Parametric bistable resonance in coherent Raman scattering in crystals

W. Gadomski* and B. Ratajska-Gadomska*
Istituto Nazionale di Ottica, Largo Enrico Fermi 6, I-50125 Firenze, Italy
(Received 12 September 1984; revised manuscript received 9 December 1985)

A parametric bistable resonance is shown to occur in a crystal irradiated with two optical beams of frequencies ω_1 and ω_2, respectively. The square of the amplitude of the lattice vibrations is resonantly enhanced when twice its frequency equals the difference frequency $\omega_1-\omega_2$. It is shown that this process results in the generation of an optical wave at the combination frequency $2\omega_1-\omega_2$ even when symmetry limitations prevent coherent anti-Stokes Raman spectroscopy. Thus it becomes possible to observe Raman-inactive modes in crystals via four-wave-mixing spectroscopy. The intensity of the generated optical field exhibits a bistable dependence on the intensities of the incident optical fields and on the difference frequency $\omega_1-\omega_2$.

I. INTRODUCTION

It has been shown recently[1–3] that a single monochromatic optical field incident on a crystal shifts the amplitude and the frequency of the crystal vibrations. These shifts are dependent on the external field intensity and are due to the mutual interaction between the dipoles optically induced in the molecules (or atoms) composing the crystal lattice. This mechanism significantly contributes to the crystal susceptibility tensors $\chi_{ijkl}(-\omega,\omega,\omega,-\omega)$ and $\chi_{ijklmn}(-\omega,\omega,\omega,-\omega,\omega,-\omega)$.

In the present paper we discuss the same model of interaction,[3] but for two optical waves of different frequencies ω_1 and ω_2. In this case both the frequencies and the amplitudes of the lattice vibration modes are modulated with the difference frequency $\omega_1-\omega_2$. For the modes of frequencies $\omega_\alpha \cong \frac{1}{2}(\omega_1-\omega_2)$ the squares of their amplitudes are resonantly enhanced. Moreover, they show bistability with respect to both the field intensity and the difference frequency $\omega_1-\omega_2$. We define this process as a parametric bistable resonance (PBR).

According to the model of crystal polarizability presented in Ref. 3, PBR accounts for the third-order polarization at the combination frequency $2\omega_1-\omega_2$. This effect may be observed in four-wave-mixing spectroscopy. PBR should not be confused with ordinary coherent anti-Stokes Raman spectroscopy (CARS),[4–6] which deals with the Raman response of the crystal and which occurs for different resonant condition, $\omega_\alpha=\omega_1-\omega_2$. PBR, in contrast, occurs also for Raman inactive modes, for which CARS is not possible. In the present paper we show that anharmonicity of the crystal lattice also leads to bistability in the Raman resonance, although the intensities necessary to observe it are much higher than those applied in the known CARS experiments.[4–6] However, the intensities required for PBR are significantly lower.

In Sec. II we present the model of the interaction of the crystal lattice with external fields and a model of the crystal polarizability. In Sec. III we derive the dynamical equations for the mean square of the vibrational amplitude. In Sec. IV we present the Maxwell equations for the optical field generated in a crystal. Section V includes the discussion of the results. The stationary solutions for PBR are compared with those obtained for CARS assuming the same model of interaction. The transient and quasistationary solutions for PBR are presented.

II. MODEL OF A CRYSTAL POLARIZABILITY

We assume the crystal lattice composed of identical, nondipolar and rigid molecules (or atoms) translationally and rotationally vibrating around their equilibrium positions.[1–3] If the crystal is subjected to an external optical field $\mathbf{E}_0(t)$ each molecule embedded in the crystal lattice interacts with a macroscopic local field $F_i(t)=f_i(\omega)E_{0i}$ (the Lorentz factor $f_i(\omega)=[\epsilon_i(\omega)+2]/3$) and with the field of dipoles induced in adjacent molecules. This model corresponds to the interaction of the macroscopic local field $\mathbf{F}(t)$ with the molecules of the effective polarizabilities modified due to their surrounding.[1–3] The effective polarizability tensor of the (ln)th molecule in the crystal (l is the number of the elementary cell and n is the number of the molecule in this cell) is given in the form[3]

$$\alpha_{ij}^{\text{eff}}(ln)=\sum_k \alpha_{ik}(ln)T_{kj}(ln) , \tag{1}$$

where $\alpha_{ik}(ln)$ denotes the polarizability of an isolated molecule and $T_{kj}(ln)=\sum_{l',n'}T_{kj}(ln,l'n')$; $T_{kj}(ln,l'n')$ being the $(iln,jl'n')$th element of the matrix $(\mathbb{1}-A)^{-1}$. $\mathbb{1}$ is the unit matrix and A, in turn, represents the dipole-dipole interaction tensor with the elements given by

$$A_{ij}(ln,l'n') = \sum_k \frac{\alpha_{kj}(l'n')}{r^3(ln,l'n')}\left[\frac{r_k(ln,l'n')r_i(ln,r'l')}{r^2(ln,l'n')}-\delta_{ik}\right] , \tag{2}$$

with the vector $\mathbf{r}(ln,l'n')$ connecting the molecules (ln) and $(l'n')$. The summation in Eq. (2) is taken over the nearest neighbors of the (ln)th molecule. The total polarizability of the crystal is the sum of the effective polarizabilities of the molecules composing the crystal lattice:[3]

$$\mathscr{P}_{ij}=\sum_{l,n}\alpha_{ij}^{\rm eff}(ln)\ . \tag{3}$$

As the effective polarizabilities [Eq. (1)] depend on the molecular positions we can expand the crystal polarizability in a power series with respect to small molecular displacements from their equilibrium positions. It yields the following form of the polarization vector $\mathbf{P}(t)$ given in normal-mode representation:

$$P_i(t)=\sum_j\langle\mathscr{P}_{ij}(t)\rangle F_j(t)=\sum_j\left[\mathscr{P}_{ij}^{(0)}+\sum_\alpha\mathscr{P}_{ij}^{(1)}(\alpha)\langle Q_\alpha(t)\rangle+\tfrac{1}{2}\sum_{q,\alpha}\mathscr{P}_{ij}^{(2)}\begin{bmatrix}q & -q\\ \alpha & \alpha\end{bmatrix}\langle\,|Q_{q\alpha}|^2\rangle+\cdots\right]F_j(t)\ , \tag{4}$$

where $Q_{q\alpha}(t)$ denotes the mass-reduced normal coordinate corresponding to the vibrational crystal mode $(q\alpha)$, q the reciprocal-lattice vector, α the mode number, and $\langle\ \rangle$ denotes the average over all crystal modes. The coefficients $\mathscr{P}_{ij}^{(1)}(\alpha)$ and $\mathscr{P}_{ij}^{(2)}(\begin{smallmatrix}q & -q\\ \alpha & \alpha\end{smallmatrix})$ are connected with the first- and second-order derivatives of $\alpha_{ij}^{\rm eff}$ with respect to molecular displacements by the known transformation relations (see Refs. 3 and 7).

Generally the amplitudes $Q_{q\alpha}(t)$ depend nonlinearly on the external field intensity. If we assume a biharmonic optical field $\mathbf{E}_0(t)=\mathbf{E}(\omega_1)\cos(\omega_1 t)+\mathbf{E}(\omega_2)\cos(\omega_2 t+\delta)$ incident on the crystal, the crystal polarizability oscillates with the combination frequencies $n\omega_1+m\omega_2$ (n,m are the integral numbers). We are interested in the crystal polarization at frequency $2\omega_1-\omega_2$. As Eq. (4) shows this occurs when $\mathbf{F}(t)=\mathbf{F}(\omega_1)\cos(\omega_1 t)$ and $\langle Q_\alpha(t)\rangle$ or $\langle\,|Q_{q\alpha}|^2(t)\rangle$ have nonzero Fourier components at frequency $\omega_1-\omega_2$. The second term in Eq. (4) corresponds to the well known CARS effect.[8] The third term, in turn, is due to the parametric excitation of a crystal (PBR) and it will be the subject of further discussion. For a suitable polarization of the optical field towards the crystallographic axes the coefficient $\mathscr{P}_{ij}^{(1)}(\alpha)=0$, which means that the second term vanishes and we can isolate the contribution of PBR to the combination-frequency polarization.

III. DYNAMICAL EQUATIONS FOR CRYSTAL VIBRATIONS

The induced-dipole–induced-dipole interaction Hamiltonian was derived in Ref. 3 to be in the form

$$H_I=-\sum_{k,l}\mathscr{H}_{kl}^{I}F_kF_l\ , \tag{5}$$

where

$$\mathscr{H}_{kl}^{I}=\tfrac{1}{2}\sum_{l,n,i,j}\alpha_{ij}(ln)T_{ik}(ln)T_{jl}(ln)\ .$$

For two optical waves interacting with the crystal, the square of the local macroscopic field $F_i(t)=f_i(\omega_1)E_{1i}(t)+f_i(\omega_2)E_{2i}(t)$ is given by

$$F_kF_l(t)=(F^2)_{kl}+(F_1F_2)_{kl}\cos[(\omega_1-\omega_2)t-\delta]\ ,$$

where we have denoted

$$(F^2)_{kl}=\tfrac{1}{2}[f_k(\omega_1)f_l(\omega_1)E_k(\omega_1)E_l(\omega_1)+f_k(\omega_2)f_l(\omega_2)E_k(\omega_2)E_l(\omega_2)]$$

and

$$(F_1F_2)_{kl}=\tfrac{1}{2}[f_k(\omega_1)f_l(\omega_2)E_k(\omega_1)E_l(\omega_2)+f_k(\omega_2)f_l(\omega_1)E_k(\omega_2)E_l(\omega_1)]\ .$$

The rapidly oscillating terms with double and sum frequencies have been neglected as they oscillate much faster than the vibrational frequency of the crystal; $\omega_1,\omega_2\sim10^{15}$ $\mathrm{s}^{-1}\gg\omega_\alpha\sim10^{13}$ s^{-1}. Then, the interaction Hamiltonian [Eq. (5)] consists of two terms, one constant in time and the other one oscillating in time with frequency $\omega_1-\omega_2$.

The total Hamiltonian of the crystal, $H=H_0+H_I$, is taken as a power series of small vibrational amplitudes with accuracy to fourth-order terms. Thus, in a normal mode representation it has the form

$$\begin{aligned}H=&\sum_{q,\alpha}\left(\tfrac{1}{2}|\dot{Q}_{q\alpha}|^2+\tfrac{1}{2}(\omega_{q\alpha}^E)^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}\,|Q_{q\alpha}|^2\right)-\sum_\alpha\mathscr{H}_{kl}^{I(1)}(\alpha)Q_\alpha F_kF_l(t)\\&-\sum_{q,\alpha,\alpha'(\neq\alpha)}\mathscr{H}_{kl}^{I(2)}\begin{bmatrix}q & -q\\ \alpha & \alpha'\end{bmatrix}Q_{q\alpha}Q_{-q\alpha'}(F_1F_2)_{kl}\cos[(\omega_1-\omega_2)t-\delta]\\&+\tfrac{1}{6}\sum_{q,q',q'',\alpha,\alpha',\alpha''}H^{(3)E}\left[\begin{matrix}q & q' & q''\\ \alpha & \alpha' & \alpha''\end{matrix}\middle|\,t\right]Q_{q\alpha}Q_{q'\alpha'}Q_{q''\alpha''}\\&+\tfrac{1}{24}\sum_{q,q',q'',q''',\alpha,\alpha',\alpha'',\alpha'''}H^{(4)E}\left[\begin{matrix}q & q' & q'' & q'''\\ \alpha & \alpha' & \alpha'' & \alpha'''\end{matrix}\middle|\,t\right]Q_{q\alpha}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''}\ ,\end{aligned} \tag{6}$$

where the time-dependent anharmonic coefficients $H^{(3)E}(\begin{smallmatrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{smallmatrix} | t)$ and $H^{(4)E}(\begin{smallmatrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{smallmatrix} | t)$ are given by

$$H^{(3)E}\left[\begin{matrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\middle| t\right] = H_0^{(3)}\left[\begin{matrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\right] - \mathscr{H}_{kl}^{I(3)}\left[\begin{matrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\right] F_k F_l(t) ,$$

$$H^{(4)E}\left[\begin{matrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{matrix}\middle| t\right] = H_0^{(4)}\left[\begin{matrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{matrix}\right] - \mathscr{H}_{kl}^{I(4)}\left[\begin{matrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{matrix}\right] F_k F_l(t) .$$

The general relations between the coefficients $H^{(i)}(\begin{smallmatrix} q_1 & q_2 & \cdots & q_i \\ \alpha_1 & \alpha_2 & \cdots & \alpha_i \end{smallmatrix})$ and the succeeding derivatives of the Hamiltonian H with respect to molecular displacements are given in Ref. 7, whereas the exact formulas for the interaction Hamiltonian [Eq. (5)] are derived in Ref. 3. As we can see in Eq. (6) the vibrational frequency $\omega_{q\alpha}$ of the mode $(q\alpha)$ is shifted by the constant part of the square of the optical field amplitude;[3]

$$(\omega_{q\alpha}^E)^2 = \omega_{q\alpha}^2(1+\eta_{q\alpha}) , \tag{7}$$

where $\eta_{q\alpha} = -\mathscr{H}_{kl}^{I(2)}(\begin{smallmatrix} q & -q \\ \alpha & \alpha \end{smallmatrix})(F^2)_{kl}/\omega_{q\alpha}^2$.

On the other hand, the vibrational frequency $\omega_{q\alpha}^E$ is modulated due to the oscillating part of the square of the optical field with the modulation coefficient $\xi_{q\alpha}$,

$$\xi_{q\alpha} = \frac{\mathscr{H}_{kl}^{I(2)}\left[\begin{matrix} q & -q \\ \alpha & \alpha \end{matrix}\right](F_1F_2)_{kl}}{(\omega_{q\alpha}^E)^2} . \tag{8}$$

As we are considering the resonant interaction of the optical field with the crystal modes we can deal with one mode which has a frequency fulfilling the resonant conditions. Thus, we treat this representative mode as the system and all other modes as the bath. The system-bath interaction is described by the anharmonic terms in the Hamiltonian defined by Eq. (6). In the case of PBR we are interested in the dynamical behavior of the square of the amplitude of this representative mode averaged over the bath $\langle |Q_{q\alpha}|^2(t)\rangle_B$ (see Sec. II). ($\langle\ \rangle_B$ denotes averaging over the bath and will be defined later.) In the case of CARS we deal with the dynamical behavior of the mean amplitude of the representative mode $\langle Q_{q\alpha}(t)\rangle_B$ and $\langle |Q_{q\alpha}|^2(t)\rangle_B \neq \langle Q_{q\alpha}(t)\rangle_B^2$ due to the system-bath interaction.

Now we will derive the dynamical equation for $\langle |Q_{q\alpha}|^2(t)\rangle_B$. The Hamilton equations for the system (see Appendix A) yield the following set of equations for the second-order products of $Q_{q\alpha}$ and $P_{q\alpha} = \dot{Q}_{q\alpha}$:

$$\frac{d}{dt}|Q_{q\alpha}|^2 = Q_{q\alpha}P_{-q\alpha} + Q_{-q\alpha}P_{q\alpha} , \tag{9a}$$

$$\begin{aligned}\frac{d}{dt}|P_{q\alpha}|^2 =& -(\omega_{q\alpha}^E)^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}(Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}) + \Delta(q)\mathscr{H}_{kl}^{I(1)}(\alpha)(P_{q\alpha}+P_{-q\alpha})F_kF_l(t) \\ &+ \sum_{\alpha'(\neq\alpha)}\left[\mathscr{H}_{kl}^{I(2)}\left[\begin{matrix} q & -q \\ \alpha & \alpha' \end{matrix}\right]P_{q\alpha}Q_{-q\alpha'} + \text{c.c.}\right](F_1F_2)_{kl}\cos[(\omega_1-\omega_2)t-\delta] \\ &- \tfrac{1}{2}\sum_{q',q'',\alpha',\alpha''}\left[H^{(3)E}\left[\begin{matrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\middle| t\right]P_{-q\alpha}Q_{q'\alpha'}Q_{q''\alpha''} + \text{c.c.}\right] \\ &- \tfrac{1}{6}\sum_{q',q'',q''',\alpha',\alpha'',\alpha'''}\left[H^{(4)E}\left[\begin{matrix} -q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{matrix}\middle| t\right]P_{-q\alpha}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''} + \text{c.c.}\right] ,\end{aligned} \tag{9b}$$

$$\begin{aligned}\frac{d}{dt}(Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}) =& 2|P_{q\alpha}|^2 - 2(\omega_{q\alpha}^E)^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}|Q_{q\alpha}|^2 + \Delta(q)\mathscr{H}_{kl}^{I(1)}(\alpha)(Q_{q\alpha}+Q_{-q\alpha})F_kF_l(t) \\ &+ \sum_{\alpha'(\neq\alpha)}\left[\mathscr{H}_{kl}^{I(2)}\left[\begin{matrix} -q & q \\ \alpha & \alpha' \end{matrix}\right]Q_{-q\alpha}Q_{q\alpha'} + \text{c.c.}\right](F_1F_2)_{kl}\cos[(\omega_1-\omega_2)t-\delta] \\ &- \tfrac{1}{2}\sum_{q',q'',\alpha',\alpha''}\left[H^{(3)E}\left[\begin{matrix} -q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\middle| t\right]Q_{-q\alpha}Q_{q'\alpha'}Q_{q''\alpha''} + \text{c.c.}\right] \\ &- \tfrac{1}{6}\sum_{q',q'',q''',\alpha',\alpha'',\alpha'''}\left[H^{(4)E}\left[\begin{matrix} -q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{matrix}\middle| t\right]Q_{-q\alpha}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''} + \text{c.c.}\right] .\end{aligned} \tag{9c}$$

On the other hand, using the Green function for the harmonic oscillator we can write down the solution of the Hamilton equations for $Q_{q'\alpha'}(t)$ $[(q'\alpha')\neq(q\alpha)]$ in the form (see Appendix A)

$$Q_{q'\alpha'}(t)=Q^{(0)}_{q'\alpha'}(t)-\int_{-\infty}^{t}\frac{\sin[\omega_{q'\alpha'}(t-t')]}{\omega_{q'\alpha'}}$$

$$\times\left\{\frac{1}{2}\sum_{q^{IV},q^{V},\alpha^{IV},\alpha^{V}}H_0^{(3)}\begin{bmatrix}-q' & q^{IV} & q^{V}\\ \alpha' & \alpha^{IV} & \alpha^{V}\end{bmatrix}Q_{q^{IV}\alpha^{IV}}(t')Q_{q^{V}\alpha^{V}}(t')\right.$$

$$+\frac{1}{6}\sum_{q^{IV},q^{V},q^{VI},\alpha^{IV},\alpha^{V},\alpha^{VI}}H_0^{(4)}\begin{bmatrix}-q' & q^{IV} & q^{V} & q^{VI}\\ \alpha' & \alpha^{IV} & \alpha^{V} & \alpha^{V}\end{bmatrix}Q_{q^{IV}\alpha^{IV}}(t')Q_{q^{V}\alpha^{V}}(t')Q_{q^{VI}\alpha^{VI}}(t')$$

$$-\Theta(t')\left[\Delta(q')\mathcal{H}^{I(1)}_{mn}(\alpha')+\sum_{\alpha^{IV}}\mathcal{H}^{I(2)}_{mn}\begin{bmatrix}-q' & q'\\ \alpha' & \alpha^{IV}\end{bmatrix}Q_{q'\alpha^{IV}}(t')\right.$$

$$+\frac{1}{2}\sum_{q^{IV},q^{V},\alpha^{IV},\alpha^{V}}\mathcal{H}^{I(3)}_{mn}\begin{bmatrix}-q' & q^{IV} & q^{V}\\ \alpha' & \alpha^{IV} & \alpha^{V}\end{bmatrix}Q_{q^{IV}\alpha^{IV}}(t')Q_{q^{V}\alpha^{V}}(t')$$

$$+\frac{1}{6}\sum_{q^{IV},q^{V},q^{VI},\alpha^{IV},\alpha^{V},\alpha^{VI}}\mathcal{H}^{I(4)}_{mn}\begin{bmatrix}-q' & q^{IV} & q^{V} & q^{VI}\\ \alpha' & \alpha^{IV} & \alpha^{V} & \alpha^{VI}\end{bmatrix}Q_{q^{IV}\alpha^{IV}}(t')$$

$$\left.\left.\times Q_{q^{V}\alpha^{V}}(t')Q_{q^{VI}\alpha^{VI}}(t')\right]F_mF_n(t')\right\}dt' , \tag{10}$$

where

$$\Theta(t')=\begin{cases}1, & t'\geq 0\\ 0, & t'<0 ,\end{cases}\quad \Delta(q)=\begin{cases}1, & q=0\\ 0, & q\neq 0\end{cases}$$

and

$$Q^{(0)}_{q'\alpha'}(t)=Q^{(0)}_{q'\alpha'}(0)\cos(\omega_{q'\alpha'}t)+\frac{\dot{Q}^{(0)}_{q'\alpha'}(0)}{\omega_{q'\alpha'}}\sin(\omega_{q'\alpha'}t)$$

is the solution of the harmonic equation. The integration of the unperturbed system starts at $t=-\infty$. The integration of the interaction Hamiltonian terms starts at $t=0$, which means that the external field is turned on at time $t=0$.

In order to get the dynamical equations for the representative mode $(q\alpha)$ we have to substitute Eq. (10) into Eqs. (9) for $Q_{q'\alpha'}\neq Q_{q\alpha}$ and average the equations obtained over all modes $(q'\alpha')\neq(q\alpha)$ according to the formula

$$\langle X\rangle_B=\frac{\mathrm{Tr}(Xe^{-H_0^B/kT})}{\mathrm{Tr}(e^{-H_0^B/kT})} \tag{11}$$

with

$$H_0^B=\frac{1}{2}\sum_{q',\alpha'(\neq q,\alpha)}(|\dot{Q}_{q'\alpha'}|^2+\omega^2_{q'\alpha'}|Q_{q'\alpha'}|^2)+\frac{1}{6}\sum_{\substack{q',q'',q'''(\neq q)\\ \alpha',\alpha'',\alpha'''(\neq\alpha)}}H_0^{(3)}\begin{bmatrix}q' & q'' & q'''\\ \alpha' & \alpha' & \alpha'''\end{bmatrix}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''}$$

$$+\frac{1}{24}\sum_{\substack{q',q'',q''',q^{IV}(\neq q)\\ \alpha',\alpha'',\alpha''',\alpha^{IV}(\neq\alpha)}}H_0^{(4)}\begin{bmatrix}q' & q'' & q''' & q^{IV}\\ \alpha' & \alpha'' & \alpha''' & \alpha^{IV}\end{bmatrix}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''}Q_{q^{IV}\alpha^{IV}} ,$$

being the Hamiltonian of the bath in the absence of external field.

In the discussion that follows we will be dealing only with optical modes $q=0$. For simplicity we put $\mathscr{H}_{kl}^{I(1)}(\alpha)=0$. This condition can be realized either by taking into account Raman-inactive modes or by choosing the suitable polarization of the external field $\mathbf{E}$ towards crystallographic axes in the case of Raman-active modes. Furthermore, we assume that $H^{(3)}\binom{0\ q'\ -q'}{\alpha\ \alpha'\ \alpha'}=0$ for all $(q'\alpha')$, which is always satisfied in Bravais lattices with inversion symmetry.[9]

We introduce the new dimensionless variables for the representative mode $(q\alpha)=(0\alpha)$:

$$x=\frac{\langle |Q_\alpha|^2\rangle_B}{\langle |Q_\alpha^{(0)}|^2\rangle_S},\quad y=\frac{\langle |P_\alpha|^2\rangle_B}{(\tilde{\omega}_\alpha^E)^2\langle |Q_\alpha^{(0)}|^2\rangle_S},$$

$$z=\frac{\langle P_\alpha Q_\alpha\rangle_B}{\tilde{\omega}_\alpha^E\langle |Q_\alpha^{(0)}|^2\rangle_S},\quad \tau=\tilde{\omega}_\alpha^E t\ ,$$

where $\tilde{\omega}_\alpha^E=\omega_\alpha^E+\Delta_\alpha^E$ and Δ_α^E is the frequency shift defined below, whereas $\langle\ \rangle_S$ denotes the average over the system in the absence of external fields, taken in the harmonic approximation.

Hence, we get the following set of equations accurate to the terms of the order of $H^{(4)}\binom{q\ -q\ q'\ -q'}{\alpha\ \alpha\ \alpha'\ \alpha'}$ and $|H^{(3)}\binom{q\ q'\ q''}{\alpha\ \alpha'\ \alpha''}|^2$ (for detailed derivation and estimation of the coefficients to be neglected see Appendix A):

$$\dot{x}=2z\ , \tag{12a}$$

$$\begin{aligned}\dot{y}=&-2z[1-\tilde{\xi}\cos(\nu\tau-\delta)]\\&-2\epsilon xz[1-\xi^\epsilon\cos(\nu\tau-\delta)]\\&-4\gamma\left[y-\frac{1}{1+\eta}\right][1-\xi^\Gamma\cos(\nu\tau-\delta)]\ ,\end{aligned} \tag{12b}$$

$$\begin{aligned}\dot{z}=&y-x[1-\tilde{\xi}\cos(\nu\tau-\delta)]\\&-\epsilon x^2[1-\xi^\epsilon\cos(\nu\tau-\delta)]\\&-2(\gamma z-\dot{\bar{\Delta}}^{(3)})[1-\xi^\Gamma\cos(\nu\tau-\delta)]\ ,\end{aligned} \tag{12c}$$

where $\nu=(\omega_1-\omega_2)/\tilde{\omega}_\alpha^E$, $\eta\equiv\eta_\alpha$, $\bar{\Delta}^{(3)}=|\Delta_\alpha^{(3)E}|/\omega_\alpha(1+\eta_\alpha)$;

$$\tilde{\xi}=\xi_\alpha+\sum_{q',\alpha'}\mathscr{H}_{kl}^{I(4)}\begin{bmatrix}0&0&q'&-q'\\\alpha&\alpha&\alpha'&\alpha'\end{bmatrix}\langle |Q_{q'\alpha'}|^2\rangle_B$$

is the frequency modulation coefficient including the second-order correction,

$$\epsilon=\frac{H_0^{(4)}\begin{bmatrix}0&0&0&0\\\alpha&\alpha&\alpha&\alpha\end{bmatrix}-\mathscr{H}_{kl}^{I(4)}\begin{bmatrix}0&0&0&0\\\alpha&\alpha&\alpha&\alpha\end{bmatrix}(F^2)_{kl}}{2(\tilde{\omega}_\alpha^E)^2}\langle |Q_\alpha^{(0)}|^2\rangle_S$$

is the coefficient of anharmonicity,

$$\xi^\epsilon=\frac{\mathscr{H}_{kl}^{I(4)}\begin{bmatrix}0&0&0&0\\\alpha&\alpha&\alpha&\alpha\end{bmatrix}(F_1F_2)_{kl}}{H_0^{(4)}\begin{bmatrix}0&0&0&0\\\alpha&\alpha&\alpha&\alpha\end{bmatrix}-\mathscr{H}_{kl}^{I(4)}\begin{bmatrix}0&0&0&0\\\alpha&\alpha&\alpha&\alpha\end{bmatrix}(F^2)_{kl}}$$

is the coefficient of modulation of ϵ. $\gamma=(\Gamma_\alpha/\tilde{\omega}_\alpha^E)(1+\eta_\alpha)$ and $\Delta_\alpha^{(3)E}=\Delta_\alpha^{(3)}(1+\eta_\alpha)$ are the damping coefficient and the frequency shift, respectively, and ξ^Γ is its modulation coefficient. In those expressions we have made use of the assumption that

$$\mathscr{H}_{kl}^{I(3)}\begin{bmatrix}q&q'&q''\\\alpha&\alpha'&\alpha''\end{bmatrix}(F_1F_2)_{kl}\sim\xi^\Gamma H_0^{(3)}\begin{bmatrix}q&q'&q''\\\alpha&\alpha'&\alpha''\end{bmatrix}(1+\eta^\Gamma)\ ,$$

$$\mathscr{H}_{kl}^{I(3)}\begin{bmatrix}q&q'&q''\\\alpha&\alpha'&\alpha''\end{bmatrix}(F^2)_{kl}\sim-\eta^\Gamma H_0^{(3)}\begin{bmatrix}q&q'&q''\\\alpha&\alpha'&\alpha''\end{bmatrix}$$

for all $(q'\alpha')$ and $(q''\alpha'')$ (see Appendix A).

Using our method the formulas defining the inverse lifetime of the mode $\Gamma_{q\alpha}$ and the frequency shift $\Delta_{q\alpha}$ are the same as those obtained by other authors (e.g., Refs. 9 and 10):

$$\Gamma_{q\alpha}=\frac{\pi}{16\omega_{q\alpha}}\sum_{\substack{q',q''(\neq q)\\ \alpha',\alpha''(\neq\alpha)}}\left|H_0^{(3)}\begin{bmatrix} q & q' & q'' \\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2 \times\left[\left[\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}+\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_0}{\omega_{q'\alpha'}}\right][\delta(\omega_{q'\alpha'}+\omega_{q''\alpha''}-\omega_{q\alpha})-\delta(\omega_{q'\alpha'}+\omega_{q''\alpha''}+\omega_{q\alpha})] + \left[\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}-\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_B}{\omega_{q'\alpha'}}\right][\delta(\omega_{q\alpha}+\omega_{q'\alpha'}-\omega_{q''\alpha''})-\delta(\omega_{q\alpha}+\omega_{q''\alpha''}-\omega_{q'\alpha'})]\right] \tag{13a}$$

and $\Delta_{q\alpha}=\Delta^{(3)}_{q\alpha}+\Delta^{(4)}_{q\alpha}$;

$$\Delta^{(4)}_{q\alpha}=\frac{1}{4\omega_{q\alpha}}\sum_{q',\alpha(\neq q,\alpha)}H_0^{(4)}\begin{bmatrix} q & -q & q' & -q' \\ \alpha & \alpha & \alpha' & \alpha'\end{bmatrix}\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B ,$$

$$\Delta^{(3)}_{q\alpha}=-\frac{1}{16\omega_{q\alpha}}\sum_{\substack{q',q''(\neq q)\\ \alpha',\alpha''(\neq\alpha)}}\left|H_0^{(3)}\begin{bmatrix} q & q' & q'' \\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2 \times\left[\left[\frac{\langle Q|^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}+\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle}{\omega_{q'\alpha'}}\right]\left[\frac{1}{(\omega_{q'\alpha'}+\omega_{q''\alpha''}-\omega_{q\alpha})_P}+\frac{1}{(\omega_{q'\alpha'}+\omega_{q''\alpha''}+\omega_{q\alpha})_P}\right] + \left[\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}-\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q'\alpha'}}\right]\left[\frac{1}{(\omega_{q\alpha}+\omega_{q'\alpha'}-\omega_{q''\alpha''})_P}-\frac{1}{(\omega_{q\alpha}+\omega_{q''\alpha''}-\omega_{q'\alpha'})_P}\right]\right]. \tag{13b}$$

In the classical picture we put

$$\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}+\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_B}{\omega_{q'\alpha'}}=\frac{\omega_{q'\alpha'}+\omega_{q''\alpha''}}{\omega^2_{q'\alpha'}\omega^2_{q''\alpha''}}kT$$

and

$$\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}-\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_B}{\omega_{q'\alpha'}}=\frac{\omega_{q''\alpha''}-\omega_{q'\alpha'}}{\omega^2_{q'\alpha'}\omega^2_{q''\alpha''}}kT$$

into Eq. (13) and we get the result of Maradudin and Fein.[9] In the quantum picture we have

$$\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}+\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_B}{\omega_{q'\alpha'}} =2\frac{\hbar}{\omega_{q'\alpha'}\omega_{q''\alpha''}}(n_{q'\alpha'}+n_{q''\alpha''}+1) ,$$

$$\frac{\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B}{\omega_{q''\alpha''}}-\frac{\langle|Q^{(0)}_{q''\alpha''}|^2\rangle_B}{\omega_{q'\alpha'}} =2\frac{\hbar}{\omega_{q'\alpha'}\omega_{q''\alpha''}}(n_{q'\alpha'}-n_{q''\alpha''})$$

[$n_{q\alpha}$ being the mean occupation number of the mode $(q\alpha)$], which leads to the result of, e.g., Califano and Schettino.[10]

The constant terms appearing in Eqs. (12) are the results of the time integration of the following correlation functions (see Appendix A):

$$4\Gamma_\alpha kT=\int_0^\infty d\tau\frac{\sin(\omega_\alpha\tau)}{\omega_\alpha}\langle\dot{f}(\tau)f(0)\rangle_B , \tag{14a}$$

$$4\frac{\Delta^{(3)}_\alpha}{\omega_\alpha}kT=\int_0^\infty d\tau\frac{\sin(\omega_\alpha\tau)}{\omega_\alpha}\langle f(\tau)f(0)\rangle_B \tag{14b}$$

(k is the Boltzmann constant and T is the temperature); where

$$f(t)=\sum_{\substack{q'(\neq 0)\\ \alpha,\alpha',\alpha''\\ (\alpha\neq\alpha'\neq\alpha'')}}H_0^{(3)}\begin{bmatrix} 0 & q' & -q' \\ \alpha & \alpha' & \alpha''\end{bmatrix}Q_{q'\alpha'}(t)Q_{-q'\alpha''}(t)$$

fulfills the condition $\langle f(t)\rangle_B=0$ and

$$\langle f(t)f(t')\rangle_B=\sum_{\substack{q'(\neq 0)\\ \alpha,\alpha',\alpha''\\ (\alpha\neq\alpha'\neq\alpha'')}}\left|H_0^{(3)}\begin{bmatrix} 0 & q' & -q' \\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2\langle|Q^{(0)}_{q'\alpha'}|^2\rangle_B\langle|Q^{(0)}_{q'\alpha''}|^2\rangle_B \times\{\cos[(\omega_{q'\alpha'}+\omega_{-q'\alpha''})(t-t')]+\cos[(\omega_{q'\alpha'}-\omega_{-q'\alpha''})(t-t')]\} .$$

For $\mathbf{E}_1=\mathbf{E}_2=0$ and $\epsilon=0$ Eqs. (12) are just the same as those obtained by the method of statistical averaging[11] for the damped oscillator driven by a random force. Thus, the given crystal mode $(q\alpha)$ described by Eqs. (12) behaves as a nonlinear damped oscillator driven by the random restoring force $f(t)$, where both the damping coefficient Γ_α and $f(t)$ are due to other crystal modes.

We are interested in the solution $x(t)$ of Eqs. (12) oscillating with frequency $\omega_1-\omega_2$. The set of Eqs. (12) reduces to the third-order differential equation for $x(t)$, where we retain only the terms of the second order in small values γ, ϵ, ξ, ξ^Γ, ξ^ϵ, and Δ/ω (see Appendix A). Following the asymptotic method of Krylov-Bogoliubov-Mitropolsky[12] we assume

$$x(t)=a(t)\cos[\nu\tau-\delta+\phi(t)]+b(t)+\epsilon v(t) \tag{15}$$

for $\nu^2=4+\epsilon\theta$ (θ is a small detuning), where $a(t)$, $b(t)$, and $\phi(t)$ are the solutions of the following equations:

$$\begin{aligned}\dot a=&4\gamma a\left[\frac{1}{\nu^2}-\frac{3}{4}+2\frac{\epsilon}{\nu^2}b\right]\\&-\frac{4\gamma}{\nu^2}\left[b(\tilde\xi+\xi^\Gamma)-\frac{\xi^\Gamma}{1+\eta}(1+2\bar\Delta^{(3)})\right]\cos\phi\\&-\frac{1}{\nu}(\tilde\xi b-2\bar\Delta^{(3)}\xi^\Gamma+\epsilon\xi^\epsilon b^2)\sin\phi\ ,\end{aligned} \tag{16a}$$

$$\begin{aligned}\dot\phi=&\frac{1}{2\nu}(4-\nu^2+8\gamma^2+6\epsilon b)\\&+4\frac{\gamma}{\nu^2 a}\left[b(\tilde\xi+\xi^\Gamma)-\frac{\xi^\Gamma}{1+\eta}(1+2\bar\Delta^{(3)})\right]\sin\phi\\&-\frac{1}{\nu a}[\tilde\xi b-2\bar\Delta^{(3)}\xi^\Gamma+\epsilon\xi^\epsilon(b^2+a^2)]\cos\phi\ ,\end{aligned} \tag{16b}$$

$$\begin{aligned}\dot b=&-\frac{8\gamma}{\nu^2}\left[b-\frac{1+2\bar\Delta^{(3)}}{1+\eta}+\epsilon(b^2+\tfrac{1}{2}a^2)\right]\\&-\frac{a}{\nu}(\tilde\xi+\epsilon\xi^\epsilon b)\sin\phi\\&+4\frac{\gamma a}{\nu}\left[\xi^\Gamma\left[1-\frac{\nu^2}{2}\right]+\tilde\xi\right]\cos\phi\ .\end{aligned} \tag{16c}$$

IV. DYNAMICAL EQUATIONS FOR THE OPTICAL FIELD

In this section we will derive the wave equation for the field $\mathbf{E}_3=\mathbf{E}(\omega_3,t,z)\cos[\omega_3 t-k_3 z+\psi(t,z)]$ ($\omega_3=2\omega_1-\omega_2$), generated in a crystal subjected to two external optical fields $\mathbf{E}_1=\mathbf{E}(\omega_1)\cos(\omega_1 t-k_1 z)$ and $\mathbf{E}_2=\mathbf{E}(\omega_2)\cos(\omega_2 t-k_2 z+\delta_0)$. The amplitude $\mathbf{E}(\omega_3,t,z)$ and the phase $\psi(t,z)$ are assumed to be the slowly varying functions of time and propagation distance. Considering a small crystal sample of length L ($L\ll 1/|k_1-k_2|$) we also can assume that their dependence on propagation distance is the same as in the stationary case,[8] that is,

$$\mathbf{E}(\omega_3,t,z)\approx z\mathbf{E}(\omega_3,t) \quad\text{and}\quad \psi(t,z)\approx\psi(t)\ .$$

In this approximation the amplitudes $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ can be treated as being constant. Thus, the dynamical equations derived in the previous section hold if we put the phase shift between both fields $\delta=(k_1-k_2)z+\delta_0$.

The nonlinear crystal polarization at frequency $2\omega_1-\omega_2$ due to the enhancement of the crystal vibrations in PBR is described by Eq. (5), where we put $\mathscr{P}_{ij}^{(1)}(\alpha)=0$ and substitute $\langle Q_\alpha^2(t)\rangle=\langle|Q_\alpha^{(0)}|^2\rangle_S x(t)$ as given by Eq. (15). Then we have

$$\begin{aligned}P_i^{\rm PBR}(t,z)=&\tfrac{1}{4}\sum_\alpha \mathscr{P}_{ij}^{(2)}\begin{bmatrix}0&0\\\alpha&\alpha\end{bmatrix}\langle|Q_\alpha^{(0)}|^2\rangle_S\{a(t)E_j(\omega_1)\cos[(2\omega_1-\omega_2)t-(2k_1-k_2)z+\phi(t)-\delta_0]\\&+2b(t)E_j(2\omega_1-\omega_2,t,z)\cos[(2\omega_1-\omega_2)t-k_3z+\psi(t,z)]\}\ .\end{aligned} \tag{17}$$

The total polarization vector is the sum of a resonant part $P^{\rm PBR}$ and a nonresonant part:[8]

$$\begin{aligned}P_i^{\rm NL}(t,z)=&P_i^{\rm PBR}(t,z)+3\chi_{ijkl}^{\rm NR}(2\omega_1-\omega_2,\omega_1,\omega_1,-\omega_2)E_j(\omega_1)E_k(\omega_1)E_l(\omega_2)\cos[(2\omega_1-\omega_2)t-(2k_1-k_2)z-\delta_0]\\&+6\tilde\chi_{ijkl}^{\rm NR}(2\omega_1-\omega_2,\omega,\omega,2\omega_1-\omega_2)E_j(\omega)E_k(\omega)E_l(2\omega_1-\omega_2,t,z)\cos[(2\omega_1-\omega_2)t-k_3z+\psi(t,z)]\ ,\end{aligned} \tag{18}$$

where $\tilde\chi_{ijkl}^{\rm NR}=\chi_{ijkl}^{\rm NR}+\Delta\chi_{ijkl}^{\rm NR}$; $\chi_{ijkl}^{\rm NR}$ is the nonresonant susceptibility tensor of the crystal and $\Delta\chi_{ijkl}^{\rm NR}(E^2)_{kl}=-\frac{1}{2}\mathscr{P}_{ij}^{(2)}(\alpha)\eta_\alpha\langle|Q_\alpha|^2\rangle_S$ is the contribution to the nonresonant susceptibility tensor connected with the shift of the vibrational amplitudes due to the constant part of the square of the field amplitude.[3]

From the wave equation for $\mathbf{E}_3(t,z)$ we find the equations for the amplitudes

$$\mathbf{A}(t)=\mathbf{E}(\omega_3,t)\cos[\psi(t)]\ ,$$

$$\mathbf{B}(t)=-\mathbf{E}(\omega_3,t)\sin[\psi(t)]\ .$$

Those equations, describing the time evolution of the signal $|E_3|^2=(A^2+B^2)L_{\rm eff}^2$ to be detected after having passed the distance $z=L_{\rm eff}$ ($L_{\rm eff}$ being the distance for which we assume the phase-matching condition to be fulfilled, $k_3=2k_1-k_2$), have the form

$$\frac{L_{\rm eff}n}{c}\left[1+\frac{4\pi}{n^2}[6\tilde{\chi}^{\rm NR}_{\sigma jj\sigma}E_j(\omega)E_j(\omega)+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}b]\right]\dot{A}_\sigma+A_\sigma$$

$$=\frac{2\pi}{cn}(-\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}\omega_\alpha A_\sigma L_{\rm eff}\dot{b}+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma j}E_j(\omega_1)\omega_\alpha[a\dot{\phi}\sin(\phi-\delta_0)-\dot{a}\phi\cos(\phi-\delta_0)]$$

$$+(2\omega_1-\omega_2)\{-[6\tilde{\chi}^{\rm NR}_{\sigma jj\sigma}E_j(\omega)E_j(\omega)+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}b]B_\sigma L_{\rm eff}-3\chi^{\rm NR}_{\sigma jkl}E_j(\omega_1)E_k(\omega_1)E_l(\omega_2)\sin\delta_0$$

$$+\tfrac{1}{4}\tilde{\mathcal{P}}^{(2)}_{\sigma j}E_j(\omega_1)a\sin(\phi-\delta_0)\}) , \tag{19a}$$

$$\frac{L_{\rm eff}n}{c}\left[1+\frac{4\pi}{n^2}[6\tilde{\chi}^{\rm NR}_{\sigma jj\sigma}E_j(\omega)E_j(\omega)+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}b]\right]\dot{B}_\sigma+B_\sigma$$

$$=\frac{2\pi}{cn}(-\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}\omega_\alpha B_\sigma L_{\rm eff}\dot{b}+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma j}E_j(\omega_1)\omega_\alpha[a\dot{\phi}\cos(\phi-\delta_0)+\dot{a}\phi\sin(\phi-\delta_0)]$$

$$+(2\omega_1-\omega_2)\{[6\tilde{\chi}^{\rm NR}_{\sigma jj\sigma}E_j(\omega)E_j(\omega)+\tfrac{1}{2}\tilde{\mathcal{P}}^{(2)}_{\sigma\sigma}b]A_\sigma L_{\rm eff}+3\chi^{\rm NR}_{\sigma jkl}E_j(\omega_1)E_k(\omega_1)E_l(\omega_2)\cos\delta_0$$

$$+\tfrac{1}{4}\tilde{\mathcal{P}}^{(2)}_{\sigma j}E_j(\omega_1)a\cos(\phi-\delta_0)\}) , \tag{19b}$$

where n is the refractive index of the crystal, c is the light velocity, and $\tilde{\mathcal{P}}^{(2)}_{ij}=\mathcal{P}^{(2)}_{ij}(\alpha)\langle\,|Q^{(0)}_\alpha|^2\rangle_S f(\omega_1)f(2\omega_1-\omega_2)$; $\mathbf{E}_3||\sigma$.

V. SOLUTION OF THE EQUATIONS AND DISCUSSION

A. Stationary case

For the duration of the external pulse τ much longer than the lifetime of the crystal mode, $\tau\gg 1/\Gamma_\alpha$, we are dealing with the stationary solutions of Eqs. (16) and (19). Then, we get the following expression for the output field intensity at frequency $2\omega_1-\omega_2$:

$$|E_{3\sigma}|^2=\frac{4\pi^2}{c^2n^2}L^2_{\rm eff}(2\omega_1-\omega_2)^2\{[3\chi^{\rm NR}_{\sigma jkl}E_j(\omega_1)E_k(\omega_1)E_l(\omega_2)]^2+[\tfrac{1}{4}\tilde{\mathcal{P}}^{(2)}_{\sigma j}E_j(\omega_1)a_S]^2$$

$$+\tfrac{3}{2}\chi^{\rm NR}_{\sigma jkl}\tilde{\mathcal{P}}^{(2)}_{\sigma m}a_S E_j(\omega_1)E_k(\omega_1)E_m(\omega_1)E_l(\omega_2)\cos\phi_S\} , \tag{20}$$

where a_S, b_S, and ϕ_S are the stationary solutions of Eqs. (16a)—(16c). In the general case the relations between the stationary values a_S, b_S, and ϕ_S are rather complicated (see Appendix B). In order to visualize the result we will discuss more exactly the case when $\xi^\Gamma=\xi^\epsilon=0$, which means that we neglect the modulation of small terms γ and ϵ. Then

$$a_S^2=\frac{\tilde{\xi}^2b_S^2\left[1+16\dfrac{\gamma^2}{\nu^2}\right]}{\nu^2\left[(4\gamma)^2\left[\dfrac{1}{\nu^2}-\dfrac{3}{4}+2\dfrac{\epsilon}{\nu^2}b_S\right]^2+\dfrac{1}{4\nu^2}(4-\nu^2+6\epsilon b_S+8\gamma^2)^2\right]} \tag{21}$$

and

$$\cos\phi_S=\frac{\dfrac{1}{2\nu}[4-\nu^2+6\epsilon b_S+8\gamma^2]+16\dfrac{\gamma^2}{\nu^2}\left[\dfrac{1}{\nu^2}-\dfrac{3}{4}+2\dfrac{\epsilon}{\nu^2}b_S\right]}{\left[(4\gamma)^2\left[\dfrac{1}{\nu^2}-\dfrac{3}{4}+2\dfrac{\epsilon}{\nu^2}b_S\right]^2+\dfrac{1}{4\nu^2}(4-\nu^2+6\epsilon b_S+8\gamma^2)^2\right]^{1/2}} \tag{22}$$

where b_S is the $\tilde{\xi}$-dependent root of the quartic equation. The expression for the component $\chi_{\sigma\mu\mu\rho}$ of the susceptibility tensor corresponding to the particular polarization of the external fields, $\mathbf{E}_1||\mu$ and $\mathbf{E}_2||\rho$, has the form

$$|\chi_{\sigma\mu\mu\rho}|^2 = |E_{3\sigma}|^2 \left[\frac{4\pi^2}{(cn)^2} L_{\text{eff}}^2 (2\omega_1-\omega_2)^2 E_\mu^2(\omega_1) E_\rho(\omega_1)\right]^{-1}$$

$$= (3\chi^{\text{NR}}_{\sigma\mu\mu\rho})^2 \frac{\left[\frac{1}{2\nu}(4-\nu^2+6\epsilon b_S+8\gamma^2)+\frac{\tilde{\mathcal{P}}^{(2)}_{\sigma\mu}\bar{\xi}_{\mu\rho}b_S}{12\nu\chi^{\text{NR}}_{\sigma\mu\mu\rho}}\right]^2+(4\gamma^2)\left[\frac{1}{\nu^2}-\frac{3}{4}+2\frac{\epsilon}{\nu^2}b_S\right]^2}{(4\gamma)^2\left[\frac{1}{\nu^2}-\frac{3}{4}+2\frac{\epsilon}{\nu^2}b_S\right]^2+\frac{1}{4\nu^2}(4-\nu^2+6\epsilon b_S+8\gamma^2)^2}, \quad (23)$$

where we have put $\tilde{\xi}=\bar{\xi}_{\mu\rho}E_\mu(\omega_1)E_\rho(\omega_2)$.

Hence, we can see that the amplitude a_S [Eq. (21)] and the susceptibility tensor [Eq. (23)] exhibit the resonant enhancement for $4-\nu^2+6\epsilon b_S+8\gamma^2=0$. If we put $\epsilon=0$ the shape of the resonance curve is just the same as in the known CARS experiments[4-6] [see Fig. 1(a) for very small values of ϵ], whereas the frequency separation between the minimum and the maximum of the curve is given by

$$\Delta\omega=\frac{\tilde{\mathcal{P}}^{(2)}_{\sigma\mu}\bar{\xi}_{\mu\rho}b_S}{12\nu\chi^{\text{NR}}_{\sigma\mu\mu\rho}} \quad \text{and} \quad b_S^{(\epsilon=0)}=\frac{1+2\bar{\Delta}^{(3)}}{1+\eta}\left[1-\frac{1}{2}\tilde{\xi}^2\frac{\left[\frac{3}{4}-\frac{1}{\nu^2}\right]-\frac{1}{2\nu^2}(4-\nu^2+8\gamma^2)}{\frac{1}{4\nu^2}(4-\nu^2+8\gamma^2)^2+16\gamma^2\left[\frac{3}{4}-\frac{1}{\nu^2}\right]}\right]^{-1}. \quad (24)$$

In contrast to CARS, in this case the frequency separation depends on the main square of the vibrational amplitude because $\tilde{\mathcal{P}}^{(2)}_{\sigma\mu}\sim\mathcal{P}^{(2)}_{\sigma\mu}(\alpha)\langle |Q_\alpha^{(0)}|^2\rangle_S$, which also involves temperature dependence. On the other hand, if we take into account $\epsilon\neq 0$, both the square of the vibrational amplitude [Eq. (21)] and the susceptibility tensor [Eq. (23)] exhibit bistable behavior. Moreover, $\epsilon\neq 0$ accounts for the significant shift of the resonant frequency. This is shown in Fig. 1(b) for different values of $\tilde{\xi}$. The plots in Fig. 1 were obtained numerically for the optical mode $q=0$, $\omega_\alpha=1332\ \text{cm}^{-1}$, in a diamond lattice, assuming the external fields to be polarized along the crystallographic axes, $\mathbf{E}_1||[100]$, and $\mathbf{E}_2||[100]$. For such a polarization of the external fields CARS does not occur in a diamond lattice.

In order to have a reasonable comparison of the stationary results for PBR with those for CARS we have calculated the susceptibility tensor for CARS following the same procedure (see Appendix C). Thus, we have derived the anharmonic equation of motion for the mean vibrational amplitude $\langle Q_\alpha(t)\rangle_B$ and we have substituted its stationary solution into the definition of the polarization vector [Eq. (5)] for $\mathcal{P}^{(1)}_{ij}(\alpha)\neq 0$. In the region of CARS resonance the term $\mathcal{P}^{(2)}_{ij}(\alpha)\langle |Q_\alpha|^2\rangle$ in Eq. (5), corresponding to PBR, is negligible. Then, for particular polarization of the external fields, $\mathbf{E}_1||\mu$ and $\mathbf{E}_2||\rho$, we obtain the following expression for the corresponding component of the susceptibility tensor:

$$|\chi_{\sigma\mu\mu\rho}|^2=(3\chi^{\text{NR}}_{\sigma\mu\mu\rho})^2 \times\frac{\left[1-\nu^2+\frac{3}{4}\tilde{\epsilon}q_S^2+\frac{\mathcal{P}^{(1)}_{\sigma\mu}h_{\mu\rho}}{6\chi^{\text{NR}}_{\sigma\mu\mu\rho}}\right]^2+4\nu^2\gamma^2}{(1-\nu^2+\frac{3}{4}\tilde{\epsilon}q_S^2)^2+4\nu^2\gamma^2}, \quad (25)$$

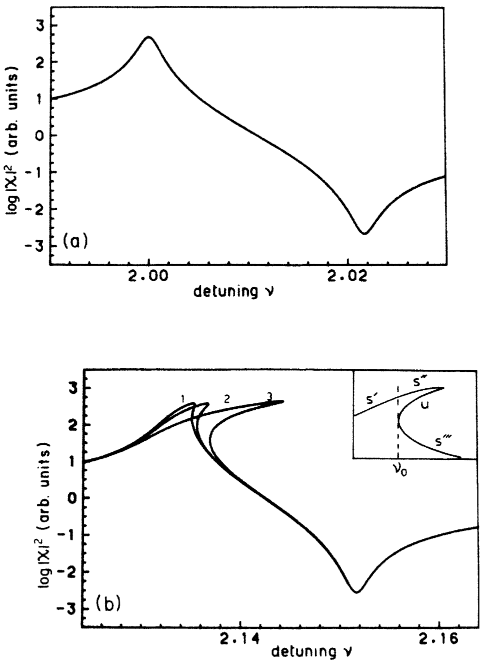

FIG. 1. Parametric resonance effect, magnitude of the nonlinear susceptibility tensor $\chi_{xxxx}(\omega_3,\omega_1,\omega_1,\omega_2)$, normalized to unity for infinite detunings, vs the relative detuning ν in diamond, for two cases: (a) $\epsilon=0$, $\xi=0.000\,24$, (b) $\epsilon=0.05$, and three different intensities of the input fields: (1) $\tilde{\xi}=0.000\,24$, (2) $\tilde{\xi}=0.0003$, (3) $\tilde{\xi}=0.0005$. Other parameters are the same for both cases: $2\gamma=0.001$ (Ref. 13), $\bar{\xi}_{xx}=\tilde{\xi}/E_{1x}E_{2x}=10^{-12}$ esu, $\tilde{\mathcal{P}}^{(2)}_{xx}=9.6\times10^{-3}$ esu. The branch u is unstable whereas the branches s are stable. The points laying on s' and s''' are reached in the transient case. The points on the branch s'' can be reached only in the quasistationary way giving hysteresis. $\omega_3=2\omega_1-\omega_2$.

where $h_{\mu\rho}=\mathscr{H}^{(1)}_{\mu\rho}(\alpha)/(\tilde{\omega}^{E}_{\alpha})^2$, $\tilde{\epsilon}=\epsilon/\langle\, |Q^{(0)}_{\alpha}|\,\rangle_S$, and q_S is the stationary amplitude of the vibration of frequency ν, $\langle Q_\alpha(t)\rangle_B=q(t)\cos[(\omega_1-\omega_2)t+\delta]$. (For the detailed derivation of the above formula see Appendix C).

The results of numerical calculations performed for an optical mode in diamond crystal (as in Fig. 1) and for the mutually perpendicular external fields, $\mathbf{E}_1$ and $\mathbf{E}_2$, are shown in Fig. 2. The value of $\mathscr{P}^{(1)}_{\sigma\mu}$ was calculated for our model of crystal polarizability, Eq. (4), and was adjusted to fit to the experimental value of the frequency separation $\Delta\omega$. As we can see in Fig. 2 also, the CARS effect exhibits bistable behavior around the resonant frequency $\nu=1$, due to the nonlinearity of the crystal lattice, $\epsilon\neq 0$. Nevertheless, the amplitudes of the external fields $E(\omega_1)$ and $E(\omega_2)$ necessary to observe it are much larger than those applied in the known CARS experiments. The above conclusions are consistent with the general considerations of Flytzanis and Tang[14] on CARS in nonlinear systems. It shoulds also be noticed that in the case of CARS the nonlinearity ϵ slightly shifts the resonant frequency from its value for $\epsilon=0$, which means $\nu=1$. The comparison of Fig. 1(b) and Fig. 2 provides that for the same conditions (diamond lattice) the field intensity necessary to observe bistability in PBR is less than the intensity necessary to observe it in CARS. In addition, the range of bistability for the same intensities of the external fields is about 3 times larger for PBR. The field intensities for which the effect of bistability is significant are less than the intensity of the field for which the breakdown in diamond crystal occurs,[15] $E=21.5$ MV/cm $=7\times 10^4$ esu. The effect of bistability in PBR can be enhanced by reducing γ; that is, assuming a long lifetime of the mode. As Fig. 3 shows, the dependence on γ is very strong. Including the modulation of the damping coefficient also increases PBR as is shown in Fig. 4.

The resonant effect of PBR permits the investigation of Raman-inactive modes by four-wave-mixing spectroscopy. The frequency separation between the maximum and the minimum of the resonance curve, Fig. 1, provides information about the nonresonant susceptibilities of the crystal, similarly to CARS. In particular, PBR could be applied in the spectroscopy of molecular crystals where all

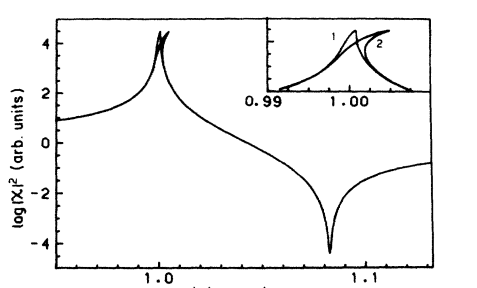

FIG. 2. CARS, magnitude of the nonlinear susceptibility tensor $\chi_{yxxy}(\omega_3,\omega_1,\omega_1,\omega_2)$, normalized to unity for infinite detunings, vs the relative detuning ν in diamond, for two intensities of the input field: (1) $\tilde{\xi}=0.000\,24$, (2) $\tilde{\xi}=0.0005$. 2γ was assumed to be 0.001 (Ref. 13), other parameters were calculated to be $\epsilon=0.05$, $\tilde{h}_{xy}=h_{xy}/(\langle\, |Q^{(0)}_{\alpha}|^2\rangle_S)^{1/2}=7.3\times 10^{-13}$ esu, $\mathscr{P}^{(1)}_{xy}(\langle\, |Q^2|\,\rangle)^{1/2}=2.6\times 10^{-2}$ esu. $\omega_3=2\omega_1-\omega_2$.

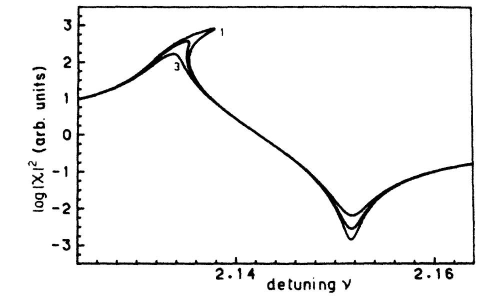

FIG. 3. Parametric resonance effect, magnitude of the nonlinear susceptibility tensor $\chi_{xxxx}(\omega_3,\omega_1,\omega_1,\omega_2)$, normalized to unity for infinite detunings, vs the relative detuning ν for different linewidths of the crystal mode: (1) $2\gamma=0.000\,75$, (2) $2\gamma=0.001$, (3) $2\gamma=0.0015$, $\tilde{\xi}=0.000\,24$ and other parameters were assumed as in the diamond lattice, e.g., $\epsilon=0.05$, $\tilde{\xi}_{xx}=10^{-12}$ esu, $\mathscr{P}^{(2)}_{xx}=9.6\times 10^{-3}$ esu. $\omega_3=2\omega_1-\omega_2$.

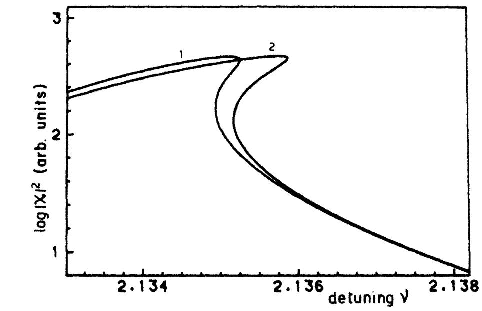

FIG. 4. The dependence of the susceptibility tensor $\chi_{xxxx}(\omega_3,\omega_1,\omega_1,\omega_2)$ on the modulation of the damping coefficient: (1) $\xi^{\Gamma}=0$, (2) $\xi^{\Gamma}=\tilde{\xi}$. In both cases $2\gamma=0.001$ and other parameters are the same as in Fig. 3.

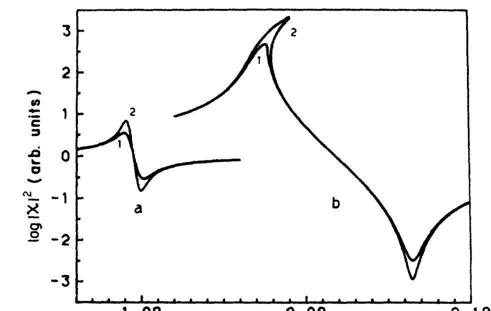

FIG. 5. Parametric resonance effect, magnitude of the nonlinear susceptibility tensors, normalized to unity for infinite detunings, vs the relative detuning ν in the crystal of benzene for two chosen vibrational modes (Ref. 3). (a) $\chi_{xxxx}(\omega_3,\omega_1,\omega_1,\omega_2)$ for the rotational mode $B_{2g}(u)$, $\omega_\alpha=56$ cm^{-1}, for two possible linewidths (Refs. 21 and 10): (1) $2\gamma=0.01$, (2) $2\gamma=0.008$. Other parameters were calculated to be $\epsilon=-0.018$, $\tilde{\xi}_{xx}=-5.6\times 10^{-12}$ esu, $\mathscr{P}^{(2)}_{xx}=9.4\times 10^{-4}$. (b) $\chi_{yyyy}(\omega_3,\omega_1,\omega_1,\omega_2)$ for the translational mode $Au(x)$, $\omega_\alpha=26.3$ cm^{-1}, for (Refs. 10 and 21) (1) $2\gamma=0.01$, (2) $2\gamma=0.008$. Other parameters were calculated to be $\epsilon=0.035$, $\tilde{\xi}_{yy}=-2.5\times 10^{-11}$ esu, $\mathscr{P}^{(2)}_{yy}=1.1\times 10^{-3}$ esu. $\omega_3=2\omega_1-\omega_2$.

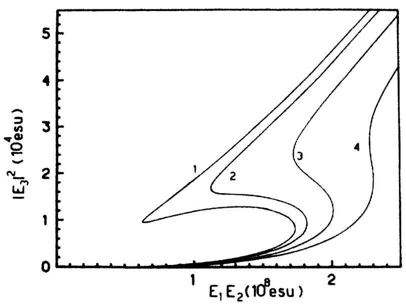

FIG. 6. The intensity of the output field $|E_3|^2$ vs the product E_1E_2, in the stationary case, for different linewidths of the crystal mode: (1) $2\gamma=0.0005$, (2) $2\gamma=0.00075$, (3) $2\gamma=0.001$, (4) $2\gamma=0.0015$. The detuning ν was assumed to lie in the region of bistability in Fig. 3, $\nu=2.1347$. Other parameters were taken as in Fig. 3.

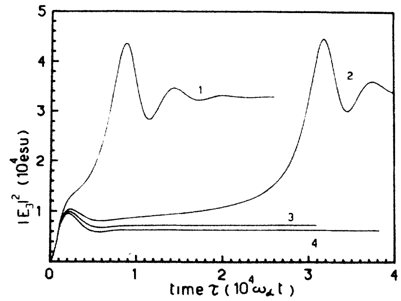

FIG. 8. Time dependence of the output field $|E_3|^2$ for the steplike input field and for the detunings as in Fig. 7.

the translationally vibrational modes of the molecular centers of mass are Raman inactive and for which the model of polarizability as proposed here is best suited.[3,10] In order to verify our suggestions we show the results of our calculations for two modes in the crystal of benzene Fig. 5. The plots correspond to different lifetimes which can be realized by changing the temperature. We have calculated the coefficients of nonlinearity by assuming a Lennard-Jones potential for atom-atom interactions.

Figure 6 shows that the intensity of the output field, given by Eq. (23), also exhibits bistable dependence on the intensities of the input fields.

B. Transient case

Here we present the time dependence of the full solutions of Eqs. (16) and (19) before the state of equilibrium is achieved. The incident fields are turned on at time $t=0$ in a steplike way. The initial values of the variables $a(t)$, $b(t)$, and $\phi(t)$ were assumed to be the stationary solutions of Eqs. (16) and (19) for $\xi=0$, which means $a(0)=0$, $b(0)=b_0=(1/2\epsilon)(-1+\sqrt{1+4\epsilon})$, $\tan[\phi(0)]=0$, and $E_3(0)=0$. However, the stationary state achieved by the system does not depend on the initial phase $\phi(0)$.

Figure 7 shows how the crystal chooses different states of vibration corresponding to different detunings of ν from the value ν_0 [Fig. 1(b)] and how the crystal tends to different states of equilibrium. For negative detuning the amplitude of vibration reaches its stationary state after having passed through a state of damped oscillations. This causes similar behavior of the intensity of the field E_3 generated in the crystal, which is shown in Fig. 8. If we start with negative detuning the system tends to the situation corresponding to the branch s' in Fig. 1(b). Similarly, for positive detuning the system achieves the branch s'''. The branch s'' is never achieved in the transient case. However, in the quasistationary case, while changing the detuning infinitesimally slowly from the negative to positive value the system reaches the branch s'' and one should observe the jump down of the output intensity to the branch s'''.

C. Quasistationary case

If we assume that the value $\tilde{\xi}$ changes very slowly in time, so that $d\tilde{\xi}/d\tau \ll \dot{a},\dot{b}$, as a trianglelike pulse, we can observe how the output intensity depends on the input intensity. Figure 9 shows that hysteresis results for different detunings. Once the input field intensity increases, the output intensity follows the lower branch, increasing rapidly up to the maximal value corresponding to the top of the trianglelike pulse. When the input field decreases, the output goes back along the upper branch. The oscilla-

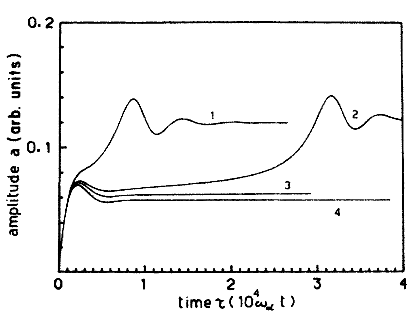

FIG. 7. Time dependence of the square of the vibrational amplitude $a=\langle |Q_\alpha^2|(t)\rangle_B/\langle |Q_\alpha^{(0)}|^2\rangle_S$, for the steplike input field, for different detunings: (1) $\nu=2.1345$, (2) $\nu=2.13465$ being smaller than ν_0 [see Fig. 1(b)] and (3) $\nu=2.13467$, (4) $\nu=2.1347$ being larger than ν_0. $\tilde{\xi}=0.00018$, $\epsilon=0.05$, $2\gamma=0.001$. Other parameters were assumed as in Fig. 3.

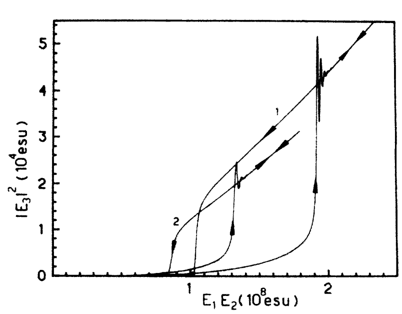

FIG. 9. The intensity of the output field $|E_3|^2$ vs the product E_1E_2, for trianglelike pulse, for two detunings: (1) $\nu=2.1347$, (2) $\nu=2.13467$ laying in the region of bistability in Fig. 1. $\epsilon=0.05$, $2\gamma=0.001$, and other parameters are taken as in Fig. 3.

tions appearing at the end of the loop are connected with the jump of the system from one state of equilibrium to the other.

VI. SUMMARY

The effect of parametric resonant enhancement presented in this paper permits the observation of the Raman-inactive modes in crystals using four-wave-mixing spectroscopy. It provides information about the second derivative of the crystal polarizability and the nonresonant susceptibility tensor. For a relatively long lifetime of the mode in the anharmonic crystal this effect exhibits bistability with respect either to the difference frequency $\omega_1-\omega_2$ or to the intensities of the incident fields. In the bistable region with respect to the input field intensities, the output field jumps to the values 1 order of magnitude higher. The four-wave-mixing spectroscopic techniques have recently been applied for investigation of two-phonon states in crystals[16–18] (the amplitude of the two phonon state called overtone[17,19] corresponds to $\langle |Q_{q\alpha}|^2\rangle$ in our paper) but none of the processes presented in those papers has the features of the parametric resonance. The dynamical equations derived by us for the material system hold not only for the crystal vibrations but also describe all the physical systems in which the interaction of the coupled nonlinear oscillators occurs, e.g., polyatomic molecules.

Although we call our effect parametric resonance, this name being usually applied to systems described by the Mathieu equation, it shows quite different features from the usual solutions of the Mathieu equation. Our solutions do not tend to infinity for $\epsilon=0$. In our equations ϵ does not play the role of damping as in Mathieu equation, but mainly shifts the resonant frequency. Thus, this shift includes the information about the anharmonic coefficients for the modes of the crystal for which it is possible to determine the frequency for $\epsilon=0$, $\nu=2$, e.g., from CARS experiments.

The name bistable parametric resonance seems to be justified in this case as the resonance occurs due to the modulation of the parameter ω (frequency) and exhibits bistable behavior.

ACKNOWLEDGMENTS

The authors would like to thank Professor F. T. Arecchi for help and interest during preparation of this paper. The authors have carried out this work with support of the "International Centre for Theoretical Physics Programme for Training and Research in Italian Laboratories, Trieste, Italy." This work was partially supported by Programme No. MR1.5 of the Polish Ministry of Science.

APPENDIX A

Using the Hamiltonian for the whole crystal as given by Eq. (6) we obtain Hamilton's equations for the chosen mode $(q\alpha)$:

$$\dot{Q}_{q\alpha}=P_{q\alpha}\ , \tag{A1a}$$

$$\begin{aligned}\dot{P}_{q\alpha}=&-(\omega_{q\alpha}^{E})^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}Q_{q\alpha}+\Delta(q)\mathscr{H}_{kl}^{I(1)}(\alpha)F_kF_l(t)\\
&+\sum_{\alpha'(\neq\alpha)}\mathscr{H}_{kl}^{I(2)}\begin{bmatrix}-q & q\\ \alpha & \alpha'\end{bmatrix}Q_{q\alpha'}(F_1F_2)_{kl}\cos[(\omega_1-\omega_2)t-\delta]-\tfrac{1}{2}\sum_{q',q'',\alpha',\alpha''}H^{(3)E}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\bigg|t\bigg]Q_{q'\alpha'}Q_{q''\alpha''}\\
&-\tfrac{1}{6}\sum_{q',q'',q''',\alpha',\alpha'',\alpha'''}H^{(4)}\begin{bmatrix}-q & q' & q'' & q'''\\ \alpha & \alpha' & \alpha'' & \alpha'''\end{bmatrix}Q_{q'\alpha'}Q_{q''\alpha''}Q_{q'''\alpha'''}\ .\end{aligned} \tag{A1b}$$

Using the Green's function for the harmonic equation the formal solution of Eq. (A1) is given in the form

$$\begin{aligned}Q_{q\alpha}(t)&\\
&=Q_{q\alpha}^{(0)}(t)+\int_{t_0}^{t}\frac{\sin[\omega_{q\alpha}(t-t')]}{\omega_{q\alpha}}\\
&\qquad\times F(Q_{q\alpha};P_{q\alpha};Q_{q'\alpha'};P_{q'\alpha'};\ldots,t)dt'\ ,\end{aligned} \tag{A2}$$

where $F(Q_{q\alpha},P_{q\alpha},Q_{q'\alpha'},P_{q'\alpha'},\ldots,t)$ is the right-hand side of Eq. (A1b) excluding the term $(\omega_{q\alpha}^E)^2Q_{q\alpha}$, $Q_{q\alpha}^{(0)}(t)$ is the solution of harmonic equation, and t_0 denotes the time when the force F is turned on. Equation (A2) corresponds to Eq. (10) in Sec. II.

In order to establish the accuracy of Eqs. (1) we estimate the orders of magnitude of the successive derivatives of the interaction Hamiltonian and the structural Hamiltonian. For the interaction Hamiltonian, Eq. (5), we have

$$\frac{\mathscr{H}_{kl}^{I(1)}(\alpha)(F^2)_{kl}}{\omega_{q\alpha}^2 Q_{q\alpha}} \sim \frac{F^2}{\sqrt{m}\,Q_{q\alpha}\omega_{q\alpha}^2}\frac{d}{dr}\left[\frac{\alpha}{\left[1-\frac{\alpha}{r^3}\right]^2}\right] \sim 10^{-11}F^2 \text{ esu} ,$$

$$\frac{\mathscr{H}_{kl}^{I(2)}\begin{bmatrix} q & q' \\ \alpha & \alpha' \end{bmatrix}(F^2)_{kl}}{\omega_{q\alpha}^2} \sim \frac{F^2}{m\omega_{q\alpha}^2}\frac{d^2}{dr^2}\left[\frac{\alpha}{\left[1-\frac{\alpha}{r^3}\right]^2}\right] \sim 10^{-12}F^2 \text{ esu} ,$$

$$\frac{\mathscr{H}_{kl}^{I(3)}\begin{bmatrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix}(F^2)_{kl}Q_{q\alpha}}{\omega_{q\alpha}^2} \sim \frac{F^2 Q_{q\alpha}}{\sqrt{m^3}\omega_{q\alpha}^2}\frac{d^3}{dr^3}\left[\frac{\alpha}{\left[1-\frac{\alpha}{r^3}\right]^2}\right] \sim 10^{-13}\, F^2 \text{ esu} , \tag{A3}$$

$$\frac{\mathscr{H}_{kl}^{I(4)}\begin{bmatrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix}(F^2)_{kl}Q_{q\alpha}^2}{\omega_{q\alpha}^2} \sim \frac{F^2 Q_{q\alpha}^2}{m^2\omega_{q\alpha}^2}\frac{d^4}{dr^4}\left[\frac{\alpha}{\left[1-\frac{\alpha}{r^3}\right]^2}\right] \sim 10^{-14}\, F^2 \text{ esu} ,$$

and for the structural Hamiltonian we have (a) for the Lennard-Jones potential

$$\Phi_1 = \frac{H_0^{(3)}\begin{bmatrix} q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{bmatrix} Q_{q\alpha}}{\omega_{q\alpha}^2} \sim 0.1 ,$$

$$\Phi_2 = \frac{H_0^{(4)}\begin{bmatrix} q & q' & q'' & q''' \\ \alpha & \alpha' & \alpha'' & \alpha''' \end{bmatrix} Q_{q'\alpha'}Q_{q\alpha}}{\omega_{q\alpha}^2} \sim 0.05 ;$$

(b) for the Morse potential[20]

$$\Phi_1 \sim 0.06 \text{ and } \Phi_2 \sim 0.005 .$$

The above estimations were performed for a diamond crystal assuming $m \sim 10^{-23}$ g, $\omega \sim 10^{14}$ s^{-1}, $\alpha \sim 10^{-24}$ cm^3, $Q_{q\alpha} = (\hbar/2\omega_{q\alpha})^{1/2} \sim \sqrt{m} \times 10^{-9}$ cm. Thus, if we derive the dynamical equation for $\langle\, |Q_{q\alpha}|^2\rangle_B$ with an accuracy of the order of $H_0^{(4)}Q_{q\alpha}^2 \sim 0.01\omega_{q\alpha}^2$ we are justified in retaining only the terms linear in the derivatives of the interaction Hamiltonian or in $H_0^{(4)}$ and quadratic in $H_0^{(3)}$. In addition we will take into account also the products $[H_0^{(3)}\mathscr{H}_{kl}^{I(3)}(F^2)_{kl}]$, although they are smaller, because they introduce the qualitative changes to the equation and will be shown to be responsible for the modulation of damping and nonlinearity.

We also must take into account the general result that $H^{(3)}\left(\begin{smallmatrix} q & q' & -q' \\ \alpha & \alpha' & \alpha' \end{smallmatrix}\right) = 0$ for Bravais crystals and nonprimitive crystals in which the atom is at a center of symmetry.[9] In molecular crystals this term has been proven to give a negligible effect.[21] For simplicity we will consider the vibrations for which $H^{(3)}\left(\begin{smallmatrix} 0 & 0 & 0 \\ \alpha & \alpha' & \alpha' \end{smallmatrix}\right) = 0$ if $q = 0$.

Substituting Eq. (10) into Eq. (9) and averaging the result over the bath we get the following set of equations with accuracy to the terms of the order of $H^{(4)}$ and $|H^{(3)}|^2$:

$$\frac{d}{dt}\langle\, |Q_{q\alpha}|^2\rangle_B = \langle Q_{q\alpha}P_{-q\alpha} + Q_{-q\alpha}P_{q\alpha}\rangle_B , \tag{A4a}$$

$$\begin{aligned}\frac{d}{dt}\langle\, |P_{q\alpha}|^2\rangle_B = &-(\omega_{q\alpha}^E)^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B + \Delta(q)\mathscr{H}_{kl}^{I(1)}\langle P_{q\alpha}+P_{-q\alpha}\rangle_B F_k F_l(t) \\ &-\tfrac{1}{2}\sum_{\substack{q'\neq q''\neq q \\ \alpha'\neq\alpha''\neq\alpha}}\left[H^{(3)E}\left[\begin{matrix} -q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\right|t\right] \langle P_{-q\alpha}(t)Q_{q'\alpha'}^{(0)}(t)Q_{q''\alpha''}^{(0)}(t)\rangle_B + \text{c.c.}\Bigg] \\ &-\frac{1}{2}\left[\sum_{q',\alpha'(\neq q,\alpha)} H^{(4)E}\left[\begin{matrix} -q & q & -q' & q' \\ \alpha & \alpha & \alpha' & \alpha' \end{matrix}\right|t\right]\langle\, |Q_{q'\alpha'}^{(0)}|^2\rangle_B\right]\langle Q_{q\alpha}P_{-q\alpha}+P_{q\alpha}Q_{-q\alpha}\rangle_B \\ &-\tfrac{1}{2}H^{(4)E}\left[\begin{matrix} -q & q & -q & q \\ \alpha & \alpha & \alpha & \alpha \end{matrix}\right|t\right]\langle\, |Q_{q\alpha}|^2\rangle_B\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B \\ &+\tfrac{1}{4}\int_{-\infty}^{t}\sum_{\substack{q',q'',q''',q^{\text{IV}} \\ \alpha',\alpha'',\alpha''',\alpha^{\text{IV}}}}\left[H^{(3)E}\left[\begin{matrix} -q & q' & q'' \\ \alpha & \alpha' & \alpha'' \end{matrix}\right|t\right]\right.\end{aligned}$$

$$\times\left\{\left[H^{(3)}\begin{bmatrix}-q' & q''' & q^{\rm IV}\\ \alpha' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}-\Theta(t')\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q' & q''' & q^{\rm IV}\\ \alpha' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}F_kF_l(t')\right]\right.$$

$$\times\langle P_{-q\alpha}(t)Q_{q''\alpha''}(t)Q_{q'''\alpha'''}(t')Q_{q^{\rm IV}\alpha^{\rm IV}}(t')\rangle_B\frac{\sin[\omega_{q'\alpha'}(t-t')]}{\omega_{q'\alpha'}}$$

$$+\left[H^{(3)}\begin{bmatrix}-q'' & q''' & q^{\rm IV}\\ \alpha'' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}-\Theta(t')\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q'' & q''' & q^{\rm IV}\\ \alpha'' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}F_kF_l(t')\right]$$

$$\left.\left.\times\langle P_{-q\alpha}(t)Q_{q'\alpha'}(t)Q_{q'''\alpha'''}(t')Q_{q^{\rm IV}\alpha^{\rm IV}}(t')\rangle_B\quad\frac{\sin[\omega_{q''\alpha''}(t-t')]}{\omega_{q''\alpha''}}\right\}+{\rm c.c.}\right]dt'\,, \tag{A4b}$$

$$\frac{d}{dt}\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B$$

$$=2\langle\,|P_{q\alpha}|^2\rangle_B-2(\omega^E_{q\alpha})^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}\langle\,|Q_{q\alpha}|^2\rangle_B+\mathscr{H}^{I(1)}_{kl}(\alpha)\langle Q_{-q\alpha}+Q_{q\alpha}\rangle_B\Delta(q)F_kF_l(t)$$

$$-\tfrac{1}{2}\sum_{\substack{q'\neq q''\neq q\\ \alpha'\neq\alpha''\neq\alpha}}\left[H^{(3)E}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}t\right]\langle Q_{-q\alpha}(t)Q^{(0)}_{q'\alpha'}(t)Q^{(0)}_{q''\alpha''}(t)\rangle_B+{\rm c.c.}\right]$$

$$-\frac{1}{2}\left[\sum_{q',\alpha'(\neq q,\alpha)}H^{(4)E}\begin{bmatrix}-q & q & -q' & q'\\ \alpha & \alpha & \alpha' & \alpha\end{bmatrix}t\right]\langle\,|Q^{(0)}_{q'\alpha'}|^2\rangle_B\right]\langle\,|Q_{q\alpha}|^2\rangle_B$$

$$-\tfrac{1}{2}H^{(4)E}\begin{bmatrix}-q & q & -q & q\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}t\right](\langle\,|Q_{q\alpha}|^2\rangle_B)^2$$

$$+\tfrac{1}{4}\int_{-\infty}^{t}\sum_{\substack{q',q'',q''',q^{\rm IV}\\ \alpha',\alpha'',\alpha''',\alpha^{\rm IV}}}\left\{H^{(3)E}\begin{bmatrix}q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}t\right]$$

$$\times\left\{\left[H^{(3)}_0\begin{bmatrix}-q' & q''' & q^{\rm IV}\\ \alpha' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}-\Theta(t')\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q' & q''' & q^{\rm IV}\\ \alpha' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}F_kF_l(t')\right]\right.$$

$$\times\langle Q^{(t)}_{-q\alpha}Q_{q''\alpha''}(t)Q_{q'''\alpha'''}(t')Q_{q^{\rm IV}\alpha^{\rm IV}}(t')\rangle_B\frac{\sin[\omega_{q'\alpha'}(t-t')]}{\omega_{q'\alpha'}}$$

$$+\left[H^{(3)}_0\begin{bmatrix}-q'' & q''' & q^{\rm IV}\\ \alpha'' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}-\Theta(t')\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q'' & q''' & q^{\rm IV}\\ \alpha'' & \alpha''' & \alpha^{\rm IV}\end{bmatrix}F_kF_l(t')\right]$$

$$\left.\left.\times\langle Q_{-q\alpha}(t)Q_{q'\alpha'}(t)Q_{q'''\alpha'''}(t')Q_{q^{\rm IV}\alpha^{\rm IV}}(t')\rangle_B\frac{\sin[\omega_{q''\alpha''}(t-t')]}{\omega_{q''\alpha''}}\right\}+{\rm c.c.}\right\}dt'\,, \tag{A4c}$$

where $\Theta(t')$ is 1 for $t'\geq 0$ and 0 for $t'<0$. In the anharmonic terms of the order of $H^{(4)}$ we have put

$$\langle |Q_{q'\alpha'}|^2(Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha})\rangle_B=\langle |Q_{q'\alpha}|^2\rangle_B\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B$$

and

$$\langle |Q_{q'\alpha'}|^2|Q_{q\alpha}|^2\rangle_B=\langle |Q_{q'\alpha'}|^2\rangle_B\langle |Q_{q\alpha}|^2\rangle_B$$

for all $(q'\alpha')$. Those equalities are satisfied with accuracy to $O(H^{(3)})$ and $O(H^{(4)})$, which is consistent with the approximation applied in Eqs. (A4).

With accuracy to the terms of the order of $|H^{(3)}|^2$ we can perform the averaging under the integrals in Eqs. (A4b) and (A4c) by putting the amplitudes $Q_{q'\alpha'}(t)$ [defined by Eq. (10)] in a harmonic approximation, $Q^{(0)}_{q'\alpha'}(t)$ and $P^{(0)}_{q'\alpha'}(t)$:

$$\begin{aligned}&\langle P^{(0)}_{-q\alpha}(t)Q^{(0)}_{q'\alpha'}(t)Q^{(0)}_{q'''\alpha'''}(t')Q^{(0)}_{q^{\mathrm{IV}}\alpha^{\mathrm{IV}}}(t')\rangle_B\\&\quad=(P^{(0)}_{-q\alpha}Q^{(0)}_{q\alpha})(t)\langle |Q^{(0)}_{q'''\alpha'''}|^2\rangle_B\Delta(q-q')\Delta(q'''+q^{\mathrm{IV}})\delta_{\alpha\alpha'}\delta_{\alpha'''\alpha^{\mathrm{IV}}}\\&\qquad+P^{(0)}_{-q\alpha}(t)Q^{(0)}_{q\alpha}(t')\langle |Q^{(0)}_{q'\alpha'}|^2\rangle_B[\Delta(q'+q''')\Delta(q-q^{\mathrm{IV}})\delta_{\alpha'\alpha'''}\delta_{\alpha\alpha^{\mathrm{IV}}}+\Delta(q'+q^{\mathrm{IV}})\Delta(q-q''')\delta_{\alpha'\alpha^{\mathrm{IV}}}\delta_{\alpha'''\alpha}]\cos[\omega_{q'\alpha'}(t-t')]\end{aligned} \tag{A5a}$$

and

$$\begin{aligned}&\langle Q^{(0)}_{-q\alpha}(t)Q^{(0)}_{q'\alpha'}(t)Q^{(0)}_{q'''\alpha'''}(t')Q^{(0)}_{q^{\mathrm{IV}}\alpha^{\mathrm{IV}}}(t')\rangle_B\\&\quad=|Q^{(0)}_{q\alpha}|^2(t)\langle |Q^{(0)}_{q'''\alpha'''}|^2\rangle_B\Delta(q-q')\Delta(q'''+q^{\mathrm{IV}})\delta_{\alpha\alpha'}\delta_{\alpha'''\alpha^{\mathrm{IV}}}\\&\qquad+Q^{(0)}_{-q\alpha}(t)Q^{(0)}_{q\alpha}(t')\langle |Q^{(0)}_{q'\alpha'}|^2\rangle_B[\Delta(q'+q''')\Delta(q-q^{\mathrm{IV}})\delta_{\alpha'\alpha'''}\delta_{\alpha\alpha^{\mathrm{IV}}}\\&\qquad\qquad+\Delta(q'+q^{\mathrm{IV}})\Delta(q-q''')\delta_{\alpha'\alpha^{\mathrm{IV}}}\delta_{\alpha\alpha'''}]\cos[\omega_{q'\alpha'}(t-t')]\ .\end{aligned} \tag{A5b}$$

Substituting Eqs. (A5a) and (A5b) into Eqs. (A4b) and (A4c), respectively, and putting $H^{(3)}\left(\begin{smallmatrix}q & q' & -q'\\ \alpha & \alpha' & \alpha'\end{smallmatrix}\right)=0$ we get the following form of the integrals: $R_1=P^{(0)}_{-q\alpha}(t)(I_1+I_2+I_3)$ in Eq. (A4b) and $R_2=Q^{(0)}_{-q\alpha}(t)(I_1+I_2+I_3)$ in Eq. (A4c), whereas

$$I_1=\tfrac{1}{8}\sum_{q'\alpha'\neq q''\alpha''\neq q\alpha}\left|H^{(3)}_0\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2(1+\eta^{\Gamma}_{q\alpha})\{1-\xi^{\Gamma}_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}\int_0^{\infty}F(t,\tau)d\tau\ , \tag{A6a}$$

$$I_2=\tfrac{1}{8}\sum_{q'\alpha'\neq q''\alpha''\neq q\alpha}\left|H^{(3)}_0\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2\frac{\eta^{\Gamma}_{q\alpha}}{1+\eta^{\Gamma}_{q\alpha}}\int_0^{t}F(t,\tau)d\tau\ , \tag{A6b}$$

$$I_3=-\tfrac{1}{8}\sum_{q'\alpha'\neq q''\alpha''\neq q\alpha}\left|H^{(3)}_0\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2\xi^{\Gamma}\int_0^{t}F(t,\tau)\cos[(\omega_1-\omega_2)\tau-\delta]d\tau\ . \tag{A6c}$$

The variable of integration in the above integrals has been changed to $\tau=t-t'$. We have also assumed that

$$\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}(F^2)_{kl}\sim-\eta^{\Gamma}_{q\alpha}H^{(3)}_0\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}$$

and

$$\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}(F_1F_2)_{kl}\sim\bar{\xi}^{\Gamma}_{q\alpha}H^{(3)}_0\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}$$

for all $(q'\alpha')$ and $(q''\alpha'')$; $\bar{\xi}^{\Gamma}_{q\alpha}=\xi^{\Gamma}_{q\alpha}(1+\eta^{\Gamma}_{q\alpha})$.

The function $F(t,\tau)$ is the result of some simple trigonometric operations and has the form

$$F(t,\tau)=Q_{qa}^{(0)}(t)\left[\left[\frac{\langle |Q_{q'a'}^{(0)}|^2\rangle_B}{\omega_{q''a''}}+\frac{\langle |Q_{q''a''}^{(0)}|^2\rangle_B}{\omega_{q'a'}}\right]\{\sin(\omega_{qa}+\omega_{q'a'}+\omega_{q''a''})\tau+\sin[(\omega_{q'a'}+\omega_{q''a''}-\omega_{qa})\tau]\}\right.$$
$$\left.-\left[\frac{\langle |Q_{q'a'}^{(0)}|^2\rangle_B}{\omega_{q''a''}}-\frac{\langle |Q_{q''a''}^{(0)}|^2\rangle}{\omega_{q'a'}}\right]\{\sin(\omega_{q'a'}-\omega_{q''a''}+\omega_{qa})\tau+\sin[(\omega_{q'a'}-\omega_{q''a''}-\omega_{qa})\tau]\}\right]$$
$$-\frac{P_{qa}^{(0)}(t)}{\omega_{qa}}\left[\left[\frac{\langle |Q_{q'a'}^{(0)}|^2\rangle_B}{\omega_{q''a''}}+\frac{\langle |Q_{q''a''}^{(0)}|^2\rangle_B}{\omega_{q'a'}}\right]\{\cos[(\omega_{q'a'}+\omega_{q''a''}-\omega_{qa})\tau]-\cos[(\omega_{q'a'}+\omega_{q''a''}+\omega_{qa})\tau]\}\right.$$
$$+\left[\frac{\langle |Q_{q'a'}^{(0)}|^2\rangle_B}{\omega_{q''a''}}-\frac{\langle |Q_{q''a''}^{(0)}|^2\rangle_B}{\omega_{q'a'}}\right]\{\cos[(\omega_{q'a'}-\omega_{q''a''}+\omega_{qa})\tau]$$
$$\left.-\cos[(\omega_{q'a'}-\omega_{q''a''}-\omega_{qa})\tau]\}\right] .$$

The harmonic vibrational amplitudes $Q_{qa}^{(0)}(t)$ and $P_{qa}^{(0)}(t)$ in the expressions on R_1 and R_2 can now be replaced by the full solutions $Q_{qa}(t)$ and $P_{qa}(t)$, which is still consistent with the assumed accuracy. Applying the relations

$$\int_0^\infty \sin(\omega t)dt=\frac{1}{(\omega)_P}$$

and

$$\int_0^\infty \cos(\omega t)dt=\pi\delta(\omega)$$

we get

$$I_1=[-\Gamma_{qa}P_{qa}(t)-\omega_{qa}\Delta_{qa}^{(3)}Q_{qa}(t)](1+\eta_{qa}^{\Gamma})\times\{1-\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\ , \tag{A7}$$

where Γ_{qa} and $\Delta_{qa}^{(3)}$ are the inverse lifetime and the frequency shift of the mode $(q\alpha)$ obtained in the form given by Eqs. (13a) and (13b). The integrals I_2 and I_3 can be neglected for the small pulses of time duration $\tau\leq 10^{-7}$ s. Then the integrals in Eqs. (A4b) and (A4c) become

$$R_1=[-2\Gamma_{qa}|P_{qa}|^2-\omega_{qa}\Delta_{qa}^{(3)}(P_{-qa}Q_{qa}+P_{qa}Q_{-qa})]\times(1+\eta_{qa}^{\Gamma})\{1-\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\ ,$$

$$R_2=[-\Gamma_{qa}(P_{-qa}Q_{qa}+P_{qa}Q_{-qa})-2\Delta_{qa}^{(3)}\omega_{qa}|Q_{qa}|^2(t)]\times(1+\eta_{qa}^{\Gamma})\{-\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\ .$$

The next terms in Eqs. (A4b) and (A4c) to be discussed are the following:

$$F_1=\sum_{q'a'\neq q''a''\neq qa}H^{(3)E}\left[\begin{vmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{vmatrix}t\right]\times\langle Q_{-qa}(t)Q_{q'a'}^{(0)}(t)Q_{q''a''}^{(0)}(t)\rangle_B\ ,$$

$$F_2=\sum_{q'a'\neq q''a''\neq qa}H^{(3)E}\left[\begin{vmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{vmatrix}t\right]\times\langle P_{-qa}(t)Q_{q'a'}^{(0)}(t)Q_{q''a''}^{(0)}(t)\rangle_B\ ,$$

which do not vanish because the amplitude of the mode $(q\alpha)$ depends on the amplitudes of the other modes, according to Eq. (10). Substituting Eq. (10) into the expressions for F_1 and F_2 yields the following terms, obtained with accuracy to the terms of the order of $|H_0^{(3)}|^2$ and $(H_0^{(3)}\mathcal{H}_{kl}^{I(3)})$,

$$F_1=\int_{-\infty}^{t}\frac{\sin[\omega_{qa}(t-t')]}{\omega_{qa}}\langle f_{qa}(t')f_{qa}(t)\rangle_B(1+\eta_{qa}^{\Gamma})\times\left[1-\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]-\Theta(t')\left[\frac{-\eta_{qa}^{\Gamma}}{1+\eta_{qa}^{\Gamma}}+\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t'-\delta]\right]\right]dt'\ , \tag{A8}$$

$$F_2=\int_{-\infty}^{t}\frac{\sin[\omega_{qa}(t-t')]}{\omega_{qa}}\langle \dot f_{qa}(t')f_{qa}(t)\rangle_B(1+\eta_{qa}^{\Gamma})\times\left[1-\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]-\Theta(t')\left[\frac{-\eta_{qa}^{\Gamma}}{1+\eta_{qa}^{\Gamma}}+\xi_{qa}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\right]\right]dt'\ , \tag{A9}$$

where

$$f_{qa}(t)=\sum_{q'a'\neq q''a''\neq qa}H_0^{(3)}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}Q_{q'a'}^{(0)}(t)Q_{q''a''}^{(0)}(t)$$

plays a role of a random restoring force exerted on a mode $(q\alpha)$ by the modes of the bath. The time correlation functions are given by

$$\langle f_{q\alpha}(t')f_{q\alpha}(t)\rangle_B=\frac{1}{4}\sum_{q'\alpha'\neq q''\alpha''\neq q\alpha}\left|H_0^{(3)}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2\langle\,|Q_{q'\alpha'}^{(0)}|^2\rangle_B\langle\,|Q_{q''\alpha''}^{(0)}|^2\rangle_B$$

$$\times\{\cos[(\omega_{q'\alpha'}+\omega_{q''\alpha''})(t-t')]+\cos[(\omega_{q'\alpha'}-\omega_{q''\alpha''})(t-t')]\} \quad \text{(A10)}$$

and

$$\langle \dot{f}_{q\alpha}(t')f_{q\alpha}(t)\rangle_B=\frac{1}{4}\sum_{q'\alpha'\neq q''\alpha''\neq q\alpha}\left|H_0^{(3)}\begin{bmatrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{bmatrix}\right|^2\langle\,|Q_{q'\alpha'}^{(0)}|^2\rangle_B\langle\,|Q_{q''\alpha''}^{(0)}|^2\rangle_B$$

$$\times\{(\omega_{q'\alpha'}-\omega_{q''\alpha''})\sin[(\omega_{q'\alpha'}-\omega_{q''\alpha''})(t-t')]+(\omega_{q'\alpha'}+\omega_{q''\alpha''})\sin[(\omega_{q'\alpha'}+\omega_{q''\alpha''})(t-t')]\}\ . \quad \text{(A11)}$$

Substituting Eqs. (A10) and (A11) into Eqs. (A8) and (A9) and performing the integration we get

$$F_1=2\left|\frac{\Delta_{q\alpha}^{(3)}}{\omega_{q\alpha}}\right|kT(1+\eta_{q\alpha}^{\Gamma})\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\ ,$$

$$F_2=2\Gamma_{q\alpha}kT(1+\eta_{q\alpha}^{\Gamma})\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}$$

for $\langle\,|Q_{q'\alpha'}^{(0)}|^2\rangle_B=kT/\omega_{q'\alpha'}^2$. Taking into account the formulas obtained for R_1, R_2, F_1, F_2, Eqs. (A4) lead to the following set of equations:

$$\frac{d}{dt}\langle\,|Q_{q\alpha}|^2\rangle_B=\langle Q_{q\alpha}P_{-q\alpha}+P_{q\alpha}Q_{-q\alpha}\rangle_B\ , \quad \text{(A12a)}$$

$$\frac{d}{dt}\langle\,|P_{q\alpha}|^2\rangle_B=-(\tilde{\omega}_{q\alpha}^E)^2\{1-(\xi_{q\alpha}+\Delta\xi_{q\alpha})\cos[(\omega_1-\omega_2)t-\delta]\}\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B$$

$$-4\Gamma_{q\alpha}^E\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\langle\,|P_{q\alpha}|^2\rangle_B+4\Gamma_{q\alpha}^E kT\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}$$

$$-\frac{1}{2}H^{(4)E}\begin{bmatrix}-q & q & -q & q\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}\langle\,|Q_{q\alpha}|^2\rangle_B\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B\{1-\xi_{q\alpha}^{\epsilon}\cos[(\omega_1-\omega_2)t-\delta]\}$$

$$+\Delta(q)\mathscr{H}_{kl}^{I(1)}(\alpha)\langle P_{q\alpha}+P_{-q\alpha}\rangle_B F_k F_l(t)\ , \quad \text{(A12b)}$$

$$\frac{d}{dt}\langle Q_{q\alpha}P_{-q\alpha}+Q_{-q\alpha}P_{q\alpha}\rangle_B=2\langle\,|P_{q\alpha}|^2\rangle_B-2(\tilde{\omega}_{q\alpha}^E)^2\{1-(\xi_{q\alpha}+\Delta\xi_{q\alpha})\cos[(\omega_1-\omega_2)t-\delta]\}\langle\,|Q_{q\alpha}|^2\rangle_B$$

$$-2\Gamma_{q\alpha}^E\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}\langle Q_{-q\alpha}P_{q\alpha}+Q_{q\alpha}P_{-q\alpha}\rangle_B$$

$$+4\left|\frac{\Delta_{q\alpha}^{(3)E}}{\omega_{q\alpha}}\right|kT\{1-\xi_{q\alpha}^{\Gamma}\cos[(\omega_1-\omega_2)t-\delta]\}$$

$$-H^{E(4)}\begin{bmatrix}-q & q & -q & q\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}(\langle\,|Q_{q\alpha}|^2\rangle_B)^2\{1-\xi_{q\alpha}^{\epsilon}\cos[(\omega_1-\omega_2)t-\delta]\}$$

$$+\Delta(q)\mathscr{H}_{kl}^{I(1)}(\alpha)\langle Q_{q\alpha}+Q_{-q\alpha}\rangle_B F_k F_l(t)\ , \quad \text{(A12c)}$$

where $\tilde{\omega}_{q\alpha}^E=\omega_{q\alpha}^E+\Delta_{q\alpha}^E$, $H^{E(4)}(\begin{smallmatrix}q & -q & q' & -q'\\ \alpha & \alpha & \alpha' & \alpha'\end{smallmatrix})=H_0^{(4)}(\begin{smallmatrix}q & -q & q' & -q'\\ \alpha & \alpha & \alpha' & \alpha'\end{smallmatrix})-\mathscr{H}_{kl}^{I(4)}(\begin{smallmatrix}q & -q & q' & -q'\\ \alpha & \alpha & \alpha' & \alpha'\end{smallmatrix})(F^2)_{kl}$;

$$\Delta\xi_{q\alpha}=\sum_{q',\alpha'}\mathscr{H}_{kl}^{I(4)}\begin{bmatrix}q & -q & q' & -q'\\ \alpha & \alpha & \alpha' & \alpha'\end{bmatrix}\langle\,|Q_{q'\alpha'}^{(0)}|^2\rangle_B$$

is the change of the frequency modulation coefficient and

$$\xi^{\epsilon}=\frac{\mathscr{H}^{I}_{kl}\begin{bmatrix}-q & q & -q & q\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}(F_1F_2)_{kl}}{H_0^{(4)E}\begin{bmatrix}-q & -q & q & q\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}} .$$

Introducing the new variables defined in Sec. II into Eqs. (A12) we get directly Eqs. (12).

APPENDIX B

The stationary solutions of Eqs. (16) are given by

$$a_S^2=\frac{\mathscr{C}^2+\mathscr{D}^2}{\mathscr{A}^2+\mathscr{B}^2+\frac{1}{\nu}\epsilon\xi^{\epsilon}a_S^2\frac{\mathscr{A}\mathscr{D}+\mathscr{C}\mathscr{B}}{\mathscr{C}^2+\mathscr{D}\left[\mathscr{D}+\frac{\epsilon\xi^{\epsilon}a_S^2}{\nu}\right]}\left[\mathscr{B}(\mathscr{C}^2+\mathscr{D}^2)+\mathscr{D}\left[\mathscr{D}+\frac{\epsilon\xi^{\epsilon}a_S^2}{\nu}\right]+\mathscr{A}\mathscr{C}\mathscr{D}\right]} , \tag{B1}$$

$$\cos\phi_S=a_S\frac{\mathscr{B}\mathscr{D}+\mathscr{A}\mathscr{C}}{\mathscr{C}^2+\mathscr{D}\left[\mathscr{D}+\frac{\epsilon\xi^{\epsilon}a_S^2}{\nu}\right]} , \tag{B2}$$

$$\frac{8\gamma}{\nu^2}\left[b_S-\frac{1+2\overline{\Delta}^{(3)}}{1+\eta}+\epsilon(b_S^2+\tfrac{1}{2}a_S^2)\right]=\frac{4\gamma}{\nu^2}a_S\left[\tilde{\xi}+\xi^{\Gamma}\left[1-\frac{\nu^2}{2}\right]\right]\sin\phi_S-\frac{a_S}{\nu}(\tilde{\xi}+\epsilon\xi^{\epsilon}b_S)\cos\phi_S , \tag{B3}$$

where

$$\mathscr{A}=4\gamma\left[\frac{1}{\nu^2}-\frac{3}{4}+2\frac{\epsilon}{\nu^2}b_S\right] ,$$

$$\mathscr{B}=\frac{1}{2\nu}(4-\nu^2+6\epsilon b_S+8\gamma^2) ,$$

$$\mathscr{C}=\frac{4\gamma}{\nu^2}\left[\xi^{\Gamma}\left[b_S-\frac{1+2\overline{\Delta}^{(3)}}{1+\eta}\right]+\tilde{\xi}\right] ,$$

$$\mathscr{D}=\frac{1}{\nu}(\tilde{\xi}b_S-2\xi^{\Gamma}\overline{\Delta}^{(3)}+\epsilon\xi^{\epsilon}b_S^2) .$$

Those equations have been solved numerically for $\xi\neq 0$, $\xi^{\Gamma}=\xi^{\epsilon}=0$ (see Figs. 1–3) and for $\xi^{\Gamma}\sim\xi\neq 0$, $\xi^{\epsilon}=0$ (see Fig. 4).

In this paper we do not discuss the influence of the modulation of the crystal nonlinearity, which means $\xi^{\epsilon}\neq 0$. It will be treated elsewhere.

APPENDIX C

In order to get the equation of motion for $\langle Q_{q\alpha}(t)\rangle_B$ we substitute $Q_{q'\alpha'}(t)$ as given by Eq. (10) into the Hamilton equations [Eqs. (A1)] for all $(q'\alpha')\neq(q\alpha)$. Averaging the result over the bath and retaining only the terms of the order of $H^{(4)}$ and $|H^{(3)}|^2$ we have

$$\langle\ddot{Q}_{q\alpha}\rangle_B+(\omega_{q\alpha}^E)^2\{1-\xi_{q\alpha}\cos[(\omega_1-\omega_2)t-\delta]\}\langle Q_{q\alpha}\rangle_B+\tfrac{1}{2}H^{(4)E}\left[\begin{matrix}-q & q & -q & q\\ \alpha & \alpha & \alpha & \alpha\end{matrix}\middle| t\right]\langle Q_{q\alpha}\rangle_B\langle|Q_{q\alpha}|^2\rangle_B$$
$$+\langle Q_{q\alpha}\rangle_B\left[\frac{1}{2}\sum_{q'\alpha'\neq q\alpha}H^{(4)E}\left[\begin{matrix}q & -q & q' & -q'\\ \alpha & \alpha & \alpha' & \alpha'\end{matrix}\middle| t\right]\langle|Q_{q'\alpha'}^{(0)}|^2\rangle_B\right]$$
$$=\mathscr{H}^{I(1)}_{kl}(\alpha)\Delta(q)F_kF_l(t)+\tfrac{1}{4}\int_{-\infty}^{t}\sum_{\substack{q',q'',q''',q^{IV},\\ \alpha',\alpha'',\alpha''',\alpha^{IV}}}H^{(3)E}\left[\begin{matrix}-q & q' & q''\\ \alpha & \alpha' & \alpha''\end{matrix}\middle| t\right]$$
$$\times\left\{\left[H_0^{(3)}\begin{bmatrix}-q' & q''' & q^{IV}\\ \alpha' & \alpha''' & \alpha^{IV}\end{bmatrix}-\Theta(t')\mathscr{H}^{I(3)}_{kl}\begin{bmatrix}-q' & q''' & q^{IV}\\ \alpha' & \alpha''' & \alpha^{IV}\end{bmatrix}F_kF_l(t')\right]\right.$$

$$\times \langle Q_{q''\alpha''}(t)Q_{q'''\alpha'''}(t')Q_{q^{IV}\alpha^{IV}}(t')\rangle_B \frac{\sin\omega_{q'\alpha'}(t-t')}{\omega_{q'\alpha'}}$$

$$+\left[H_0^{(3)}\begin{bmatrix}-q'' & q''' & q^{IV}\\ \alpha'' & \alpha''' & \alpha^{IV}\end{bmatrix}-\Theta(t')\mathscr{H}_{kl}^{I(3)}\begin{bmatrix}-q'' & q''' & q^{IV}\\ \alpha'' & \alpha''' & \alpha^{IV}\end{bmatrix}F_kF_l(t')\right]$$

$$\times \langle Q_{q'\alpha'}(t)Q_{q'''\alpha'''}(t')Q_{q^{IV}\alpha^{IV}}(t')\rangle_B \frac{\sin[\omega_{q''\alpha''}(t-t')]}{\omega_{q''\alpha''}(t-t')}\Bigg\}dt' , \quad \text{(C1)}$$

where

$$\Theta(t')=\begin{cases}1, & t'\geq 0\\ 0, & t'<0 .\end{cases}$$

The approximations applied in this equation were explained in Appendix A. The integral is just the sum $I_1+I_2+I_3$. The integral I_1 was calculated in Appendix A and is defined by Eq. (A7), whereas the integrals I_2 and I_3 are negligible (see Appendix A). Equation (C1) does not include any terms connected with the random restoring force $f(t)$ because $\langle f(t)\rangle_B=0$. Substituting Eq. (A7) into Eq. (C1) and introducing the new time variable, $\tau=\tilde{\omega}_\alpha^E t$, we get the Duffing-Mathieu equation for an optical mode $q=0$:

$$\langle \ddot{Q}_\alpha\rangle_B+2\gamma\langle \dot{Q}_\alpha\rangle_B[1-\xi^\Gamma\cos(\nu\tau-\delta)]$$
$$+\langle Q_\alpha\rangle_B[1-\tilde{\xi}\cos(\nu\tau-\delta)]$$
$$+\tilde{\epsilon}\langle Q_\alpha\rangle_B^3[1-\xi^\epsilon\cos(\nu\tau-\delta)]=h_{kl}F_kF_l(t) , \quad \text{(C2)}$$

where

$$\nu=\frac{\omega_1-\omega_2}{\tilde{\omega}_\alpha^E},\quad \gamma=\frac{\Gamma_\alpha^E}{\tilde{\omega}_\alpha^E} ,$$

$$\tilde{\epsilon}=\frac{\epsilon}{\langle |Q_\alpha^{(0)}|^2\rangle_S}=\frac{H^{(4)E}\begin{bmatrix}0 & 0 & 0 & 0\\ \alpha & \alpha & \alpha & \alpha\end{bmatrix}}{2(\tilde{\omega}_\alpha^E)^2},\quad h_{kl}=\frac{\mathscr{H}_{kl}^{I(1)}(\alpha)}{(\tilde{\omega}_\alpha^E)^2} .$$

Applying the asymptotic method of Krylov-Bogoliubov-Mitropolsky[12] we assume a solution of Eq. (C2) in the form

$$\langle Q_\alpha(t)\rangle_B=q(t)\cos[\nu\tau+\zeta(\tau)-\delta]+\epsilon u(\tau) , \quad \text{(C3)}$$

where $\nu^2=1+\epsilon\theta$ (θ being a small detuning). $q(\tau)$ and $\zeta(\tau)$ are slowly varying amplitude and phase, respectively, to be found as the solutions of the equations

$$\dot{q}=-\gamma q-\frac{h_{kl}(F_1F_2)_{kl}}{2\nu}\sin\zeta , \quad \text{(C4a)}$$

$$\dot{\zeta}=\frac{1}{2\nu}(1-\nu^2+\tfrac{3}{4}\tilde{\epsilon}q^2)-\frac{h_{kl}(F_1F_2)_{kl}}{2\nu q}\cos\zeta , \quad \text{(C4b)}$$

where $u(\tau)$ contains the vibrations with frequencies 2ν, 3ν, or $\nu=0$. In this approximation the modulation of the frequency as well as of the damping and the nonlinearity do not influence the vibration of frequency $\omega_1-\omega_2$.

The stationary solutions of Eqs. (C4a) and (C4b) have the form

$$q_S=\frac{h_{kl}(F_1F_2)_{kl}}{[(1-\nu^2+\frac{3}{4}\epsilon q_S^2)^2+\nu^2\gamma^2]^{1/2}} , \quad \text{(C5)}$$

$$\cos\zeta_S=\frac{1-\nu^2+\frac{3}{4}\tilde{\epsilon}q_S^2}{[(1-\nu^2+\frac{3}{4}\tilde{\epsilon}q_S^2)^2+\nu^2\gamma^2]^{1/2}} . \quad \text{(C6)}$$

As we can see q_S exhibits nonlinear dependence on the difference frequency $\omega_1-\omega_2$. In the stationary case the square of the amplitude of the optical field generated in a crystal at frequency $2\omega_1-\omega_2$ is given by the formula[8]

$$|E_{3\sigma}|^2=\frac{4\pi^2}{c^2n^2}L_{\text{eff}}^2(2\omega_1-\omega_2)^2\{[3\chi_{\sigma jkl}^{\text{NR}}E_j(\omega_1)E_k(\omega_1)E_l(\omega_2)]^2+[\tfrac{1}{2}\mathscr{P}_{\sigma j}^{(1)}E_j(\omega_1)q_S]^2$$
$$+3\chi_{\sigma jkl}^{\text{NR}}\mathscr{P}_{\sigma m}^{(1)}q_SE_j(\omega_1)E_k(\omega_1)E_m(\omega_1)E_l(\omega_2)\cos\zeta_S\} , \quad \text{(C7)}$$

where $\mathscr{P}_{\sigma j}^{(1)}=\mathscr{P}_{\sigma j}^{(1)}(\alpha)f(\omega_1)f(2\omega_1-\omega_2)$; $\mathbf{E}_3||\sigma$. Substituting Eqs. (C5) and (C6) into Eq. (C7) and assuming the particular polarizations of the external fields we obtain Eq. (25) for the susceptibility tensor.

---

*Permanent address: Laboratory of Physicochemistry of Dielectrics, Department of Chemistry, University of Warsaw, ul. Zwirki i Wigury 101, PL-02-089 Warsaw, Poland.

[1]A. H. Piekara, Jpn. J. Appl. Phys. **10**, 226 (1971); in *Coherence and Quantum Optics*, edited by E. Wolf (Plenum, New York, 1973), p. 533; Jpn. J. Appl. Phys. Suppl. **14**, 1 (1975); **14**, 7 (1978).

[2]A. H. Piekara and B. Ratajska, Appl. Opt. **17**, 689 (1978); Acta

Phys. Pol. A **53**, 115 (1978); Opt. Laser Technol. **10**, 200 (1978); Appl. Opt. **19**, 2556 (1980); B. Ratajska and A. H. Piekara, Appl. Opt. **17**, 3815 (1978).

[3]B. Ratajska-Gadomska, Phys. Rev. B **26**, 1942 (1982).

[4]M. D. Levenson and N. Bloembergen, Phys. Rev. B **10**, 4447 (1974).

[5]M. D. Levenson, C. Flytzanis, and N. Bloembergen, Phys. Rev. B **6**, 3962 (1972).

[6]M. D. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).

[7]M. Born and K. Huang, *Dynamical Theory of Crystal Lattice* (Clarendon, Oxford, 1954).

[8]A. Penzkofer, A. Laubereau, and W. Kaiser, Prog. Quantum Electron. **2**, 55 (1979).

[9]A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

[10]S. Califano, V. Schettino, and N. Neto, in *Lattice Dynamics of Molecular Crystals*, Vol. 26 of *Springer Lecture Notes in Chemistry* (Springer, Berlin, 1981).

[11]W. I. Kliatzkin, *Statistical Description of Dynamical Systems with Fluctuating Parameters* (Nauka, Moscow, 1975) (in Russian).

[12]N. Minorsky, *Nonlinear Oscillators* (Van Nostrand, Princeton, N.J., 1962).

[13]E. Anastassakis and E. Burstein, Phys. Rev. B **6**, 1952 (1970).

[14]Chr. Flytzanis and C. Tang, Phys. Rev. Lett. **46**, 441 (1980).

[15]P. Lin, R. Yen, and N. Bloembergen, IEEE J. Quantum Electron. **QE-14**, 574 (1978).

[16]M. L. Geirnaert, G. M. Gale, and C. Flytzanis, Phys. Rev. Lett. **52**, 815 (1984). The experiment presented in this paper shows the decay of the coherent bound two-phonon state generated by two optical waves in the molecular crystal CS_2. The condition of the resonance is the same as in our case. Anyway, there is no correspondence in theoretical description. The authors assume *a priori* the model of a harmonic oscillator for the existing bound two-phonon state and are interested in its decay. Our equations describe the creation of the two-phonon state in the presence of two optical fields in the process of parametric excitation.

[17]Chr. Flytzanis, G. M. Gale, and M. L. Geirnaert, in *Applications of Picosecond Spectroscopy to Chemistry*, edited by K. B. Eisenthal (Reidel, Dordrecht, 1984), pp. 205–235.

[18]G. L. Eesley and M. D. Levenson, Opt. Lett. **3**, 178 (1978).

[19]R. Loudon, Adv. Phys. **13**, 432 (1964).

[20]S. Ganesan, A. A. Maradudin, and I. Oitmaa, Ann. Phys. (N.Y.) **56**, 556 (1970).

[21]R. G. Della Valle, P. F. Fracassi, R. Righini, and S. Califano, Chem. Phys. **74**, 179 (1983).