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Theory of second-harmonic generation of molecular systems: The steady-state case

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In this paper, a general formalism for treating both steady-state and time-resolved second-harmonic generation for molecular systems is presented. Here, only the steady-state case will be reported. The adiabatic approximation is introduced. Four important cases, resonance-resonance, resonance–off-resonance, off-resonance–resonance, and off-resonance–off-resonance transitions, have been considered. Finally, numerical calculations of rhodamine 6G are performed to demonstrate the applications of theoretical results.

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I. INTRODUCTION

Since the pioneering work of Bloembergen on nonlinear optical susceptibilities [1], theoretical descriptions including macroscopic as well as microscopic theories in rarefied and dense media have been done [2,3]. Second-order effects in molecules have been considered in the Born-Oppenheimer approximation, and simple models as different as the two-δ-function potential [4] or the charge transfer model [5] have been used to clarify the dependence of the second-order hyperpolarizability on the charge asymmetry in a molecular system.

Steady-state and time-resolved second-harmonic generation (SHG) has begun to be actively used experimentally for studying molecular systems [6–13]. An understanding of the dynamics of molecules at surfaces or interfaces is of great importance in the study of heterogeneous catalysis, corrosion, and biological processes. Considerable progress has been made in determining static properties, such as the orientation and bonding of molecules that are chemisorbed to metal surfaces like, for example, pyridine on silver [14]. A central interest lies in investigating the dynamics of vibrationally or electronically excited polyatomic molecules at surfaces. Important issues include the nature of the interactions between an excited molecule and its ground-state neighbors, and the coupling of electronic excited states of the adsorbate to the vibrational modes (phonons) of the surface.

Recently, second-order nonlinear optical spectroscopy has emerged as a unique probe of the dynamic and static properties of molecules and surfaces. In a second-order optical process, the molecule undergoes at least two interactions with the applied fields. Examples are sum and difference frequency generation, in which coherent electric fields with components at frequencies ω_1 and ω_2 are applied to the sample, and a coherent signal with frequency $\omega_1 \pm \omega_2$ is detected. A special case of sum generation is SHG, in which $\omega_1 = \omega_2$. Second-order processes are forbidden in centrosymmetric media within the electric dipole approximation. Since inversion symmetry is broken at an interface, SHG can only occur at or very near to the surface, and thus provides a surface-specific probe.

Interesting applications of this sensitivity have been developed. As an example, the intensity of the SHG signal has been demonstrated to show a submonolayer sensitivity to the degree of coverage of molecules adsorbed on a surface. This technique has been applied in a variety of contexts by Shen [7], including determination of adsorption isotherms, studies of spectral properties of adsorbed dye molecules, and investigation of an orientational phase transition in a monolayer of fatty acid at an air-water interface [15].

SHG experiments are currently interpreted with phenomenological models in which the absorbing molecules do not interact with each other. A microscopic theory of second-order spectroscopic processes in interacting molecules at surfaces is lacking. We plan to develop a theory which will permit the interpretation of nonlinear band shapes in terms of interactions among the adsorbate molecules and the atoms or molecules that compose the surface.

The purpose of this paper is to study the steady-state and ultrafast time-resolved SHG of molecular systems by using the generalized susceptibility approach developed in a previous work [16]. The paper is organized as follows. In Sec. II, the general theory of SHG is presented. Section III is devoted to the derivation of the expression of the steady-state SHG. Then, adiabatic approximation is introduced in Sec. IV to treat the SHG of molecular systems. Several cases, like resonance-resonance, resonance–off-resonance, off-resonance–resonance, and off-resonance–resonance, are studied. Finally, in Sec. V, we show an application to the particular case of rhodamine 6G.

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II. GENERAL THEORY

Among the theoretical approaches to SHG by molecules [2,3], the Liouvillan formalism is of particular interest to describe the usual Liouville equation [17], which takes the form

$$\frac{\partial\rho(t)}{\partial t}=-\frac{i}{\hbar}L_0\rho(t)-\frac{i}{\hbar}L_1(t)\rho(t)-\Gamma\rho(t)\ . \qquad (2.1)$$

Here, L_0 and Γ are, respectively, the zero-order Liouville and the damping operator describing the dynamics of the system. In addition, $L_1(t)$ denotes the Liouville operator for the interaction between the system and radiation fields. If we define the transformation as

$$\rho(t)=e^{-(i/\hbar)L_0' t}\sigma(t)\ , \qquad (2.2)$$

where the usual notation $L_0'=L_0-i\hbar\Gamma$ has been introduced, then Eq. (2.1) becomes

$$\frac{\partial\sigma(t)}{\partial t}=-\frac{i}{\hbar}\bar{L}_1(t)\sigma(t)\ , \qquad (2.3)$$

with the notation

$$\bar{L}_1(t)=e^{(i/\hbar)L_0' t}L_1(t)e^{-(i/\hbar)L_0' t}\ . \qquad (2.4)$$

A formal solution to Eq. (2.3) can be easily deduced. It can be written as

$$\Delta\sigma(t)=\sigma(t)-\sigma_i=-\frac{i}{\hbar}\int_{t_i}^{t}d\tau\,\bar{L}_1(\tau)\sigma(\tau)\ , \qquad (2.5)$$

where σ_i denotes the $\sigma(t)$ value at $t=t_i$. As long as the radiation-matter interaction is weak enough, the solution can be expanded perturbatively. The first-order term $\Delta\sigma^{(1)}(t)$, and second-order term $\Delta\sigma^{(2)}(t)$ are obtained straightforwardly. They take the forms

$$\Delta\sigma^{(1)}(t)=-\frac{i}{\hbar}\int_{t_i}^{t}d\tau\,\bar{L}_1(\tau)\sigma_i \qquad (2.6)$$

and

$$\Delta\sigma^{(2)}(t)=-\frac{1}{\hbar^2}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\,\bar{L}_1(\tau_1)\bar{L}_1(\tau_2)\sigma_i\ . \qquad (2.7)$$

Notice that the polarization $\mathbf{P}(t)$, which is our basic quantity, is given by

$$\mathbf{P}(t)=\mathrm{Tr}[\rho(t)\boldsymbol{\mu}]=\mathrm{Tr}[G(t)\sigma(t)\boldsymbol{\mu}] \qquad (2.8)$$

and can be expressed as

$$\mathbf{P}(t)=\sum_n\sum_m\{G_{nm\,nm}(t)\sigma_{nm}(t)\boldsymbol{\mu}_{mn}(1-\delta_{mn}) + G_{nn\,mm}(t)\sigma_{mm}(t)\boldsymbol{\mu}_{nn}\}\ . \qquad (2.9)$$

As usual, $\boldsymbol{\mu}$ denotes the dipole moment operator and the free evolution is described by the Liouville operator

$$G(t)=e^{-(i/\hbar)L_0' t}\ . \qquad (2.10)$$

If the set of molecules does not have permanent dipole moment, the previous expression reduces to

$$\mathbf{P}(t)=\sum_n\sum_m G_{nm\,nm}(t)\Delta\sigma_{nm}(t)\boldsymbol{\mu}_{mn} \qquad (2.11)$$

because to zero order there is no coherence preexisting in the molecular system, and the initial density matrix is diagonal. Of course, for the second-harmonic generation, we are concerned with the second-order contribution of the polarization $\mathbf{P}^{(2)}(t)$, which can be expressed by

$$\mathbf{P}^{(2)}(t)=\sum_n\sum_m G_{nm\,nm}(t)\Delta\sigma_{nm}^{(2)}(t)\boldsymbol{\mu}_{mn}\ . \qquad (2.12)$$

For the sake of convenience, the quantity $\Delta\sigma_{nm}^{(2)}(t)$ can be written as

$$\Delta\sigma_{nm}^{(2)}(t)=\sum_{i=1}^{4}\Delta\sigma_{i\,nm}^{(2)}(t)\ , \qquad (2.13)$$

where the various contributions take the form

$$\begin{aligned}
\Delta\sigma_{1\,nm}^{(2)}(t)&=-\frac{1}{\hbar^2}\sum_{n'}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\,e^{i\omega_{nm}'\tau_1}V_{nn'}(\tau_1)e^{-i\omega_{n'm}'(\tau_1-\tau_2)}V_{n'm}(\tau_2)\rho_{mm}(t_i)\ ,\\
\Delta\sigma_{2\,nm}^{(2)}(t)&=\frac{1}{\hbar^2}\sum_{n'}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\,e^{i\omega_{nm}'\tau_1}V_{nn'}(\tau_1)e^{-i\omega_{n'm}'(\tau_1-\tau_2)}V_{n'm}(\tau_2)\rho_{n'n'}(t_i)\ ,\\
\Delta\sigma_{3\,nm}^{(2)}(t)&=\frac{1}{\hbar^2}\sum_{n'}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\,e^{i\omega_{nm}'\tau_1}V_{n'm}(\tau_1)e^{-i\omega_{nn'}'(\tau_1-\tau_2)}V_{nn'}(\tau_2)\rho_{n'n'}(t_i)\ ,\\
\Delta\sigma_{4\,nm}^{(2)}(t)&=-\frac{1}{\hbar^2}\sum_{n'}\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2\,e^{i\omega_{nm}'\tau_1}V_{n'm}(\tau_1)e^{-i\omega_{nn'}'(\tau_1-\tau_2)}V_{nn'}(\tau_2)\rho_{nn}(t_i)\ .
\end{aligned} \qquad (2.14)$$

In the previous expression, we took advantage of the fact that the system is initially in a stable distribution of states of the ground electronic configuration, so that

$$G(t-t_i)\rho(t_i)=\rho(t_i)\ . \qquad (2.15)$$

The initial density matrix $\rho(t_i)$ will be described by a stable Boltzmann distribution of vibrational states of the ground electronic configuration g

$$\rho(t_i)=\frac{1}{Z}\sum_{v'}e^{-E_{gv}/kT}|gv\rangle\langle gv|,\quad Z=\sum_{v'}e^{-E_{gv'}/kT}\ . \qquad (2.16)$$

In these previous expressions, the radiation-matter interaction can be expressed as

$$V(t)=-\boldsymbol{\mu}\cdot[\mathbf{E}(\omega)e^{-i\omega t}+\mathbf{E}^*(\omega)e^{i\omega t}]A(t)\ , \tag{2.17}$$

where $A(t)$ denotes the laser-pulse shape function. It is convenient to use $A(t)$ given by

$$A(t)=e^{-\gamma|t-t_p|}\ . \tag{2.18}$$

Here, $T=2\gamma^{-1}$ represents the pulse duration and t_p denotes the probing time.

The expression for $\mathbf{P}^{(2)}(t)$ given in this section, can be applied to both steady-state and ultrafast time-resolved SHG. For the latter case, both population and coherence make contributions to SHG. In addition, if the pulses overlap, various chronological ordering must be considered for time-resolved SHG, while they give a trivial dependence in the steady-state regime. In appendix A, a different approach for deriving $\mathbf{P}^{(2)}(t)$ is presented.

III. STEADY-STATE CASE

When the experiment is performed in the stationary regime, the amplitude of the electric field is constant and the relation (2.17) takes the form

$$V(t)=-\boldsymbol{\mu}\cdot\sum_{\alpha=\pm 1}\mathbf{E}(\alpha\omega)e^{-i\alpha\omega t},\quad \mathbf{E}(-\omega)=\mathbf{E}^*(\omega)\ . \tag{3.1}$$

In this case, the various expressions of $\Delta\sigma^{(2)}_{j\,nm}(t)$ can be evaluated easily. For instance, $\Delta\sigma^{(2)}_{1\,nm}(t)$ becomes

$$\Delta\sigma^{(2)}_{1\,nm}(t)=-\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{mm}(t_i)[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\beta\omega)]\int_{t_i}^{t}d\tau_1\int_{t_i}^{\tau_1}d\tau_2 e^{i(\omega'_{nm}-\omega'_{n'm}-\alpha\omega)\tau_1}e^{i(\omega'_{n'm}-\beta\omega)\tau_2}\ , \tag{3.2}$$

where we have substituted Eq. (3.1) into Eq. (2.14). Performing the time integration, we get

$$\Delta\sigma^{(2)}_{1\,nm}(t)=\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{mm}(t_i)[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\beta\omega)]$$
$$\times\frac{1}{\omega'_{n'm}-\beta\omega}\left[\frac{e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t}-e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t_i}}{\omega'_{nm}-\alpha\omega-\beta\omega}\right.$$
$$\left.-e^{i(\omega'_{n'm}-\beta\omega)t_i}\frac{e^{i(\omega'_{nm}-\omega'_{n'm}-\alpha\omega)t}-e^{i(\omega'_{nm}-\omega'_{n'm}-\alpha\omega)t_i}}{\omega'_{nm}-\omega'_{n'm}-\alpha\omega}\right]\ . \tag{3.3}$$

When the initial condition, $\lim_{t_i\to-\infty}$ is introduced and if t is large enough to reach the steady-state regime, the expressions of the various contributions are greatly simplified. The previous quantities result in the form

$$\Delta\sigma^{(2)}_{1\,nm}(t)=\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{mm}(t_i)e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t}\frac{[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\beta\omega)]}{(\omega'_{n'm}-\beta\omega)(\omega'_{nm}-\alpha\omega-\beta\omega)}\ . \tag{3.4}$$

Similarly, we obtain for the other contributions

$$\begin{aligned}
\Delta\sigma^{(2)}_{2\,nm}(t)&=-\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{n'n'}(t_i)e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t}\frac{[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\beta\omega)]}{(\omega'_{n'm}-\beta\omega)(\omega'_{nm}-\alpha\omega-\beta\omega)}\ ,\\
\Delta\sigma^{(2)}_{3\,nm}(t)&=-\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{n'n'}(t_i)e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t}\frac{[\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\beta\omega)]}{(\omega'_{nn'}-\beta\omega)(\omega'_{nm}-\alpha\omega-\beta\omega)}\ ,\\
\Delta\sigma^{(2)}_{4\,nm}(t)&=\frac{1}{\hbar^2}\sum_{n'}\sum_{\alpha}\sum_{\beta}\rho_{nn}(t_i)e^{i(\omega'_{nm}-\alpha\omega-\beta\omega)t}\frac{[\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\alpha\omega)][\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\beta\omega)]}{(\omega'_{nn'}-\beta\omega)(\omega'_{nm}-\alpha\omega-\beta\omega)}\ .
\end{aligned} \tag{3.5}$$

In the second-harmonic-generation experiment, the phase-matching conditions are satisfied, and consequently the wave-vector dependence can be ignored from the electric field. Then, only the terms $\alpha=\beta=\pm 1$ contribute to the process.

From the previous results, the polarization is straightforwardly obtained. If we consider the formal development valid in the steady-state regime

$$\mathbf{P}^{(2)}(t)=\mathbf{P}^{(2)}(2\omega)e^{-2i\omega t}+\mathbf{P}^{(2)}(-2\omega)e^{2i\omega t} \tag{3.6}$$

and again, introduce the previous partition

$$\mathbf{P}^{(2)}(\pm 2\omega)=\sum_{j=1}^{4}\mathbf{P}_j^{(2)}(\pm 2\omega)\ , \tag{3.7}$$

the various contributions to the polarization are given by

$$
\begin{aligned}
\mathbf{P}_1^{(2)}(\pm 2\omega) &= \frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{mm}(t_i)\boldsymbol{\mu}_{mn} \frac{[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\pm\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\pm\omega)]}{(\omega'_{n'm}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\mathbf{P}_2^{(2)}(\pm 2\omega) &= -\frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{n'n'}(t_i)\boldsymbol{\mu}_{mn} \frac{[\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\pm\omega)][\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\pm\omega)]}{(\omega'_{n'm}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\mathbf{P}_3^{(2)}(\pm 2\omega) &= -\frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{n'n'}(t_i)\boldsymbol{\mu}_{mn} \frac{[\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\pm\omega)][\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\pm\omega)]}{(\omega'_{nn'}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\mathbf{P}_4^{(2)}(\pm 2\omega) &= \frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{nn}(t_i)\boldsymbol{\mu}_{mn} \frac{[\boldsymbol{\mu}_{n'm}\cdot\mathbf{E}(\pm\omega)][\boldsymbol{\mu}_{nn'}\cdot\mathbf{E}(\pm\omega)]}{(\omega'_{nn'}\mp\omega)(\omega'_{nm}\mp 2\omega)} .
\end{aligned}
\tag{3.8}
$$

From these expressions, it is quite easy to deduce the corresponding second-order nonlinear optical susceptibilities. They correspond to the third-order rank tensors described by

$$
\chi^{(2)}(\pm 2\omega) = \sum_{j=1}^{4} \chi_j^{(2)}(\pm 2\omega) ,
\tag{3.9}
$$

where

$$
\begin{aligned}
\chi_1^{(2)}(\pm 2\omega) &= \frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{mm}(t_i) \frac{\boldsymbol{\mu}_{mn}\otimes\boldsymbol{\mu}_{nn'}\otimes\boldsymbol{\mu}_{n'm}}{(\omega'_{n'm}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\chi_2^{(2)}(\pm 2\omega) &= -\frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{n'n'}(t_i) \frac{\boldsymbol{\mu}_{mn}\otimes\boldsymbol{\mu}_{nn'}\otimes\boldsymbol{\mu}_{n'm}}{(\omega'_{n'm}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\chi_3^{(2)}(\pm 2\omega) &= -\frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{n'n'}(t_i) \frac{\boldsymbol{\mu}_{mn}\otimes\boldsymbol{\mu}_{n'm}\otimes\boldsymbol{\mu}_{nn'}}{(\omega'_{nn'}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,\\
\chi_4^{(2)}(\pm 2\omega) &= \frac{1}{\hbar^2}\sum_n \sum_m \sum_{n'} \rho_{nn}(t_i) \frac{\boldsymbol{\mu}_{mn}\otimes\boldsymbol{\mu}_{n'm}\otimes\boldsymbol{\mu}_{nn'}}{(\omega'_{nn'}\mp\omega)(\omega'_{nm}\mp 2\omega)} ,
\end{aligned}
\tag{3.10}
$$

and ⊗ denotes the tensorial product. In the next sections, these quantities will be evaluated explicitly by using the adiabatic approximation on a particular molecular system.

IV. ADIABATIC APPROXIMATION IN THE STEADY-STATE REGIME

Using the adiabatic approximation, we have to consider the three vibronic manifolds depicted on Fig. 1. From the structure of the denominator of the nonlinear susceptibility, and depending on whether the transition frequencies of the system are resonant or not with ω and 2ω, we are faced with the four following cases which are termed resonance-resonance, resonance–off-resonance, off-resonance–resonance, and finally off-resonance–off-resonance cases, respectively.

A. Resonance-resonance case

This case is represented in Fig. 1(a). Here, only $\chi_1^{(2)}(2\omega)$ needs to be considered. It corresponds to

$$
\chi_1^{(2)}(2\omega) = \frac{1}{\hbar^2}\sum_v \sum_{v'} \sum_{v''} P_{gv} \frac{\boldsymbol{\mu}_{gv\,e''v''}\otimes\boldsymbol{\mu}_{e''v''\,e'v'}\otimes\boldsymbol{\mu}_{e'v'\,gv}}{(\omega'_{e'v'\,gv}-\omega)(\omega'_{e''v''\,gv}-2\omega)} ,
\tag{4.1}
$$

where P_{gv} denotes the Boltzmann distribution, (g,e',e'') represent the three electronic configurations involved in the second-harmonic generation, and (v,v',v'') denote their corresponding vibrational states. For allowed transitions, the Condon approximation can be used and Eq. (4.1) becomes

$$
\chi_1^{(2)}(2\omega) = K_{e''e'g} \sum_v \sum_{v'} \sum_{v''} P_{gv} \frac{\langle \Theta_{gv}|\Theta_{e''v''}\rangle \langle \Theta_{e''v''}|\Theta_{e'v'}\rangle \langle \Theta_{e'v'}|\Theta_{gv}\rangle}{(\omega'_{e'v'\,gv}-\omega)(\omega'_{e''v''\,gv}-2\omega)} ,
\tag{4.2}
$$

if the third-rank tensor $K_{e''e'g}$ is given by

$$K_{e''e'g}=\frac{1}{\hbar^2}\boldsymbol{\mu}_{ge''}\otimes\boldsymbol{\mu}_{e''e'}\otimes\boldsymbol{\mu}_{e'g} \tag{4.3}$$

and $\langle\Theta_{gv}|\Theta_{e''v''}\rangle$ denotes the vibrational overlap integral. In the following, it will be of interest to introduce the integral representation

$$\frac{1}{\omega'_{e'v'\,gv}-\omega}=\int_0^{\wp}dt\, e^{-(\omega'_{e'v'\,gv}-\omega)t}\,, \tag{4.4}$$

where the upper limit, $\wp=\pm\infty$, must be chosen such that the primitive of $\exp[-(\omega'_{e'v'\,gv}-\omega)t]$ vanishes at this point. Moreover, the same representation is introduced for the second factor of the denominator. It should be noted that $\chi_1^{(2)}(2\omega)$ represents the dominant contribution. Equation (4.2) can be written as

$$\chi_1^{(2)}(2\omega)=K_{e''e'g}\int_0^{\infty}dt_1 e^{-(\omega'_{e'g}-\omega)t_1}\int_0^{\infty}dt_2 e^{-(\omega'_{e''g}-\omega)t_2}\langle e^{-(1/\hbar)H_V(e'')t_2}e^{-(1/\hbar)H_V(e')t_1}e^{(1/\hbar)H_V(g)(t_1+t_2)}\rangle_g\,, \tag{4.5}$$

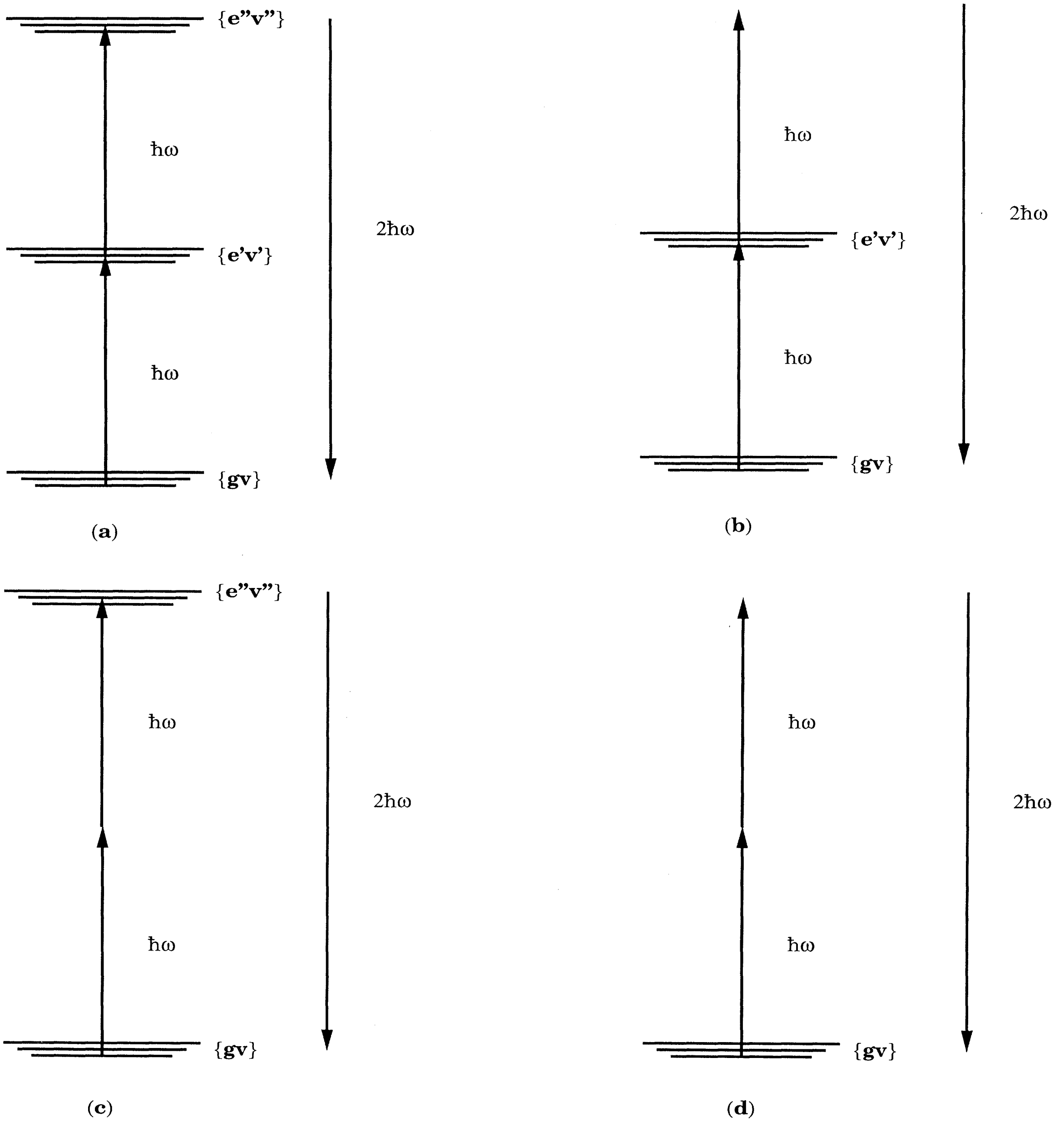

FIG. 1. Energy-level schemes for (a) resonance-resonance SHG; (b) resonance–off-resonance SHG; (c) off-resonance–resonance SHG; (d) off-resonance–off-resonance SHG.

assuming that the electronic dephasing gives the main contribution to the dephasing constants. Here, $\langle\ \rangle_g$ means that the thermal average over the ground electronic manifold should be taken. Also, $H_V(j)$ stands for the vibrational Hamiltonian in the j electronic configuration.

The SHG is most efficient for the resonance-resonance case. Let us first consider the particular case in which the potential surfaces of the electronic configurations e' and e'' are identical. In this case, Eq. (4.2) reduces to

$$\chi_1^{(2)}(2\omega)=K_{e''e'g}\sum_v\sum_{v'}P_{gv}\frac{\langle\Theta_{gv}|\Theta_{e''v'}\rangle\langle\Theta_{e'v'}|\Theta_{gv}\rangle}{(\omega'_{e'v'\,gv}-\omega)(\omega'_{e''v'\,gv}-2\omega)}\ , \tag{4.6}$$

where $\Theta_{e''v'}=\Theta_{e'v'}$. Notice that the total vibrational wave functions can be developed as a product of the wave functions of the various individual vibrational modes, so that

$$\begin{aligned}\Theta_{gv}&=\prod_i\chi_{gv_i}(Q_i)\ ,\\ \Theta_{e'v'}&=\prod_i\chi_{e'v_i'}(Q_i')\ .\end{aligned} \tag{4.7}$$

With the previous assumption of negligible vibrational dephasing, we get the expression

$$\chi_1^{(2)}(2\omega)=K_{e''e'g}\int_0^{\wp}dt_1e^{-\Delta_1\omega'_{e'g}t_1}\int_0^{\wp}dt_2e^{-\Delta_2\omega'_{e''g}t_2}\prod_i G_i(t_1,t_2)\ , \tag{4.8}$$

where the definitions

$$\begin{aligned}\Delta_1\omega'_{e'g}&=\omega_{e'g}-i\Gamma_{e'g}-\omega\ ,\\ \Delta_2\omega'_{e''g}&=\omega_{e''g}-i\Gamma_{e''g}-2\omega\ ,\end{aligned} \tag{4.9}$$

and

$$G_i(t_1,t_2)=\sum_{v_i}\sum_{v_i'}P_{gv_i}|\langle\chi_{gv_i}|\chi_{e'v_i'}\rangle|^2\exp\left[-\left\{\left[v_i'+\frac{1}{2}\right]\omega_i'-\left[v_i+\frac{1}{2}\right]\omega_i\right\}(t_1+t_2)\right]\ , \tag{4.10}$$

have been introduced. Here, $\hbar\omega_{e'g}$ and $\hbar\omega_{e''g}$ represent the electronic energy gaps. The function $G_i(t_1,t_2)$ has been evaluated in connection with radiationless transitions and resonance Raman scattering [18–20]. For the case of displaced oscillators, $\omega_i'=\omega_i$, and we have

$$G_i(t_1,t_2)=\exp\left[-S_i\left\{\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i(t_1+t_2)\right]\right\}\right] \tag{4.11}$$

if S_i stands for the quantity

$$S_i=\frac{\omega_i(d_i'-d_i)^2}{2\hbar}\ . \tag{4.12}$$

Here, d_i' and d_i are the displacements of the normal mode coordinate with frequency ω_i in the electronic configurations e' and g, respectively. Then, the expression of $\chi_1^{(2)}(2\omega)$ is readily established. It takes the form

$$\begin{aligned}\chi_1^{(2)}(2\omega)=K_{e''e'g}&\int_0^{\wp}dt_1e^{-\Delta_1\omega'_{e'g}t_1}\int_0^{\wp}dt_2e^{-\Delta_2\omega'_{e''g}t_2}\\ &\times\exp\left[-\sum_i S_i\left\{\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i(t_1+t_2)\right]\right\}\right]\ .\end{aligned} \tag{4.13}$$

For the case in which only one mode has $S_i\neq0$, Eq. (4.13) becomes

$$\begin{aligned}\chi_1^{(2)}(2\omega)=K_{e''e'g}e^{-S_i(1+2\bar{n}_i)}&\sum_{n_i=0}^{\infty}\sum_{m_i=0}^{\infty}\frac{(S_i\bar{n}_i)^{m_i}[S_i(1+\bar{n}_i)]^{n_i}}{n_i!m_i!}\\ &\times\frac{1}{[\omega_{e'g}+(n_i-m_i)\omega_i-i\Gamma_{e'g}-\omega][\omega_{e''g}+(n_i-m_i)\omega_i-i\Gamma_{e''g}-2\omega]}\ .\end{aligned} \tag{4.14}$$

Therefore, at $T=0$, the expression of the second-order susceptibility reduces to

$$\chi_1^{(2)}(2\omega)=K_{e''e'g}e^{-S_i}\sum_{n_i=0}^{\infty}\frac{S_i^{n_i}}{n_i!}\frac{1}{[\omega_{e'g}+n_i\omega_i-i\Gamma_{e'g}-\omega][\omega_{e''g}+n_i\omega_i-i\Gamma_{e''g}-2\omega]}\ . \tag{4.15}$$

Next, we come to the more general case. Here, the potential surfaces are different. Then, we have

$$\chi_1^{(2)}(2\omega)=K_{e''e'g}\int_0^{\wp}dt_1 e^{-\Delta_1\omega'_{e'g}t_1}\int_0^{\wp}dt_2 e^{-\Delta_2\omega'_{e''g}t_2}\prod_i H_i(t_1,t_2)\ , \tag{4.16}$$

where

$$H_i(t_1,t_2)=2\sinh\left\{\frac{\hbar\omega_i}{2kT}\right\}\sum_{v_i}\sum_{v'_i}\sum_{v''_i}e^{-\lambda_i(v_i+1/2)}e^{-\lambda'_i(v'_i+1/2)}e^{-\lambda''_i(v''_i+1/2)}\langle\chi_{gv_i}|\chi_{e''v''_i}\rangle\langle\chi_{e''v''_i}|\chi_{e'v'_i}\rangle\langle\chi_{e'v'_i}|\chi_{gv_i}\rangle\ , \tag{4.17}$$

and

$$\lambda_i=\frac{\hbar\omega_i}{kT}-\omega_i(t_1+t_2),\ \ \lambda'_i=\omega'_i t_1,\ \ \lambda''_i=\omega'_i t_2\ . \tag{4.18}$$

Using the Mehler formula [18], $H_i(t_1,t_2)$ can be evaluated as shown in Appendix B. The result is given by

$$H(t_1,t_2)=M\left[\frac{\pi^3}{a_i a'_i a''_i}\right]^{1/2}\exp\left\{\frac{b_i''^2}{4a''_i-c''_i}\right\}\ ,$$
$$M=\frac{2\beta_i^{3/2}\sinh\dfrac{\hbar\omega_i}{2kT}}{\sqrt{8\pi^3\sinh\lambda'_i\,\sinh\lambda''_i}}\ . \tag{4.19}$$

The quantities a_i, a'_i, a''_i, b''_i, and c''_i are defined in Appendix B. In fact, the same type of calculation can be applied to third-harmonic generation [21–23].

B. Resonance–off-resonance case

In this case, both $\chi_1^{(2)}(2\omega)$ and $\chi_3^{(2)}(2\omega)$ have significant contributions to SHG. The third term $\chi_3^{(2)}(2\omega)$ can be rewritten as

$$\chi_3^{(2)}(2\omega)=\frac{1}{\hbar^2}\sum_{mv_m}\sum_{v'}\sum_{v}P_{gv}\frac{\boldsymbol{\mu}_{mv_m\ e'v'}\otimes\boldsymbol{\mu}_{gv\ mv_m}\otimes\boldsymbol{\mu}_{e'v'\ gv}}{(\omega'_{e'v'gv}-\omega)(-\omega'_{e'v'\ mv_m}+2\omega)}\ , \tag{4.20}$$

where now we are summing over all the electronic configurations above the first one. In the adiabatic approximation, we find

$$\chi_1^{(2)}(2\omega)=\sum_m\sum_{v'}\sum_v K_{me'g}P_{gv}\frac{|\langle\Theta_{gv}|\Theta_{e'v'}\rangle|^2}{(\omega'_{e'v'\ gv}-\omega)(\omega_{mg}-2\omega)} \tag{4.21}$$

and

$$\chi_3^{(2)}(2\omega)=\sum_m\sum_{v'}\sum_v K'_{me'g}P_{gv}\frac{|\langle\Theta_{gv}|\Theta_{e'v'}\rangle|^2}{(\omega'_{e'v'\ gv}-\omega)(\omega_{me'}+2\omega)}\ . \tag{4.22}$$

Here, the Placzek approximation [24], has been used. Because the second factor in the denominator is nonresonant, the vibrational structure as well as the imaginary part are irrelevant. Notice that $K_{me'g}=\hbar^{-2}\boldsymbol{\mu}_{gm}\otimes\boldsymbol{\mu}_{me'}\otimes\boldsymbol{\mu}_{e'g}$ and $k'_{me'g}=\hbar^{-2}\boldsymbol{\mu}_{me'}\otimes\boldsymbol{\mu}_{gm}\otimes\boldsymbol{\mu}_{e'g}$.

From an inspection of Eqs. (4.21) and (4.22), we can see that the imaginary parts of both $\chi_1^{(2)}(2\omega)$ and $\chi_3^{(2)}(2\omega)$ will approximately give the bandshape function of ordinary one-photon absorption spectra. We shall rewrite these equations as

$$\chi_1^{(2)}(2\omega)=K_1(\omega)\alpha(\omega)\ ,$$
$$\chi_3^{(2)}(2\omega)=K_3(\omega)\alpha(\omega)\ , \tag{4.23}$$

where

$$\alpha(\omega)=\frac{1}{\pi}\sum_{v'}\sum_v P_{gv}\frac{|\langle\Theta_{gv}|\Theta_{e'v'}\rangle|^2}{\omega'_{e'v'gv}-\omega} \tag{4.24}$$

and

$$K_1(\omega)=\pi\sum_m \frac{K_{me'g}}{\omega_{mg}-2\omega}\ ,\qquad K_3(\omega)=\pi\sum_m \frac{K'_{me'g}}{\omega_{me'}+2\omega}\ . \tag{4.25}$$

By using the method described in Sec. IV A, the quantity $\alpha(\omega)$ can be easily evaluated and takes the form

$$\alpha(\omega)=\frac{1}{\pi}\int_0^{\wp} dt\, e^{-\Delta_1\omega'_{e'g}t}\prod_i G_i(t)\ , \tag{4.26}$$

where

$$G_i(t)=\sum_{v_i'}\sum_{v_i} P_{gv_i}|\langle\chi_{gv_i}|\chi_{e'v_i'}\rangle|^2 \exp\left\{-\left[\left[v_i'+\frac{1}{2}\right]\omega_i'-\left[v_i+\frac{1}{2}\right]\omega_i\right]t\right\}\ . \tag{4.27}$$

Again, in the particular case of displaced oscillators, $\omega_i'=\omega_i$, and we have

$$G_i(t)=\exp\left[-S_i\left\{\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i t\right]\right\}\right] \tag{4.28}$$

so that

$$\alpha(\omega)=\frac{1}{\pi}\int_0^{\wp} dt\, \exp\left\{-\Delta_1\omega'_{e'g}t-\sum_i S_i\left[\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i t\right]\right]\right\}\ . \tag{4.29}$$

For the single-mode case, Eq. (4.29) reduces to

$$\alpha(\omega)=\frac{1}{\pi}e^{-S_i(1+2\bar{n}_i)}\sum_{n_i=0}^{\infty}\sum_{m_i=0}^{\infty}\frac{(S_i\bar{n}_i)^{m_i}[S_i(1+\bar{n}_i)]^{n_i}}{m_i!n_i![\omega_{e'g}+(n_i-m_i)\omega_i-\omega-i\Gamma_{e'g}]}\ . \tag{4.30}$$

The case of distorted oscillators could also be considered. It just requires the evaluation of the corresponding function $G_i(t)$.

C. Off-resonance–resonance case

In the present case, only the term $\chi_1^{(2)}(2\omega)$ makes a significant contribution to SHG. Again, using the adiabatic and Placzek approximations, it takes the following form:

$$\chi_1^{(2)}(2\omega)=\frac{1}{\hbar^2}\sum_{v''}\sum_{nv_n}\sum_{v}P_{gv}\frac{\boldsymbol{\mu}_{gv\;e''v''}\otimes\boldsymbol{\mu}_{e''v''\;nv_n}\otimes\boldsymbol{\mu}_{nv_n\;gv}}{(\omega_{ng}-\omega)(\omega'_{e''v''\;gv}-2\omega)}\ . \tag{4.31}$$

For allowed transitions, the previous equation becomes

$$\begin{aligned}\chi_1^{(2)}(2\omega)&=\sum_{v''}\sum_{n}\sum_{v}P_{gv}K_{e''ng}\frac{|\langle\Theta_{gv}|\Theta_{e''v''}\rangle|^2}{(\omega_{ng}-\omega)(\omega'_{e''v''gv}-2\omega)}\\ &=K_1'(\omega)\alpha_2(\omega)\ ,\end{aligned} \tag{4.32}$$

where now

$$\alpha_2(\omega)=\frac{1}{\pi}\sum_{v''}\sum_{v}P_{gv}\frac{|\langle\Theta_{gv}|\Theta_{e''v''}\rangle|^2}{\omega'_{e''v''gv}-2\omega} \tag{4.33}$$

and

$$K_1'(\omega)=\pi\sum_n\frac{K_{e''ng}}{\omega_{ng}-\omega}\ . \tag{4.34}$$

Again, the quantity $\alpha_2(\omega)$ can be evaluated similarly. Therefore, for the off-resonance–resonance case we obtain

$$\alpha_2(\omega)=\frac{1}{\hbar^2}\int_0^{\wp} dt\, e^{-\Delta_2\omega'_{e''g}t}\prod_i \bar{G}_i(t)\ , \tag{4.35}$$

where

$$\bar{G}_i(t)=\sum_{v_i''}\sum_{v_i}P_{gv_i}|\langle\chi_{gv_i}|\chi_{e''v_i''}\rangle|^2\exp\left\{-\left[\left(v_i''+\tfrac{1}{2}\right)\omega_i''-\left(v_i+\tfrac{1}{2}\right)\omega_i\right]t\right\} . \tag{4.36}$$

For displaced operators, we have

$$\bar{G}_i(t)=\exp\left[-S_i'\left\{\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i t\right]\right\}\right] , \tag{4.37}$$

where now S_i' denotes the coupling constant between the electronic configurations e'' and g for the ith vibrational mode. It follows that

$$\alpha_2(\omega)=\frac{1}{\pi}\int_0^{\wp}dt\,\exp\left[-\Delta_2\omega'_{e''g}t-\sum_i S_i'\left\{\coth\frac{\hbar\omega_i}{2kT}-\operatorname{csch}\frac{\hbar\omega_i}{2kT}\cosh\left[\frac{\hbar\omega_i}{2kT}-\omega_i t\right]\right\}\right] . \tag{4.38}$$

The final integrated expressions of $\alpha_2(\omega)$ can be obtained straightforwardly, as done in the previous case, from the comparison of relations (4.29) and (4.38).

D. Off-resonance–off-resonance case

In this case, all four contributions to the second-order susceptibility contribute. Notice that if the Placzek approximation is introduced as previously done, we get

$$\begin{aligned}\chi_1^{(2)}(2\omega)&=\frac{1}{\hbar^2}\sum_m\sum_n\frac{\mu_{gm}\otimes\mu_{mn}\otimes\mu_{ng}}{(\omega_{ng}-\omega)(\omega_{mg}-2\omega)} ,\\ \chi_2^{(2)}(2\omega)&=\frac{1}{\hbar^2}\sum_m\sum_n\frac{\mu_{nm}\otimes\mu_{mg}\otimes\mu_{gn}}{(\omega ng+\omega)(\omega_{mn}-2\omega)} ,\\ \chi_3^{(2)}(2\omega)&=\frac{1}{\hbar^2}\sum_m\sum_n\frac{\mu_{mn}\otimes\mu_{gm}\otimes\mu_{ng}}{(\omega_{ng}-\omega)(\omega_{mn}+2\omega)} ,\\ \chi_4^{(2)}(2\omega)&=\frac{1}{\hbar^2}\sum_m\sum_n\frac{\mu_{mg}\otimes\mu_{nm}\otimes\mu_{gn}}{(\omega_{ng}+\omega)(\omega_{mg}+2\omega)} .\end{aligned} \tag{4.39}$$

These terms represent the electronic contributions to SHG. In the previous Equation (4.39), because we are always far from resonance, the temperature effects have been ignored.

From this section, we can see that SHG depends on the triple product of electronic transition moments $\mu_{ge''}\otimes\mu_{e''e'}\otimes\mu_{e'g}$. Therefore, for a randomly oriented system the SHG vanishes, and for an oriented or partially oriented system with an inversion center of internal symmetry, the SHG also vanishes. This characteristic of SHG has been used for studying the so-called "cold melting" of solids induced by nanosecond, picosecond, and femtosecond laser pulses [8,25]. In addition, from the theoretical treatments presented in this paper for SHG of molecular systems, to design a molecular system with a large SHG signal, we observe that it is important to prepare a molecular system with not only large electronic transition moments but also proper energy levels so that resonance transitions can be involved in SHG.

V. DISCUSSION

To show the application of the theoretical results presented in the previous sections, we note that Heinz *et al.* [6] have recently obtained the spectra of the $S_0\rightarrow S_2$ electronic transition of rhodamine dyes adsorbed at monolayer coverages on a fused silica substrate by resonance SHG. The results are presented in Figs. 2 and 3. This corresponds to our off-resonance–resonance case.

If the incoming light has polarization $\mathbf{e}_\omega$, then the intensity of the forward or reflected harmonic light of polarization $\mathbf{e}_{2\omega}$ is given by [1,3]

$$I_{2\omega}=\frac{32\pi^3\omega^3}{c^3}\sec^2\varphi I_\omega^2|\mathbf{e}_{2\omega}\cdot\chi_s^{(2)}(2\omega):\mathbf{e}_\omega\mathbf{e}_\omega|^2 , \tag{5.1}$$

where φ denotes the incidence angle. From Eq. (4.32), we

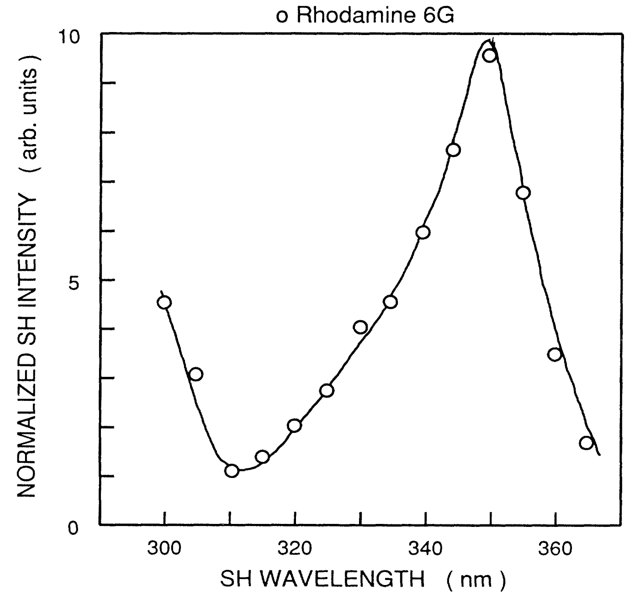

FIG. 2. Normalized SH intensity for p-polarized excitation of monolayer samples rhodamine 6G on fused silica as a function of the SH wavelength in the region of the S_0-S_2 transition.

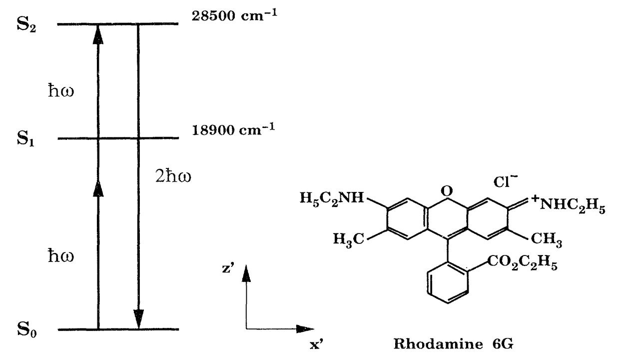

FIG. 3. Energy-level diagram for rhodamine 6G adsorbed on fused silica, with the energies of the electronic configurations deduced from the fit between the experimental results of Heinz *et al.* and our theory. The structure of the dyes and the molecular axes referred to in the text are indicated.

have

$$\chi^{(2)}(2\omega)=\chi_1^{(2)}(2\omega)=K_1'(\omega)\alpha_2(\omega)\ , \tag{5.2}$$

where

$$\alpha_2(\omega)=\frac{1}{\pi}\sum_{v''}\sum_{v}P_{gv}\frac{|\langle\Theta_{gv}|\Theta_{e''v''}\rangle|^2}{\omega_{e''v''\,gv}-2\omega-i\Gamma_{e''v''\,gv}}\ . \tag{5.3}$$

Notice that from the real and imaginary parts, we have

$$\alpha_2(\omega)=\mathrm{Re}[\alpha_2(\omega)]+i\ \mathrm{Im}[\alpha_2(\omega)]\ , \tag{5.4}$$

where

$$\mathrm{Re}[\alpha_2(\omega)]=\frac{1}{\pi}\sum_{v''}\sum_{v}P_{gv}\frac{\omega_{e''v''\,gv}-2\omega}{(\omega_{e''v''\,gv}-2\omega)^2+\Gamma^2_{e''v''\,gv}}|\langle\Theta_{gv}|\Theta_{e''v''}\rangle|^2\ ,$$
$$\mathrm{Im}[\alpha_2(\omega)]=\frac{1}{\pi}\sum_{v''}\sum_{v}P_{gv}\frac{\Gamma_{e''v''\,gv}}{(\omega_{e''v''\,gv}-2\omega)^2+\Gamma^2_{e''v''\,gv}}|\langle\Theta_{gv}|\Theta_{e''v''}\rangle|^2\ . \tag{5.5}$$

That is, $\mathrm{Im}[\alpha_2(\omega)]$ denotes the band-shape function of absorption spectra with frequency 2ω, while $\mathrm{Re}[\alpha_2(\omega)]$ represents the corresponding dispersion band-shape function.

For comparison with the SHG of rhodamine in Fig. 2, we show the absorption spectra of rhodamine 6G in alcohol in Fig. 4. We can see that Fig. 2 and 4 are quite similar. We shall rigorously analyze the relation between the SHG spectra and the absorption spectra. Notice that in the Condon approximation,

$$I_{2\omega}\alpha|\mathrm{Re}[\alpha_2(\omega)]|^2+|\mathrm{Im}[\alpha_2(\omega)]|^2\ . \tag{5.6}$$

To analyze the results given in Figs. 2 and 4, we need the real and imaginary parts of $\alpha_2(\omega)$ obtained in the off-resonance–resonance case. Here, $\alpha_2(\omega)$ is given by

$$\alpha_2(\omega)=\frac{1}{\pi}e^{-S_i'(1+2\bar{n}_i)}\sum_{n_i=0}^{\infty}\sum_{m_i=0}^{\infty}\frac{(S_i'\bar{n}_i)^{m_i}[S_i'(1+\bar{n}_i)]^{n_i}}{m_i!n_i![\omega_{e''g}+(n_i-m_i)\omega_i-2\omega-i\Gamma_{e''g}]}\ , \tag{5.7}$$

and we get, respectively,

$$\mathrm{Re}[\alpha_2(\omega)]=\frac{1}{\pi}e^{-S_i'(1+2\bar{n}_i)}\sum_{n_i=0}^{\infty}\sum_{m_i=0}^{\infty}\frac{(S_i'\bar{n}_i)^{m_i}[S_i'(1+\bar{n}_i)]^{n_i}}{m_i!n_i!}\frac{\omega_{e''g}+(n_i-m_i)\omega_i-2\omega}{[\omega_{e''g}+(n_i-m_i)\omega_i-2\omega]^2+\Gamma^2_{e''g}} \tag{5.8}$$

and

$$\mathrm{Im}[\alpha_2(\omega)]=\frac{1}{\pi}e^{-S_i'(1+2\bar{n}_i)}\sum_{n_i=0}^{\infty}\sum_{m_i=0}^{\infty}\frac{(S_i'\bar{n}_i)^{m_i}[S_i'(1+\bar{n}_i)]^{n_i}}{m_i!n_i!}\frac{\Gamma_{e''g}}{[\omega_{e''g}+(n_i-m_i)\omega_i-2\omega]^2+\Gamma^2_{e''g}}\ , \tag{5.9}$$

where S_i',ω_i, and $\Gamma_{e''g}$ could be determined from Fig. 4. In fact, it will be more convenient to fit the experimental data of the SHG signal by using the expression of the SHG intensity deduced from our model, and given by Eq. (5.1). Then, the values of the constants S_i',ω_i, $\Gamma_{e''g}$, and $\omega_{e''g}$ for the adsorbed rhodamine 6G are easily determined. There are given in the caption of Fig. 5. The value of the dephasing constant Γ_{ng} as well as the one of ω_{ng}, have been introduced in the numerical simulations. They have very little influence because of the nonresonant character of the first electronic transition. Therefore, the value of ω_{ng} has been taken from the ab-

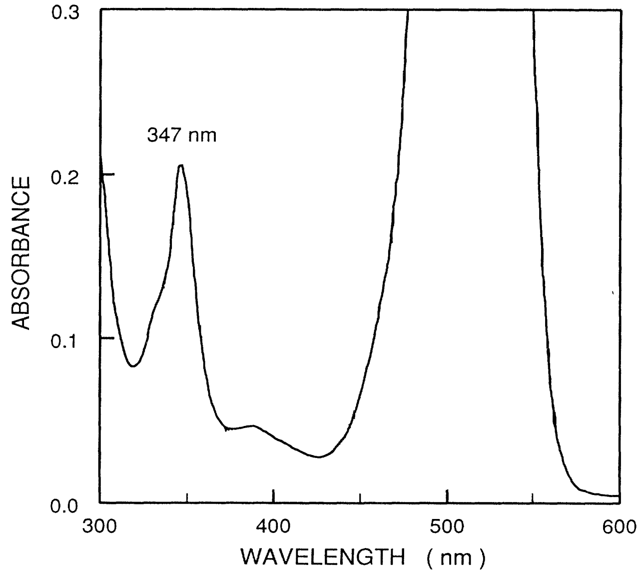

FIG. 4. Absorption spectrum of rhodamine 6G in alcohol.

sorption spectrum of the isolated molecule, and corresponds to 18 900 cm^{-1}. Of course, the fit cannot describe the increase of the absorbance as well as the two experimental points in the range 290–310 nm. This is because this resonant variation involves electronic levels which are not accounted for in our description. But, concerning this part of the frequency range, first, there is no way to get precise information about the nature of these higher excited states, and second, we are here in the nonresonant-resonant case, which implies that 2ω must be near resonant with the frequency transition between S_2 and the ground electronic configuration. Finally, it can be mentioned that this enhancement has been discussed by Heinz *et al.* [6] as resulting from the resonant process when ω is nearly degenerate with the frequency transition E_{S_1}-E_g. However, our numerical simulations clearly show that this process cannot justify alone the strong increase observed in Fig. 5.

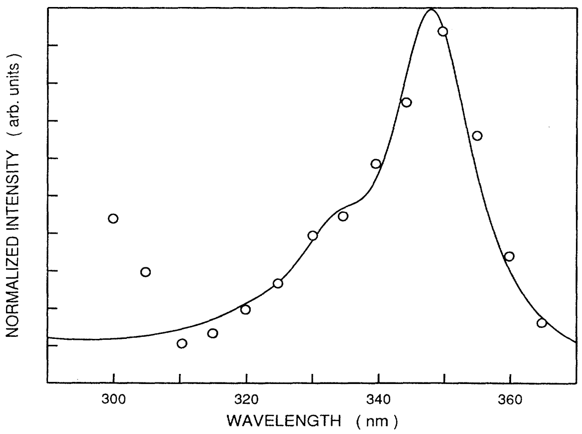

FIG. 5. Comparison of theoretical and experimental SHG. The parameters used to model the SHG data are given by $\omega_{e''g}=28\,500$ cm^{-1}, $S_i'=0.23$, $\Gamma_{e''g}=650$ cm^{-1}, and $\omega_i=1130$ cm^{-1}.

The frequency shift obtained between the transition frequencies for the adsorbed and the isolated molecule is a signature of the binding energy of the molecule with the surface.

VI. CONCLUSION

In the present work, we have developed a general microscopic theory of second-order optical processes, with a particular emphasis on second-harmonic generation in the steady-state regime. Four different typical cases, which can be encountered in experimental situations, have been explicitly evaluated. They are classified according to the magnitude of the off-resonance parameters characteristic of the one- and two-photon processes taking place in SHG. Simple relations of the second-order susceptibility with the band-shape function of the absorption spectra as well as with the dispersion band-shape function have been established. In the particular case of rhodamines, these functions have been used to calculate the second-harmonic-generation spectra.

In the future, it will be of the interest to model the second-harmonic generation of molecular systems adsorbed on surfaces, in the pulsed case. Such a theoretical description could give detailed information on the recent experiments done by Prybyla, Tom, and Aumillek [26,27], which have applied SHG to study the laser-induced desorption of CO from the Cu(III) surface. Both steady-state and time-resolved SHG techniques have been used in their investigations. An important feature in these investigations is that they have succeeded in using the femtosecond time-resolved SHG to probe the desorption mechanism induced by femtosecond laser pulses.

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APPENDIX A

In this Appendix, we provide a different derivation of the polarization for the second harmonic generation. Notice that

$$\frac{\partial\rho(1)}{\partial t}=-\frac{i}{\hbar}L_0'\rho(t)-\frac{i}{\hbar}\lambda L_1(t)\rho(t)\ , \tag{A1}$$

where λ denotes the perturbation parameter. With the development

$$\rho(t)=\rho^{(0)}(t)+\lambda\rho^{(1)}(t)+\lambda^2\rho^{(2)}(t)+\cdots \tag{A2}$$

the various contributions to the perturbational expansion will result from the equations

$$\frac{\partial\rho^{(0)}(t)}{\partial t}=-\frac{i}{\hbar}L_0'\rho^{(0)}(t)\ , \tag{A3}$$

$$\frac{\partial\rho^{(1)}(t)}{\partial t}=-\frac{i}{\hbar}L_0'\rho^{(1)}(t)-\frac{i}{\hbar}L_1(t)\rho^{(0)}(t)\ , \tag{A4}$$

$$\frac{\partial\rho^{(2)}(t)}{\partial t}=-\frac{i}{\hbar}L_0'\rho^{(2)}(t)-\frac{i}{\hbar}L_1(t)\rho^{(1)}(t)\ . \tag{A5}$$

$$\cdots$$

Solutions of Eqs. (A3)–(A5) yield

$$\rho^{(0)}(t)=e^{-(i/\hbar)L_0'(t-t_i)}\rho(t_i)=e^{-(i/\hbar)L_0'\sigma_i}\ , \tag{A6}$$

$$\rho^{(1)}(t)=-\frac{i}{\hbar}e^{-(i/\hbar)L_0't}\int_{t_i}^{t}d\tau\,\overline{L}_1(\tau)\sigma_i\ , \tag{A7}$$

and

$$\rho^{(2)}(t)=-\frac{1}{\hbar^2}e^{-(i/\hbar)L_0't}\int_{t_i}^{t}d\tau\,\overline{L}_1(\tau)\int_{t_i}^{\tau}d\tau_1\overline{L}_1(\tau_1)\sigma_i$$
$$=e^{-(i/\hbar)L_0't}\Delta\sigma^{(2)}(t)\ . \tag{A8}$$

The second-order polarization is given by

$$\mathbf{P}^{(2)}(t)=\sum_{n}\sum_{m}\rho_{nm}^{(2)}(t)\boldsymbol{\mu}_{mn}\ , \tag{A9}$$

where

$$\frac{\partial\rho_{mn}^{(2)}(t)}{\partial t}=-i\omega_{mn}'\rho_{mn}^{(2)}(t)-\frac{i}{\hbar}\sum_{m'}[V_{mm'}(t)\rho_{m'n}^{(1)}(t)-\rho_{mm'}^{(1)}(t)V_{m'n}(t)]\ , \tag{A10}$$

$$\frac{\partial\rho_{m'n'}^{(1)}(t)}{\partial t}=-i\omega_{m'n'}'\rho_{m'n'}^{(1)}(t)+\frac{i}{\hbar}V_{m'n'}(t)[\rho_{m'm'}^{(0)}(t)-\rho_{n'n'}^{(0)}(t)]\ . \tag{A11}$$

If as usual the system is initially thermalized, the zero-order populations are independent of time and we have

$$\rho_{m'm'}^{(0)}(t)=\rho_{m'm'}(t_i),\quad \rho_{n'n'}^{(0)}(t)=\rho_{n'n'}(t_i)\ , \tag{A12}$$

so that

$$\rho_{m'n'}^{(1)}(t)=\frac{i}{\hbar}e^{-\omega_{m'n'}'t}\int_{t_i}^{t}d\tau\,V_{m'n'}(\tau)e^{i\omega_{m'n'}'\tau}[\rho_{m'm'}(t_i)-\rho_{n'n'}(t_i)] \tag{A13}$$

and

$$\rho_{mn}^{(2)}(t)=\frac{1}{\hbar^2}e^{-i\omega_{mn}'t}\sum_{m'}\int_{t_i}^{t}d\tau\left[V_{mm'}(\tau)e^{i\omega_{mm'}'\tau}\int_{t_i}^{\tau}d\tau_1V_{m'n}(\tau_1)e^{i\omega_{m'n}'\tau_1}[\rho_{m'm'}(t_i)-\rho_{nn}(t_i)]\right.$$
$$\left.-V_{m'n}(\tau)e^{i\omega_{m'n}'\tau}\int_{t_i}^{\tau}d\tau_1V_{mm'}(\tau_1)e^{i\omega_{mm'}'\tau_1}[\rho_{mm}(t_i)-\rho_{m'm'}(t_i)]\right]\ . \tag{A14}$$

Using the following expression

$$V(t)=-\boldsymbol{\mu}\cdot[\mathbf{E}(\omega)e^{-i\omega t}+\mathbf{E}(-\omega)e^{i\omega t}]\ , \tag{A15}$$

valid for the steady-state case, we obtain in the rotating-wave approximation

$$\rho_{mn}^{(2)}(t)=\frac{1}{\hbar^2}\sum_{m'}\left[\left\{\frac{[\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(\omega)][\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(\omega)]}{(\omega_{m'n}'-\omega)(\omega_{mn}'-2\omega)}e^{-2i\omega t}+\frac{[\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(-\omega)][\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(-\omega)]}{(\omega_{m'n}'+\omega)(\omega_{mn}'+2\omega)}e^{2i\omega t}\right\}[\rho_{nn}(t_i)-\rho_{m'm'}(t_i)]\right.$$
$$\left.+\left\{\frac{[\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(\omega)][\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(\omega)]}{(\omega_{mm'}'-\omega)(\omega_{mn}'-2\omega)}e^{-2i\omega t}+\frac{[\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(-\omega)][\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(-\omega)]}{(\omega_{mm'}'+\omega)(\omega_{mn}'+2\omega)}e^{2i\omega t}\right\}[\rho_{mm}(t_i)-\rho_{m'm'}(t_i)]\right]\ . \tag{A16}$$

Therefore, we get for the expression of the second-order polarization

$$\mathbf{P}^{(2)}(t)=\mathbf{P}^{(2)}(2\omega)e^{-2i\omega t}+\mathbf{P}^{(2)}(-2\omega)e^{2i\omega t}\ , \tag{A17}$$

where

$$\mathbf{P}^{(2)}(2\omega)=\frac{1}{\hbar^2}\sum_{n}\sum_{m}\sum_{m'}\boldsymbol{\mu}_{nm}\left[\frac{[\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(\omega)][\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(\omega)]}{(\omega_{m'n}'-\omega)(\omega_{mn}'-2\omega)}[\rho_{nn}(t_i)-\rho_{m'm'}(t_i)]\right.$$
$$\left.+\frac{[\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(\omega)][\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(\omega)]}{(\omega_{mm'}'-\omega)(\omega_{mn}'-2\omega)}[\rho_{mm}(t_i)-\rho_{m'm'}(t_i)]\right] \tag{A18}$$

and

$$\mathbf{P}^{(2)}(-2\omega)=\frac{1}{\hbar^2}\sum_n\sum_m\sum_{m'}\boldsymbol{\mu}_{nm}\left[\frac{[\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(-\omega)][\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(-\omega)]}{(\omega'_{m'n}+\omega)(\omega'_{mn}+2\omega)}[\rho_{nn}(t_i)-\rho_{m'm'}(t_i)]\right.$$
$$\left.+\frac{[\boldsymbol{\mu}_{m'n}\cdot\mathbf{E}(-\omega)][\boldsymbol{\mu}_{mm'}\cdot\mathbf{E}(-\omega)]}{(\omega'_{mm'}+\omega)(\omega'_{mn}+2\omega)}[\rho_{mm}(t_i)-\rho_{m'm'}(t_i)]\right]. \tag{A19}$$

The theoretical approach presented in this Appendix is given for convenience and is commonly described in textbooks [1–3].

APPENDIX B

To evaluate $H_i(t_1,t_2)$, we use the Mehler formula to obtain

$$H_i(t_1,t_2)=M\int_{-\infty}^{\infty}dQ_i\int_{-\infty}^{\infty}d\bar{Q}_i\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\exp\left[-\frac{\beta_i}{4}\left\{(Q_i+\bar{\bar{Q}}_i)^2\tanh\frac{\lambda_i}{2}+(Q_i-\bar{\bar{Q}}_i)^2\coth\frac{\lambda_i}{2}+(Q_i''+\bar{Q}_i'')^2\tanh\frac{\lambda_i''}{2}\right.\right.$$
$$\left.\left.+(Q_i''-\bar{Q}_i'')^2\coth\frac{\lambda_i''}{2}+(\bar{Q}_i'+\bar{\bar{Q}}_i')^2\tanh\frac{\lambda_i'}{2}+(\bar{Q}_i'-\bar{\bar{Q}}_i')^2\coth\frac{\lambda_i'}{2}\right\}\right], \tag{B1}$$

where $Q_i'=Q_i+d_i'$ and $Q_i''=Q_i+d_i''$, d_i' and d_i'' being the normal coordinate displacements. Also, we have to bear in mind that here λ_i, λ_i', and λ_i'' are depending on t_1 and t_2. To carry out the integration with respect to Q_i, we write Eq. (B1) as

$$H_i(t_1,t_2)=M\int_{-\infty}^{\infty}dQ_i\int_{-\infty}^{\infty}d\bar{Q}_i\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\,\exp[-a_iQ_i^2-b_iQ_i-c_i]$$
$$=M\left[\frac{\pi}{a_i}\right]^{1/2}\int_{-\infty}^{\infty}d\bar{Q}_i\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\,\exp\left[-c_i+\frac{b_i^2}{4a_i}\right], \tag{B2}$$

where

$$a_i=\frac{\beta_i}{4}\left[\left\{\tanh\frac{\lambda_i}{2}+\coth\frac{\lambda_i}{2}\right\}+\left\{\tanh\frac{\lambda_i''}{2}+\coth\frac{\lambda_i''}{2}\right\}\right]$$
$$=\frac{\beta_i}{2}[\coth\lambda_i+\coth\lambda_i''], \tag{B3}$$

$$b_i=\frac{\beta_i}{2}\left[\bar{\bar{Q}}_i\left\{\tanh\frac{\lambda_i}{2}-\coth\frac{\lambda_i}{2}\right\}+\bar{Q}_i\left\{\tanh\frac{\lambda_i''}{2}-\coth\frac{\lambda_i''}{2}\right\}+2d_i''\tanh\frac{\lambda_i''}{2}\right]$$
$$=\beta_i\left[-\bar{\bar{Q}}_i\operatorname{csch}\lambda_i-\bar{Q}_i\operatorname{csch}\lambda_i''+d_i''\tanh\frac{\lambda_i''}{2}\right], \tag{B4}$$

and

$$c_i=\frac{\beta_i}{4}\left[\bar{\bar{Q}}_i^2\left\{\tanh\frac{\lambda_i}{2}+\coth\frac{\lambda_i}{2}\right\}+\{\bar{Q}_i+2d_i''\}^2\tanh\frac{\lambda_i''}{2}+\bar{Q}_i^2\coth\frac{\lambda_i''}{2}+\{\bar{\bar{Q}}_i+\bar{Q}_i+2d_i'\}^2\tanh\frac{\lambda_i'}{2}+\{\bar{Q}_i-\bar{\bar{Q}}_i\}^2\coth\frac{\lambda_i'}{2}\right] \tag{B5}$$

$$=\frac{\beta_i}{2}\left[\bar{\bar{Q}}_i^2\{\coth\lambda_i+\coth\lambda_i'\}+\bar{Q}_i^2\{\coth\lambda_i''+\coth\lambda_i'\}-2\bar{Q}_i\bar{\bar{Q}}_i\operatorname{csch}\lambda_i'+2\bar{Q}_i\left\{d_i''\tanh\frac{\lambda_i''}{2}+d_i'\tanh\frac{\lambda_i'}{2}\right\}\right.$$
$$\left.+2\bar{\bar{Q}}_id_i'\tanh\frac{\lambda_i'}{2}+2d_i''^2\tanh\frac{\lambda_i''}{2}+2d_i'^2\tanh\frac{\lambda_i'}{2}\right]. \tag{B6}$$

Similarly, we have

$$H_i(t_1,t_2)=M\left[\frac{\pi}{a_i}\right]^{1/2}\int_{-\infty}^{\infty}d\bar{Q}_i\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\,\exp[-a_i'\bar{Q}_i^2-b_i'\bar{Q}_i-c_i'] \tag{B7}$$

$$=M\left[\frac{\pi^2}{a_ia_i'}\right]^{1/2}\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\,\exp\left[-c_i'+\frac{b_i'^2}{4a_i'}\right], \tag{B8}$$

where the additional constants have been introduced

$$a_i'=\frac{\beta_i}{2}\left[\coth\lambda_i'+\coth\lambda_i''-\frac{\operatorname{csch}^2\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right], \tag{B9}$$

$$b_i'=\beta_i\left[-\bar{\bar{Q}}_1\left\{\operatorname{csch}\lambda_i'+\frac{\operatorname{csch}\lambda_i\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}+d_i'\tanh\frac{\lambda_i'}{2}+d_i''\tanh\frac{\lambda_i''}{2}\left\{1+\frac{\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}\right], \tag{B10}$$

and

$$c_i'=\frac{\beta_i}{2}\left[\bar{\bar{Q}}_i^{(2)}\left\{\coth\lambda_i+\coth\lambda_i'-\frac{\operatorname{csch}^2\lambda_i}{\coth\lambda_i+\coth\lambda_i''}\right\}+2\bar{\bar{Q}}_i\left\{d_i'\tanh\frac{\lambda_i'}{2}+\frac{d_i''\operatorname{csch}\lambda_i\tanh\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}\right.$$
$$\left.+2d_i''^2\tanh\frac{\lambda_i''}{2}+2d_i'^2\tanh\frac{\lambda_i'}{2}-\frac{d_i''^2\tanh^2\frac{\lambda_i''}{2}}{\coth\lambda_i+\coth\lambda_i''}\right]. \tag{B11}$$

It follows that

$$H_i(t_1,t_2)=M\left[\frac{\pi^2}{a_ia_i'}\right]^{1/2}\int_{-\infty}^{\infty}d\bar{\bar{Q}}_i\,\exp[-a_i''\bar{\bar{Q}}_i^2-b_i''\bar{\bar{Q}}_i-c_i'']$$

$$=M\left[\frac{\pi^3}{a_ia_i'a_i''}\right]^{1/2}\exp\left[-c_i''+\frac{b_i''^2}{4a_i''}\right], \tag{B12}$$

where the following notations,

$$a_i''=\frac{\beta_i}{2}\left[\left\{\coth\lambda_i+\coth\lambda_i'-\frac{\operatorname{csch}^2\lambda_i}{\coth\lambda_i+\coth\lambda_i''}\right\}-\frac{\left\{\operatorname{csch}\lambda_i'+\dfrac{\operatorname{csch}\lambda_i\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}^2}{\{\coth\lambda_i'+\coth\lambda_i''\}-\dfrac{\operatorname{csch}^2\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}}\right], \tag{B13}$$

$$b_i''=\beta_i\left\{d_i'\tanh\frac{\lambda_i'}{2}+\frac{d_i''\operatorname{csch}\lambda_i\tanh\frac{\lambda_i''}{2}}{\coth\lambda_i+\coth\lambda_i''}\right\}$$
$$+\frac{\beta_i^2}{2a_i'}\left\{\operatorname{csch}\lambda_i'+\frac{\operatorname{csch}\lambda_i\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}\left[d_i'\tanh\frac{\lambda_i'}{2}+d_i''\tanh\frac{\lambda_i''}{2}\left\{1+\frac{\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}\right], \tag{B14}$$

$$c_i''=\beta_i\left[\left\{d_i''^2\tanh\frac{\lambda_i''}{2}+d_i'^2\tanh\frac{\lambda_i'}{2}\right\}-\frac{d_i''^2\tanh^2\frac{\lambda_i''}{2}}{2\{\coth\lambda_i+\coth\lambda_i''\}}\right]$$
$$-\frac{\beta_i^2}{4a_i'}\left[d_i'\tanh\frac{\lambda_i'}{2}+d_i''\tanh\frac{\lambda_i''}{2}\left\{1+\frac{\operatorname{csch}\lambda_i''}{\coth\lambda_i+\coth\lambda_i''}\right\}\right]^2, \tag{B15}$$

have been introduced for convenience.

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