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Coherent light scattering in isotropic media: Theory of degenerate four-wave mixing in vibrational spectroscopy

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The expression for the light-scattering intensity is deduced using the general perturbation expansion for a stationary solution of the Liouville equation. The principal importance of translational symmetry for coherent spectroscopy is rigorously shown. The expressions for the degenerate four-wave mixing (DFWM) signal intensity as well as for its polarization are derived in the case of fast translational relaxation (Dicke narrowing). The instructive relationship between the index of refraction, the absorption spectrum, and the DFWM is established.

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I. INTRODUCTION

Among nonlinear spectroscopic techniques the coherent light scattering is especially favorable as a diagnostic tool. The interest in spatial and temporal resolved measurements of temperature and special concentration has motivated intensive development of coherent spectroscopy methods over the past decades [1–5]. The desirable thermodynamic parameters have to be extract- from optical spectra on the basis of an appropriate statistical theory describing the influence of the thermal molecular motion on the observed line shape. Existing theories of degenerate four-wave mixing [6–10] are developed for electronic spectra and based practically on the evaluation of the spectrum shape for an isolated molecule. The broadening of spectral components due to the interaction with other particles is considered independently for each line. This approach is justified in the presence of strong quenching and dephasing processes. However, in vibrational spectroscopy [11] the independent line broadening determined by the vibrational dephasing rate [12] as well as the spectral exchange phenomenon [13,14] connected with rotational relaxation have to be considered simultaneously. When a single linewidth becomes comparable with the spacing between neighboring rotational components the spectrum drastically changes with increasing density and it cannot be represented as a composition of independently broadening lines [15,16]. To explain this behavior on the basis of details of the relaxation mechanism in the medium the correspondence between the observed contour and time correlation function of an appropriate molecular operator has to be first established. In general, in a nonlinear molecular spectroscopy the line shape is not expressed through the one-dimensional time-dependent correlation function. To reproduce the spectrum under thermal equilibrium in the time scale, it is necessary to know the function, which depends on several arguments:

$$K(t_2-t_1,t_3-t_1,\ldots,t_n-t_1)=\frac{1}{\langle d^n\rangle}\left\langle\prod_{l=1}^{n} d(t_l)\right\rangle , \tag{1}$$

where n is the order of perturbation theory and d is a molecular operator providing interaction with the external field.

In particular, the general expression for the four-wave-mixing (FWM) signal intensity derived in [17] involves an eight-point time correlation function of the dipole operator. Obviously, the correlation function (1) cannot be calculated exactly from a one-dimensional spectrum. Thus, the processing of the spectroscopic data can give only quite poor information about the mechanism of molecular mobility in the medium. On the other hand, the results of different techniques may not be strictly compared with each other. Nevertheless, in some cases the approximated solution for this problem can be found. For instance, in [18] the coherent anti-Stokes Raman-scattering (CARS) intensity was expressed via the ordinary correlation function of the molecular polarizability tensor. The main purpose of this paper is to find out the relationship between the degenerate-four-wave-mixing (DFWM) spectrum and the appropriate correlation function. We will assume further that the incident beams are coherent and monochromatic.

It is easy to see that, if the Doppler shift can be neglected, the final state of the molecule after the interaction with two degenerated photons ($\omega_1=\omega_2$) coincides with its initial equilibrium state. This circumstance is reflected in the singularity occurring in the frequency dependence of the third-order susceptibility [see (14.3b) in [6] at $m=g$]. In [19] this property of the DFWM spectrum is used to evaluate the line shape of the two-level system within the impact approximation. In this case of many-level interacting molecules among all corrections to the density matrix which appear due to the twofold interaction with radiation, only the part belonging to the equilibrium distribution should be retained to describe the stationary spectrum. This is because all other components have finite lifetimes determined by the re-

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laxation mechanism in the medium. As a result, the third-order susceptibility can be factorized and represented as a multiplication of the two susceptibilities of the first order. Since the influence of the Doppler broadening on the line shape of rovibrational spectra is comparatively weak, their analysis is simplified considerably. In general, the factorization cannot be attained when the electronic transition is observed. If pump and probe waves travel in different directions the Doppler linewidth usually exceeds the characteristic relaxation time and the rotational line strengths [20] entirely describe the spectrum shape. However, the approach is invalid when laser beams are near to being parallel. This is the special case that is similar to DFWM in vibrational spectroscopy and will be also considered in the present paper.

II. THEORY

A. General approach

The expression for the observed spectral intensity will be derived here in the form of the perturbation series. The matter-radiation interaction operator V will be treated as a perturbation to the Hamiltonian operator H_0 of the entire system (the matter and the radiation) in the absence of a coupling. As an initial point let us consider the general definition for radiation intensity of normal mode α. In the Schrödinger picture it can be expressed using the density matrix of the system,

$$W_\alpha = \hbar\omega_\alpha \frac{d}{dt}\langle n_\alpha + \tfrac{1}{2}\rangle = \hbar\omega_\alpha \mathrm{Tr}\left[(a_\alpha^\dagger a_\alpha + \tfrac{1}{2}) \frac{d}{dt}\rho(t) \right] , \tag{2}$$

where $a_\alpha^\dagger$ and a_α are creation and annihilation operators, respectively; ω_α is the frequency of the photon. The complete set of states here is assumed to be eigenvectors of the unperturbed Hamiltonian operator H_0. For the closed dynamical system the time evolution of density matrix $\rho(t)$ is determined by the Liouville–von Neumann equation

$$\begin{aligned} \frac{d}{dt}\rho(t) &= -\frac{i}{\hbar}[H_0,\rho(t)]_- - \frac{i}{\hbar}[V,\rho(t)]_- \\ &= -\frac{i}{\hbar}H_0^\times \rho(t) - \frac{i}{\hbar}V^\times \rho(t) . \end{aligned} \tag{3}$$

Here $A^\times B$ is the shorthand notation for commutator $[A,B]_-$.

The interaction between matter and radiation will be considered below within the framework of the dipole approximation [17–19]

$$V = \sum_{j=1}^{N} [\mathbf{d}_j \cdot \mathbf{E}(\mathbf{r}_j)] = \sum_{j,\alpha} \{ \mathbf{d}_j \cdot [a_\alpha \mathbf{A}_\alpha(\mathbf{r}_j) + a_\alpha^\dagger \mathbf{A}_\alpha^\dagger(\mathbf{r}_j)] \} , \tag{4}$$

where N is the number of actively participating particles, $\mathbf{d}_j$ is the dipole-moment operator for molecule j, and $\mathbf{E}(\mathbf{r}_j)$ is the transverse electric-field operator at the center of mass of the molecule,

$$\mathbf{A}_\alpha(\mathbf{r}) = i\mathbf{e}_\alpha \left[\frac{2\pi\hbar\omega_\alpha}{\mathcal{V}} \right]^{1/2} \exp[i(\mathbf{k}_\alpha \cdot \mathbf{r})] . \tag{5}$$

Here $\mathbf{e}_\alpha$ and $\mathbf{k}_\alpha$ are polarization and wave vectors, respectively, for normal mode α of a field quantized in a volume $\mathcal{V}$.

Taking into account the commutation relations for photons and the conservation of the number of photons in the absence of scattering,

$$[a_\alpha, a_\beta^\dagger] = \delta_{\alpha,\beta} , \tag{6a}$$

$$H_0^\times a a^\dagger = 0 , \tag{6b}$$

and inserting Eqs. (3) and (4) into (2), one readily arrives at

$$\begin{aligned} W_\alpha &= i\omega_\alpha \mathrm{Tr}[\rho(t) V^\times (a_\alpha^\dagger a_\alpha + \tfrac{1}{2})] \\ &= -N\omega_\alpha \left[\frac{2\pi\hbar\omega_\alpha}{\mathcal{V}} \right]^{1/2} \mathrm{Tr}[(a_\alpha d_{\alpha,1} e^{i(\mathbf{k}\cdot\mathbf{r}_1)} \\ &\qquad + a_\alpha^\dagger d_{\alpha,1}^\dagger e^{-i(\mathbf{k}_\alpha \cdot \mathbf{r}_1)}) \rho(t)] , \end{aligned} \tag{7}$$

where $d_{\alpha,j} = (\mathbf{e}_\alpha \cdot \mathbf{d}_j)$.

The formal stationary solution $\rho = \rho(t)|_{t\to\infty}$ of the Liouville equation (3) will be found for the practically important case when the initial distribution $\rho_0 = \rho(t)|_{t\to 0}$ is diagonal in the basis of H_0 eigenvectors, i.e.,

$$H_0^\times \rho_0 = 0 . \tag{8}$$

In the other words, $\rho_0 = \rho_{\mathrm{rad}}\rho_{\mathrm{eq}}$, where ρ_{rad} and ρ_{eq} are the stationary density matrix for radiation in the absence of a coupling with medium and the equilibrium Boltzmann distribution over the states of the matter, respectively.

The limit $\rho = \lim_{t\to\infty}\rho(t)$ for the equilibrium system can be rewritten in the more convenient form

$$\rho = \lim_{\varepsilon\to 0} \left\{ \varepsilon \int_0^\infty \exp(-\varepsilon t)\rho(t)dt \right\} . \tag{9}$$

Then for the desirable solution ρ we have from Eqs. (3), (8), and (9)

$$\begin{aligned} \rho &= \lim_{\varepsilon\to 0} [\varepsilon (H_0^\times + V^\times + \varepsilon)^{-1} \rho_0] \\ &= \sum_{n=1}^{\infty} [(-1)(H_0^\times)^{-1} V^\times]^{n-1} \rho_0 \\ &= [1 + (H_0^\times)^{-1} V^\times]^{-1} \rho_0 . \end{aligned} \tag{10}$$

Thus, expression (7) takes the final form

$$\begin{aligned}W_\alpha&=i\omega_\alpha \mathrm{Tr}\{(V^\times a_\alpha^\dagger a_\alpha)[1+(H_0^\times)^{-1}V^\times]^{-1}\rho_0\}\\&=-N\omega_\alpha\left[\frac{2\pi\hbar\omega_\alpha}{\mathcal{V}}\right]^{1/2}\mathrm{Tr}\left\{(a_\alpha d_{\alpha,1}e^{i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)}+a_\alpha^\dagger d_{\alpha,1}^\dagger e^{-i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)})\right.\\&\qquad\times\sum_{n=1}^{\infty}\left[\left[\frac{2\pi}{\hbar\mathcal{V}}\right]^{1/2}\sum_{\alpha',j}\sqrt{\omega_{\alpha'}}\left[\frac{i}{\hbar}H_0^\times\right]^{-1}(a_{\alpha'}d_{\alpha',j}e^{i(\mathbf{k}_\alpha\cdot\mathbf{r}_j)}\right.\\&\qquad\qquad\left.\left.-a_{\alpha'}^\dagger d_{\alpha',j}^\dagger e^{-i(\mathbf{k}_\alpha\cdot\mathbf{r}_j)})^\times\right]^{n-1}\rho_0\right\}\;.\end{aligned}\tag{11}$$

The factor N here results from the invariance of the trace over all permutations of identical particles [21]. It is easy to see that terms in Eq. (11) corresponding to $n=2$ and $n=4$ describe the infrared absorption (IR) and Raman-scattering experiments, respectively. In particular, for $n=2$ one obtains from (11)

$$\begin{aligned}W_\alpha^{\mathrm{IR}}&=-\frac{4\pi N}{\mathcal{V}}\omega_\alpha^2\mathrm{Re}\left\{\mathrm{Tr}\left[a_\alpha^\dagger d_{\alpha,1}^\dagger e^{-i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)}\left[\frac{i}{\hbar}H_0^\times\right]^{-1}(a_\alpha d_{\alpha,1}e^{i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)})^\times\rho_0\right]\right\}\\&\approx-\frac{4\pi N}{\mathcal{V}}\omega_\alpha I_\alpha\mathrm{Re}\left\{\mathrm{Tr}_M\left[d_{\alpha,1}^\dagger e^{-i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)}\left[\frac{i}{\hbar}H_M^\times-i\omega_\alpha\right]^{-1}(d_{\alpha,1}e^{i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)}\rho_{\mathrm{eq}}-\rho_{\mathrm{eq}}d_{\alpha,1}e^{i(\mathbf{k}_\alpha\cdot\mathbf{r}_1)})\right]\right\}\;.\end{aligned}\tag{12}$$

Here H_M is the Hamiltonian operator of the medium. Tr_M denotes the trace over the states of the matter ($\mathrm{Tr}=\mathrm{Tr}_M\mathrm{Tr}_{\mathrm{rad}}$). Deriving the second equality in (12) we have neglected the commutation rule (6a) for the case of the classical field ($I_\alpha/\hbar\omega_\alpha\gg1$),

$$\mathrm{Tr}_{\mathrm{rad}}[(a_\alpha a_\alpha^\dagger)\rho_{\mathrm{rad}}]\approx\mathrm{Tr}_{\mathrm{rad}}[(a_\alpha^\dagger a_\alpha)\rho_{\mathrm{rad}}]\;.\tag{13}$$

Let us assume now that ρ_{eq} is a diagonal operator,

$$\langle\nu|\rho_{\mathrm{eq}}|\nu'\rangle=\delta_{\nu,\nu'}\rho_\nu\rho_{\mathrm{R-T}}\;,\quad\rho_{\mathrm{R-T}}=\sum_{\nu=0}^{\infty}\langle\nu|\rho_{\mathrm{eq}}|\nu\rangle\;,\tag{14}$$

in the basis of vibrational states $|\nu\rangle$ [22],

$$\langle\nu|H_M|\nu'\rangle=\delta_{\nu,\nu'}(H_{\mathrm{R-T}}(\nu)+E_\nu)\;,\tag{15}$$

where R-T denotes rotation-translation. Equation (12) can be then rearranged as

$$W_\alpha^{\mathrm{IR}}=-\frac{4\pi N}{3\mathcal{V}}\omega_\alpha I_\alpha\mathrm{Re}\left[\sum_{\nu,\nu'=0}^{\infty}[G_{\nu',\nu}(\omega_\alpha,k_\alpha)\rho_\nu-G_{\nu,\nu'}(-\omega_\alpha,-k_\alpha)\rho_{\nu'}]\right]\;,\tag{16}$$

where we adopt the following definition for the susceptibility:

$$\begin{aligned}G_{\nu',\nu}(\omega,k)&=\mathrm{Tr}'\left[\langle\nu|d|\nu'\rangle e^{-i(\mathbf{k}\cdot\mathbf{r}_1)}\left[\frac{i}{\hbar}H_M^\times-i\omega\right]^{-1}\Bigg|_{\substack{\nu'\\ \nu}}\langle\nu'|d|\nu\rangle e^{i(\mathbf{k}\cdot\mathbf{r}_1)}\rho_{\mathrm{R-T}}\right]\\&=\mathrm{Tr}'\left[\langle\nu|d|\nu'\rangle e^{-i(\mathbf{k}\cdot\mathbf{r}_1)}\left[\frac{i}{\hbar}H_{\mathrm{R-T}}^\times+i\omega_{\nu',\nu}-i\omega\right]^{-1}\langle\nu'|d|\nu\rangle e^{i(\mathbf{k}\cdot\mathbf{r}_1)}\rho_{\mathrm{R-T}}\right]\;.\end{aligned}\tag{17}$$

Here the transition ($\nu\rightarrow\nu'$) implies $\hbar\omega_{\nu',\nu}=E_{\nu'}-E_\nu$. Tr' means that the sum over vibrational states is excluded from the trace (Tr_M). Equations (16) and (17) lead to the usual expression for the absorption intensity via the dipole-moment correlation function (see Appendix).

B. Coherent scattering

As was mentioned in [17–19], the selection rules for wave vectors in coherent light-scattering experiments are caused by the interaction of the same photon with different molecules. By using isotropy of the medium we now derive the phase-matching conditions on the basis of the general expansion (11). First, let us introduce the integral representation $L(\mathbf{r}_f,\mathbf{r}_f';\mathbf{r},\mathbf{r}')$ for the differential superoperator $L(\mathbf{r}_f,\mathbf{r}_f')$ describing the motion of particle in a space of translational coordinates ($|\mathbf{r}\rangle\langle\mathbf{r}'|$)

$$\begin{aligned}L(\mathbf{r}_f,\mathbf{r}_f')\rho(\mathbf{r}_f,\mathbf{r}_f')&=\int\int\rho(\mathbf{r},\mathbf{r}')[L(\mathbf{r}_f,\mathbf{r}_f')\delta(\mathbf{r}_f-\mathbf{r})\delta(\mathbf{r}_f'-\mathbf{r}')]d\mathbf{r}\,d\mathbf{r}'\\&=\int\int L(\mathbf{r}_f,\mathbf{r}_f';\mathbf{r},\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'\;.\end{aligned}\tag{18}$$

Thus, for example, the free translational motion of a molecule is determined by the integral superoperator:

$$L(\mathbf{r}_f,\mathbf{r}'_f;\mathbf{r},\mathbf{r}')=\frac{1}{(2\pi)^6}\int\int d\mathbf{k}\,d\mathbf{k}'\exp\left[-\frac{i}{\hbar}[H(\mathbf{r})-H(\mathbf{r}')]t\right]\exp[i\mathbf{k}\cdot(\mathbf{r}_f-\mathbf{r})-i\mathbf{k}'\cdot(\mathbf{r}'_f-\mathbf{r}')]$$
$$=\left[\frac{m}{2\pi\hbar t}\right]^3\exp\left[-\frac{i}{2}\frac{m}{\hbar t}(|\mathbf{r}_f-\mathbf{r}|^2-|\mathbf{r}'_f-\mathbf{r}'|^2)\right]\ . \tag{19}$$

The major advantage of the integral form for the equation of motion in an isotropic medium is the simplicity of defining the invariance of the operators over any translational transformation ($\mathbf{r}\rightarrow\mathbf{r}+\mathbf{r}_0$)

$$L(\mathbf{r}_f,\mathbf{r}'_f;\mathbf{r},\mathbf{r}')=L(\mathbf{r}_f+\mathbf{r}_0,\mathbf{r}'_f+\mathbf{r}_0;\mathbf{r}+\mathbf{r}_0,\mathbf{r}'+\mathbf{r}_0)\ . \tag{20}$$

In the momentum representation the invariance principle (20) yields the usual momentum-conservation law, which in the integral superoperator terms takes the form

$$L(\mathbf{p}_f,\mathbf{p}'_f;\mathbf{p},\mathbf{p}')=\int\int\int\int L(\mathbf{r}_f,\mathbf{r}'_f;\mathbf{r},\mathbf{r}')\exp[i(\mathbf{r}_f\cdot\mathbf{p}_f)-i(\mathbf{r}'_f\cdot\mathbf{p}'_f)-i(\mathbf{r}\cdot\mathbf{p})+i(\mathbf{r}'\cdot\mathbf{p}')]d\mathbf{r}\,d\mathbf{r}'d\mathbf{r}_fd\mathbf{r}_f{}'$$
$$=\delta[\tfrac{1}{2}(\mathbf{p}_f+\mathbf{p}'_f)-\tfrac{1}{2}(\mathbf{p}+\mathbf{p}')]L_r(\mathbf{p}_f,\mathbf{p}'_f;\mathbf{p},\mathbf{p}')\ , \tag{21}$$

where L_r is the regular superoperator corresponding to L.

Analogously, for a system consisting from N particles the translational invariance principle provides the conservation of the full moment $\mathbf{P}=\frac{1}{2}\sum_{l\le j\le N}(\mathbf{p}_{(j)}+\mathbf{p}'_{(j)})$:

$$L(\mathbf{p}_{f(1)},\mathbf{p}'_{f(1)},\mathbf{p}_{f(2)},\mathbf{p}'_{f(2)},\ldots,\mathbf{p}_{f(N)},\mathbf{p}'_{f(N)};\mathbf{p}_{(1)},\mathbf{p}'_{(1)},\mathbf{p}_{(2)},\mathbf{p}'_{(2)},\ldots,\mathbf{p}_{(N)},\mathbf{p}'_{(N)})$$
$$=\delta(\mathbf{P}_f-\mathbf{P})L_r(\mathbf{p}_{f(1)},\mathbf{p}'_{f(1)},\mathbf{p}_{f(2)},\mathbf{p}'_{f(2)},\ldots,\mathbf{p}_{f(N)},\mathbf{p}'_{f(N)};\mathbf{p}_{(1)},\mathbf{p}'_{(1)},\mathbf{p}_{(2)},\mathbf{p}'_{(2)},\ldots,\mathbf{p}_{(N)},\mathbf{p}'_{(N)})\ . \tag{22}$$

It can be supposed that the well-known restriction on wave vectors in coherent light scattering is a manifestation of the equality (22). To prove this let us consider the translational averaging in Eq. (11). Through the nth order of perturbation theory one obtains

$$\mathrm{Tr}_T\left\{\sum_{j_n}(a_\alpha A_{\alpha,j_n}-a_\alpha^\dagger A_{\alpha,j_n}^\dagger)[(-1)(H_0^\times)^{-1}V^\times]^{n-1}\rho_0\right\}$$
$$=N\mathrm{Tr}_T\left\{(a_\alpha A_{\alpha,1}-a_\alpha^\dagger A_{\alpha,1}^\dagger)\sum_{\alpha_l,j_l}\prod_{l=1}^{n-1}[(-1)(H_0^\times)^{-1}(a_{\alpha_l}A_{\alpha_l,j_1}+a_{\alpha_l}^\dagger A_{\alpha_l,j_l}^\dagger)^\times]\rho_0\right\}$$
$$=N\sum_{\{\alpha_l,j_l,\beta_l,\gamma_l\}_n}\mathrm{Tr}_T\left\{(-1)^{\beta_n}A_{\alpha_n,J_n}^{\beta_n,\gamma_n}\prod_{l=1}^{n-1}[(-1)^{\gamma_l}(H_0^\times)^{-1}(-1)A_{\alpha_l,J_l}^{\beta_j,\gamma_l}]\rho_0\right\}\ . \tag{23}$$

Here $A_{\alpha,j}=\mathbf{d}_j\cdot\mathbf{A}_\alpha(\mathbf{r}_j)$, the subscript T denotes that the trace has to be evaluated only over the translation states of the medium. $\sum_{\{\alpha_l,j_l,\beta_l,\gamma_l\}_n}$ implies the summation over all n-term sequences $\{\alpha_l,j_l,\beta_l,\gamma_l\}_n$ with $\alpha_n=\alpha$, $j_n=1$, $\gamma_n=0$. Each term (α,j,β,γ) in the sequence corresponds to the onefold interaction of a photon of normal mode α with a certain molecule (j). The details of the process are described by the parameters $\beta(=0,1)$ and $\gamma(=0,1)$, namely

$$A_{\alpha,j}^{\beta=0,\gamma=0}\rho=a_\alpha A_{\alpha,j}\rho\ ,\quad A_{\alpha,j}^{\beta=1,\gamma=0}\rho=a_\alpha^\dagger A_{\alpha,j}^\dagger\rho\ ,$$
$$A_{\alpha,j}^{\beta=0,\gamma=1}\rho=\rho a_\alpha A_{\alpha,j}\ ,\quad A_{\alpha,j}^{\beta=1,\gamma=1}\rho=\rho a_\alpha^\dagger A_{\alpha,j}^\dagger\ , \tag{24}$$

Obviously, every ordered sequence can be displayed graphically by the appropriate double-sided Fermi diagram (see Fig. 1).

Since the operator of the full momentum and the Hamiltonian for the N-particles system can be diagonalized in the same basis of eigenvectors $|\mathbf{P}\rangle$, the initial Boltzmann distribution in medium ρ_{eq} can be written in this basis as $\rho_{\mathrm{eq}}=\sum_P|\mathbf{P}\rangle\rho_P\langle\mathbf{P}|$. According to Eqs. (4) and (5), each

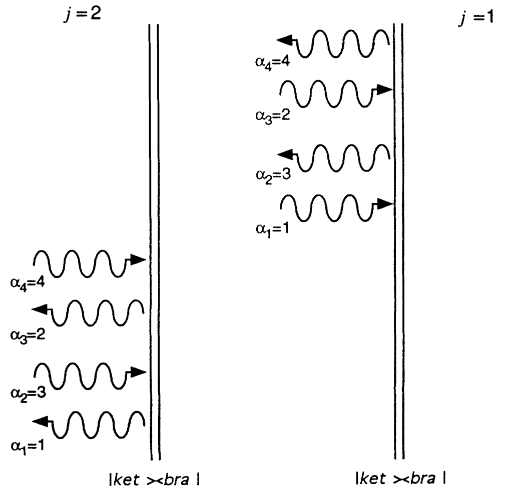

FIG. 1. Bimolecular ($j=1,2$) double-sided diagram that corresponds to the ordered sequence $\{1,2,1,0;\ 3,2,0,0;\ 2,2,1,0;\ 4,2,0,0;\ 1,1,0,0;\ 3,1,1,0;\ 2,1,0,0;\ 4,1,1,0\}_8$.

diagonal matrix element ρ_P transforms into nondiagonal elements due to the interaction with the photon:

$$A_{\alpha,j}^{\beta,\gamma=0}|\mathbf{P}\rangle\langle\mathbf{P}| \rightarrow |\mathbf{P}+(-1)^{\beta}\mathbf{k}_\alpha\rangle\langle\mathbf{P}| \ , \tag{25a}$$

$$A_{\alpha,j}^{\beta,\gamma=1}|\mathbf{P}\rangle\langle\mathbf{P}| \rightarrow |\mathbf{P}\rangle\langle\mathbf{P}-(-1)^{\beta}\mathbf{k}_\alpha| \ . \tag{25b}$$

In agreement with Eq. (22), the $(H_0^\times)^{-1}$ operator couples only vectors $|\mathbf{P}\rangle\langle\mathbf{P}'|$ having the same values of full momentum: $|\mathbf{P}\rangle\langle\mathbf{P}'| \leftrightarrow |\mathbf{P}+\mathbf{Q}\rangle\langle\mathbf{P}'-\mathbf{Q}|$. Taking into consideration that only the diagonal final states $|\mathbf{P}\rangle\langle\mathbf{P}|$ should be retained in Eq. (23), one may readily see that all nonzero scattering terms have the following property:

$$\sum_{\substack{l=1 \\ \alpha_l,\beta_l \in \{\alpha_l, j_l, \beta_l, \gamma_l\}_n}}^{n} (-1)^{\beta_l}\mathbf{k}_{\alpha_l} = \sum_\alpha (n_\alpha - n_\alpha^\dagger)\mathbf{k}_\alpha = 0 \ , \tag{26}$$

where $n_\alpha^\dagger = \sum_{j=1}^{N} n_{\alpha,j}^\dagger$ and $n_\alpha = \sum_{j=1}^{N} n_{\alpha,j}$, respectively.

$n_{\alpha,j}^\dagger$ and $n_{\alpha,j}$ are the total numbers of $a_\alpha^\dagger$ and a_α operators acting on the *j*th molecule in the selected sequence $\{\alpha_l, j_l, \beta_l, \gamma_l\}_n$:

$$\begin{aligned} n_{\alpha,j}^\dagger &= \sum_{\substack{k=1 \\ \alpha_k,\beta_k,j_k \in \{\alpha_l, j_l, \beta_l, \gamma_l, j_l\}_n}}^{n} \delta_{\alpha,\alpha_k}\delta_{1,\beta_k}\delta_{j,j_k} \ , \\ n_{\alpha,j} &= \sum_{\substack{k=1 \\ \alpha_k,\beta_k,j_k \in \{\alpha_l, j_l, \beta_l, \gamma_l, j_l\}_n}}^{n} \delta_{\alpha,\alpha_k}\delta_{0,\beta_k}\delta_{j,j_k} \ . \end{aligned} \tag{27}$$

The equality (26) is trivial when the interaction with one molecule is considered (e.g., ir absorption, Raman scattering). This is because the nonzero contribution to the scattering intensity (11) arises only from terms with

$$n_\alpha^\dagger = n_\alpha \ . \tag{28}$$

However, the situation is changed drastically when the radiation acts on several independent molecules. When the interaction between the selected molecules can be neglected the expression (26) holds for each molecule separately. In particular, for two molecules (1,2), both conservation conditions Eqs. (26) and (28) have the form

$$\sum_\alpha (n_{\alpha,1} - n_{\alpha,1}^\dagger)\mathbf{k}_\alpha = 0 \ , \tag{29a}$$

$$\sum_\alpha (n_{\alpha,2} - n_{\alpha,2}^\dagger)\mathbf{k}_\alpha = 0 \ , \tag{29b}$$

$$n_{\alpha,1}^\dagger + n_{\alpha,2}^\dagger = n_{\alpha,1} + n_{\alpha,2} \ . \tag{29c}$$

The equality (29c) leads to the coincidence of the phase-matching conditions (29a) and (29b) for both molecules.

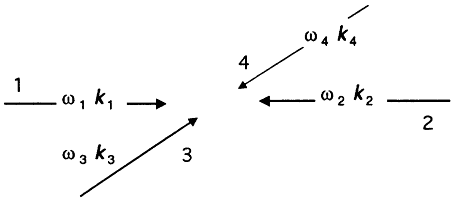

FIG. 2. Geometry for degenerate four-wave mixing. $\omega_1, \mathbf{k}_1$ and $\omega_2, \mathbf{k}_2$ correspond to the pumping beams. 3 and 4 are probing and signal beams, respectively.

Before proceeding to the analysis of the spectral properties of the coherent scattering let us consider, for instance, one of the sequences belonging to the four-wave mixing: $\{1,2,1,0;\ 3,2,0,0;\ 2,2,1,0;\ 4,2,0,0;\ 1,1,0,0;\ 3,1,1,0;\ 2,1,0,0;\ 4,1,1,0\}_8$ (see Fig. 1). Then from Eqs. (29) one obtains the momentum-conservation condition, which is usual for CARS and DFWM,

$$\mathbf{k}_4 = \mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 \ . \tag{30}$$

C. Vibrational DFWM spectroscopy

The results of the preceeding sections will be employed here to find out the expression for the spectrum shape via susceptibility (17). The analysis will be performed in the lowest order of perturbation theory for the case when the frequencies of all applied modes are in resonance with the frequency of the vibrational transition of the molecule.

By extracting from Eq. (11) terms which describe the coherent interaction with two molecules (V_1, V_2) for the system of *N* identical particles one obtains

$$\begin{aligned} W_\alpha^{(2)} = {} & i\omega_\alpha N(N-1) \\ & \times \mathrm{Tr}((V_1^\times a_\alpha^\dagger a_\alpha)\{[1+(H_0^\times)^{-1}(V_1^\times + V_2^\times)]^{-1} \\ & - [1+(H_0^\times)^{-1}V_1^\times]^{-1}\}\rho_0) \ . \end{aligned} \tag{31}$$

Since we intend now to deal with the four radiation modes (see Fig. 2), we immediately see from Eq. (28) that in this case the perturbation expansion (11) provides nonvanishing results only at the eighth and higher orders. Additionally, to satisfy Eq. (30) the interaction of the molecule with different modes has to be considered. Then the corresponding terms in the expression (31) can be written as

$$\begin{aligned} W_\alpha^{\mathrm{DFWM}} &\approx i\omega_\alpha N(N-1) \sum_{\{\alpha_l, j_l, \beta_l, \gamma_l\}_8'} \mathrm{Tr}\left\{(-1)^{\beta_8} A_{\alpha_8, J_8}^{\beta_8,\gamma_8} \prod_{l=1}^{7} \left[(-1)^{\gamma_l} \left[\frac{i}{\hbar} H_0^\times\right]^{-1} \left[-\frac{i}{\hbar}\right] A_{\alpha_l, j_l}^{\beta_l,\gamma_l}\right] \rho_0\right\} \\ &= i\omega_\alpha N(N-1) \sum_{\{\alpha_l, j_l, \beta_l, \gamma_l\}_8'} \mathrm{Tr}\left\{(-1)^{\beta_8} A_{\alpha_8, j_8}^{\beta_8,\gamma_8} \prod_{l=1}^{7} \left[(-1)^{\gamma_l} \left[\frac{i}{\hbar} H_M^\times - i \sum_{k=1}^{l} (-1)^{\beta_k} \omega_{\alpha_k}\right]^{-1} \left[-\frac{i}{\hbar}\right] A_{\alpha_l, j_l}^{\beta_l,\gamma_l}\right] \rho_0\right\} \ . \end{aligned} \tag{32}$$

The prime ($\{\ \}'$) here means that the sequence comprises the interaction of each molecule with one and the same photon only once.

It is easy to see that the most important contribution to the sum (32) comes from the ordered sequences for which the interaction of both molecules with the radiation is shared in time: at first, all photons act on one molecule and afterwards on another one. Actually, in this case the interaction of the four successive photons with the medium can be considered as an open process for which three fundamental conservation conditions are fulfilled:

$$\omega_{\alpha_1}-\omega_{\alpha_2}+\omega_{\alpha_3}-\omega_{\alpha_4}=0\ , \tag{33a}$$

$$\sum_{\substack{m,l,k,\\ h,q,q'}}(\mathbf{e}^m\cdot\mathbf{e}_{\alpha_1}^{(\beta_1)})C_{l,m;1,l}^{L,q}(\mathbf{e}^l\cdot\mathbf{e}_{\alpha_2}^{(\beta_2)})C_{L,q;1,k}^{L',q'}\times(\mathbf{e}^k\cdot\mathbf{e}_{\alpha_3}^{(\beta_3)})C_{L',q';1,h}^{L'',q''}(\mathbf{e}^h\cdot\mathbf{e}_{\alpha_4}^{(\beta_4)})=\delta_{L'',0}\delta_{q'',0}\ , \tag{33b}$$

$$\mathbf{k}_{\alpha_1}-\mathbf{k}_{\alpha_2}+\mathbf{k}_{\alpha_3}-\mathbf{k}_{\alpha_4}=\mathbf{0}\ , \tag{33c}$$

where $\mathbf{e}^{(0)}=\mathbf{e}$, $\mathbf{e}^{(1)}=\mathbf{e}^*$. Equation (33b) is valid for any $L\in\{0,1,2\}$, $\mathbf{e}^m$ and $C_{1,m;1,l}^{L,q}$ being, respectively, spherical basis vectors and Clebsch-Gordon coefficients. In general, for four different polarization vectors the tensor constructed from products of their components has 3^4 elements. The equality (33b) means that only those linear combinations of these elements are essential for coherent scattering, which belong to the fully symmetric (scalar) representation of the rotational symmetry group [23]; in other words, when the interaction with the radiation does not change the angular momentum.

Considering Eqs. (33a)–(33c) we first remark that the process obeying these conditions does not disturb the equilibrium distribution ρ_{eq}. Then the product of the first four factors ($l=1$–4) in Eq. (32) reads

$$\begin{aligned}
&\prod_{l=1}^{4}\left[(-1)^{\gamma_l}\left[\frac{i}{\hbar}H_M^{\times}-i\sum_{k=1}^{l}(-1)^{\beta_k}\omega_{\alpha_k}\right]^{-1}\left[-\frac{i}{\hbar}\right]A_{\alpha_l,j_l}^{\beta_l,\gamma_l}\right]\rho_0\\
&\quad=\rho_{\mathrm{rad}}(\{\alpha_l,\beta_l,\gamma_l\}_4)\left[\frac{i}{\hbar}H_M^{\times}-i\sum_{k=1}^{4}(-1)^{\beta_k}\omega_{\alpha_k}\right]^{-1}\left[\chi_{\{a_l,\beta_l,\gamma_l\}_4}\left[\prod_{l=1}^{4}\delta_{1,j_l}+\prod_{l=1}^{4}\delta_{2,j_l}\right]\rho_{\mathrm{eq}}+\delta\rho\right]\\
&\quad=\left[\prod_{l=1}^{4}\delta_{1,j_l}+\prod_{l=1}^{4}\delta_{2,j_l}\right]\rho_{\mathrm{rad}}(\{\alpha_l,\beta_l,\gamma_l\}_4)\chi_{\{\alpha_l,\beta_l,\gamma_l\}_4}\rho_{\mathrm{eq}}\lim_{\varepsilon\to 0}\frac{1}{\varepsilon-i\sum_{k=1}^{4}(-1)^{\beta_k}\omega_{\alpha_k}}\ ,
\end{aligned} \tag{34}$$

where

$$\rho_{\mathrm{rad}}(\{\alpha_l,\beta_l,\gamma_l\}_4)=\left\{\prod_{l=1}^{4}[\delta_{0,\gamma_l}(\delta_{0,\beta_l}a_{\alpha_l}+\delta_{1,\beta_l}a_{\alpha_l}^{\dagger})+\delta_{1,\gamma_l}]\right\}\rho_{\mathrm{rad}}\left\{\prod_{l=1}^{4}[\delta_{0,\gamma_l}+\delta_{1,\gamma_l}(\delta_{0,\beta_l}a_{\alpha_l}+\delta_{l,\beta_l}a_{\alpha_l}^{\dagger})]\right\}\ ,$$

and

$$\chi_{\{\alpha_l,\beta_l,\gamma_l\}_4}=\mathrm{Tr}_M\left\{(-1)^{\gamma_4}\left[-\frac{i}{\hbar}\right]\tilde{A}_{\alpha_4}^{\beta_4,\gamma_4}\prod_{l=1}^{3}\left[(-1)^{\gamma_l}\left[\frac{i}{\hbar}H_M^{\times}-i\sum_{k=1}^{l}(-1)^{\beta_k}\omega_{\alpha_k}\right]^{-1}\left[-\frac{i}{\hbar}\right]\tilde{A}_{\alpha_l}^{\beta_l,\gamma_l}\right]\rho_{\mathrm{eq}}\right\}\ .$$

Here $\tilde{A}_{\alpha}^{\beta,\gamma}$ are equal to $A_{\alpha,l=2}^{\beta,\gamma}$ at $a_\alpha=a_\alpha^{\dagger}=1$.

The limit $\varepsilon\to 0$ will be taken, as usual [18], at the end of the calculations. The nonequilibrium part $\delta\rho$ ($H_M^{\times}\delta\rho\neq 0$) of the density matrix is produced by the diagrams which violate the conditions (33). Thus the denominator at $l=4$ plays here the role of a projector onto the equilibrium distribution as a consequence of Eq. (8). So, to confirm Eqs. (33) it is sufficient to show that the factor in front of the limit in the scattering amplitude determined by (34) differs from zero. Before this let us recall the well-known commutation relation,

$$\begin{aligned}
&e^{-i(\mathbf{k}\cdot\mathbf{r})}H_M e^{i(\mathbf{k}\cdot\mathbf{r})}\\
&\quad=\sum_{n=0}^{\infty}\frac{1}{n!}[-i(\mathbf{k}\cdot\mathbf{r}),[\dots,[-i(\mathbf{k}\cdot\mathbf{r}),H_M]_-]_-]_-^{(n)}\\
&\quad=H_M+\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})+\frac{\hbar^2}{2m}k^2\\
&\quad\approx H_M+\frac{\hbar}{m}(\mathbf{k}\cdot\mathbf{p})\ .
\end{aligned} \tag{35}$$

In the present paper we concentrate on the case of fast translational relaxation (Dicke narrowing [24]),

$$|\mathbf{k}_{\alpha_1}-\mathbf{k}_{\alpha_2}|\left[\frac{k_BT}{m}\right]^{1/2}\tau_v\ll 1\ , \tag{36}$$

where τ_v is the time of the translational velocity ($\mathbf{v}$) relaxation [25],

$$\tau_v=\frac{m}{3k_BT}\int_0^{\infty}(\mathbf{v}(t)\cdot\mathbf{v})dt\ . \tag{37}$$

If the rotational relaxation rate ($1/\tau_J$ [26-28]) is substantial,

$$|\mathbf{k}_{\alpha_1}-\mathbf{k}_{\alpha_2}|^2\frac{k_BT}{m}\tau_v\ll 1/\tau_J\ , \tag{38}$$

the condition (36) permits a writing of the following expression:

$$\left[\frac{i}{\hbar}H_M^{\times}+\frac{i}{m}(\mathbf{k}_{\alpha_1}\cdot\mathbf{p})-\frac{i}{m}(\mathbf{k}_{\alpha_2}\cdot\mathbf{p}')\right]^{-1}\rho_M\approx\left[\frac{i}{\hbar}H_M^{\times}+\left|\mathbf{k}_{\alpha_1}-\mathbf{k}_{\alpha_2}\right|^2\frac{k_BT}{m}\tau_v\right]^{-1}\rho_{\mathrm{R-T}}\mathrm{Tr}'\rho_M\,, \tag{39}$$

for any density matrix ρ_M in an isotropic medium.

With the help of Eqs. (38) and (39) it is possible now to trace the rotational-translational states in Eq. (34),

$$\begin{aligned}
\chi_{\{\alpha_l,\beta_l,\gamma_l\}_4}=&\frac{(2\pi\hbar\omega)^2}{9\mathcal{V}}(-1)^{\sum_{1-4}(\gamma_l+\beta_l)}(\mathbf{e}_{\alpha_1}^{(\beta_1)}\cdot\mathbf{e}_{\alpha_2}^{(\beta_2)})(\mathbf{e}_{\alpha_3}^{(\beta_3)}\cdot\mathbf{e}_{\alpha_4}^{(\beta_4)})S_{\mathcal{V}}\left[\sum_{1-4}(-1)^{\beta_l}\mathbf{k}_{\alpha_l}\right]\\
&\times\sum_{\nu,\nu'=0}^{\infty}\Biggl\{\frac{\delta_{\beta_1,1-\beta_2}\delta_{\beta_3,1-\beta_4}}{|\mathbf{k}_{\alpha_1}-\mathbf{k}_{\alpha_2}|^2\dfrac{k_BT}{m}\tau_v}\Biggl\{[\delta_{\beta_3,0}\delta_{\gamma_3,0}G_{\nu',\nu}(\omega,k)+\delta_{\beta,_1}\delta_{\gamma_3,1}G_{\nu',\nu}(\omega,k)^*]\\
&\qquad\times\{[\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu',\nu}(\omega,k)+\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu',\nu}(\omega,k)^*]\rho_\nu\\
&\qquad+[\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu,\nu'}(-\omega,-k)+\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu,\nu'}(-\omega,-k)^*]\rho_{\nu'}\}\\
&\qquad+[\delta_{\beta_3,1}\delta_{\gamma_3,0}G_{\nu,\nu'}(-\omega,-k)+\delta_{\beta_3,0}\delta_{\gamma_3,1}G_{\nu,\nu'}(-\omega,-k)^*]\\
&\qquad\times\{[\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu',\nu}(\omega,k)+\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu',\nu}(\omega,k)^*]\rho_\nu\\
&\qquad+[\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu,\nu'}(-\omega,-k)+\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu,\nu'}(-\omega,-k)^*]\rho_{\nu'}\}\\
&\qquad+\sum_{\nu''=0}^{\infty}([\delta_{\beta_3,0}\delta_{\gamma_3,0}G_{\nu'',\nu'}(\omega,k)+\delta_{\beta_3,1}\delta_{\gamma_3,1}G_{\nu'',\nu'}(\omega,k)^*]\\
&\qquad\times\{[\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu',\nu}(\omega,k)+\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu',\nu}(\omega,k)^*]\rho_\nu\\
&\qquad+[\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu,\nu'}(-\omega,-k)+\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu,\nu'}(-\omega,-k)^*]\rho_{\nu'}\}\\
&\qquad+[\delta_{\beta_3,1}\delta_{\gamma_3,0}G_{\nu,\nu'}(-\omega,-k)+\delta_{\beta_3,0}\delta_{\gamma_3,1}G_{\nu,\nu'}(-\omega,-k)^*]\\
&\qquad\times\{[\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu',\nu''}(-\omega,-k)+\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu',\nu''}(-\omega,-k)^*]\rho_{\nu''}\\
&\qquad+[\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu'',\nu'}(\omega,k)+\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu'',\nu'}(\omega,k)^*]\rho_{\nu'}\})\Biggr]\\
&+\sum_{\nu''=0}^{\infty}\frac{\delta_{\beta_1,\beta_2}\delta_{\beta_3,\beta_4}}{i(-1)^{\beta_1}(\omega_{\nu'',\nu}-2\omega)+|\mathbf{k}_{\alpha_1}+\mathbf{k}_{\alpha_2}|^2\dfrac{k_BT}{m}\tau_v}\\
&\times\{[\delta_{\beta_3,0}\delta_{\gamma_3,0}G_{\nu'',\nu';\nu',\nu}(\omega,k)+\delta_{\beta_3,0}\delta_{\gamma_3,1}G_{\nu,\nu';\nu',\nu''}(-\omega,-k)^*]\\
&\times[\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu'',\nu';\nu',\nu}(\omega,k)^*\rho_\nu+\delta_{\beta_1,1}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu',\nu;\nu'',\nu'}(\omega,k)^*\rho_{\nu'}\\
&+\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu',\nu'';\nu,\nu'}(-\omega,-k)\rho_{\nu'}+\delta_{\beta_1,1}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu,\nu';\nu',\nu''}(-\omega,-k)\rho_{\nu''}]\\
&+[\delta_{\beta_3,1}\delta_{\gamma_3,0}G_{\nu,\nu';\nu',\nu''}(-\omega,-k)+\delta_{\beta_3,1}\delta_{\gamma_3,1}G_{\nu'',\nu';\nu',\nu}(\omega,k)^*]\\
&\times[\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,0}G_{\nu'',\nu';\nu',\nu}(\omega,k)\rho_\nu+\delta_{\beta_1,0}\delta_{\gamma_1,0}\delta_{\gamma_2,1}G_{\nu',\nu;\nu'',\nu'}(\omega,k)\rho_{\nu'}\\
&\times\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,0}G_{\nu',\nu'';\nu,\nu'}(-\omega,-k)^*\rho_{\nu'}+\delta_{\beta_1,0}\delta_{\gamma_1,1}\delta_{\gamma_2,1}G_{\nu,\nu';\nu',\nu''}(-\omega,-k)^*\rho_{\nu''}]\}\Biggr\}\,.
\end{aligned} \tag{40}$$

Here $\omega=\omega_{\alpha_4}\approx\omega_{\alpha_3}\approx\omega_{\alpha_2}\approx\omega_{\alpha_1};k=k_{\alpha_4}\approx k_{\alpha_3}\approx k_{\alpha_2}\approx k_{\alpha_1}$, and

$$G_{\nu''',\nu'';\nu',\nu}(\omega,k)=\mathrm{Tr}'\left\{\langle\nu'''|d|\nu''\rangle e^{-i(\mathbf{k}\cdot\mathbf{r}_1)}\left[\frac{i}{\hbar}H_{\mathrm{R-T}}^{\times}(\nu)+i\omega_{\nu',\nu}-i\omega\right]^{-1}\langle\nu'|d|\nu\rangle e^{i(\mathbf{k}\cdot\mathbf{r}_1)}\rho_{\mathrm{R-T}}\right\}\,. \tag{41}$$

In particular, $G_{\nu''',\nu'';\nu',\nu}(\omega,k)$ is a real symmetrical matrix when vibrational levels of the molecule are nongenerated. As follows from Eq. (17), $G_{\nu',\nu}(\omega,k)\equiv G_{\nu,\nu';\nu',\nu}(\omega,k)$.

It should be noted here that the translational invariance (20) is the exact identity only for infinite media. This circumstance is reflected in Eq. (40) by the factor $S_{\mathcal{V}}$,

$$S_{\mathcal{V}}\left[\sum_{1-4}(-1)^{\beta_l}\mathbf{k}_{\alpha_l}\right]=\int_{\mathcal{V}}\exp\left[i\left[\mathbf{r}\sum_{1-4}(-1)^{\beta_l}\mathbf{k}_{\alpha_l}\right]\right]\frac{d\mathbf{r}}{\mathcal{V}}\ . \tag{42}$$

The value of the integral depends on volume as well as on boundary conditions. For periodic boundary conditions [18], for instance, $S_{\mathcal{V}}$ is equal to the Kronecker δ.

Now we substitute (40) for χ into Eq. (34) and carry out similar calculations for another molecule in Eq. (32). Then, after summation of diagrams in (32) we come to the final relation:

$$\begin{aligned}W^{\mathrm{DFWM}}\approx{}&\frac{2^7\pi^5}{3^4\hbar^6\mathcal{V}^4}N(N-1)\omega^2 I_1 I_2 I_3\delta(\omega-\omega_0)|S_{\mathcal{V}}(\mathbf{k}-\mathbf{k}_0)|^2\\&\times\Bigg|\sum_{\nu,\nu'=0}^{\infty}\Bigg\{P_1(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})\Bigg[\bigg[G_{\nu',\nu}(\omega,k)+G_{\nu,\nu'}(-\omega,-k)^*-\sum_{\nu''=0}G_{\nu'',\nu'}(\omega,k)\bigg]\\&\qquad\times\mathrm{Re}\{G_{\nu',\nu}(\omega,k)\rho_\nu-G_{\nu,\nu'}(-\omega,-k)\rho_{\nu'}\}-G_{\nu,\nu'}(-\omega,-k)^*\sum_{\nu''=0}^{\infty}\mathrm{Re}\{G_{\nu'',\nu'}(\omega,k)\rho_{\nu'}\\&\qquad-G_{\nu',\nu''}(-\omega,-k)\rho_{\nu''}\}\Bigg]\\&\quad+\sum_{\nu''=0}^{\infty}(P_2(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})[G_{\nu'',\nu';\nu',\nu}(\omega,k)-G_{\nu,\nu';\nu',\nu''}(-\omega,-k)^*]\\&\quad\times\{G_{\nu'',\nu';\nu',\nu}(\omega,k)^*\rho_\nu-[G_{\nu',\nu;\nu'',\nu'}(\omega,k)^*+G_{\nu',\nu'';\nu,\nu'}(-\omega,-k)]\rho_{\nu'}+G_{\nu,\nu';\nu',\nu''}(-\omega,-k)\rho_{\nu''}\})\Bigg\}\Bigg|^2\ .\end{aligned}\tag{43}$$

Here $\omega_0=\omega_1-\omega_3+\omega_2$, $\mathbf{k}_0=\mathbf{k}_1-\mathbf{k}_3+\mathbf{k}_2$, and

$$\begin{aligned}P_1(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})&=\frac{(\mathbf{e}_1\mathbf{e}_3^*)(\mathbf{e}_2\mathbf{e}^*)}{|\mathbf{k}_1-\mathbf{k}_3|^2\frac{k_BT}{m}\tau_v}+\frac{(\mathbf{e}_2\mathbf{e}_3^*)(\mathbf{e}_1\mathbf{e}^*)}{|\mathbf{k}_2-\mathbf{k}_3|^2\frac{k_BT}{m\tau_v}}\ ,\\P_2(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})&=\frac{(\mathbf{e}_1\mathbf{e}_2)(\mathbf{e}_3^*\mathbf{e}^*)}{-i(\omega_{\nu'',\nu}-2\omega)+|\mathbf{k}_1+\mathbf{k}_2|^2\frac{k_BT}{m}\tau_v}\ .\end{aligned}\tag{44}$$

As with Eq. (16), the relation (13) was used for all field operators except the signal one ($\alpha_4=4$). The δ function is defined here as

$$\delta(\omega)=\frac{1}{\pi}\mathrm{Re}\left\{\lim_{\varepsilon\to 0}\frac{1}{i\omega+\varepsilon}\right\}\ . \tag{45}$$

Deriving the expression (43) we have neglected the lifetime of the vibrational state. However, assuming statistical independence of vibrational relaxation one may show that the influence of the process is reduced to the alteration of denominators in Eq. (44). So, instead of Eq. (44) we have

$$\begin{aligned}P_1(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})&=\frac{(\mathbf{e}_1\cdot\mathbf{e}_3{}^*)(\mathbf{e}_2\cdot\mathbf{e}^*)}{|\mathbf{k}_1-\mathbf{k}_3|^2\frac{k_\beta T}{m}\tau_v+\frac{1}{T_1}}+\frac{(\mathbf{e}_2\cdot\mathbf{e}_3{}^*)(\mathbf{e}_1\cdot\mathbf{e}^*)}{|\mathbf{k}_2-\mathbf{k}_3|^2\frac{k_BT}{m}\tau_v+\frac{1}{T_1}}\ ,\\P_2(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})&=\frac{(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{e}_3{}^*\cdot\mathbf{e}^*)}{-i(\omega_{\nu'',\nu}-2\omega)+|\mathbf{k}_1+\mathbf{k}_2|^2\frac{k_BT}{m}\tau_v+\frac{1}{T_2}}\ .\end{aligned}\tag{46}$$

Here T_1 and T_2 are longitudinal and transversal vibrational relaxation times, respectively.

The last remark concerns the special case when the angle between pumping $\mathbf{k}_1$ and probing $\mathbf{k}_3$ beams (see Fig. 1) is relatively small. Then, the second term in Eqs. (44a) and (44b) is much less than the first one and the contribution to the signal from the corresponding diagrams can be neglected. The necessary condition can be written as $|\mathbf{k}_1-\mathbf{k}_3|^2(k_B T\tau_v/m) \ll |\mathbf{k}_2-\mathbf{k}_3|\,(k_B T/m)^{1/2}$. This circumstance allows the present theory to be applied not only to vibrational spectra but also to evaluate electronic spectra. The resonant electronic transition will be designated below as $n_e, v \rightarrow n_e', v'$.

III. RESULTS AND CONCLUSIONS

The general relation (43) can be simplified considerably when both pumping beams are orthogonally polarized ($\mathbf{e}_1 \perp \mathbf{e}_2$). In this case we have from Eqs. (44) and (46) $P_2(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})=0$ and polarization of the scattering beam is

$$\mathbf{e} \propto \left[\mathbf{P}-\frac{1}{|k|^2}(\mathbf{Pk})\mathbf{k}\right], \tag{47}$$

where the vector $\mathbf{P}$ is equal to the gradient $\nabla_e P_1(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})^*$.

Using the symmetry of the susceptibility matrix (A5) the expression (43) can be represented in the more acceptable form for applications:

$$\begin{aligned} W^{\mathrm{DFWM}}=B\Bigg| \sum_{v,v'=0}^{\infty} \Bigg\{ & \left[G_{v',v}(\omega,k)-\sum_{v''=0}^{\infty} G_{v'',v'}(\omega,k)\right]\mathrm{Re}\{G_{v',v}(\omega,k)\}\rho_v \\ & +G_{v,v'}(-\omega,-k)^*\left[\mathrm{Re}\{G_{v',v}(\omega,k)\}\rho_v-\rho_{v'}\sum_{v''=0}^{\infty}\mathrm{Re}\{G_{v'',v'}(\omega,k)\}\right]\Bigg\}\Bigg|^2, \end{aligned} \tag{48}$$

where

$$B=\frac{2^7\pi^5}{3^4\hbar^6 \mathcal{V}^4}N(N-1)\omega^2\left[1-\exp\left[-\frac{\hbar\omega}{k_B T}\right]\right]^2 I_1 I_2 I_3 \delta(\omega-\omega_0)|P_1(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3,\mathbf{e})S_{\mathcal{V}}(\mathbf{k}-\mathbf{k}_0)|^2 . \tag{49}$$

The comparison of the above expression with Eq. (16) demonstrates the principal distinction between DFWM and IR techniques. The line shape in DFWM spectroscopy depends both on the imaginary and on the real parts of the susceptibility, whereas the ir spectrum is described only by the real part of the one. The similar difference is characterized by the CARS method with respect to spontaneous Raman scattering. However, in contrast to CARS with contribution to the DFWM signal from the excited vibrational band ($v'=1 \rightarrow v''=2$) cannot be ignored even at sufficiently low temperature. Except for the rarefied gases spectra, the width of a single rotational line observed at moderate temperatures in the stretching vibrational band considerably exceeds line splitting on account of vibrational anharmonicity when the normal vibration does not involve hydrogen [29],

$$\{\,|\omega_{v+2,v+1}-\omega_{v+1,v}|;\alpha_e\langle j(j+1)\rangle_T\} \ll 1/\tau_J . \tag{50}$$

Here α_e is the vibrational-rotational coupling constant.

Under condition (50) the dependence of rotational-translational Hamiltonian $H_{\mathrm{R-T}}(v)$ in Eq. (14) on vibrational quantum number v can be neglected. Hence, to estimate the spectrum shape the approximate equality of the susceptibility for fundamental ($G_{1,0}(\omega)$) and excited ($G_{2,1}(\omega)$) vibrational bands can be used in Eq. (48):

$$W_{\mathrm{vibr}}^{\mathrm{DFWM}} \approx B\left|\sum_{v,v'=0}^{\infty}\left\{\left[1-\exp\left[-\frac{\hbar\omega_{v',v}}{k_B T}\right]\right]G_{v,v'}(-\omega,-k)^*\mathrm{Re}\{G_{v',v}(\omega,k)\rho_v\right\}\right|^2 . \tag{51}$$

On the contrary, for electronic transitions ($n_e=0 \rightarrow n_e=1$ and $n_e=1 \rightarrow n_e=2$) the corresponding frequencies $\omega_{1,0}$ and $\omega_{2,1}$ are quite different. Therefore the overlapping of $G_{n_e=1;n_e=0}(\omega)$ and $G_{n_e=2;n_e=1}(\omega)$ in Eq. (48) is negligible:

$$W_{\mathrm{electr}}^{\mathrm{DFWM}} \approx B\left|\sum_{v,v'=0}^{\infty}([G_{n_e=1,v';n_e=0,v}(\omega,k)+G_{n_e=0,v;n_e=1,v'}(-\omega,-k)^*]\mathrm{Re}\{G_{n_e=1,v';n_e=0,v}(\omega,k)\}\rho_v)\right|^2 . \tag{52}$$

The sum here runs over vibrational sublevels of the electronic state n_e. It is easy to see that the expressions (51) and (52) are very similar and for isolated Lorenz line $G_{v',v}(\omega)=1/[i(\omega-\omega_{v',v})+\gamma]$, both of them reproduced the well-known result [7] $W^{\mathrm{DFWM}} \propto 1/[(\omega-\omega_{v',v})^2+\gamma^2]^3$.

Let us recall now the influence of the imaginary part of the susceptibility on the propagation of radiation in the medium. In this context the usual expression for the index of refraction $n(\omega)$ [30] in nonmagnetic media can be represented in the following form:

$$n^2(\omega)=1-\frac{4i\pi}{3\hbar}\frac{N}{\mathcal{V}}\sum_{\nu,\nu'=0}^{\infty}\{G_{\nu',\nu}(\omega,k)\rho_\nu - G_{\nu,\nu'}(-\omega,-k)^*\rho_{\nu'}\} . \quad (53)$$

To illustrate the connection of $n(\omega)$ with DFWM we restrict ourselves now to the case of comparatively large frequencies of the vibrational transition: $\hbar\omega_{\nu',\nu} \gg k_B T$. Then, the sum over the vibrational levels in Eqs. (51) and (53) reduces to one term belonging to the fundamental transition $\nu=0\rightarrow\nu'=1$. Substituting $G_{1,0}(\omega)$ and $\mathrm{Re}[G_{1,0}(\omega)]$ in Eqs. (51) and (52) with the help of expressions (53), (16), and (A7), we have finally

$$W_{\mathrm{vibr}}^{\mathrm{DFWM}} \approx \tfrac{1}{4} W_{\mathrm{electr}}^{\mathrm{DFWM}} \approx \widetilde{B}\,|n^2(\omega)-1|^2 W_1^{\mathrm{IR}} W_2^{\mathrm{IR}} , \quad (54)$$

where

$$\widetilde{B}=\frac{\pi}{2\hbar^2 N^2} I_3 \delta(\omega-\omega_0) |P_1(\mathbf{e}_1,\mathbf{e}_2\mathbf{e}_3,\mathbf{e}) S_{\mathcal{V}}(\mathbf{k}-\mathbf{k}_0)|^2 . \quad (55)$$

In summary, it is necessary to emphasize the principal significance of the approximation (36) for resulting relations presented in this section. The evident drawback of our analysis is the limited power of applied laser beams and, consequently, low signal levels. To overcome this obstacle and to take into account the saturation effect [31], terms of higher orders in the general expansion (11) should be evaluated. Proposed in the preceding section, the ordered sequences algorithm is oriented to conduct such analytical calculations on a computer.

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APPENDIX

The susceptibility $G_{\nu',\nu}(\omega,k)$ introduced in Eq. (17) can be regarded as an analytic function of the complex variable ω. The main properties of this function briefly discussed in this Appendix determine the symmetry of the observed line shape. Assuming that the domain of analyticity is the half plane $\mathrm{Im}(\omega)>0$, Eq. (17) can be represented as Laplace transform

$$G_{\nu',\nu}(\omega,k)=\int_0^\infty K_{\nu',\nu}(t,k)\exp(i(\omega-\omega_{\nu',\nu})t)dt \quad (\mathrm{A}1)$$

of the time-dependent correlation function

$$K_{\nu',\nu}(t,k)=\mathrm{Tr}'\left[\langle\nu|d|\nu'\rangle e^{-i(k\cdot r_1)} \times\exp\left[-\frac{i}{\hbar}H_{\mathrm{R-T}}(\nu')t\right] \times\langle\nu'|d|\nu\rangle e^{i(k\cdot r_1)}\rho_{\mathrm{R-T}} \times\exp\left[\frac{i}{\hbar}H_{\mathrm{R-T}}(\nu)t\right]\right] . \quad (\mathrm{A}2)$$

The summation of Eq. (A2) over vibrational states evidently leads to the total correlation function of the dipole momentum [26]

$$K(t)=\sum_{\nu',\nu=0}^{\infty} K_{\nu',\nu}(t,k)\rho_\nu . \quad (\mathrm{A}3)$$

Now we notice that the equilibrium distribution operator $\rho_{\mathrm{R-T}}$ that has to be in accord with the definition (14) and (15) proportional to $\exp[-H_{\mathrm{R-T}}(\nu)/k_B T]$. By performing the cyclic permutation of operators in Eq. (A2), the following expressions can be derived in the case of levels (ν',ν) of the same degeneracy:

$$K_{\nu',\nu}(-t,k)^* = K_{\nu',\nu}(t,k) , \quad (\mathrm{A}4\mathrm{a})$$

$$K_{\nu',\nu}(-t,k)=K_{\nu,\nu'}\left[t-\frac{i\hbar}{k_B T},-k\right] . \quad (\mathrm{A}4\mathrm{b})$$

Equations (A4) are a generalization of the well-known symmetry properties of $K(t)$ [32]. Taking the complex conjugation of Eq. (A1) and using (A4), we finally get

$$\mathrm{Re}[G_{\nu,\nu'}(-\omega,-k)] =\exp\left[-\frac{\hbar}{k_B T}(\omega-\omega_{\nu',\nu})\right]\mathrm{Re}[G_{\nu',\nu}(\omega,k)] . \quad (\mathrm{A}5)$$

The similar relation holds for the imaginary part of the susceptibility as well:

$$\mathrm{Im}[G_{\nu,\nu'}(-\omega,-k)]=-\exp\left[-\frac{\hbar}{k_B T}(\omega-\omega_{\nu',\nu})\right]\left\{\mathrm{Im}[G_{\nu',\nu}(\omega,k)]+i\int_0^{-i\hbar/k_B T} K_{\nu',\nu}(t,k)\exp[i(\omega-\omega_{\nu',\nu})t]dt\right\} . \quad (\mathrm{A}6)$$

It is clear that nearby the vibrational resonance ($\hbar|\omega-\omega_{\nu',\nu}| \ll k_B T$), both Eqs. (A5) and (A6) result in

$$G_{\nu',\nu}(\omega,k)\approx G_{\nu,\nu'}(-\omega,-k)^* . \quad (\mathrm{A}7)$$

As was shown in [33], the rotational and translational relaxation can be considered as statistical independent random processes $K_{\nu',\nu}(t,k)\approx K_{\mathrm{rot}}(t;\nu',\nu)K_{\mathrm{tr}}(t,k)$. In fact, the problem of the calculation of the line shape is reduced to the evaluation of the rotational contribution $K_{\mathrm{rot}}(t;\nu',\nu)$. In the gas phase it can be solved using the model for the relaxation operator proposed in [34] within the infinite-order sudden approximation.

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