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Theoretical description of steady-state sum-frequency generation in molecular adsorbates

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In this paper, we present a density-matrix formalism for treating second-order sum-frequency generation (SFG) and difference-frequency generation (DFG). The theory can treat both steady-state and time-resolved SFG and DFG. However, only the steady-state SFG will be described in this paper. As a practical application, we show how the theory can be applied to study the infrared-visible SFG. The band-shape function of SFG is derived, which consists of both real and imaginary parts. The real part of the SFG band-shape function is related to the infrared spectral band-shape function and the imaginary part is related to the real part by Kramers-Krönig relations. The temperature effect on SFG is taken into account in our expression of the SFG band-shape function. We show that for a vibrational mode to be SFG active in infrared-visible SFG measurements, it has to be both infrared and Raman active.

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I. INTRODUCTION

The surfaces and the bulk of a medium generally have different structural symmetries. Therefore, their optical responses often obey different selection rules. Accordingly, optical probes could be made surface specific. This is particularly obvious with second-order nonlinear optical processes [1]. Infrared-visible sum-frequency generation (SFG), as a surface vibrational spectroscopic technique, has been demonstrated [2–7]. As pointed out by Burstein and his co-workers [5–7], surface SFG is ideal for probing surface or interface states of metals and semiconductors. Using SFG, they were able to identify an interface state resulting from the CaF_2/Si(111) interface, formed by epitaxial growth. They have also used SFG to study surface states on Cu(110) and observed anisotropic transitions consistent with the prediction from the anisotropic surface structure of Cu(110). The recent experiments on vibrational energy and coherence relaxations observed on adsorbed molecular compounds constitute an important tool to study the dynamical processes taking place between the adsorbates and the surfaces [8–13]. Former measurements of the vibrational relaxation lifetime, obtained from spectral analysis [14], were misleading because of the dominating contribution to the infrared linewidth of an adsorbate vibration provided by the pure dephasing processes [15]. To circumvent this difficulty, vibrational relaxation lifetimes have been determined by using the transient bleaching method in conjunction with the sum-frequency generation [16]. While measurements of population and relaxation rates have first been performed in semiconductor surfaces by free-induction decay and photon echo experiments to probe the coherence of H adsorbed on Si(111) [17], it is just quite recently that the first measurement of a vibrational coherent transient of CO adsorbed on a metal surface of Cu(111) has been realized [18]. This is because of the higher time resolution needed for the metal surfaces. In addition, it should be mentioned that the SFG spectrum displays interferences which are induced by the cross terms between the resonant and nonresonant contributions of the second-order susceptibility [19–21]. These interferences enable the determination of the relative amplitude and the phase of the resonant and nonresonant parts. From the spectral analysis of these interferences [18], the band center and the linewidth of the vibrational resonance of the surface SFG spectrum of CO on Cu(111) are consistent with the results obtained in reflection-absorption infrared spectroscopy experiments [22].

Recently, infrared-visible SFG has been used by Chin *et al.* [23] to obtain vibrational spectra of hydrogen on diamond C(111). They found that from a fully relaxed (1×1) surface, a single sharp peak of approximately 2830 cm^{-1} was observed, which can be identified as the CH stretch mode from H on-top sites and with the surface freshly transformed from (2×1) to (1×1). However, another peak at a higher frequency was detected, which is attributed to H adsorbed on a metastable (1×1) structure. It appears that, although the general expression for steady-state SFG is available [1], detailed expressions of SFG, which treat infrared-visible SFG and provide the band-shape functions of SFG for studying the temperature effect and selection rules for SFG, are needed. It is the main purpose of this paper to provide this information. In Sec. II, we present the general formalism required to describe the SFG process for molecules adsorbed on surfaces and undergoing relaxation and dephasing processes. Then, in Sec. III, we give the theoretical descriptions of SFG and difference-frequency generation (DFG) in the steady-state regime and establish the expressions of the second-order susceptibility for these

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processes. Section IV is dedicated to the determination of the band-shape function of the SFG signal. The resonant and nonresonant contributions are evaluated in the framework of the adiabatic approximation for the adsorbed system. Finally, in Sec. V, we give a general discussion of the results as well as some numerical calculations.

II. GENERAL CONSIDERATIONS

It has been shown that the density matrix $\rho(t)$ for a system embedded in a heat bath can be expressed as [24]

$$\begin{aligned}\frac{\partial\rho(t)}{\partial t}&=-\frac{i}{\hbar}L_0\rho(t)-\Gamma\rho(t)-\frac{i}{\hbar}[V(t),\rho(t)]\\&=-\frac{i}{\hbar}L_0'\rho(t)-\frac{i}{\hbar}L_v(t)\rho(t)\ ,\end{aligned}\tag{2.1}$$

where $L_0'=L_0-i\hbar\Gamma$. Here L_0 denotes the Liouville operator of the free system, Γ represents the damping operator describing the interaction between the system and the heat bath, and $V(t)$ is the interaction between the system and the radiation fields. In the dipole approximation, $V(t)$ is given by

$$V(t)=-\boldsymbol{\mu}\cdot\mathbf{E}_1(t)-\boldsymbol{\mu}\cdot\mathbf{E}_2(t)\ ,\tag{2.2}$$

where $\boldsymbol{\mu}$ is the dipole operator and $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$ denote the radiation fields. Also, $L_v(t)$ stands for its corresponding Liouvillian. As usual, by making the substitution

$$\rho(t)=e^{-(i/\hbar)L_0't}\sigma(t)\ ,\tag{2.3}$$

the dynamical evolution, previously given by Eq. (2.1), becomes

$$\frac{\partial\sigma(t)}{\partial t}=-\frac{i}{\hbar}\bar{L}_v(t)\sigma(t)\ ,\tag{2.4}$$

where the notation

$$\bar{L}_v(t)=e^{(i/\hbar)L_0't}L_v(t)e^{-(i/\hbar)L_0't}\tag{2.5}$$

has been introduced. It follows that

$$\sigma(t)=\sigma_i-\frac{i}{\hbar}\int_{t_i}^{t}d\tau\,\bar{L}_v(\tau)\sigma(\tau)\ ,\tag{2.6}$$

where σ_i denotes the value of $\sigma(t)$ at $t=t_i$. As long as the radiation-matter interaction is weak enough, the solution can be expanded perturbatively. The contributions to different orders are obtained straightforwardly. The second-order term, of particular interest here, can be written as

$$\sigma^{(2)}(t)=-\frac{1}{\hbar^2}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\bar{L}_v(\tau_1)\bar{L}_v(\tau_2)\sigma_i\ .\tag{2.7}$$

For the SFG process under investigation here, we are concerned with the calculations of the second-order polarization

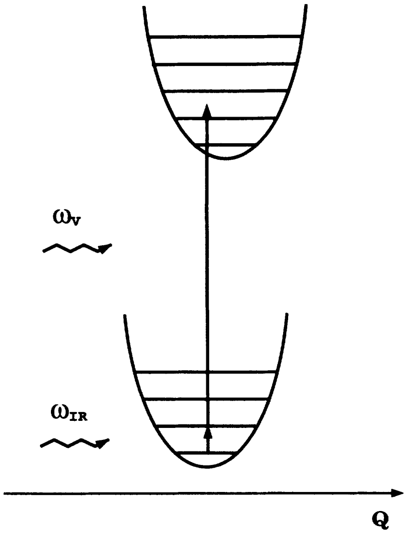

FIG. 1. Level scheme of the electronic and vibrational configurations involved in the SFG process. The infrared beam with frequency $\omega_1=\omega_{\rm ir}$ excites the vibrational states of the ground electronic configuration while the electronic transition is induced by the visible beam with frequency $\omega_2=\omega_V$.

$$\mathbf{P}^{(2)}(t)=\mathrm{Tr}\{\rho^{(2)}(t)\boldsymbol{\mu}\}\ ,\tag{2.8}$$

where $\rho^{(2)}(t)=\exp\{-(i/\hbar)L_0't\}\sigma^{(2)}(t)$. We restrict our description to systems having no diagonal matrix element of the dipole moment. It should be noted that the above results can be applied to both steady-state and transient phenomena. For the steady-state case, the system is assumed to be, at the initial time t_i, in the Boltzmann equilibrium distribution. On the other hand, for the transient case of nonoverlapping laser pulses, σ_i is determined by the preparation of the system by the pumping laser. Notice that

$$\mathbf{P}^{(2)}(t)=\sum_k\sum_l[e^{-i\omega_{kl}'t}\sigma_{kl}^{(2)}(t)\boldsymbol{\mu}_{lk}+\mathrm{c.c.}]\ ,\tag{2.9}$$

where the symbol c.c. stands for the complex conjugate part and ω_{kl}' for the diagonal matrix elements of the Liouvillian L_0', as long as $k\neq l$. Also, we have

$$\begin{aligned}\sigma_{kl}^{(2)}(t)=-\frac{1}{\hbar^2}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\sum_p\{&\bar{V}_{kp}(\tau)[\bar{L}_v(\tau')\sigma_i]_{pl}\\&-[\bar{L}_v(\tau')\sigma_i]_{kp}\bar{V}_{pl}(\tau)\}\ .\end{aligned}\tag{2.10}$$

With the quantity

$$\bar{V}_{kp}(\tau)=e^{i\omega_{kp}'\tau}V_{kp}(\tau)\ ,\tag{2.11}$$

the density-matrix elements take the explicit form

$$\sigma_{kl}^{(2)}(t)=-\frac{1}{\hbar^2}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\sum_p\sum_q\{\bar{V}_{kp}(\tau)[\bar{V}_{pq}(\tau')\sigma_{iql}-\sigma_{ipq}\bar{V}_{ql}(\tau')]+\bar{V}_{pl}(\tau)[\sigma_{ikq}\bar{V}_{qp}(\tau')-\bar{V}_{kq}(\tau')\sigma_{iqp}]\}\tag{2.12}$$

if the matrix elements of the initial density matrix are not necessarily diagonal.

The results obtained in this section are general and can be applied to second-harmonic generation or sum- and difference-frequency generation. In this paper, we shall focus on the treatment of steady-state SFG. But any other case could be described along the same lines, if required.

III. THEORETICAL DESCRIPTION OF STEADY-STATE SFG AND DFG

In the following, we shall consider the model depicted in Fig. 1. It involves two electronic configurations associated with a vibrational structure made of a set of modes. The applied fields couple either states of different electronic configurations or vibrational states of the same electronic configuration. Therefore, the corresponding field frequencies are in the visible or the infrared frequency range, respectively.

In this case, assuming that there is no coherence preexisting on the molecular system, its initial density matrix is diagonal and Eq. (2.12) becomes

$$\sigma_{kl}^{(2)}(t)=-\frac{1}{\hbar^2}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\sum_{g}\sum_{p}\sigma_{igg}\{\bar{V}_{kp}(\tau)[\bar{V}_{pg}(\tau')\delta_{gl}-\bar{V}_{gl}(\tau')\delta_{gp}]+\bar{V}_{pl}(\tau)[\bar{V}_{gp}(\tau')\delta_{kg}-\bar{V}_{kg}(\tau')\delta_{gp}]\}\ . \tag{3.1}$$

From expression (3.1), it is quite easy to deduce the polarization required to evaluate the SFG signal. It takes the form

$$\mathbf{P}^{(2)}(t)=-\frac{1}{\hbar^2}\sum_{g,p,k,l}\sigma_{igg}e^{-i\omega'_{kl}t}\boldsymbol{\mu}_{lk}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\{\bar{V}_{kp}(\tau)[\bar{V}_{pg}(\tau')\delta_{gl}-\bar{V}_{gl}(\tau')\delta_{gp}]+\bar{V}_{gp}(\tau)[\bar{V}_{gp}(\tau')\delta_{kg}-\bar{V}_{kg}(\tau')\delta_{gp}]\}+\text{c.c.} \tag{3.2}$$

As usually done in steady-state SHG [25], it will be convenient to specify the four different contributions to the polarization induced in a SFG process. This can be done by introducing

$$\mathbf{P}^{(2)}(t)=\sum_{i=1}^{4}[\mathbf{P}_i^{(2)}(t)+\text{c.c.}]\ , \tag{3.3}$$

where the various terms correspond to

$$\begin{aligned}\mathbf{P}_1^{(2)}(t)&=-\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}e^{-i\omega'_{kg}t}\boldsymbol{\mu}_{gk}\\&\quad\times\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\bar{V}_{kp}(\tau)\bar{V}_{pg}(\tau')\ ,\\\mathbf{P}_2^{(2)}(t)&=\frac{1}{\hbar^2}\sum_{g,k,l}\sigma_{igg}e^{-i\omega'_{kl}t}\boldsymbol{\mu}_{lk}\\&\quad\times\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\bar{V}_{kg}(\tau)\bar{V}_{gl}(\tau')\ ,\end{aligned} \tag{3.4}$$

$$\mathbf{P}_3^{(2)}(t)=\frac{1}{\hbar^2}\sum_{g,k,l}\sigma_{igg}e^{-i\omega'_{kl}t}\boldsymbol{\mu}_{lk}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\bar{V}_{gl}(\tau)\bar{V}_{kg}(\tau')\ ,$$

$$\mathbf{P}_4^{(2)}(t)=-\frac{1}{\hbar^2}\sum_{g,p,l}\sigma_{igg}e^{-i\omega'_{gl}t}\boldsymbol{\mu}_{lg}\int_{t_i}^{t}d\tau\int_{t_i}^{\tau}d\tau'\bar{V}_{pl}(\tau)\bar{V}_{gp}(\tau')\ .$$

Notice that the same combinations of resonant and nonresonant terms are obtained for pulsed SHG [26,27]. From the previous expressions, it can easily be shown that

$$\mathbf{P}_4^{(2)}(t)=[\mathbf{P}_1^{(2)}(t)]^* \tag{3.5}$$

and

$$\mathbf{P}_3^{(2)}(t)=[\mathbf{P}_2^{(2)}(t)]^*\ . \tag{3.6}$$

To evaluate $\mathbf{P}^{(2)}(t)$ in the general case, we shall express the electric field in the form

$$\mathbf{E}_i(t)=[\mathscr{E}_i(\omega_i)e^{-i\omega_i t}+\mathscr{E}_i(-\omega_i)e^{i\omega_i t}]\mathscr{L}_i(t)\ , \tag{3.7}$$

where $\mathscr{L}_i(t)$ denotes the pulse-shape function. For simplicity, we shall use

$$\mathscr{L}_i(t)=e^{-\gamma_i|t_p-t|}\ , \tag{3.8}$$

where $T_i=\gamma_i^{-1}$ is the pulse duration and t_p denotes the probing time chosen such that $t_p\geq t$. Substituting Eqs. (3.7) and (3.8) into the expression of the polarization terms (3.4) and rejecting strongly nonresonant contributions yields

$$\mathbf{P}_1^{(2)}(t_p)=\mathbf{P}_{1,1}^{(2)}(t_p)+\mathbf{P}_{1,2}^{(2)}(t_p)\ , \tag{3.9}$$

where

$$\mathbf{P}_{1,1}^{(2)}(t_p)=-\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{gk}\frac{\boldsymbol{\mu}_{pg}\cdot\mathscr{E}_1(\omega_1)}{i(\omega'_{pg}-\omega_1)+\gamma_1}\left[\frac{[\boldsymbol{\mu}_{kp}\cdot\mathscr{E}_2(\omega_2)]e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{kg}-\omega_1-\omega_2)+\gamma_1+\gamma_2}+\frac{[\boldsymbol{\mu}_{kp}\cdot\mathscr{E}_2(-\omega_2)]e^{-i(\omega_1-\omega_2)t_p}}{i(\omega'_{kg}-\omega_1+\omega_2)+\gamma_1+\gamma_2}\right] \tag{3.10}$$

and

$$\mathbf{P}_{1,2}^{(2)}(t_p)=-\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{gk}\frac{\boldsymbol{\mu}_{pg}\cdot\mathscr{E}_2(\omega_2)}{i(\omega'_{pg}-\omega_2)+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{kp}\cdot\mathscr{E}_1(\omega_1)]e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{kg}-\omega_1-\omega_2)+\gamma_1+\gamma_2}+\frac{[\boldsymbol{\mu}_{kp}\cdot\mathscr{E}_1(-\omega_1)]e^{i(\omega_1-\omega_2)t_p}}{i(\omega'_{kg}+\omega_1-\omega_2)+\gamma_1+\gamma_2}\right]\ . \tag{3.11}$$

Similarly, we obtain, for the other term,

$$\mathbf{P}_2^{(2)}(t_p)=\mathbf{P}_{2,1}^{(2)}(t_p)+\mathbf{P}_{2,2}^{(2)}(t_p)\ , \tag{3.12}$$

where

$$\mathbf{P}_{2,1}^{(2)}(t_p)=\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{pk}\frac{\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_1(-\omega_1)}{i(\omega'_{gp}+\omega_1)+\gamma_1}\left[\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_2(\omega_2)]e^{i(\omega_1-\omega_2)t_p}}{i(\omega'_{kp}+\omega_1-\omega_2)+\gamma_1+\gamma_2}+\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_2(-\omega_2)]e^{i(\omega_1+\omega_2)t_p}}{i(\omega'_{kp}+\omega_1+\omega_2)+\gamma_1+\gamma_2}\right] \tag{3.13}$$

and

$$\mathbf{P}_{2,2}^{(2)}(t_p)=\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{pk}\frac{\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_2(-\omega_2)}{i(\omega'_{gp}+\omega_2)+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_1(\omega_1)]e^{-i(\omega_1-\omega_2)t_p}}{i(\omega'_{kp}-\omega_1+\omega_2)+\gamma_1+\gamma_2}+\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_1(-\omega_1)]e^{i(\omega_1+\omega_2)t_p}}{i(\omega'_{kp}+\omega_1+\omega_2)+\gamma_1+\gamma_2}\right]. \tag{3.14}$$

All the other contributions can be deduced by complex conjugation from Eqs. (3.5) and (3.6). It should be noted that the expressions given by Eqs. (3.9)–(3.14) can be rearranged to get the result

$$\begin{aligned}\mathbf{P}_1^{(2)}(t_p)=&-\frac{1}{\hbar^2}\sum_{g,p,k}\frac{\sigma_{igg}\boldsymbol{\mu}_{gk}e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{kg}-\omega_1-\omega_2)+\gamma_1+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{pg}-\omega_1)+\gamma_1}+\frac{[\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{pg}-\omega_2)+\gamma_2}\right]\\&-\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{gk}\left[\frac{[\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_2(-\omega_2)]e^{-i(\omega_1-\omega_2)t_p}}{[i(\omega'_{pg}-\omega_1)+\gamma_1][i(\omega'_{kg}-\omega_1+\omega_2)+\gamma_1+\gamma_2]}\right.\\&\left.+\frac{[\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_2(\omega_2)][\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_1(-\omega_1)]e^{i(\omega_1-\omega_2)t_p}}{[i(\omega'_{pg}-\omega_2)+\gamma_2][i(\omega'_{kg}+\omega_1-\omega_2)+\gamma_1+\gamma_2]}\right].\end{aligned} \tag{3.15}$$

Similarly, the second contribution can be reorganized into the form

$$\begin{aligned}\mathbf{P}_2^{(2)}(t_p)=&\frac{1}{\hbar^2}\sum_{g,p,k}\frac{\sigma_{igg}\boldsymbol{\mu}_{pk}e^{i(\omega_1+\omega_2)t_p}}{i(\omega'_{kp}+\omega_1+\omega_2)+\gamma_1+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_2(-\omega_2)][\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_1(-\omega_1)]}{i(\omega'_{gp}+\omega_1)+\gamma_1}+\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_1(-\omega_1)][\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_2(-\omega_2)]}{i(\omega'_{gp}+\omega_2)+\gamma_2}\right]\\&+\frac{1}{\hbar^2}\sum_{g,p,k}\sigma_{igg}\boldsymbol{\mu}_{pk}\left[\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_2(\omega_2)][\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_1(-\omega_1)]e^{i(\omega_1-\omega_2)t_p}}{[i(\omega'_{gp}+\omega_1)+\gamma_1][i(\omega'_{kp}+\omega_1-\omega_2)+\gamma_1+\gamma_2]}\right.\\&\left.+\frac{[\boldsymbol{\mu}_{kg}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{gp}\cdot\mathcal{E}_2(-\omega_2)]e^{-i(\omega_1-\omega_2)t_p}}{[i(\omega'_{gp}+\omega_2)+\gamma_2][i(\omega'_{kp}-\omega_1+\omega_2)+\gamma_1+\gamma_2]}\right].\end{aligned} \tag{3.16}$$

Notice that the terms such as $\exp\{\pm i(\omega_1+\omega_2)t\}$ contribute to SFG, while the terms such as $\exp\{\pm i(\omega_1-\omega_2)t\}$ contribute to DFG.

For infrared-visible SFG, ω_1 denotes the infrared frequency, while ω_2 denotes the visible frequency. Therefore, for the particular combination $\exp\{-i(\omega_1+\omega_2)t\}$, only one term of $\mathbf{P}_1^{(2)}(t_p)$ contributes and none of $[\mathbf{P}_1^{(2)}(t_p)]^*$. This polarization term reduces to

$$\mathbf{P}_1^{(2)}(\omega_1+\omega_2;t_p)=-\frac{2}{\hbar^2}\sum_{g,p,k}\frac{\sigma_{igg}\boldsymbol{\mu}_{gk}e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{kg}-\omega_1-\omega_2)+\gamma_1+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{pg}-\omega_1)+\gamma_1}+\frac{[\boldsymbol{\mu}_{kp}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{pg}-\omega_2)+\gamma_2}\right]. \tag{3.17}$$

Similarly, among the terms of $\mathbf{P}_2^{(2)}(t_p)$ and $[\mathbf{P}_2^{(2)}(t_p)]^*$, only one term contributes to the same combination and it arises from $[\mathbf{P}_2^{(2)}(t_p)]^*$. Again, this contribution takes the form

$$[\mathbf{P}_2^{(2)}(\omega_1+\omega_2;t_p)]^*=\frac{2}{\hbar^2}\sum_{g,p,k}\frac{\sigma_{igg}\boldsymbol{\mu}_{kp}e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{pk}-\omega_1-\omega_2)+\gamma_1+\gamma_2}\left[\frac{[\boldsymbol{\mu}_{gk}\cdot\mathcal{E}_2(\omega_2)][\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_1(\omega_1)]}{i(\omega'_{pg}-\omega_1)+\gamma_1}+\frac{[\boldsymbol{\mu}_{gk}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{pg}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{pg}-\omega_2)+\gamma_2}\right]. \tag{3.18}$$

The second terms in the square bracket of Eqs. (3.17) and (3.18) are less important because they are off resonance. In the present case, states $\{|p\rangle\}$ and $\{|g\rangle\}$ belong to the same electronic configuration, which is the ground electronic configuration, and states $\{|k\rangle\}$ belong to the excited electronic configuration. In the adiabatic approximation [28], we have

$$|g\rangle \rightarrow |gv\rangle\ , \quad |p\rangle \rightarrow |gv'\rangle\ , \quad |k\rangle \rightarrow |eu\rangle\ . \tag{3.19}$$

The polarization terms result in the form

$$\mathbf{P}_1^{(2)}(\omega_1+\omega_2;t_p) = -\frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \frac{\sigma_{igvgv}\boldsymbol{\mu}_{gveu}e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{eugv}-\omega_1-\omega_2)+\gamma_1+\gamma_2} \times \left[\frac{[\boldsymbol{\mu}_{gv'gv}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{eugv'}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{gv'gv}-\omega_1)+\gamma_1} + \frac{[\boldsymbol{\mu}_{eugv'}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{gv'gv}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{gv'gv}-\omega_2)+\gamma_2} \right], \tag{3.20}$$

and similarly

$$[\mathbf{P}_2^{(2)}(\omega_1+\omega_2;t_p)]^* = \frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \frac{\sigma_{igvgv}\boldsymbol{\mu}_{eugv'}e^{-i(\omega_1+\omega_2)t_p}}{i(\omega'_{gv'eu}-\omega_1-\omega_2)+\gamma_1+\gamma_2} \times \left[\frac{[\boldsymbol{\mu}_{gv'gv}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{gveu}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{gv'gv}-\omega_1)+\gamma_1} + \frac{[\boldsymbol{\mu}_{gveu}\cdot\mathcal{E}_1(\omega_1)][\boldsymbol{\mu}_{gv'gv}\cdot\mathcal{E}_2(\omega_2)]}{i(\omega'_{gv'gv}-\omega_2)+\gamma_2} \right]. \tag{3.21}$$

We shall introduce the components of the second-order susceptibility defined by

$$P_k^{(2)}(t_p) = \sum_i \sum_j \chi_{ijk}^{(2)}(\omega_1+\omega_2)E_{1i}(\omega_1)E_{2j}(\omega_2)e^{-i(\omega_1+\omega_2)t_p}\ , \tag{3.22}$$

where E_{ni} represents the ith component of field n and

$$\chi_{ijk}^{(2)}(\omega_1+\omega_2) = \chi_{1,ijk}^{(2)}(\omega_1+\omega_2) + \chi_{2,ijk}^{(2)}(\omega_1+\omega_2) \tag{3.23}$$

if the contributions are given by

$$\chi_{1,ijk}^{(2)}(\omega_1+\omega_2) = -\frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \frac{\sigma_{igvgv}\mu_{gveu}(k)}{i(\omega'_{eugv}-\omega_1-\omega_2)+\gamma_1+\gamma_2} \left[\frac{\mu_{gv'gv}(i)\mu_{eugv'}(j)}{i(\omega'_{gv'gv}-\omega_1)+\gamma_1} + \frac{\mu_{eugv'}(i)\mu_{gv'gv}(j)}{i(\omega'_{gv'gv}-\omega_2)+\gamma_2} \right], \tag{3.24}$$

and similarly

$$\chi_{2,ijk}^{(2)}(\omega_1+\omega_2) = \frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \frac{\sigma_{igvgv}\mu_{eugv'}(k)}{i(\omega'_{gv'eu}-\omega_1-\omega_2)+\gamma_1+\gamma_2} \left[\frac{\mu_{gv'gv}(i)\mu_{gveu}(j)}{i(\omega'_{gv'gv}-\omega_1)+\gamma_1} + \frac{\mu_{gveu}(i)\mu_{gv'gv}(j)}{i(\omega'_{gv'gv}-\omega_2)+\gamma_2} \right]. \tag{3.25}$$

Here higher-order terms have been neglected. Also, the notation $\mu_{gveu}(i)$ has been introduced, where i denotes the ith component of $\boldsymbol{\mu}_{gveu}$.

In the infrared-visible SFG, the frequency ω_1 is chosen to be in the infrared frequency range, so that $\omega_1 \simeq \omega_{gv'gv}$. In this case, the second-order term in Eqs. (3.24) and (3.25) is negligible and we get, for the first contribution,

$$\chi_{1,ijk}^{(2)}(\omega_1+\omega_2) = -\frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \sigma_{igvgv} \frac{\langle\Theta_{gv}|\mu_{ge}(k)|\Theta_{eu}\rangle\langle\Theta_{eu}|\mu_{eg}(j)|\Theta_{gv'}\rangle\langle\Theta_{gv'}|\mu_{gg}(i)|\Theta_{gv}\rangle}{[i(\omega'_{eugv}-\omega_1-\omega_2)+\gamma_1+\gamma_2][i(\omega'_{gv'gv}-\omega_1)+\gamma_1]}\ , \tag{3.26}$$

and for the second contribution,

$$\chi_{2,ijk}^{(2)}(\omega_1+\omega_2) = \frac{2}{\hbar^2}\sum_e \sum_{v,v',u} \sigma_{igvgv} \frac{\langle\Theta_{eu}|\mu_{eg}(k)|\Theta_{gv'}\rangle\langle\Theta_{gv'}|\mu_{gg}(i)|\Theta_{gv}\rangle\langle\Theta_{gv}|\mu_{ge}(j)|\Theta_{eu}\rangle}{[i(\omega'_{gv'eu}-\omega_1-\omega_2)+\gamma_1+\gamma_2][i(\omega'_{gv'gv}-\omega_1)+\gamma_1]}\ , \tag{3.27}$$

where Θ_{gv} and Θ_{eu} denote the vibrational wave functions of the ground and excited electronic states. Because the field frequency ω_2 is not in resonance with the electronic transition, we can use the Placzek approximation [28]. We obtain

$$\chi_{1,ijk}^{(2)}(\omega_1+\omega_2) = \frac{2i}{\hbar}\sum_{v,v'} \sigma_{igvgv} \frac{\langle\Theta_{gv}|\alpha_{1g}(k,j)|\Theta_{gv'}\rangle\langle\Theta_{gv'}|\mu_{gg}(i)|\Theta_{gv}\rangle}{i(\omega_{gv'gv}-\omega_1)+\Gamma_{gv'gv}+\gamma_1}\ , \tag{3.28}$$

and for the second contribution

$$\chi_{2,ijk}^{(2)}(\omega_1+\omega_2) = \frac{2i}{\hbar}\sum_{v,v'} \sigma_{igvgv} \frac{\langle\Theta_{gv}|\alpha_{2g}(k,j)|\Theta_{gv'}\rangle\langle\Theta_{gv'}|\mu_{gg}(i)|\Theta_{gv}\rangle}{i(\omega_{gv'gv}-\omega_1)+\Gamma_{gv'gv}+\gamma_1}\ . \tag{3.29}$$

Therefore the second-order susceptibility for the SFG process can be written in the form

$$\chi^{(2)}_{ijk}(\omega_1+\omega_2)=\frac{2i}{\hbar}\sum_{v,v'}\sigma_{igvgv}\frac{\langle\Theta_{gv}|\alpha_g(k,j)|\Theta_{gv'}\rangle\langle\Theta_{gv'}|\mu_{gg}(i)|\Theta_{gv}\rangle}{i(\omega_{gv'gv}-\omega_1)+\Gamma_{gv'gv}+\gamma_1}\ . \tag{3.30}$$

where $\Gamma_{gv'gv}$ denotes the vibrational dephasing constant, and we have

$$\alpha_{1g}(k,j)=\frac{1}{\hbar}\sum_e\frac{\mu_{ge}(k)\mu_{eg}(j)}{\omega_{eg}-\omega_1-\omega_2}\ ,$$
$$\alpha_{2g}(k,j)=\frac{1}{\hbar}\sum_e\frac{\mu_{ge}(j)\mu_{eg}(k)}{\omega_{eg}+\omega_1+\omega_2}\ . \tag{3.31}$$

It should be noted that

$$\alpha_g(k,j)=\alpha_{1g}(k,j)+\alpha_{2g}(k,j)$$
$$=\frac{1}{\hbar}\sum_e\left[\frac{\mu_{ge}(k)\mu_{eg}(j)}{\omega_{eg}-\omega_1-\omega_2}+\frac{\mu_{ge}(j)\mu_{eg}(k)}{\omega_{eg}+\omega_1+\omega_2}\right]\ , \tag{3.32}$$

which is the conventional optical polarizability. Expanding $\alpha_g(k,j)$ and $\mu_{gg}(i)$ in terms of vibrational coordinates Q_l, we get

$$\mu_{gg}(i)=\mu_{gg}^{(0)}(i)+\sum_l\left[\frac{\partial\mu_{gg}(i)}{\partial Q_l}\right]_0 Q_l+\cdots\ ,$$
$$\alpha_g(k,j)=\alpha_g^{(0)}(k,j)+\sum_l\left[\frac{\partial\alpha_g(k,j)}{\partial Q_l}\right]_0 Q_l+\cdots\ . \tag{3.33}$$

From these expansions, the second-order susceptibility takes the form

$$\chi^{(2)}_{ijk}(\omega_1+\omega_2)=\frac{2i}{\hbar}\sum_{v,v'}\sum_l\sigma_{igvgv}\left[\frac{\partial\alpha_g(k,j)}{\partial Q_l}\right]_0\left[\frac{\partial\mu_{gg}(i)}{\partial Q_l}\right]_0\times\frac{|\langle\Theta_{gv}|Q_l|\Theta_{gv'}\rangle|^2}{[i(\omega_{gv'gv}-\omega_1)+\Gamma_{gv'gv}+\gamma_1]}\ . \tag{3.34}$$

Equation (3.34) indicates that for a vibrational mode to be observed in infrared-visible SFG (i.e., SFG active), that particular mode has to be both infrared and Raman active, that is,

$$\left[\frac{\partial\mu_{gg}(i)}{\partial Q_l}\right]_0\neq 0 \tag{3.35}$$

and

$$\left[\frac{\partial\alpha_g(k,j)}{\partial Q_l}\right]_0\neq 0\ . \tag{3.36}$$

Therefore, the infrared-visible SFG can be used to determine Raman scattering cross section and infrared absorption cross section and vice versa.

In infrared-visible SFG measurements, the picosecond laser pulses are commonly used. The contribution of the laser pulse width in this case may not be negligible, as can be seen from Eq. (3.34). In other words, the observed linewidth can be contributed from $\Gamma_{gv'gv}$ and γ_1. In particular, if the temperature effect is negligible (see Sec. IV) and Q_l is harmonic, then Eq. (3.34) reduces to

$$\chi^{(2)}_{ijk}(\omega_1+\omega_2)=\frac{2}{\hbar}\sum_l\frac{\left[\frac{\partial\alpha_g(k,j)}{\partial Q_l}\right]_0\left[\frac{\partial\mu_{gg}(i)}{\partial Q_l}\right]_0|\langle\Theta_{g0}|Q_l|\Theta_{g1}\rangle|^2}{\omega_{g1g0}-\omega_1-i(\Gamma_{g1g0}+\gamma_1)} \tag{3.37}$$

In fact, Eq. (3.37) shows that if various vibrational bands do not overlap, the SFG band shape is approximately related to that of infrared spectra. The restriction to nonoverlaping bands comes from the fact that $\alpha_g(k,j)$ involves a summation over the excited electronic configurations. For this reason, this equation has been used by Shen and his co-workers in analyzing their SFG data [2–4,23] in the form

$$\chi^{(2)}_{ijk}(\omega_1+\omega_2)=\sum_l\frac{\mathcal{A}_l}{\omega_{g1g0}-\omega_1-i\Gamma_{g1g0}}\ , \tag{3.38}$$

where

$$\mathcal{A}_l=\frac{2}{\hbar}\left[\frac{\partial\alpha_g(k,j)}{\partial Q_l}\right]_0\left[\frac{\partial\mu_{gg}(i)}{\partial Q_l}\right]_0\ . \tag{3.39}$$

It should be noted that in Eq. (3.38), the pulse-width contribution γ_1^{-1} has been ignored.

IV. BAND-SHAPE FUNCTIONS IN SFG EXPERIMENTS

Due to the fact that, in infrared-visible experiments, the SFG active mode interacts with either local modes or phonon modes, or both, the observed SFG band shape cannot be described by a single Lorentzian. In this section, we shall evaluate explicitly the band-shape function obtained in a sum-frequency generation experiment. For this purpose, we define the SFG band-shape function $\mathcal{F}_l(\omega_1)$ for the lth mode by

$$\mathcal{F}_l(\omega_1)=\sum_{v}\sum_{v'}\sigma_{igvgv}\frac{|\langle\Theta_{gv}|Q_l|\Theta_{gv'}\rangle|^2}{i(\omega_{gv'gv}-\omega_1)+\overline{\Gamma}_{gv'gv}}\ , \tag{4.1}$$

where $\overline{\Gamma}_{gv'gv}=\Gamma_{gv'gv}+\gamma_1$ and σ_{igvgv} represents the Boltzmann distribution

$$\sigma_{igvgv}=\frac{e^{-E_{gv}/kT}}{Z}\ ,\quad Z=\sum_{v'}e^{-E_{gv'}/kT}\ . \tag{4.2}$$

If we introduce the real and the imaginary parts, noted $\mathrm{Re}\{\mathcal{F}_l(\omega_1)\}$ and $\mathrm{Im}\{\mathcal{F}_l(\omega_1)\}$, respectively, we have

$$\mathcal{F}_l(\omega_1)=\mathrm{Re}\{\mathcal{F}_l(\omega_1)\}+i\,\mathrm{Im}\{\mathcal{F}_l(\omega_1)\}\ , \tag{4.3}$$

where

$$\begin{aligned}\mathrm{Re}\{\mathcal{F}_l(\omega_1)\}&=\sum_{vv'}\sigma_{igvgv}\overline{\Gamma}_{gv'gv}\frac{|\langle\Theta_{gv}|Q_l|\Theta_{gv'}\rangle|^2}{(\omega_{gv'gv}-\omega_1)^2+\overline{\Gamma}^2_{gv'gv}}\ ,\\ \mathrm{Im}\{\mathcal{F}_l(\omega_1)\}&=\sum_{vv'}\sigma_{igvgv}(\omega_1-\omega_{gv'gv})\\ &\quad\times\frac{|\langle\Theta_{gv}|Q_l|\Theta_{gv'}\rangle|^2}{(\omega_{gv'gv}-\omega_1)^2+\overline{\Gamma}^2_{gv'gv}}\ .\end{aligned} \tag{4.4}$$

Here $\mathrm{Re}\{\mathcal{F}_l(\omega_1)\}$ is the infrared band-shape function in the long pulse limit, or, equivalently, in the limit $\gamma_1\to 0$, and $\mathrm{Im}\{\mathcal{F}_l(\omega_1)\}$ is related to $\mathrm{Re}\{\mathcal{F}_l(\omega_1)\}$ by the usual Kramers-Kronig relations.

In infrared-visible SFG measurements, the frequency of an observed SFG mode is usually much higher than the frequencies of local modes and phonon modes. In this case, the adiabatic approximation can be used to separate the "system" modes from the "bath" modes [29–37].

This adiabatic approximation theory will be applied to treat the SFG band-shape function. Note that the Hamiltonian operator of the total system consisting of intramolecular vibration, the SFG active mode H_M^0, heat bath vibrations H_L^0, and interaction between these two motions H_{ML} is given by

$$H=H_M^0+H_L^0+H_{ML}\ , \tag{4.5}$$

where

$$H_M^0=-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_l^2}+\frac{1}{2}\omega_l^2Q_l^2\ . \tag{4.6}$$

Next we expand H_{ML} in terms of Q_l to get

$$H_{ML}=H_{ML}(0)+\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0 Q_l+\frac{1}{2}\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2}\right]_0 Q_l^2+\cdots\ . \tag{4.7}$$

To solve the Schrödinger equation for H, we shall use the adiabatic approximation. To this end, we separate the intramolecular vibration of high-frequency from low-frequency local or phonon modes. On the basis of the adiabatic approximation, we first solve the Schrödinger equation for the intramolecular vibration

$$\begin{aligned}&\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_l^2}+\frac{1}{2}\omega_l^2Q_l^2+\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0 Q_l\right.\\ &\qquad\left.+\frac{1}{2}\left[\frac{\partial^2 H_{mL}}{\partial Q_l^2}\right]_0 Q_l^2+\cdots\right]\Phi_{v_l}=U_{v_l}\Phi_{v_l}\ ,\end{aligned} \tag{4.8}$$

where the notation

$$U_{v_l}=(v_l+\tfrac{1}{2})\hbar\omega_l'-\frac{1}{2\omega_l'^2}\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0^2 \tag{4.9}$$

has been introduced, as well as

$$\omega_l'^2=\omega_l^2+\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2}\right]_0\ . \tag{4.10}$$

To the lower order in H_{ML}, the expression of U_{v_l} can be written as

$$\begin{aligned}U_{v_l}&=(v_l+\tfrac{1}{2})\hbar\omega_l-\frac{1}{2\omega_l^2}\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0^2\\ &\quad+\frac{(v_l+\frac{1}{2})\hbar}{2\omega_l}\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2}\right]_0+\cdots\end{aligned} \tag{4.11}$$

and will play the role of a potential energy for the motion of the low-frequency modes.

Then we consider the Schrödinger equation for the low-frequency motion. Its Hamiltonian in the v_lth intramolecular vibrational state can be expressed as

$$H_{v_l}=H_L^0+H_{ML}(0)+U_{v_l} \tag{4.12}$$

and

$$H_{v_l}\Psi_{v_l,n}=E_{v_l,n}\Psi_{v_l,n}\ . \tag{4.13}$$

Substituting Eq. (4.11) into Eq. (4.12) yields

$$H_{v_l}=H_L^0+(v_l+\tfrac{1}{2})\hbar\omega_l+V_{v_l,L}\ , \tag{4.14}$$

where the notation

$$\begin{aligned}V_{v_l,L}&=H_{ML}(0)-\frac{1}{2\omega_l^2}\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0^2\\ &\quad+\frac{(v_l+\frac{1}{2})\hbar}{2\omega_l}\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2}\right]_0+\cdots\end{aligned} \tag{4.15}$$

is introduced. We shall let $\{q_i\}$ represent the vibrational coordinates of the heat bath modes. Suppose that

$$\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2}\right]_0=\alpha+\sum_i\alpha_iq_i+\cdots\ . \tag{4.16}$$

Again, substituting Eq. (4.16) into Eq. (4.15) yields

$$\begin{aligned}V_{v_l,L}&=H_{ML}(0)-\frac{1}{2\omega_l^2}\left[\frac{\partial H_{ML}}{\partial Q_l}\right]_0^2\\ &\quad+\frac{(v_l+\frac{1}{2})\hbar\alpha}{2\omega_l}+\frac{(v_l+\frac{1}{2})\hbar}{2\omega_l}\sum_i\alpha_iq_i+\cdots\ .\end{aligned} \tag{4.17}$$

If H_L^0 is given by

$$H_L^0=\sum_i \left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_i^2}+\frac{1}{2}\omega_i^2 q_i^2 \right] , \tag{4.18}$$

the solution of Eq. (4.13) can be expressed as

$$\begin{aligned} E_{v_l,n}=&(v_l+\tfrac{1}{2})\hbar \left[\frac{\alpha}{\omega_l}+\omega_l \right] +\sum_i (n_i+\tfrac{1}{2})\hbar\omega_i \\ &+H_{ML}^0-\frac{1}{2\omega_l^2}\left[\frac{\partial H_{ML}}{\partial Q_l} \right]_0^2 \\ &-(v_l+\tfrac{1}{2})^2\sum_i \frac{\hbar^2\alpha_i^2}{8\omega_i^2\omega_l^2}+\dots \end{aligned} \tag{4.19}$$

and

$$\Psi_{v_l,n}=\prod_i \chi_{v_l,n_i}(q_i') , \tag{4.20}$$

where q_i' and Δq_i stand for

$$q_i'=q_i+\Delta q_i \; , \quad \Delta q_i=\frac{(v_l+\frac{1}{2})\hbar\alpha_i}{2\omega_i^2\omega_l} . \tag{4.21}$$

That is, Δq_i denotes the normal coordinate displacement induced by H_{ML}. It should be noted that α_i describes the spectral shift of the intramolecular vibration due to the heat bath effect. In the adiabatic approximation, we have

$$\Theta_{v_l,n}=\Phi_{v_l}\Psi_{v_l,n} . \tag{4.22}$$

Let us consider a particular case. We will assume, for example, that H_{ML} can be written in the form

$$H_{ML}=\tfrac{1}{2}Q_l\sum_i a_iQ_i+\frac{1}{3!}Q_l\sum_{i<j} b_{ij}q_iq_j+\frac{1}{3!}Q_l^2\sum_i b_iq_i+\dots . \tag{4.23}$$

Therefore, the previous quantities can be evaluated explicitly to give

$$H_{ML}(0)=0 ,$$

$$\left[\frac{\partial H_{ML}}{\partial Q_l} \right]_0=\frac{1}{2}\sum_i a_iq_i+\frac{1}{3!}\sum_{i<j} b_{ij}q_iq_j+\frac{1}{3}Q_l\sum_i b_iq_i+\dots ,$$

$$\left[\frac{\partial^2 H_{ML}}{\partial Q_l^2} \right]_0=\frac{1}{3}\sum_i b_iq_i+\dots . \tag{4.24}$$

In general, the term $(\partial H_{ML}/\partial Q_l)_0^2$ will affect the vibrational frequencies of the heat bath modes. In this paper, this effect will be ignored.

Now we are ready to calculate $\mathcal{F}_l(\omega_1)$. Notice that

$$\langle \Theta_{gv}|Q_l|\Theta_{gv'}\rangle=\langle \Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle\prod\nolimits_i\langle \chi_{v_l,n_i}|\chi_{v_l',n_i'}\rangle , \tag{4.25}$$

where the initial conditions are now given by

$$\sigma_{igvgv}=\prod_i P_{v_ln_i} , \tag{4.26}$$

where $P_{v_ln_i}$ denotes the Boltzmann factor of the ith low-frequency mode. Here we have neglected the temperature effect due to the intramolecular vibrational mode. If we introduce the integral representation

$$\frac{1}{i(\omega_{gv'gv}-\omega_1)+\overline{\Gamma}_{gv'gv}}=\int_0^\infty dt\, e^{-[i(\omega_{gv'gv}-\omega_1)+\overline{\Gamma}_{gv'gv}]t} \tag{4.27}$$

and substitute Eqs. (4.25)–(4.27) into Eq. (4.1), we obtain

$$\begin{aligned} \mathcal{F}_l(\omega_1)=&|\langle \Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2 \\ &\times\int_0^\infty dt\, e^{-[i(\omega_l-\omega_1)+\overline{\Gamma}]t}\prod_j \mathcal{G}_j(t) , \end{aligned} \tag{4.28}$$

where $v_l'=v_l+1$ if we retain only the resonant modes and

$$\begin{aligned} \mathcal{G}_j(t)=&\sum_{n_j}\sum_{n_j'} P_{v_l,n_j}|\langle \chi_{v_ln_j}|\chi_{v_l'n_j'}\rangle|^2 \\ &\times e^{-it[(n_j'+1/2)\omega_j-(n_j+1/2)\omega_j]} . \end{aligned} \tag{4.29}$$

In Eq. (4.28), for simplicity an average $\overline{\Gamma}$ has been introduced for $\overline{\Gamma}_{gv'gv}$. Also, $\mathcal{G}_j(t)$ has been evaluated in previous papers [36,37] and is given by

$$\mathcal{G}_j(t)=\exp\{-S_j[(2\bar{n}_j+1)-(\bar{n}_j+1)e^{-i\omega_jt}-\bar{n}_je^{i\omega_jt}]\} , \tag{4.30}$$

where $S_j=(v_l+1/2)^2\hbar\alpha_j^2/8\omega_l^2\omega_j^3$ and $\bar{n}_j$ denotes the phonon distribution $\bar{n}_j=[\exp(\hbar\omega_j/kT)-1]^{-1}$. It follows that

$$\mathcal{F}_l(\omega_1)=|\langle \Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2\int_0^\infty dt\,\exp\{-[i(\omega_l-\omega_1)+\overline{\Gamma}]t-\sum_j S_j[(2\bar{n}_j+1)-(\bar{n}_j+1)e^{-i\omega_jt}-\bar{n}_je^{i\omega_jt}]\} , \tag{4.31}$$

where ω_l is the frequency of the intramolecular mode and ω_1 denotes the infrared optical frequency. Equation (4.31) can be simplified by introducing an average frequency $\bar{\omega}$ for the frequencies of the bath ω_j. Then we have

$$\mathcal{F}_l(\omega_1)=|\langle \Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2e^{-S(2\bar{n}+1)}\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\frac{[S(\bar{n}+1)]^m[S\bar{n}]^p}{m!p!}\frac{1}{\overline{\Gamma}+i[(\omega_l-\omega_1)+\bar{\omega}(m-p)]} . \tag{4.32}$$

The real and imaginary parts of $\mathcal{F}_l(\omega_1)$ are given by

$$\mathrm{Re}\{\mathcal{J}_l(\omega_1)\}=|\langle\Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2e^{-S(2\bar{n}_j+1)}\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\frac{[S(\bar{n}+1)]^m[S\bar{n}]^p}{m!p!}\frac{\bar{\Gamma}}{\bar{\Gamma}^2+[(\omega_l-\omega_1)+\bar{\omega}(m-p)]^2} \tag{4.33}$$

and

$$\mathrm{Im}\{\mathcal{J}_l(\omega_1)\}=-|\langle\Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2e^{-S(2\bar{n}_j+1)}\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\frac{[S(\bar{n}+1)]^m[S\bar{n}]^p}{m!p!}\frac{(\omega_l-\omega_1)+\bar{\omega}(m-p)}{\bar{\Gamma}^2+[(\omega_l-\omega_1)+\bar{\omega}(m-p)]^2} . \tag{4.34}$$

Here the notation $S=\sum_j S_j$ has been introduced and we have

$$|\langle\Phi_{v_l}|Q_l|\Phi_{v_l'}\rangle|^2=\frac{(v_l+1)\hbar}{2\omega_l}\delta_{v_l,v_l'+1} . \tag{4.35}$$

It should be noted that the coupling constant S_j is related to $a_j=b_j/3$, which in turn is related to the anharmonic effect $(\partial^3V/\partial Q_l^2\partial q_j)$, V being the potential function. Finally, it should be mentioned that the magnitude of a_j determines the relative importance of the q_j mode in the SFG band-shape function.

V. DISCUSSIONS

It is well known that the output of SFG measurements is proportional to the absolute square of the nonlinear susceptibility $\chi_{ijk}^{(2)}(\omega_1+\omega_2)$. In other words, the observed SFG intensity band-shape function $\mathcal{J}_l^{\mathrm{BS}}(\omega_1)$ is given by

$$\mathcal{J}_l^{\mathrm{BS}}(\omega_1)=\mathrm{Im}\{\mathcal{J}_l(\omega_1)\}^2+\mathrm{Re}\{\mathcal{J}_l(\omega_1)\}^2 . \tag{5.1}$$

For example, for the case given by Eqs. (4.33) and (4.34), we find

$$\mathcal{J}_l^{\mathrm{BS}}(\omega_1)=\frac{(v_l+1)^2\hbar^2}{4\omega_l^2}e^{-2S(2\bar{n}+1)}\left\{\left|\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\frac{[S(\bar{n}+1)]^m[S\bar{n}]^p}{m!p!}\frac{\bar{\Gamma}}{\bar{\Gamma}^2+[(\omega_l-\omega_1)+\bar{\omega}(m-p)]^2}\right|^2\right.$$
$$\left.+\left|\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\frac{[S(\bar{n}+1)]^m[S\bar{n}]^p}{m!p!}\frac{(\omega_l-\omega_1)+\bar{\omega}(m-p)}{\bar{\Gamma}^2+[(\omega_l-\omega_1)+\bar{\omega}(m-p)]^2}\right|^2\right\} . \tag{5.2}$$

Equation (5.2) could be used to perform numerical calculations. In this case, the influence of a number of physical parameters, such as anharmonicity, electronic and vibrational dephasing, reduced displacement, as well as temperature effects on the band-shape function $\mathcal{J}_l^{\mathrm{BS}}(\omega_1)$, could be discussed. Also, it will be of interest to compare the band-shape functions of infrared spectra and SFG.

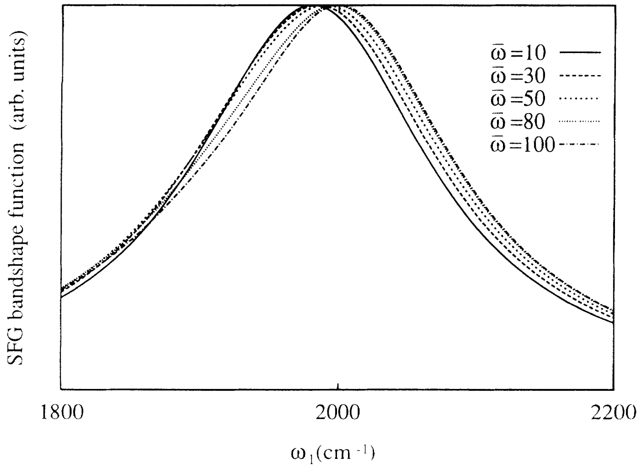

FIG. 2. We represent the variations of the band-shape function $\mathcal{J}_l^{\mathrm{BS}}(\omega_1)$ with the infrared field frequency ω_1. The cases of various average phonon frequencies of the bath $\bar{\omega}$ are considered. The values of the parameters introduced for the numerical simulation are $\omega_l=2000$ cm^{-1}, $T=200$ cm^{-1}, $\bar{\Gamma}=100$ cm^{-1}, and $S=0.1$. The peak heights are normalized.

For the moment, we just want to emphasize the role of the average surface phonon frequency on the band-shape

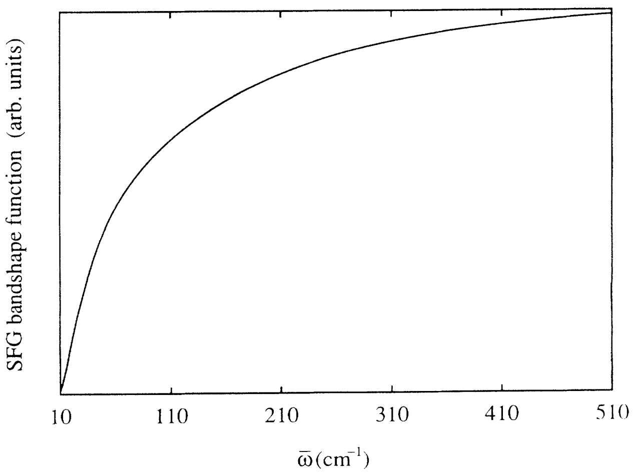

FIG. 3. Dependence of the band-shape function $\mathcal{J}_l^{\mathrm{BS}}(\omega_1)$ with $\bar{\omega}$. The other values of the parameters are identical to the ones introduced in Fig. 2. The infrared field frequency has been taken as $\omega_1=\omega_l$.

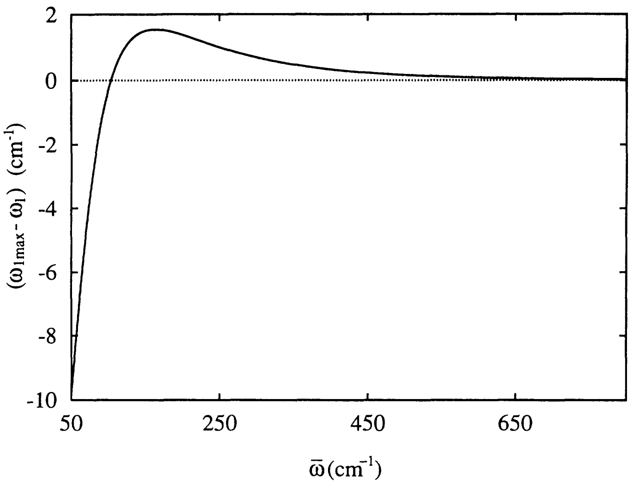

FIG. 4. We represent the peak shift $(\omega_{1\,\max}-\omega_l)$ of the maximum of $\mathcal{F}_l^{BS}(\omega_1)$ as a function of the average phonon frequency $\bar{\omega}$. The other values are identical to the ones of Fig. 3.

function. Of course, from the frequency dependence of the band-shape function, a resonant variation of the SFG signal centered in the vicinity of the molecular vibrational mode ω_l can be expected. The maximum of $\mathcal{F}_l^{BS}(\omega_1)$ is shifted to frequencies lower than ω_l and this shift increases for decreasing values of the average surface phonon frequencies $\bar{\omega}$, as can be seen from Fig. 2. While in this picture the peak heights have been normalized, in Fig. 3 we have drawn the peak height of $\mathcal{F}_l^{BS}(\omega_1=\omega_l)$ as a function of $\bar{\omega}$. We note that the SFG process is increased when increasing the average surface phonon frequency. This is because the nonradiative process induced by the coupling between the high-frequency mode and the phonon modes of the surface is more efficient for low $\bar{\omega}$. In addition, we show in Fig. 4 the peak shift $(\omega_{1\,\max}-\omega_l)$ as a function of $\bar{\omega}$. Here $\omega_{1\,\max}$ corresponds to the frequency of the maximum of $\mathcal{F}_l^{BS}(\omega_1)$. While for large $\bar{\omega}$ the peak is centered on the frequency of the vibrational mode l, for decreasing values of $\bar{\omega}$ it increases and then decreases to negative values. This is very similar to what is observed in the case of a discrete state coupled to a quasicontinuum. A simple examination of the analytical expression of the band-shape function also shows a drastic reduction of the SFG signal with an increase of the anharmonicity; this is also true if we increase the vibrational dephasing. However, all these variations will be better discussed in the future, in relation to experimental results.

VI. CONCLUSION

In the present work, we have developed a theoretical description of sum- and difference-frequency generation applied to molecules adsorbed on surfaces, with a particular emphasis on infrared-visible sum-frequency generation. While the theory can treat both steady-state and time-resolved regimes, for the sake of convenience, only the steady-state case has been studied extensively here. We have shown that for a vibrational mode to participate in an infrared-visible sum-frequency generation process, it has to be both infrared and Raman active. As previously done for second-harmonic generation, the time dependence could be described similarly.

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