\times\Biggl[\frac{\partial^2}{\partial\mathbf{Q}^2}\Biggl(V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})$$
$$+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle$$
$$+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Biggr)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\Biggr]^{-1}, \tag{3.17}$$

which specifies the variation of the oscillator equilibrium position induced by the electrostatic field. If we introduce the expression of the unperturbed oscillator frequency given by

$$\Omega_n^{(0)}=\Biggl[\frac{1}{M}\frac{\partial^2}{\partial\mathbf{Q}^2}[V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})$$
$$+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle]_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\Biggr]^{1/2} \tag{3.18}$$

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

$$\delta\mathbf{Q}_n^{(0)}=-\left[\frac{\partial}{\partial\mathbf{Q}}\left(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\right)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\right]$$
$$\times\Biggl[M\Omega_n^{(0)^2}+\frac{\partial^2}{\partial\mathbf{Q}^2}\Biggl(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s$$
$$+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Biggr)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\Biggr]^{-1}. \tag{3.19}$$

We still have to determine the frequency change due to the perturbation. From the $\mathbf{Q}$ expansion of $\mathcal{V}(\mathbf{Q})$ up to $\mathbf{Q}^2$, we obtain from Eq. (3.12), if the substrate electrostatic field is not applied,

$$\Bigg[T(\mathbf{Q}-\mathbf{Q}_n^{(0)})+\frac{1}{2}\left(\left.\frac{\partial^2\{V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\}}{\partial\mathbf{Q}^2}\right|_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}\right)(\mathbf{Q}-\mathbf{Q}_n^{(0)})^2-\mathcal{E}_{n\nu}^{(0)}+V(\mathbf{Q}_n^{(0)})+E_n^{(BO)}(\mathbf{Q}_n^{(0)})$$
$$+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)})\rangle\Bigg]|\chi_{n\nu}^{(0)}(\mathbf{Q}-\mathbf{Q}_n^{(0)})\rangle=0, \tag{3.20}$$

because the sum of the first derivatives is zero from equilibrium conditions. From this previous equation (3.20), usual eigenstates and eigenenergies of the unperturbed harmonic oscillator can be determined and are given in Appendix B. In the presence of the substrate surface electrostatic field, we get, in turn,

$$\Bigg[T(\mathbf{Q}-\mathbf{Q}_n^{(0)}-\delta\mathbf{Q}_n^{(0)})+\frac{1}{2}(\mathbf{Q}-\mathbf{Q}_n^{(0)}-\delta\mathbf{Q}_n^{(0)})^2\frac{\partial^2}{\partial\mathbf{Q}^2}\Bigg(V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}$$
$$\times K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Bigg)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}-\delta\mathbf{Q}_n^{(0)}}-\mathcal{E}_{n\nu}+V(\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})+E_n^{(BO)}(\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})|T(\mathbf{Q})$$
$$\times|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})\rangle+\sum_s C_{nn}^{(s)}(\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)})\vartheta_s\sum_{\vartheta_u}\Bigg]|\chi_{n\nu}^{(0)}(\mathbf{Q}-\mathbf{Q}_n^{(0)}-\delta\mathbf{Q}_n^{(0)})\rangle=0, \tag{3.21}$$

whose eigenstates and eigenenergies of the perturbed harmonic oscillator are given in Appendix B. Its vibrational frequency corresponds to

$$\Omega_n=\Bigg[\frac{1}{M}\frac{\partial^2}{\partial\mathbf{Q}^2}\Bigg(V(\mathbf{Q})+E_n^{(BO)}(\mathbf{Q})+\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Bigg)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)}}\Bigg]^{1/2}. \tag{3.22}$$

Notice that radiative and nonradiative relaxation processes are accounted for by the introduction of the additional constants $\Gamma_{n\nu}$. From the previous analysis, the perturbed vibrational eigenfunctions can be deduced from the unperturbed ones at the cost of the displacement $\delta\mathbf{Q}_n^{(0)}$ and frequency change $\delta\Omega_n=\Omega_n-\Omega_n^{(0)}$ given by

$$\delta\Omega_n\sim\frac{1}{2M\Omega_n^{(0)}}\frac{\partial^2}{\partial\mathbf{Q}^2}\Bigg(\sum_s C_{nn}^{(s)}(\mathbf{Q})\vartheta_s+\sum_{s,u}K_n^{(su)}(\mathbf{Q})\vartheta_s\vartheta_u\Bigg)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}+\delta\mathbf{Q}_n^{(0)}}, \tag{3.23}$$

according to the expansion $\sqrt{1+x}\sim1+x/2$. Of course, frequency change and displacement are interdependent, as shown in Appendix B. At this stage, it can be mentioned for the case of an homogeneous substrate electrostatic field that we have neither displacement nor frequency change of the oscillator associated with the normal mode.

In the next section, we will take advantage of these quantities to describe the vibrational structure on account of the influence of the electrostatic field substrate for the particular process of sum-frequency generation.

IV. APPLICATION TO THE STUDY OF A SUM-FREQUENCY GENERATION PROCESS

To discuss and evaluate more quantitatively the role played by the substrate surface electrostatic field on sum-frequency generation we first establish, from the general dynamical equation, the second-order optical susceptibility.

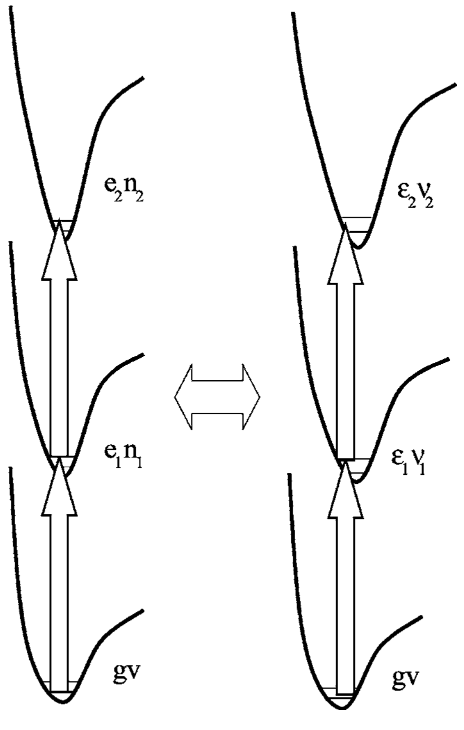

FIG. 1. Electronic configurations participating to the sum-frequency process. The unperturbed and perturbed configurations are drawn on the right and left sides, respectively. As discussed in the paper, the ground configuration is not altered by the electrostatic field of the substrate surface.

With this goal in mind, the density matrix in the Schrödinger picture will be written in the following as

$$\rho^{(2)}(t) = -\frac{1}{\hbar^2}\int_{t_i}^{t} d\tau_2 \int_{t_i}^{\tau_2} d\tau_1\, G(t-\tau_2) \times L_V(\tau_2) G(\tau_2-\tau_1) L_V(\tau_1)\rho(t_i), \tag{4.1}$$

with $G(\tau_1 - t_i) = 1$, if the adsorbate molecule is initially in a stable state. From the analysis done in the previous section, we know that vibronic levels associated with different electronic configurations are coupled. In the initial ground configuration, at least at room temperature, there is no quasi-isoenergetic vibronic states pertaining to the upper electronic configuration and the eigenstates $|\xi_\alpha(\mathbf{q},\mathbf{Q})\rangle$ reduce to the BO vibronic states in the ground configuration as shown in Fig. 1. Then the initial density matrix of the adsorbates can be conveniently described by

$$\rho(t_i) = \sum_v \mathcal{P}_v |\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle |\theta_{gv}(\mathbf{q},\mathbf{Q})\rangle\langle\theta_{gv}(\mathbf{q},\mathbf{Q})| \langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|, \tag{4.2}$$

where $\mathcal{P}_v = \mathrm{e}^{-E_{gv}/kT}/Z$, with $Z = \Sigma_{v'}\mathrm{e}^{-E_{gv'}/kT}$ the partition function. The various pathways participating to the evaluation of $\rho^{(2)}(t)$ are given in Table I. Therefore, we are left with the evaluation of the various matrix elements of the interaction terms

$$\begin{aligned}
L_{Vgv\epsilon_1\nu_1 gvgv}(\tau_1) &= \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})| \\
&\quad \times \boldsymbol{\mu}|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle \cdot \mathbf{E}_1 \mathrm{e}^{i\omega_1\tau_1 - i\mathbf{k}_1\cdot\mathbf{r}}, \\
L_{Vgv\epsilon_2\nu_2 gv\epsilon_1\nu_1}(\tau_2) &= \langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})| \\
&\quad \times \boldsymbol{\mu}|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle \cdot \mathbf{E}_2 \mathrm{e}^{i\omega_2\tau_2 - i\mathbf{k}_2\cdot\mathbf{r}}, \\
L_{V\epsilon_1\nu_1 gvgvgv}(\tau_1) &= -L^{\star}_{Vgv\epsilon_1\nu_1 gvgv}(\tau_1), \\
L_{V\epsilon_2\nu_2 gv\epsilon_1\nu_1 gv}(\tau_2) &= -L^{\star}_{Vgv\epsilon_2\nu_2 gv\epsilon_1\nu_1}(\tau_2),
\end{aligned} \tag{4.3}$$

assuming the rotating-wave approximation and both fields 1 and 2 quasiresonant with vibronic transitions $gv \leftrightarrow \epsilon_1\nu_1$ and $\epsilon_1\nu_1 \leftrightarrow \epsilon_2\nu_2$, respectively. Also, the matrix elements of the evolution Liouvillian are given by

$$\begin{aligned}
G_{gv\epsilon_1\nu_1 gv\epsilon_1\nu_1}(\tau_2-\tau_1) &= \mathrm{e}^{-(i/\hbar)[E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})](\tau_2-\tau_1)}, \\
G_{gv\epsilon_2\nu_2 gv\epsilon_2\nu_2}(t-\tau_2) &= \mathrm{e}^{-(i/\hbar)[E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})](t-\tau_2)}, \\
G_{\epsilon_1\nu_1 gv\epsilon_1\nu_1 gv}(\tau_2-\tau_1) &= G^{\star}_{gv\epsilon_1\nu_1 gv\epsilon_1\nu_1}(\tau_2-\tau_1), \\
G_{\epsilon_2\nu_2 gv\epsilon_2\nu_2 gv}(t-\tau_2) &= G^{\star}_{gv\epsilon_2\nu_2 gv\epsilon_2\nu_2}(t-\tau_2).
\end{aligned} \tag{4.4}$$

To evaluate the second-order optical susceptibility, we first perform the time integration to get the explicit expression of $\rho^{(2)}(t)$. It can be expressed as

$$\begin{aligned}
\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})|\rho^{(2)}(t)|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle &= -\frac{1}{\hbar^2}\int_{t_i}^{t} d\tau_2 \int_{t_i}^{\tau_2} d\tau_1 \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})|G(t-\tau_2) \\
&\quad \times |\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle\langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})| \\
&\quad \times \boldsymbol{\mu}|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle \cdot \mathbf{E}_2 \mathrm{e}^{i\omega_2\tau_2 - i\mathbf{k}_2\cdot\mathbf{r}} \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})| \\
&\quad \times G(\tau_2-\tau_1)|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})| \\
&\quad \times \boldsymbol{\mu}|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle \cdot \mathbf{E}_1 \mathrm{e}^{i\omega_1\tau_1 - i\mathbf{k}_1\cdot\mathbf{r}} \rho_{gvgv}(t_i).
\end{aligned} \tag{4.5}$$

Performing the double time integration we get, in the limit $t_i \to -\infty$, the expression of the second-order optical polarization $\mathbf{P}(\omega_1+\omega_2, \mathbf{k}_1+\mathbf{k}_2, t) = \mathrm{Tr}[\rho^{(2)}(t)\boldsymbol{\mu}]$ in the direction $\mathbf{k}_1+\mathbf{k}_2$. It takes the form

$$\begin{aligned}
\mathbf{P}(\omega_1+\omega_2, \mathbf{k}_1+\mathbf{k}_2, t) &= \frac{\mathrm{e}^{i(\omega_1+\omega_2)t - i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}}}{[E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q}) + \hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q}) + \hbar\omega_1 + \hbar\omega_2]} \langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})| \\
&\quad \times \boldsymbol{\mu}\cdot\mathbf{E}_2|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})|\boldsymbol{\mu}\cdot\mathbf{E}_1|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle\langle \xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})|\boldsymbol{\mu} \\
&\quad \times |\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\rangle.
\end{aligned} \tag{4.6}$$

From the identification of the l component of the polarization just established and the definition of the second-order optical susceptibility,

$$P_l(\omega_1+\omega_2, \mathbf{k}_1+\mathbf{k}_2, t) = \sum_{m,n} \chi_{lmn}(\omega_1+\omega_2) E_{1,m}(t) E_{2,n}(t), \tag{4.7}$$

if $E_{f,p}$ stands for the p component of the f field, we obtain

TABLE I. Description of the various pathways entering in the evaluation of the sum-frequency signal induced on the adsorbed molecule and generating the contributions to $\rho^{(2)}(t)$.

$G(t-\tau_2)$	$L_V(\tau_2)$	$G(\tau_2-\tau_1)$	$L_V(\tau_1)$	$\rho(t_i)$
$gv\epsilon_2\nu_2\, gv\epsilon_2\nu_2$	$gv\epsilon_2\nu_2\, gv\epsilon_1\nu_1$	$gv\epsilon_1\nu_1\, gv\epsilon_1\nu_1$	$gv\epsilon_1\nu_1\, gvgv$	$gvgv$
$\epsilon_2\nu_2gv\, \epsilon_2\nu_2gv$	$\epsilon_2\nu_2gv\, \epsilon_1\nu_1gv$	$\epsilon_1\nu_1gv\, \epsilon_1\nu_1gv$	$\epsilon_1\nu_1gv\, gvgv$	

$$\chi_{lmn}(\omega_1+\omega_2) = \frac{\langle \xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q}) + \hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q}) + \hbar\omega_1 + \hbar\omega_2]}\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q})|\mu_m|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle \times\langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})|\mu_n|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle. \tag{4.8}$$

As long as the perturbation induced by the surface electrostatic field on the adsorbed molecule is weak enough, $\chi_{lmn}(\omega_1+\omega_2)$ can be expressed from the perturbative expressions of the energies and molecular states given by Eqs. (2.7) and (2.8). It provides the basic expression which enables us to discuss the peculiar role played by the surface field on a particular second-order process. From the previous evaluation, we have all the required informations to evaluate the various contributions of $\chi_{lmn}(\omega_1+\omega_2)$.

At this stage, we would like to stress the influence of the substrate electrostatic field on the nonlinear optical susceptibility associated to a sum-frequency generation process. In fact, this field modifies simultaneously the electronic energies and the vibrational frequencies, as well as the Franck-Condon factors, because of the conformational changes resulting from the different equilibrium positions of the normal modes in presence of the electrostatic field. To discuss the various additional contributions to the nonlinear optical susceptibility resulting of the presence of the substrate field, we will introduce in the following a partition of $\chi_{lmn}(\omega_1+\omega_2)$ in terms of the different additional processes induced by the electrostatic field.

In the following, we will consider successively the homogeneous and the inhomogeneous cases. To this end, we show in Fig. 2, the vibrational states which participate to the dynamics on account of our approximation, implying that the quasi-isoenergetic states give the dominant contribution in the perturbation expansion.

We first consider the case of an homogeneous electrostatic field. Therefore, $C_{ij}^{(s)}(\mathbf{Q})$ is not anymore $\mathbf{Q}$ dependent and can be taken arbitrarily at $\mathbf{Q}^{(0)}$, the minimum of the potential surface energy. In the Condon approximation, the various matrix elements can be factorized. In the general case, the perturbed vibrational states and their corresponding frequencies can be expressed in terms of the previous unperturbed vibrational states associated with the displaced equilibrium positions $\delta\mathbf{Q}_n^{(0)}$ and their corresponding frequency shifts $\delta\Omega_n$. From the evaluation of $\chi_{lmn}^{hom}(\omega_1+\omega_2)$ done in the first part of Appendix C, we are able to discuss the contributions introduced by the homogeneous electrostatic field in the nonlinear susceptibility of the sum-frequency process. The contributions to $\chi_{lmn}^{hom}(\omega_1+\omega_2)$ can be decomposed first into a zeroth-order part $\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)$ given by

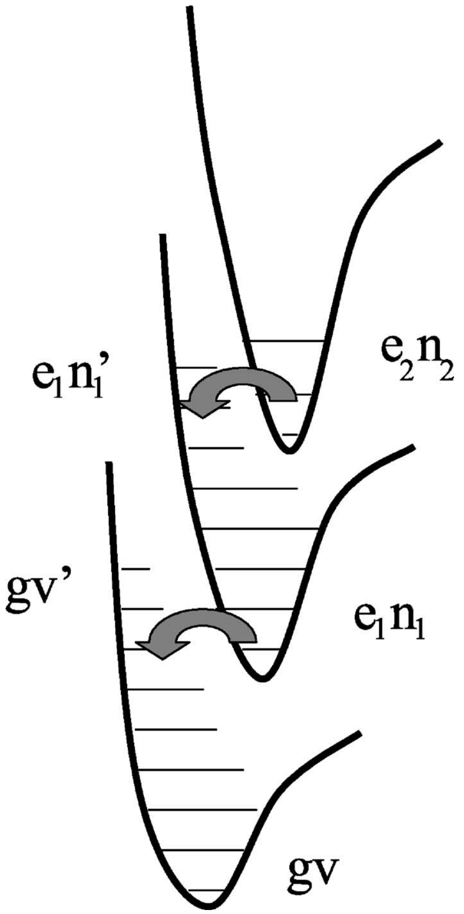

FIG. 2. We show the dynamical processes giving the main contributions to the sum-frequency process in the unperturbed electronic configurations. Also, the lowest vibronic states of the ground electronic configuration are not modified by the electrostatic field of the substrate surface.

$$\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)=\frac{1}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}^{(BO)}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}^{(BO)}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\langle\Phi_{\epsilon_2}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})| \times\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle\langle\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})\rangle \times\langle\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}\ \rangle \tag{4.9}$$

and generated by the induced dipole moment between ground and excited states or between the excited states themselves. Notice that in the limit of negligible homogeneous electrostatic field substrate, the eigenenergies $\mathcal{E}_{\epsilon_j\nu_j}\to E_{e_jn_j}$ for $j=1,2$, and we recover the usual sum-frequency optical susceptibility. Next, we get as expected a contribution induced by the presence of the substrate electrostatic field (IDM) on the induced dipole moment and corresponding to

$$\chi_{lmn}^{(\mathrm{IDM})hom}(\omega_1+\omega_2)=\frac{\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}^{(BO)}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}^{(BO)}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\Bigg[\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \times\frac{\sum_s C_{ge_1}^{(s)\star}\vartheta_s^\star}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\frac{\sum_s C_{e_1e_2}^{(s)\star}\vartheta_s^\star}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \times\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\Bigg]\langle\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle\langle\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})\rangle \times\langle\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)})\rangle. \tag{4.10}$$

Finally, we have an additional contribution (PDM) which only exists if the adsorbate has a permanent dipole moment in the electronic excited states e_1 and e_2, in presence of the substrate electrostatic field. It takes the form

$$\chi_{lmn}^{(\mathrm{PDM})hom}(\omega_1+\omega_2)=\frac{\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\Bigg[\frac{\sum_s C_{ge_1}^{(s)}\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})| \times\mu_m|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n \times|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\frac{\sum_s C_{e_1e_2}^{(s)}\vartheta_s}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\Bigg]\langle\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle\langle\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})\rangle \times\langle\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)})\rangle. \tag{4.11}$$

Of course, there are many other high-order contributing terms which are not considered here. This leaves the optical susceptibility for sum-frequency generation into the form

$$\chi_{lmn}^{hom}(\omega_1+\omega_2)=\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{IDM})hom}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{PDM})hom}(\omega_1+\omega_2)+\cdots\ . \tag{4.12}$$

Therefore, from Eqs. (3.21)–(3.23) as well as Eqs. (4.9)–(4.11), we see that the influence of the electrostatic field is twofold. It shifts the electronic transition energies through the modifications of the electronic energies in the various electronic configurations and alters the efficiency of the dynamical process by introducing additional contributions which can enhance or decrease significantly the optical response associated to the sum-frequency generation process.

We come now to the more intricate case of an inhomogeneous electrostatic field. Here, because of the inhomogeneities of the field, the $\mathbf{Q}$ dependence needs to be preserved and will be introduced explicitly for the sake of simplicity. For our purpose, we assume a weak dependence so that

$$C_{ij}^{(s)}(\mathbf{Q})=\Lambda_{ij}^{(s)(0)}(\mathbf{Q}^{(0)})+\Lambda_{ij}^{(s)(1)}(\mathbf{Q}^{(0)})\mathbf{Q}+\frac{1}{2}\Lambda_{ij}^{(s)(2)}(\mathbf{Q}^{(0)})\mathbf{Q}^2+\cdots\ . \tag{4.13}$$

As a consequence, we will have displacements and distorsions of the oscillators as discussed previously. Then, starting from Eq. (4.8), the second-order optical susceptibility clearly shows that, due to the presence of the field inhomogeneity, the couplings of the vibrational states pertaining to different electronic configurations strongly modify the optical susceptibility with respect to the homogeneous case. Then the second-order optical susceptibility for a sum-frequency process acting on adsorbates sticking on a surface with an inhomogeneous electrostatic field can be decomposed as

$$\chi_{lmn}^{inh}(\omega_1+\omega_2)=\chi_{lmn}^{(0)inh}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{IDM})inh}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{PDM})inh}(\omega_1+\omega_2)+\cdots, \tag{4.14}$$

where the zeroth-order term is straightforwardly obtained from the homogeneous case

$$\chi_{lmn}^{(0)inh}(\omega_1+\omega_2)=\lambda_{lmn}^{(0)hom}(\omega_1+\omega_2) \tag{4.15}$$

if the change of notation $C_{ij}^{(s)}\rightarrow\Lambda_{ij}^{(s)(0)}(\mathbf{Q}_0)$ is introduced. Then the next term associated with the presence of the surface electrostatic field corresponds to

$$\begin{aligned}\chi_{lmn}^{(\mathrm{IDM})inh}(\omega_1+\omega_2)={}&\frac{\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\Bigg[\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}\\&-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2,\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}\\&-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})|\mu_l\frac{\sum_s C_{e_1e_2}^{(s)^+}(\mathbf{Q})\vartheta_s^{\star}}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle+\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}\\&-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})|\mu_n\frac{\sum_s C_{ge_1}^{(s)^+}(\mathbf{Q})\vartheta_s^{\star}}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})\rangle\\&\times\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle\Bigg].\end{aligned} \tag{4.16}$$

Finally, the contribution induced by the existence of permanent dipole moments takes the form

$$\begin{aligned}\chi_{lmn}^{(\mathrm{PDM})inh}(\omega_1+\omega_2)={}&\frac{\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\Bigg[\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}\\&-\mathbf{Q}_g^{(0)})|\mu_m\frac{\sum_s C_{ge_1}^{(s)}(\mathbf{Q})\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}\\&-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})\rangle+\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\\&\times\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})\rangle\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)}-\delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}+\delta\Omega_{e_1})|\\&\times\mu_n\frac{\sum_s C_{e_1e_2}^{(s)}(\mathbf{Q})\vartheta_s}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)}-\delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}+\delta\Omega_{e_2})\rangle\Bigg].\end{aligned} \tag{4.17}$$

Expressions (4.16) and (4.17) describe the contributions of the induced transition dipole moment $\chi_{lmn}^{(\mathrm{IDM})inh}(\omega_1+\omega_2)$ and permanent dipole moment $\chi_{lmn}^{(\mathrm{PDM})inh}(\omega_1+\omega_2)$ to the nonlinear optical susceptibility for sum-frequency generation associated with the inhomogeneous electrostatic field. We note that the main difference with respect to the homogeneous case lies on the many-phonon transitions resulting from the **Q** dependence of the substrate field and the modifications of the electronic potential surface which imply distorsions of the adsorbate structure.

V. NUMERICAL SIMULATIONS AND DISCUSSION

In the present section, we will perform some numerical simulations on the formal results previously established. The cases of an homogeneous and next of an inhomogeneous substrate electrostatic field will be analyzed successively. For this purpose, we first introduce the main physical parameters which characterize the molecular adsorbate sticked on the substrate surface.

The electronic energies of the ground $|g\rangle$ and excited $|e_1\rangle$ and $|e_2\rangle$ configurations correspond to 0, 10 000, and 16 500 cm^{-1}, respectively. The vibronic levels participating to the sum-frequency signal are $|g0\rangle$, $|e_11\rangle$, and $|e_20\rangle$ and their corresponding linewidths are given by $\Gamma_{g0g0g0g0}=0$, $\Gamma_{e_11e_11e_11e_11}=10$ cm^{-1}, and $\Gamma_{e_20e_20e_20e_20}=15$ cm^{-1}. Since we are dealing with the most general case of displaced and distorted oscillators, the equilibrium positions of the normal coordinate are set to $\mathbf{Q}_g^{(0)}=1$, $\mathbf{Q}_{e_1}^{(0)}=1.2$, and $\mathbf{Q}_{e_2}^{(0)}=1.5$ in the

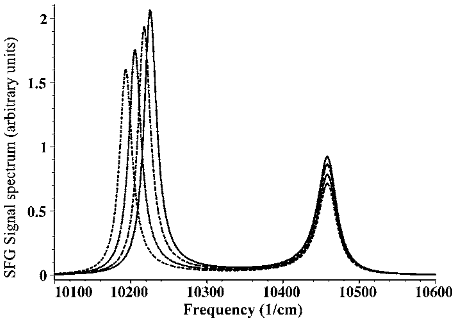

FIG. 3. We show the spectra $I_{SFG}^{(0)}(\omega_1)$ of the sum-frequency signal as a function of the laser frequency ω_1 for the case of an homogeneous electrostatic field substrate. Four different values of $\Lambda_{ge_1}^{(0)}$ which characterize the perturbation induced by the substrate electrostatic field have been considered, say, $\Lambda_{ge_1}^{(0)}=0$ (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line). The values of the other physical parameters are given in the text.

three different electronic configurations with their corresponding frequencies $\omega_g=300$, $\omega_{e_1}=250$, and $\omega_{e_2}=220$ cm^{-1}. Also, the constant $\hbar$ and the reduced mass M of the mode under investigation are set arbitrarily equal to 1 and 0.01, respectively. To deeply analyze the influence of the substrate electrostatic field, it is more convenient to adopt resonant-nonresonant laser excitation conditions. To this end, the first laser beam frequency ω_1 is tuned around the first electronic transition, while the second laser beam frequency is chosen strongly nonresonant by lower value at 6000 cm^{-1}. Then, only the $n=0$ vibrational level of the highest electronic configurations will participate to the dynamics of the sum-frequency process. Finally, the induced dipole moments are chosen equal and the permanent dipole moments in the excited configurations are given by $\mu_{gg}=0.5\mu_{ge_1}$ and $\mu_{e_1e_1}=0.8\mu_{ge_1}$. Besides, the perturbation parameter in the higher electronic configuration is fixed all along, at the value $\Lambda_{e_1e_2}^{(1)}=-1$.

We first discuss the results presented in Fig. 3 showing the spectrum $I_{SFG}^{(0)}(\omega_1)$ of the sum-frequency signal as a function of the laser frequency ω_1 for the case of an homogeneous substrate electrostatic field. This spectrum is related to the nonlinear susceptibility of the sum-frequency process by the relation

$$I_{SFG}^{(0)}(\omega_1+\omega_2)=|\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)|^2 \tag{5.1}$$

and has been drawn for different magnitudes of the perturbation induced by the substrate electrostatic field. Each spectrum is characterized by two resonances corresponding to the cases where either the laser frequency ω_1 is resonant with the first vibronic transition $|g0\rangle\rightarrow|e_1 1\rangle$ or the sum of the laser frequencies $\omega_1+\omega_2$ is resonant with the $|g0\rangle\rightarrow|e_2 0\rangle$ transition. For increasing values of $\Lambda_{ge_j}^{(0)}$ we observe an overall decrease of the spectrum. In addition, the resonance around 10 460 cm^{-1} is weakly affected because of the small magnitude of the perturbation $\Lambda_{e_1e_2}^{(0)}$ acting on the upper configuration. Concerning the variations of the resonance around 10 220 cm^{-1}, we note a redshift of the peak resonance and a decrease of their corresponding amplitude with the increase of $|\Lambda_{ge_j}^{(0)}|$. As previously discussed, these observations reflect the change of just the resonance frequencies under the influence of the perturbating electrostatic field. At this stage, it is important to stress that the variations observed on the spectra strongly depend on the initial equilibrium positions of the normal coordinate in the various electronic configurations as well as on the sign and magnitude of the perturbating field terms. It means that different variation patterns could be obtained as well, revealing the high sensitivity of the spectrum to the substrate electrostatic field effect. We come now to the influence of the perturbating substrate field on the additional contribution generated by the induced transition dipole moment. The associated variations can be expressed by the relation

$$\begin{aligned}\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)=&|\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{IDM})hom}(\omega_1+\omega_2)|^2\\&-I_{SFG}^{(0)}(\omega_1+\omega_2),\end{aligned} \tag{5.2}$$

and the values of the perturbating substrate field chosen for the simulations are identical to the ones of Fig. 3. If the substrate electrostatic field cancels, $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)=0$. When the substrate field is acting on the adsorbate, we recover the same resonance structure as in the case of the spectra of the sum-frequency signal, except that the contributions are negative. This implies for the molecular adsorbate characterized by the set of physical parameters chosen here that the presence of the substrate electrostatic field is unfavorable to the realization of the sum-frequency processes. Of course, for different molecular adsorbates, the opposite situation can be found as well, depending on the sign of $\Lambda_{ge_1}^{(0)}$. We recover the high sensitivity of this additional contribution induced by the perturbating field, and the additional contribution $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$ increases with the increase of the electrostatic field. Notice that while arbitrary units have been used to represent the spectra of the sum-frequency signal, the same scaling is adopted to represent the various contributions to the total sum-frequency signal intensity. This is a required condition to make a comparative analysis of the various terms shown in Figs. 4 and 5. Finally, we discuss the contribution induced by the substrate electrostatic field through the permanent dipole moment for the homogeneous case. It corresponds to

$$\begin{aligned}\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)=&|\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)+\chi_{lmn}^{(\mathrm{IDM})hom}(\omega_1+\omega_2)\\&+\chi_{lmn}^{(\mathrm{PDM})hom}(\omega_1+\omega_2)|^2-I_{SFG}^{(0)}(\omega_1+\omega_2)\\&-\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2).\end{aligned} \tag{5.3}$$

A similar resonance structure is recovered because the three terms $\chi_{lmn}^{(0)hom}(\omega_1+\omega_2)$, $\chi_{lmn}^{(\mathrm{IDM})hom}(\omega_1+\omega_2)$, and $\chi_{lmn}^{(\mathrm{PDM})hom}(\omega_1+\omega_2)$ have the same resonant factor, as can be seen from their respective expressions (4.9)–(4.11). Also, the influence of the substrate field is comparable to the one resulting from the induced transition dipole moment. It shows a redshift and an increase of the resonance magnitude with the increase of the electrostatic field strength. In the limit of zero-field amplitude, this contribution goes almost linearly to zero within our approximation, and the weakness of this contribution is

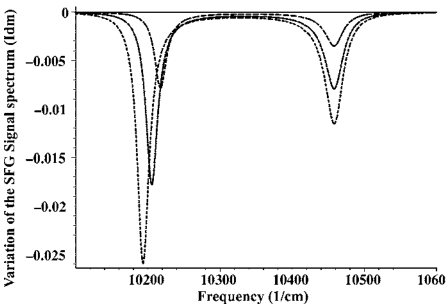

FIG. 4. We represent the additional contribution $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$ induced by the substrate electrostatic field through the induced transition dipole moment for the homogeneous case. Again, the values of $\Lambda_{ge_1}^{(0)}$ are set equal to 0 (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line). While the variations of $I_{SFG}^{(0)}(\omega_1)$ have been done in Fig. 3 in arbitrary units, the present variations are done using the same scaling.

just the consequence of the respective values chosen for the induced transition and permanent dipole moments. As mentioned in the discussion of the previous term $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$, here again $\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)$ is negative and the presence of the substrate electrostatic field tends to decrease the sum-frequency signal intensity. No general conclusion can be drawn since this is just a matter of a particular model. Depending on the relative positions of the electronic energy curves and sign of the perturbation parameter $\Lambda_{ge_1}^{(0)}$, the opposite situation could be obtained as well. However, for a given configuration, the comparative analysis and sensitivity of the substrate field are relevant.

We still have to discuss the case of an inhomogeneous substrate electrostatic field. From previous analysis developed in Sec. III, we have seen that in the inhomogeneous case, the perturbating electrostatic field can displace and distort the electronic energy curves of the various configurations. These changes which are expressed by Eqs. (3.17) and (3.23), can be approximated to lower order by

$$\delta\mathbf{Q}_{e_j}^{(0)} = -\Lambda_{ge_j}^{(1)}/M\Omega_{e_j}^{(0)2}, \quad j=1,2, \tag{5.4}$$

which is a first-order term while

$$\delta\Omega_{e_j} = \Lambda_{ge_j}^{(2)}/2M\Omega_{e_j}^{(0)}, \quad j=1,2, \tag{5.5}$$

is a second-order term which is arbitrarily chosen as $\Lambda_{ge_j}^{(2)} = \sqrt{|\Lambda_{ge_j}^{(1)}|}$ because $\Lambda_{ge_j}^{(1)} \leqslant 0$. Now the Franck-Condon factors are deeply altered because of the $\mathbf{Q}$ dependence of the electronic partial charge. Assuming the Condon approximation and a linear $\mathbf{Q}$ dependence of the interaction term, the additional contributions $\chi_{lmn}^{(\mathrm{IDM})inh}(\omega_1+\omega_2)$ and $\chi_{lmn}^{(\mathrm{PDM})inh}(\omega_1+\omega_2)$ have been evaluated and are given explicitly in the last part of Appendix C. From their expressions we emphasize, in Fig. 6, the influence of the substrate electrostatic field inhomogeneity on the spectra of the sum-frequency signal. All the values of the physical parameters are kept identical to the homogeneous case except that we will consider here the contribution associated with the inhomogeneity as described in relation (4.16). In order to compare the influence of the inhomogeneous term with respect to the homogeneous one previously analyzed, we set $\Lambda_{ge_1}^{(0)} = \Lambda_{e_1e_2}^{(0)} = 0$. Also, the values of $\Lambda_{ge_1}^{(1)}$, the inhomogeneous linear $\mathbf{Q}$ term of $C_{ge_1}^{(s)}(\mathbf{Q})$, are chosen in a similar range as previously considered for $\Lambda_{ge_1}^{(0)}$ in the homogeneous contribution. This is required to make a comparable analysis between the two different situations. Like previously observed for the homogeneous case, we observe a redshift of the sum-frequency spectrum which increases with $\Lambda_{ge_1}^{(1)}$. Even if the magnitude of the resonance lines decreases more slowly than for the homogeneous case, there is no drastic difference. Next, in Fig. 7, we show the additional contribution $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$ induced by the substrate electrostatic field through the induced transition dipole moment for the inhomogeneous case. Two points are relevant here. Again, we note that a redshift is observed in presence of field inhomogeneities. In addition, the magnitude of $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$ is increased roughly by a factor of 4. Finally, in the last Fig. 8, we represent the frequency dependence of $\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)$ associated with the presence of permanent dipole moments. Here a remarkable feature is the

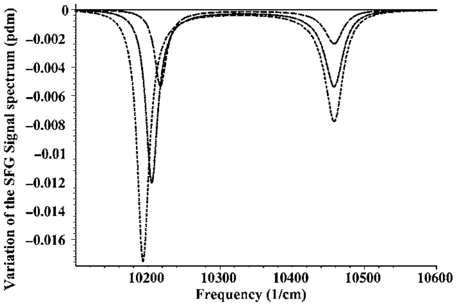

FIG. 5. We exhibit the additional contribution $\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)$ induced by the substrate electrostatic field through the permanent dipole moment for the homogeneous case. The values of $\Lambda_{ge_1}^{(0)}$ are still set equal to 0 (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line), and the frequency dependence is again done with the same scaling adopted in Figs. 3 and 4.

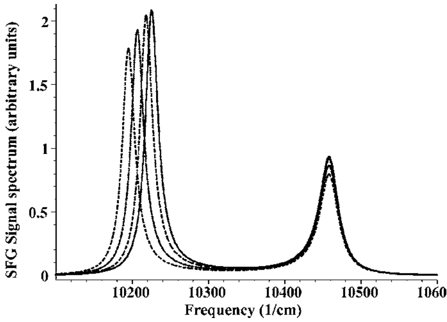

FIG. 6. We show the spectra $I_{SFG}^{(0)}(\omega_1)$ of the sum-frequency signal as a function of the laser frequency ω_1 for the case of an inhomogeneous substrate electrostatic field. Like previously, four different values of $\Lambda_{ge_1}^{(0)} = \Lambda_{ge_1}^{(1)}$ have been considered—say, $\Lambda_{ge_1}^{(0)} = 0$ (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line). The values of the other physical parameters are given in the text. The frequency dependence is again done with the same scaling adopted from Figs. 3–5.

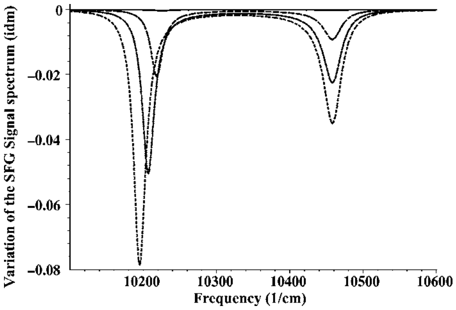

FIG. 7. We represent the additional contribution $\Delta I_{SFG}^{(\mathrm{IDM})}(\omega_1+\omega_2)$ induced by the substrate electrostatic field through the induced transition dipole moment for the inhomogeneous case. Again, the values of $\Lambda_{ge_1}^{(1)}$ are set equal to 0 (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line). The present variations are done using the same scaling used from Figs. 3–6.

change of sign of the contribution $\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)$, meaning that while for the homogeneous case the permanent dipole moments tend to decrease the sum-frequency spectrum, on the contrary the presence of field inhomogeneities tends to increase the sum-frequency spectrum in presence of permanent dipole moments. Of course, as discussed before, these variations are specific to a particular electronic structure. However, the differences obtained for the homogeneous and inhomogeneous cases in the same model demonstrate the peculiar effects and the sensitivity of the substrate electrostatic field. It can be noted that for higher-order processes these differences could still be enhanced because of the multiplicative structure of the Frank-Condon factors in the expression of the higher-order nonlinear susceptibility and also because the inhomogeneities of the electrostatic field can induce large values of the parameters $\Lambda_{ij}^{(n)}$.

VI. CONCLUSION

In this work, we took advantage of the work initiated by Cho on the correlation existing between the electronic distribution and the molecular structure changes when a molecular adsorbate undergoes the electrostatic field of the substrate to describe and next evaluate the influence of the molecular structure distorsions on the nonlinear optical response associated to a sum-frequency generation process. Of course, any other second-order process can be obtained, as well. From our analytical description, we have described the role of the frequency changes and equilibrium displacements of the potential energy surfaces induced by the substrate surface electrostatic field on the nonlinear susceptibility. Two different cases have been stressed. For the homogeneous electrostatic field case, we have shown that the perturbating electrostatic field generates, through the induced dipole moment, additional contributions to the nonlinear susceptibility. Besides, we obtain supplementary contributions which only exist if the molecule has permanent dipole moments in the excited electronic configurations. In addition, the electrostatic field shifts the electronic energies and introduces internal couplings among the vibronic states which are weighted by the Franck-Condon factors associated to the unperturbed molecular structure of the adsorbate participating to the sum-frequency process. Finally, owing to the inhomogeneous substrate electrostatic field case, while previous observations are still pertinent, we have a strong modification of the couplings in the vibronic structure which comes from the **Q** dependence of the effective charge operator. Here, the coupling strengths induced by the electrostatic substrate field are redistributed through the matrix elements of the various powers of the normal mode coordinate operator which is a signature of the field inhomogeneity. Also, the coupling strengths are weighted by the Franck-Condon factors of the perturbed molecule, implying that they depend on the molecular structure modified by the substrate electrostatic field.

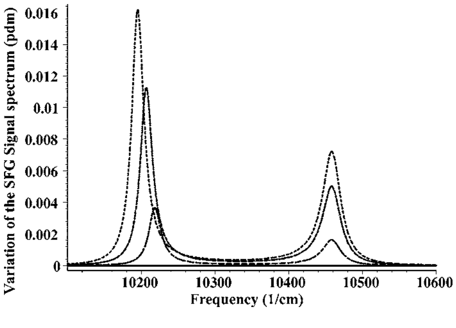

FIG. 8. We exhibit the additional contribution $\Delta I_{SFG}^{(\mathrm{PDM})}(\omega_1+\omega_2)$ induced by the substrate electrostatic field through the permanent dipole moment for the inhomogeneous case. The values of $\Lambda_{ge_1}^{(1)}$ are still set equal to 0 (solid line), −8 (dotted line), −20 (dashed line), and −32 (dash-dotted line). The frequency dependence is again done with the same scaling adopted in Figs. 3–7.

APPENDIX A

Here we evaluate the diagonal $(n=p)$ and nondiagonal $(n\neq p)$ contributions of the last term in Eq. (2.12). To this end, we first note that $T(\mathbf{Q})$ is a second-order differential operator $(-\hbar^2/2M)(\partial^2/\partial\mathbf{Q}^2)$ so that

$$\begin{aligned}T(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{pi}(\mathbf{Q})\rangle &= -\frac{\hbar^2}{2M}\Bigg[\left(\frac{\partial^2}{\partial\mathbf{Q}^2}|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)|\theta_{pi}(\mathbf{Q})\rangle \\ &\quad + 2\left(\frac{\partial}{\partial\mathbf{Q}}|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)\left(\frac{\partial}{\partial\mathbf{Q}}|\theta_{pi}(\mathbf{Q})\rangle\right) \\ &\quad + |\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\ &\quad \times\left(\frac{\partial^2}{\partial\mathbf{Q}^2}|\theta_{pi}(\mathbf{Q})\rangle\right)\Bigg], \qquad \text{(A1)}\end{aligned}$$

and a similar expression is true for the nondiagonal terms. We then get

$$
\begin{aligned}
&[E_p^{(BO)}(\mathbf{Q}) - \mathcal{E}_i]|\theta_{pi}(\mathbf{Q})\rangle + \sum_n \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\Bigg[\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{Q}^2}|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)|\theta_{pi}(\mathbf{Q})\rangle \\
&\quad - \frac{\hbar^2}{M}\left(\frac{\partial}{\partial \mathbf{Q}}|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)\left(\frac{\partial}{\partial \mathbf{Q}}|\theta_{pi}(\mathbf{Q})\rangle\right) + |\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{Q}^2}|\theta_{pi}(\mathbf{Q})\rangle\right)\Bigg] + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|V(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{pi}(\mathbf{Q})\rangle \\
&\quad + \sum_{n\neq p} \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\Bigg[\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{Q}^2}|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)|\theta_{ni}(\mathbf{Q})\rangle - \frac{\hbar^2}{M}\left(\frac{\partial}{\partial \mathbf{Q}}|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)\left(\frac{\partial}{\partial \mathbf{Q}}|\theta_{ni}(\mathbf{Q})\rangle\right) + |\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\
&\quad \times\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{Q}^2}|\theta_{ni}(\mathbf{Q})\rangle\right)\Bigg] + \sum_{n\neq p} \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|V(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle = 0. \qquad \text{(A2)}
\end{aligned}
$$

Note that the term

$$
\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{Q}^2}\right)|\theta_{ni}(\mathbf{Q})\rangle
$$

cancels for $n \neq p$. Next, taking advantage of the very weak $\mathbf{Q}$ dependence of the electronic part of the molecular state we have, on account of the adiabatic approximation,

$$
\begin{aligned}
&\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|V(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{pi}(\mathbf{Q})\rangle \sim V(\mathbf{Q})|\theta_{pi}(\mathbf{Q})\rangle \\
&\quad \times \sum_{n\neq p} \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|V(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle|\theta_{ni}(\mathbf{Q})\rangle \sim 0. \qquad \text{(A3)}
\end{aligned}
$$

In addition, it is well known that the average value of the momentum operator for an electronic bound state vanishes, so that

$$
-\frac{\hbar^2}{M}\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\frac{\partial}{\partial \mathbf{Q}}|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle = 0. \qquad \text{(A4)}
$$

This leaves Eq. (2.11) into the more convenient form

$$
\begin{aligned}
&\Bigg[E_p^{(BO)}(\mathbf{Q}) - \mathcal{E}_i + \sum_s C_{pp}^{(s)}(\mathbf{Q})\vartheta_s + V(\mathbf{Q}) + T(\mathbf{Q}) \\
&\quad + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\Bigg]|\theta_{pi}(\mathbf{Q})\rangle \\
&\quad + \sum_{n\neq p}\Bigg[\sum_s C_{pn}^{(s)}(\mathbf{Q})\vartheta_s + \langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle \\
&\quad - \frac{\hbar^2}{M}\left(\langle \Phi_p^{(BO)}(\mathbf{q},\mathbf{Q})|\frac{\partial}{\partial \mathbf{Q}}|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right)\frac{\partial}{\partial \mathbf{Q}}\Bigg]|\theta_{ni}(\mathbf{Q})\rangle \\
&= 0. \qquad \text{(A5)}
\end{aligned}
$$

APPENDIX B

The eigenenergies and their corresponding eigenfunctions of the unperturbed harmonic oscillator described in Eq. (3.20) have the usual forms

$$
\begin{aligned}
\mathcal{E}_{n\nu}^{(0)} &= E_n^{(BO)}(\mathbf{Q}_n^{(0)}) + V(\mathbf{Q}_n^{(0)}) \\
&\quad + \langle \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)}))\rangle \\
&\quad + \left(\nu + \frac{1}{2}\right)\hbar\Omega_n^{(0)} + i\frac{\Gamma_{n\nu}}{2},
\end{aligned}
$$

$$
\begin{aligned}
\chi_{n\nu}^{(0)}(\mathbf{Q} - \mathbf{Q}_n^{(0)}) &= \left[\frac{1}{2^\nu \nu!}\left(\frac{\hbar}{M\Omega_n^{(0)}}\right)^\nu\right]^{1/2}\left(\frac{M\Omega_n^{(0)}}{\pi\hbar}\right)^{1/4} \\
&\quad \times\left[\frac{M\Omega_n^{(0)}}{\hbar}(\mathbf{Q} - \mathbf{Q}_n^{(0)}) - \frac{d}{d\mathbf{Q}}\right]^\nu \\
&\quad \times e^{-(M\Omega_n^{(0)}/2\hbar)(\mathbf{Q} - \mathbf{Q}_n^{(0)})^2}, \qquad \text{(B1)}
\end{aligned}
$$

where we have introduced the imaginary part which accounts for the finite lifetime of the vibronic state. For the perturbed harmonic oscillator described by Eq. (3.21), we have in turn

$$
\begin{aligned}
\mathcal{E}_{n\nu} &= E_n^{(BO)}(\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)}) + V(\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)}) \\
&\quad + \langle \Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)})|T(\mathbf{Q})|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)}))\rangle \\
&\quad + \sum_s C_{nn}^{(s)}(\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)})\vartheta_s \\
&\quad + \sum_{s,u} K_n^{(su)}(\mathbf{Q}_n^{(0)} + \delta\mathbf{Q}_n^{(0)})\vartheta_s\vartheta_u + \left(\nu + \frac{1}{2}\right)\hbar\Omega_n + i\frac{\Gamma_{n\nu}}{2},
\end{aligned}
$$

$$
\begin{aligned}
&\chi_{n\nu}(\mathbf{Q} - \mathbf{Q}_n^{(0)} - \delta\mathbf{Q}_n^{(0)}) \\
&\quad = \left[\frac{1}{2^\nu \nu!}\left(\frac{\hbar}{M\Omega_n}\right)^\nu\right]^{1/2}\left(\frac{M\Omega_n}{\pi\hbar}\right)^{1/4}\Bigg[\frac{M\Omega_n}{\hbar}(\mathbf{Q} - \mathbf{Q}_n^{(0)} \\
&\qquad - \delta\mathbf{Q}_n^{(0)}) - \frac{d}{d\mathbf{Q}}\Bigg]^\nu \\
&\qquad \times e^{-(M\Omega_n/2\hbar)(\mathbf{Q} - \mathbf{Q}_n^{(0)} - \delta\mathbf{Q}_n^{(0)})^2}, \qquad \text{(B2)}
\end{aligned}
$$

where Ω_n stands for the vibrational frequency of the harmonic oscillator. 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

$$\delta\Omega_n \sim \frac{1}{2M\Omega_n^{(0)}}\frac{\partial^2}{\partial \mathbf{Q}^2}\left[1+\delta\mathbf{Q}_n^{(0)}\frac{\partial}{\partial \mathbf{Q}}\right]\Bigg(\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_{m\neq n}\frac{\langle\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_s \hat{c}_s(\mathbf{Q})\vartheta_s|\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_m^{(BO)}(\mathbf{q},\mathbf{Q})|\sum_u \hat{c}_u(\mathbf{Q})\vartheta_u|\Phi_n^{(BO)}(\mathbf{q},\mathbf{Q})\rangle}{E_n^{(BO)}(\mathbf{Q})-E_m^{(BO)}(\mathbf{Q})}\Bigg)_{\mathbf{Q}=\mathbf{Q}_n^{(0)}}, \tag{B3}$$

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 perturbating electrostatic field increases, this dependence becomes more intricate.

APPENDIX C

For an homogeneous field, the situation is quite simple because $\delta\mathbf{Q}_n^{(0)}=\delta\Omega_n=0$, and we get

$$\chi_{lmn}^{hom}(\omega_1+\omega_2)=\frac{\langle\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\rangle\langle\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})|\mu_n|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\rangle}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\langle\chi_{\epsilon_2\nu_2}(\mathbf{Q})|\theta_{gv}(\mathbf{Q})\rangle \times\langle\theta_{gv}(\mathbf{Q})|\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle\langle\chi_{\epsilon_1\nu_1}(\mathbf{Q})|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle. \tag{C1}$$

In the weak-perturbation limit, electronic eigenstates and eigenenergies can be introduced according Eqs. (2.7) and (2.8). Also, because the vibrational states of the electronic configurations ϵ_1 and ϵ_2 have been evaluated exactly from Eq. (3.21), we do not need their expressions in terms of the unperturbed vibrational states. They can be expressed straightforwardly as $|\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle=|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)},\omega_{e_1})\rangle$ and $|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle=|\theta_{e_1\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)},\omega_{e_2})\rangle$. Therefore, we get the final expression for $\chi_{lmn}^{hom}(\omega_1+\omega_2)$ in the form

$$\begin{aligned}\chi_{lmn}^{hom}(\omega_1+\omega_2)={}&\frac{1}{[E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\\&\times\left[\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\frac{\sum_s C_{e_1e_2}^{(s)\star}\vartheta_s^\star}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right]\\&\times\left[\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\frac{\sum_s C_{ge_1}^{(s)}\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\right]\\&\times\Bigg[\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\frac{\sum_s C_{e_1e_2}^{(s)}\vartheta_s}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\\&+\frac{\sum_s C_{ge_1}^{(s)\star}\vartheta_s^\star}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\frac{\sum_s C_{ge_1}^{(s)\star}\vartheta_s^\star}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\langle\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\\&\times\frac{\sum_s C_{e_1e_2}^{(s)}\vartheta_s}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\Bigg]\langle\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)},\omega_{e_2})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})\rangle\langle\theta_{gv}(\mathbf{Q}-\mathbf{Q}_g^{(0)})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)},\omega_{e_1})\rangle\\&\times\langle\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}_{e_1}^{(0)},\omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}_{e_2}^{(0)},\omega_{e_2})\rangle,\end{aligned} \tag{C2}$$

because, for the present purpose, the electronic eigenstates reduce to

$$\langle\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})|=\langle\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})|+\frac{\sum_s C_{e_1e_2}^{(s)\star}\vartheta_s^\star}{E_{e_2}^{(BO)}(\mathbf{Q})-E_{e_1}^{(BO)}(\mathbf{Q})}\times\langle\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|,$$

$$|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\rangle=|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle+\frac{\sum_s C_{ge_1}^{(s)}\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q})-E_g^{(BO)}(\mathbf{Q})}\times|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle. \tag{C3}$$

As long as perturbation expansion is valid, relation (C2) describes the adsorbate optical susceptibility for sum-frequency generation in presence of an homogeneous substrate electrostatic field.

Owing to the inhomogeneous case, with the restriction previously introduced for the perturbational expansion, say, the lowest vibronic ground states are not perturbed and the lowest vibronic states in the excited electronic configurations are coupled to the isoenergetic vibronic states of the nearest lower electronic configuration only, we have

$$\langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})| = \langle \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})| + \sum_s \frac{\vartheta_s^\star}{E_{\epsilon_1}^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})} \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})| C_{ge_1}^{(s)\,+}(\mathbf{Q})$$

$$|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\rangle = |\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle + \sum_s \frac{\vartheta_s}{E_{\epsilon_2}^{(BO)}(\mathbf{Q}) - E_{\epsilon_1}^{(BO)}(\mathbf{Q})} C_{e_1e_2}^{(s)}(\mathbf{Q}) |\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle. \tag{C4}$$

Therefore, the various matrix elements of the dipole moment can be expressed as

$$\begin{aligned}\langle \xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q})\rangle &= \langle \Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \chi_{\epsilon_2\nu_2}(\mathbf{Q})|\,\theta_{gv}(\mathbf{Q})\rangle + \sum_s \frac{\vartheta_s^\star}{E_{e_2}^{(BO)}(\mathbf{Q}) - E_{e_1}^{(BO)}(\mathbf{Q})}\\ &\quad\times \langle \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \chi_{\epsilon_2\nu_2}(\mathbf{Q})|C_{e_1e_2}^{(s)\,+}(\mathbf{Q})|\,\theta_{gv}(\mathbf{Q})\rangle + \cdots\end{aligned}$$

$$\begin{aligned}\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q})|\mu_m|\xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle &= \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \theta_{gv}(\mathbf{Q})|\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle + \sum_s \frac{\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})}\\ &\quad\times \langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \theta_{gv}(\mathbf{Q})|C_{ge_1}^{(s)}(\mathbf{Q})|\chi_{\epsilon_1\nu_1}(\mathbf{Q})\rangle + \cdots\end{aligned}$$

$$\begin{aligned}\langle \xi_{\epsilon_1}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_1\nu_1}(\mathbf{Q})|\mu_n|\xi_{\epsilon_2}(\mathbf{q},\mathbf{Q})\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle &= \langle \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \chi_{\epsilon_1\nu_1}(\mathbf{Q})|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle + \sum_s \frac{\vartheta_s}{E_{\epsilon_2}^{(BO)}(\mathbf{Q}) - E_{e_1}^{(BO)}(\mathbf{Q})}\\ &\quad\times \langle \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \chi_{\epsilon_1\nu_1}(\mathbf{Q})|C_{e_1e_2}^{(s)}(\mathbf{Q})|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle\\ &\quad+ \sum_s \frac{\vartheta_s^\star}{E_{e_1}^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})}\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\langle \chi_{\epsilon_1\nu_1}(\mathbf{Q})|C_{ge_1}^{(s)}(\mathbf{Q})|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle\\ &\quad+ \sum_{s,s'} \frac{\vartheta_s\vartheta_{s'}^\star}{[E_{e_1}^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})][E_{e_2}^{(BO)}(\mathbf{Q}) - E_{e_1}^{(BO)}(\mathbf{Q})]}\langle \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\rangle\\ &\quad\times\langle \chi_{\epsilon_1\nu_1}(\mathbf{Q})|C_{ge_1}^{(s')+}(\mathbf{Q})C_{e_1e_2}^{(s)}(\mathbf{Q})|\chi_{\epsilon_2\nu_2}(\mathbf{Q})\rangle + \cdots\ .\end{aligned} \tag{C5}$$

As long as the Condon approximation is valid, the various contributions to the second-order optical susceptibility can be obtained similarly, except that the Franck-Condon factors are now replaced by the matrix elements of the various powers of the normal coordinate operator, so that

$$\begin{aligned}\chi_{lmn}^{inh}(\omega_1+\omega_2) &= \{[E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q}) + \hbar\omega_1][E_{gv}^{(BO)}(\mathbf{Q}) - \mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q}) + \hbar\omega_1 + \hbar\omega_2]\}^{-1}\Bigg[\ \langle\ \Phi_{e_2}^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q} - \mathbf{Q}_{e_2}^{(0)}\\ &\quad- \delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2} + \delta\Omega_{e_2})|\mu_l|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q} - \mathbf{Q}_g^{(0)})\ \rangle\ +\ \langle\ \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q} - \mathbf{Q}_{e_2}^{(0)} - \delta\mathbf{Q}_{e_2}^{(0)},\omega_{e_2}\\ &\quad+ \delta\Omega_{e_2})|\mu_l\frac{\sum_s C_{e_1e_2}^{(s)^+}(\mathbf{Q})\,\vartheta_s^\star}{E_{e_2}^{(BO)}(\mathbf{Q}) - E_{e_1}^{(BO)}(\mathbf{Q})}|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q} - \mathbf{Q}_g^{(0)})\ \rangle\ \Bigg]\Bigg[\ \langle\ \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q} - \mathbf{Q}_g^{(0)})|\mu_m|\Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\\ &\quad\times\theta_{e_1\nu_1}(\mathbf{Q} - \mathbf{Q}_{e_1}^{(0)} - \delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1} + \delta\Omega_{e_1})\ \rangle\ +\ \langle\ \Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{gv}(\mathbf{Q} - \mathbf{Q}_g^{(0)})|\mu_m\frac{\sum_s C_{ge_1}^{(s)}(\mathbf{Q})\,\vartheta_s}{E_{e_1}^{(BO)}(\mathbf{Q}) - E_g^{(BO)}(\mathbf{Q})}\\ &\quad\times|\Phi_g^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{e_1\nu_1}(\mathbf{Q} - \mathbf{Q}_{e_1}^{(0)} - \delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1} + \delta\Omega_{e_1})\ \rangle\ \Bigg]\Bigg[\ \langle\ \Phi_{e_1}^{(BO)}(\mathbf{q},\mathbf{Q})\,\theta_{e_1\nu_1}(\mathbf{Q} - \mathbf{Q}_{e_1}^{(0)} - \delta\mathbf{Q}_{e_1}^{(0)},\omega_{e_1}\end{aligned}$$

$$
\begin{aligned}
&+\delta\Omega_{e_1})|\mu_n|\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\,\rangle \;+\; \langle\,\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}\\
&+\delta\Omega_{e_1})|\mu_n\frac{\sum_s C^{(s)}_{e_1e_2}(\mathbf{Q})\vartheta_s}{E^{(BO)}_{e_2}(\mathbf{Q})-E^{(BO)}_{e_1}(\mathbf{Q})}|\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\,\rangle\\
&+\;\langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\mu_n\frac{\sum_s C^{(s)\,+}_{ge_1}(\mathbf{Q})\vartheta^{\star}_s}{E^{(BO)}_{e_1}(\mathbf{Q})-E^{(BO)}_{g}(\mathbf{Q})}|\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}\\
&-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\,\rangle \;+\; \langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\frac{\sum_s C^{(s)\,+}_{ge_1}(\mathbf{Q})\vartheta^{\star}_s}{E^{(BO)}_{e_1}(\mathbf{Q})-E^{(BO)}_{g}(\mathbf{Q})}\mu_n\\
&\times\frac{\sum_s C^{(s)}_{e_1e_2}(\mathbf{Q})\vartheta_s}{E^{(BO)}_{e_2}(\mathbf{Q})-E^{(BO)}_{e_1}(\mathbf{Q})}\;|\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle\Bigg].
\end{aligned}
\tag{C6}
$$

Finally, we give the expressions of $\chi^{(\mathrm{IDM})inh}_{lmn}(\omega_1+\omega_2)$ and $\chi^{(\mathrm{PDM})inh}_{lmn}(\omega_1+\omega_2)$ for the case of an inhomogeneous field on account of the $\mathbf{Q}$ dependence modelized by the relation (4.13)

$$
\begin{aligned}
\chi^{(\mathrm{IDM})inh}_{lmn}(\omega_1+\omega_2) = {} & \frac{\langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})\rangle}{[E^{(BO)}_{gv}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E^{(BO)}_{gv}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\Bigg[\;\langle\,\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})|\\
&\times\mu_n|\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle\\
&\times\frac{\langle\,\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\rangle}{E^{(BO)}_{e_2}(\mathbf{Q})-E^{(BO)}_{e_1}(\mathbf{Q})}(\Lambda^{(0)\,\star}_{e_1e_2}\,\langle\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})\rangle\\
&+\Lambda^{(1)}_{e_1e_2}\,\langle\,\theta_{e_2\nu_2+1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})\rangle)+\frac{\langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})\rangle}{E^{(BO)}_{e_1}(\mathbf{Q})-E^{(BO)}_{g}(\mathbf{Q})}\\
&\times(\Lambda^{(0)\,\star}_{ge_1}\,\langle\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle+\Lambda^{(1)\,\star}_{ge_1}\,\langle\,\theta_{e_1\nu_1-1}(\mathbf{Q}\\
&-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle+\sqrt{2}\Lambda^{(1)\,\star}_{ge_1}\,\langle\,\theta_{e_1\nu_1+1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}\\
&-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle)\,\langle\,\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}\\
&-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})\rangle\Bigg]
\end{aligned}
\tag{C7}
$$

and

$$
\begin{aligned}
\chi^{(PDM)inh}_{lmn}(\omega_1+\omega_2) = {} & \frac{\langle\,\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})|\mu_l|\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})|\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})\rangle}{[E^{(BO)}_{gv}(\mathbf{Q})-\mathcal{E}_{\epsilon_1\nu_1}(\mathbf{Q})+\hbar\omega_1][E^{(BO)}_{gv}(\mathbf{Q})-\mathcal{E}_{\epsilon_2\nu_2}(\mathbf{Q})+\hbar\omega_1+\hbar\omega_2]}\\
&\times\Bigg[\frac{\langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})\rangle}{E^{(BO)}_{e_1}(\mathbf{Q})-E^{(BO)}_{g}(\mathbf{Q})}(\Lambda^{(0)}_{ge_1}\,\langle\,\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})|\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})\rangle\\
&+\sqrt{2}\Lambda^{(1)}_{ge_1}\,\langle\,\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})|\theta_{e_1\nu_1+1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})\rangle+\Lambda^{(0)}_{ge_1}\,\langle\,\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})|\theta_{e_1\nu_1-1}(\mathbf{Q}\\
&-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})\rangle)\,\langle\,\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi^{(BO)}_{e_2}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}\\
&+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle+\;\langle\,\Phi^{(BO)}_{g}(\mathbf{q},\mathbf{Q})|\mu_m|\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\rangle\,\langle\,\theta_{gv}(\mathbf{Q}-\mathbf{Q}^{(0)}_{g})|\theta_{e_1\nu_1}(\mathbf{Q}\\
&-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})\rangle\,\langle\,\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})|\mu_n|\Phi^{(BO)}_{e_1}(\mathbf{q},\mathbf{Q})\rangle\frac{1}{E^{(BO)}_{e_2}(\mathbf{Q})-E^{(BO)}_{e_1}(\mathbf{Q})}(\Lambda^{(0)}_{e_1e_2}\,\langle\,\theta_{e_1\nu_1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}\\
&-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}+\delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_2}-\delta\mathbf{Q}^{(0)}_{e_2},\omega_{e_2}+\delta\Omega_{e_2})\rangle+\sqrt{2}\Lambda^{(1)}_{e_1e_2}\,\langle\,\theta_{e_1\nu_1+1}(\mathbf{Q}-\mathbf{Q}^{(0)}_{e_1}-\delta\mathbf{Q}^{(0)}_{e_1},\omega_{e_1}
\end{aligned}
$$

$$+ \delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q} - \mathbf{Q}_{e_2}^{(0)} - \delta\mathbf{Q}_{e_2}^{(0)}, \omega_{e_2} + \delta\Omega_{e_2})\rangle + \Lambda_{e_1e_2}^{(1)} \langle \theta_{e_1\nu_1-1}(\mathbf{Q} - \mathbf{Q}_{e_1}^{(0)} - \delta\mathbf{Q}_{e_1}^{(0)}, \omega_{e_1} + \delta\Omega_{e_1})|\theta_{e_2\nu_2}(\mathbf{Q} - \mathbf{Q}_{e_2}^{(0)} - \delta\mathbf{Q}_{e_2}^{(0)}, \omega_{e_2} + \delta\Omega_{e_2})\rangle\rangle\Bigg]. \tag{C8}$$

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