# Low-frequency asymptotic behavior of the Raman susceptibility of molecules

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Raman scattering with transformation of the frequency into the radio-frequency range as the pump frequency $\omega_p$ approaches the scattering transition frequency $\omega_{21}$ is studied. The method of a generalized two-level system, adjusted to the presence of a low-frequency field, is used to calculate the Raman susceptibility of molecules (generally without distinguishing between polar and nonpolar molecules) at the Stokes frequency $\omega_s$. This quantity is shown to be determined by the interaction of Raman scattering proper and two-photon absorption, and by saturation effects. The spectrum of the imaginary part of the Raman susceptibility is studied as a function of $\omega_s$ and the shift $\omega_p-\omega_{21}$ for the most typical situations. In polar molecules the imaginary part of the Raman susceptibility for transitions allowed in one-photon absorption and in Raman scattering via other virtual levels is found to depend on the ratio of the real and imaginary parts of the dipole-moment matrix element and the polarizability of such a transition. In other cases, the imaginary part of the Raman susceptibility tends to zero as $\omega_p \to \omega_{21}$ as $\omega_s^2$ if $\omega_s=\omega_p-\omega_{21}$, and as $\omega_p-\omega_{21}$ when observed at the frequency of the peak of the imaginary part of the Raman susceptibility. Finally, the transition to Raman scattering in the optical range is examined. © *1996 American Institute of Physics.* © *1996 American Institute of Physics.* [S1063-7761(96)00401-0]

Raman scattering is one of the most powerful basic methods of spectroscopy for various media.[1] It is also a widespread method for radiation frequency transformation.[2] Therefore, interest in the frequency behavior of the Raman scattering characteristics of various substances appears natural. In particular, it has been established that inelasticity in the scattering leads to deviation of the high-frequency asymptotic behavior of the differential cross section of Raman scattering from the Rayleigh law: the fourth power of the frequency $\omega_p$ of the incident radiation (the pump frequency) is replaced with the factor $\omega_p\omega_s^3$, where $\omega_s$ is the frequency of the Stokes component in the scattered radiation.[3] It has also been found that as $\omega_p$ approaches the lower edge of the medium's continuous spectrum, the Raman characteristics increase resonantly fast. Such an increase is also observed when the pump frequency is close to the frequency $\omega_{mn}$ of one of the allowed one-photon transitions between the $m$th and $n$th levels in the energy spectrum of the substance. A brief survey of the first studies of these phenomena is given in Ref. 1. In what follows we examine the low-frequency behavior of the Raman susceptibility of molecules as the pump frequency approaches the Raman-active transition frequency $\omega_{21}$, and hence the Stokes frequency approaches zero. Note that Raman scattering with the transformation of the frequency into the radio-frequency range has begun to attract researchers.[4] The characteristics of spontaneous Raman scattering such as the cross section, the probability, and the extinction coefficient are related to the imaginary part of the Raman susceptibility through the fluctuation–dissipation theorem;[5] the stimulated gain coefficient for stimulated Raman scattering is also proportional to the imaginary part of the Raman susceptibility.[2]

Following Faĭn,[5] we define the Raman susceptibility $\chi_s$ of a molecule at the frequency $\omega_s$ by the relationship $\mathscr{P}_s=\chi_s\mathscr{E}_s$, where $\mathscr{P}_s$ and $\mathscr{E}_s$ are the amplitudes of the Stokes components of the molecule's polarization

$$\mathbf{P}=\sum \mathscr{P}_j \exp\{i\omega_j t\}+\text{c.c.}=\mathrm{Tr}(\hat{\mathbf{d}}\hat{\rho})$$

and the electric field acting on the molecule,

$$\mathbf{E}=\sum \mathscr{E}_j \exp\{i\omega_j t\}+\text{c.c.},$$

where $\hat{\mathbf{d}}$ is the molecule's dipole moment operator, $\hat{\rho}$ is the density matrix in the Schrödinger representation, and the $\omega_j$ are the pump frequency $(j=p)$ and the frequency of the Stokes component of Raman scattering $(j=s)$.

## 1. TRUNCATED KINETIC EQUATIONS

To calculate $\mathscr{P}_s$ we employ the approach developed in Ref. 6, based on applying the averaging method to the equation for the density matrix in the interaction representation. Here we allow for the fact that, in contrast to Raman scattering in the optical range, not only the shift $\nu_0=\omega_p-\omega_{21}$ and widths $T_{km}^{-1}$ of the lines corresponding to transitions between the $k$th and $m$th levels but also the frequency $\omega_s$ are much smaller than all other frequencies and frequency combinations. The general case, which includes both polar and nonpolar molecules, requires the second approximation of the averaging method to be used.

In this method we use the density matrix in the form of the sum of a slow component and a series of rapidly varying terms with a smallness parameter of the order of the ratio of the molecule–field interaction energy to the characteristic energy of transitions in the molecule's energy spectrum. The

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truncated kinetic equations of the $q$th approximation are derived by averaging the expression obtained through substituting the sum of the slow component and $q-1$ terms of the rapidly varying component into the initial kinetic equations; here the slowly varying functions of time including $\exp\{i\omega_s t\}$ are taken outside the integral sign. For the rapidly varying first-approximation density matrix we use the forced solutions of equations obtained by subtracting the first-order averaged equations from the original kinetic equations, in which the density matrix is replaced by its slow component. The resulting second-order equations for the elements $\sigma_{mn}$ of the slow density matrix in the interaction representation have the form

$$\left(\frac{d}{dt}+\frac{1}{T_{12}}+i\Omega_{12}\right)\sigma_{12}=\frac{i}{\hbar}(\sigma_{11}-\sigma_{22})\mathscr{V}'_{12}, \tag{1}$$

$$\left(\frac{d}{dt}+\frac{1}{T_{1n}}+i\Omega_{1n}\right)\sigma_{1n}+\frac{i}{\hbar}\mathscr{V}'_{12}\sigma_{2n}=0, \quad n\neq 1, \tag{2}$$

$$\left(\frac{d}{dt}+\frac{1}{T_{2n}}+i\Omega_{2n}\right)\sigma_{2n}+\frac{i}{\hbar}\mathscr{V}'_{21}\sigma_{1n}=0, \quad n\neq 2, \tag{3}$$

$$\left(\frac{d}{dt}+\frac{1}{T_{mn}}+i\Omega_{mn}\right)\sigma_{mn}=0, \quad m,\ n\neq 1,\ 2, \tag{4}$$

$$\frac{d\sigma_{mn}}{dt}+\sum_k\left[\sigma_{mn}(W_{mk}+Q_{mk})-\sigma_{kk}(W_{km}+Q_{km})\right]=0, \qquad m\neq 1,\ 2, \tag{5}$$

$$\frac{d\sigma_{11}}{dt}+\sum_k\left[\sigma_{11}(W_{1k}+Q_{1k})-\sigma_{kk}(W_{k1}+Q_{k1})\right] =-\frac{2}{\hbar}\,\mathrm{Im}(\sigma_{12}\mathscr{V}'_{21}), \tag{6}$$

$$\frac{d\sigma_{22}}{dt}+\sum_k\left[\sigma_{22}(W_{2k}+Q_{2k})-\sigma_{kk}(W_{k2}+Q_{k2})\right] =\frac{2}{\hbar}\mathrm{Im}(\sigma_{12}\mathscr{V}'_{21}). \tag{7}$$

Here the subscripts 1 and 2 refer, respectively, to the lower and upper levels in the Raman–active transition considered, $\sigma_{kk}$ the population of the $k$th level (whose off-diagonal elements meet the condition $\sigma^*_{mn}=\sigma_{nm}$), $W_{mn}$ is the probability of the molecule relaxing from the $m$th state into the $n$th state, and $T_{mn}$ is the transverse relaxation time for the $m-n$ transition. The quantities

$$\Omega_{mn}=\Omega^{(1)}_{mn}+\Omega^{(2)}_{mn}(\omega_p)+\Omega^{(2)}_{mn}(\omega_s) \tag{8}$$

consist of shifts of the $m-n$ transition lines caused by the linear Stark effect in the presence of a Stokes-frequency field,

$$\Omega^{(1)}_{mn}=\frac{1}{\hbar}\left[(V^s_{mm}-V^s_{nn})\exp(i\omega_s t)+(V^{-s}_{mm}-V^{-s}_{nn})\times\exp(-i\omega_s t)\right], \tag{9}$$

by quadratic Stark shifts caused by the pump field,

$$\Omega^{(2)}_{mn}(\omega_p)=\frac{1}{\hbar^2}\sum_k\left(\frac{V^p_{mk}V^{-p}_{km}}{\omega_{km}-\omega_p}+\frac{V^{-p}_{mk}V^p_{km}}{\omega_{km}+\omega_p}+\frac{V^{-p}_{nk}V^p_{kn}}{\omega_{nk}-\omega_p}+\frac{V^p_{nk}V^{-p}_{kn}}{\omega_{nk}+\omega_p}\right), \tag{10}$$

and by quadratic Stark shifts caused by the Stokes-frequency field,

$$\begin{aligned}\Omega^{(2)}_{mn}(\omega_s)=\frac{1}{\hbar^2}\Bigg[&\sum_k\left(\frac{V^s_{mk}V^{-s}_{km}}{\omega_{km}-\omega_s}+\frac{V^{-s}_{mk}V^s_{km}}{\omega_{km}+\omega_s}+\frac{V^{-s}_{nk}V^s_{kn}}{\omega_{nk}-\omega_s}+\frac{V^s_{nk}V^{-s}_{kn}}{\omega_{nk}+\omega_s}\right)\\&+\sum_k\left(\frac{V^s_{mk}V^s_{km}}{\omega_{km}+\omega_s}+\frac{V^s_{nk}V^s_{kn}}{\omega_{nk}+\omega_s}\right)\exp\{i2\omega_s t\}\\&+\sum_k\left(\frac{V^{-s}_{mk}V^{-s}_{km}}{\omega_{km}-\omega_s}+\frac{V^{-s}_{nk}V^{-s}_{kn}}{\omega_{nk}-\omega_s}\right)\exp\{-i2\omega_s t\}\Bigg].\end{aligned} \tag{11}$$

In Eqs. (10) and (11) we must exclude resonant terms; for example, in (11) there must be no terms with $k=m$ and $k=n$ (the reader is reminded of the smallness of $\omega_s$). Equations (9) and (10) show that the linear Stark shift oscillates at frequency $\omega_s$, while the frequency of oscillations of the quadratic shift is higher by a factor of two. In Eqs. (1)–(4) we excluded terms describing nonlinear line broadening, which are small compared to the nonlinear shift, $(\omega_{mn}T_{kl})^{-1}\ll 1$; for this reason one must not overstate the accuracy of the expression for the small broadening oscillating with a frequency $2\omega_s$ (the imaginary part of the second and third sums over $k$ are of order $\omega_s/\omega_{km}\ll 1$). In Eqs. (9)–(11), $V^j_{mn}=-d^j_{mn}\mathscr{E}_j$ is the $j$th complex-valued amplitude of the matrix element of the operator $\hat{V}=-\hat{\mathbf{d}}\cdot\mathbf{E}$ of the molecule radiation interaction energy for the $m-n$ transition, and $d^j_{mn}$ is the projection of the respective dipole=moment matrix element on the direction of polarization of the field's spectral component at the frequency $\omega_j$.

The matrix element $\mathscr{V}'_{12}=\mathscr{V}^*_{21}$ of the averaged Hamiltonian, which is present in Eqs. (1)–(3), (6), and (7), is

$$\mathscr{V}'_{12}=\sum\mathscr{V}'^{q}_{12}\exp\{i\nu_q t\}, \tag{12}$$

where the $\{q\}=\{0,Rs,tpa\}$ correspond to the following resonances (Fig. 1): the one-photon resonance of the pump frequency with the 2–1 transition frequency (the $\nu_0=\omega_p-\omega_{21}$ shift), the Raman resonance (the $\nu_{Rs}=\omega_p-\omega_s-\omega_{21}$ shift), and the resonance associated with two-photon absorption (the $\nu_{tpa}=\omega_p+\omega_s-\omega_{21}$ shift). The corresponding amplitudes are

$$\begin{aligned}\mathscr{V}'^{0}_{12}&=-d^p_{12}\mathscr{E}_p,\\ \mathscr{V}'^{Rs}_{12}&=-\kappa^{Rs}_{12}\mathscr{E}_p\mathscr{E}_{-s},\\ \mathscr{V}'^{tpa}_{12}&=-\kappa^{tpa}_{12}\mathscr{E}_p\mathscr{E}_s.\end{aligned} \tag{13}$$

The nonresonant polarizabilities in Raman scattering and two-photon absorption for the 1–2 transition,

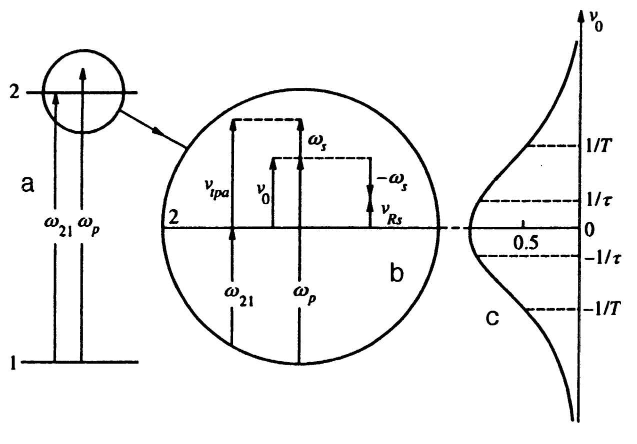

FIG. 1. The resonances $\omega_p-\omega_{21}=\nu_0$, $\omega_p-\omega_s-\omega_{21}=\nu_{Rs}$, and $\omega_p+\omega_s-\omega_{21}=\nu_{tpa}$, (a) and (b), and the one-photon absorption lineshape (c).

$$\kappa_{12}^{Rs}=\frac{1}{\hbar}\left[\sum_{m\neq 1,2}\left(\frac{d_{1m}^{p}d_{m2}^{-s}}{\omega_{m1}-\omega_p}+\frac{d_{1m}^{-s}d_{m2}^{p}}{\omega_{m1}+\omega_s+\nu_{Rs}}\right)+\frac{(d_{22}^{p}-d_{11}^{p})d_{12}^{-s}}{\omega_{21}+\omega_s+\nu_{Rs}}\right],$$
$$\kappa_{12}^{tpa}=\frac{1}{\hbar}\left[\sum_{m\neq 1,2}\left(\frac{d_{1m}^{p}d_{m2}^{s}}{\omega_{m1}-\omega_p}+\frac{d_{1m}^{s}d_{m2}^{p}}{\omega_{m1}-\omega_s+\nu_{tpa}}\right)+\frac{(d_{22}^{p}-d_{11}^{p})d_{12}^{s}}{\omega_{21}-\omega_s+\nu_{tpa}}\right], \tag{14}$$

are for all practical purposes the same for linearly polarized fields (since in this case $d_{mn}^{-j}=d_{mn}^{j}$ and all the shifts $\nu_q$ and $\omega_s$ are much smaller than $\omega_{m1}$). In what follows we use the notation $\kappa_{12}=\kappa$ for these polarizabilities. The probabilities $Q_{mk}=Q_{km}$ in Eqs. (5)–(7) of nonresonant stimulated transitions between the levels $m$ and $k$ that take place owing to the presence of fields with frequencies $\omega_p$ and $\omega_s$ differ from the respective quantities calculated in Ref. 7 by terms like

$$\frac{2}{\hbar^2}V_{mk}^{s}V_{km}^{s}\frac{T_{mk}(i-\omega_sT_{mk})}{T_{mk}^2\omega_{mk}^2-(i+\omega_sT_{mk})}\exp(2i\omega_st)+\text{ c.c.},$$

which oscillate at twice the Stokes frequency. Since we are dealing with weak Stokes fields, these terms can be ignored. In a similar manner we ignore the quadratic Stark shift associated with the Stokes field. The probability of nonresonant stimulated transitions produced by the pump field can be included in $W_{mk}$ or discarded, depending on pump intensity.

## 2. SLOW POLARIZATION OF A MOLECULE

The polarization's slow part $\mathbf{P}_{sl}$ that we are interested in can be calculated by averaging the polarization after the density matrix, represented as the sum of a slow component and a series of rapidly varying terms, has been substituted into it. Its projection in the direction of the Stokes field proves to be

$$\mathbf{P}_{sl}^{s}=\sum_{m}\sigma_{mm}\{d_{mm}^{s}+\kappa_{mm}(\omega_s)[\mathscr{E}_s\exp(i\omega_st)+\mathscr{E}_{-s}\exp(-i\omega_st)]\}+\sigma_{21}\kappa_{12}\mathscr{E}_p\exp(i\nu_0t)+\sigma_{12}\kappa_{21}\mathscr{E}_{-p}\exp(-i\nu_0t), \tag{15}$$

where $\kappa_{mm}(\omega_s)$ is the polarizability responsible for the contribution of molecules in the $m$th state to the nonresonant part of the refractive index at the Stokes frequency. At $\omega_s=0$ Eq. (15) yields the polarization responsible for the effect of resonant optical detection.[8] The contribution to the Stokes-frequency polarization related to the diagonal dipole-moment matrix elements $d_{mm}^{s}$ is produced by the Stokes components $\sigma_{mm}^{s}$ in the spectrum of populations $\sigma_{mm}$. The constant components $\sigma_{mm}^{c}$ with the corresponding polarizabilities $\kappa_{mm}$ (the second term with $\mathscr{E}_{-s}$) are contained in the refractive index but have no effect on the imaginary part of the Raman susceptibility. The contribution of the next-to-last term in (15) to this susceptibility comes from the spectral component $\sigma_{12}$ at the frequency $\nu_{Rs}-\sigma_{12}^{Rs}$, and that of the last term from the spectral component $\sigma_{12}^{tpa}$ at the frequency $\nu_{tpa}$. To determine the DC susceptibility, these components $\sigma_{12}$ and the Stokes components of the populations must be calculated by using the steady-state solutions of Eqs. (1)–(7).

## 3. GENERALIZED TWO-LEVEL SYSTEM IN A SLOWLY VARYING FIELD

The forced solutions of Eqs. (2)–(4) are equal to zero. Stokes-frequency oscillations of the populations of the levels not belonging to the Raman-active 1–2 transition (see Eq.(5)) may emerge if the populations $\sigma_{11}$ and $\sigma_{22}$ undergo such oscillations. But if the populations of the levels with $k\neq 1,2$ are negligible or are relaxationally coupled to each other more strongly than to the populations of levels 1 and 2, with the result that their distribution in the presence of fields remains at equilibrium, then of the diagonal elements of the slow density matrix $\hat{\sigma}$ contribution only those that refer to the levels 1 and 2 (the solutions of Eqs. (6) and (7)) contribute to the Raman susceptibility. Here it has proved convenient to go over to the population difference $\eta=\sigma_{11}-\sigma_{22}$ by using normalization based on the fact that the fraction of populations belonging to the levels 1 and 2 remains constant.

Equation (1) and the equation

$$\frac{d\eta}{dt}+\frac{\eta-\eta_0}{\tau}=-\frac{4}{\hbar}\operatorname{Im}(\sigma_{12}\mathscr{V}_{21}) \tag{16}$$

for the population difference, together with the expressions (8)–(13), constitute a system of equations of a generalized two-level system[9] adjusted to the case where, in addition to fields belonging to the optical range, there is a slowly varying field acting on the molecule ($\eta_0$ is the equilibrium population difference in the absence of fields).

By introducing the complex-valued amplitude of the Stokes spectral component $\eta_s$ of the population difference we can write the imaginary part of the Raman susceptibility of a generalized two-level system as

$$\operatorname{Im}\ \chi_s=\{0.5(d_{11}^{s}-d_{22}^{s})\operatorname{Im}\eta_s\mathscr{E}_s^{*}+\operatorname{Im}[(\sigma_{12}^{Rs})^{*}\kappa_{12}\mathscr{E}_p\mathscr{E}_s^{*}]+\operatorname{Im}(\sigma_{12}^{tpa}\kappa_{21}\mathscr{E}_p^{*}\mathscr{E}_s^{*})\}|\mathscr{E}_s|^{-2}. \tag{17}$$

The transition to ordinary Raman scattering occurs when $\omega_p$ and $\omega_s$ increase in such a manner that the shift $\nu_{Rs}$ remains small. Then both $\nu_0$ and $\nu_{tpa}$ become large. If we now average Eqs. (1) and (17) once more with these facts taken into account, the equations remain unchanged but the oscillating terms in $\Omega_{12}^{2}(\omega_s)$ (see Eq. (11)) and $Q_{mn}$ vanish, as do the terms with $\mathscr{V}_{12}^{0}$ and $\mathscr{V}_{12}^{tpa}$ in Eq. (12). Only the second term with the polarizability of the type of the first formula in (14) remains in the expression (17) for the imaginary part of the Raman susceptibility. If $\omega_p$ and $\omega_s$ are varied in such a way that $\nu_{tpa}$ remains small, then $\nu_0$ and $\nu_{Rs}$, while remaining negative, increase in absolute value. Again the oscillating terms in $\Omega_{12}^{(2)}(\omega_s)$ and $Q_{mn}$ vanish, Eq. (12) retains only the term with $\mathscr{V}_{12}^{tpa}$, and Eq. (17) retains only the last term with the polarizability of the type of the second formula in (14). The transition to ordinary two-photon absorption is complete.

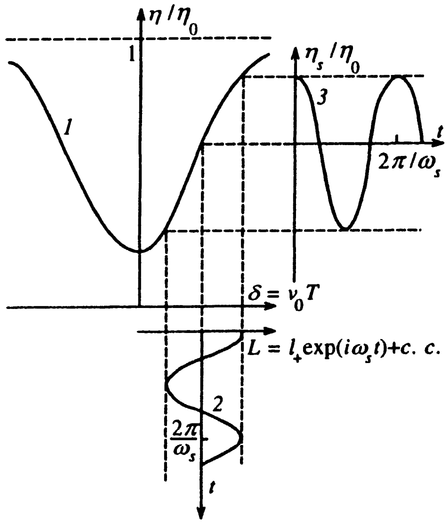

FIG. 2. Modulation of the population difference due to the linear Stark shift of the levels produced by the Stokes field (the quasistationary approach): *1* is the saturation curve for the stationary population difference $\eta$ normalized to the equilibrium population difference $\eta_0$, and *2* and *3* are the curves representing the time dependence of the linear Stark shift $L$ normalized to the linewidth and the variable component of the population difference $\eta_s$, respectively.

## 4. AMPLITUDES OF THE STOKES COMPONENTS OF THE AVERAGED DENSITY MATRIX

We write Eqs. (1) and (16) using the dimensionless time $\vartheta=t/T_{12}$, the parameters $\Theta=\tau/T_{12}$, $\Delta=\omega_s T_{12}$, and $\delta=\nu_0 T_{12}$, the normalized linear Stark shift $L=\Omega_{12}^{(1)}T_{12}$, and the normalized averaged Hamiltonian $u=2\mathscr{V}_{12}\sqrt{\tau T_{12}}/\hbar^{-1}$ and going over to the variable $S=2\sqrt{\tau/T_{12}}\sigma_{12}\exp\{i\delta\vartheta\}$:

$$\Theta\dot{\eta}+(\eta-\eta_0)=-\mathrm{Im}\ Su^*, \tag{18}$$

$$\dot{S}+[1+i(\delta+L)]S=i\eta u. \tag{19}$$

Here

$$u=u_0+u_+\exp\{i\Delta\vartheta\}+u_-\exp\{-i\Delta\vartheta\},$$

$$L=l_+\exp\{i\Delta\vartheta\}+\text{ c.c},$$

$$u_0=2\mathscr{V}_{12}^{0}\sqrt{\tau T_{12}}\hbar^{-1},\quad u_+=2\mathscr{V}_{12}^{tpa}\sqrt{\tau T_{12}}\hbar^{-1},$$

$$u_-=2\mathscr{V}_{12}^{Rs}\sqrt{\tau T_{12}}\hbar^{-1},\quad l_+=(V_{11}^{2}-V_{22}^{s})T_{12}\hbar,$$

and $\Omega_{12}^{(2)}(\omega_p)T_{12}$ is incorporated in the offset $\delta$ but can be ignored if the pump intensities are not too high. Where the field $\mathscr{E}_s$ is absent, $u_+=u_-=l_+=0$ and Eqs. (18) and (19) transform into the equations of an ordinary two-level system with well-known stationary solutions. In our notation these have the form (below $\Gamma(x)=(1+ix)^{-1}$)

$$\eta_{\text{st}}=\eta_0[1+|u_0|^2|\Gamma(\delta)|^2]^{-1},\quad S_{\text{st}}=i\eta_{\text{st}}u_0\Gamma(\delta). \tag{20}$$

Clearly, modulation of the shift due to the linear Stark effect results, through the quantity $L$ that enters into $\delta$ additively, in oscillations of the population difference (Fig. 2) and the amplitude $S$ at frequency $\omega_s$ and hence in the formation of Im $\chi_s$. Therein lies the mechanism of formation of the resonant Raman susceptibility specific to polar molecules.

To calculate it in general form we use iterative refinement, representing $\eta$ and $S$ in the form

$$\eta=\eta_{\text{st}}+\eta_s\exp\{i\Delta\vartheta\}+\eta_s^*\exp\{-i\Delta\vartheta\}+O(|\mathscr{E}_s|^2),$$

$$S=S_{\text{st}}+S_{tpa}\exp\{i\Delta\vartheta\}+S_{Rs}\exp\{-i\Delta\vartheta\}+O(|\mathscr{E}_s|^2),$$

where $\eta_{\text{st}}$ and $S_{\text{st}}$ satisfy Eqs. (20). Substituting these representations into (18) and (19), using (20), and discarding small second-order terms in $|\mathscr{E}_s|$, we can easily see that the quantities $S_{tpa}$ and $S_{Rs}^*$, which are proportional to the Stokes amplitudes $\sigma_{12}^{tpa}$ and $(\sigma_{12}^{Rs})^*$ of the off-diagonal element of the density matrix determining Im $\chi_s$, are related only to each other and to the Stokes amplitude of the population difference $\eta_s$:

$$\begin{aligned}&2(1+i\Theta\Delta)\eta_s-iu_0^*S_{tpa}+iu_0S_{Rs}^*=i(S_{\text{st}}u_-^*-S_{\text{st}}^*u_+),\\&-iu_0\eta_s+[1+i(\delta+\Delta)]S_{tpa}=i(\eta_{\text{st}}u_+-S_{\text{st}}l_+),\\&iu_0^*\eta_s+[1-i(\delta-\Delta)]S_{Rs}^*=i(\eta_{\text{st}}u_-^*-S_{\text{st}}^*l_+).\end{aligned} \tag{21}$$

In terms of these variables the imaginary part of the Raman susceptibility is

$$\mathrm{Im}\ \chi_s=-\hbar(4\tau|\mathscr{E}_s|^2)^{-1}\mathrm{Im}(2\Theta l_+^*\eta_s+S_{tpa}u_+^*+S_{Rs}^*u_-). \tag{22}$$

From (21) we find the Stokes amplitude of the population difference:

$$\begin{aligned}\eta_s=0.5\eta_{\text{st}}\{&i|u_0|^2l_+[\Gamma(\delta)\Gamma(\delta+\Delta)-\Gamma^*(\delta)\Gamma^*(\delta-\Delta)]\\&-u_0u_-^*[\Gamma(\delta)+\Gamma^*(\delta-\Delta)]\\&-u_0^*u_+[\Gamma^*(\delta)+\Gamma(\delta+\Delta)]\}\{1+i\Theta\Delta+0.5|u_0|^2\\&\times[\Gamma(\delta+\Delta)+\Gamma^*(\delta-\Delta)]\}^{-1}.\end{aligned} \tag{23}$$

Combining (20) and (21), we obtain

$$S_{tpa}=i[\eta_{\text{st}}(u_+-i\Gamma(\delta)u_0l_+)+\eta_su_0]\Gamma(\delta+\Delta), \tag{24}$$

$$S_{Rs}^*=-i[\eta_{\text{st}}(u_-^*+i\Gamma^*(\delta)u_0^*l_+)+\eta_su_0^*]\Gamma^*(\delta-\Delta). \tag{25}$$

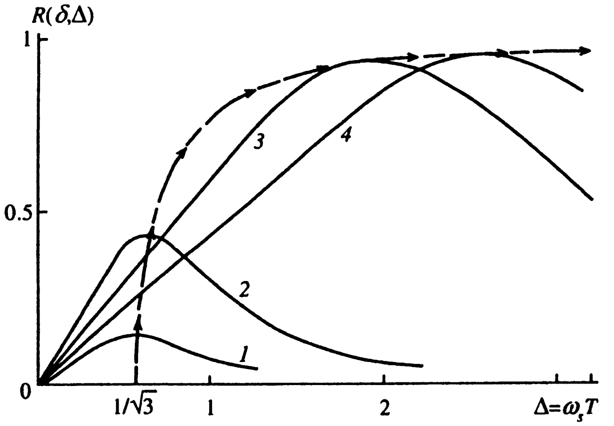

FIG. 3. The evolution of the spectrum of the imaginary part of the Raman susceptibility of a nonpolar transition (see Eq. (27)) as the dimensionless shift $\delta=(\omega_p-\omega_{21})T$ increases. Curves *1–4* correspond to the values $\delta_1<\delta_2<1<\delta_3<\delta_4$. The dashed curve with arrows depicts the line along which the maximum shifts as $\delta$ grows.

## 5. RAMAN SUSCEPTIBILITY OF TRANSITIONS WITH FORBIDDEN ONE-PHOTON ABSORPTION

In this case $d_{12}$ and $u_0$ vanish and $|u_+|^2=|u_-|^2$ are finite; in nonpolar molecules $l_+=0$. From Eqs. (20) and (23) we find that $\eta_{\text{st}}=\eta_0$ and $\eta_s=0$, and combining Eqs. (22), (24), and (25) we get

$$\text{Im}\ \chi_s=\eta_0 T_{12}\hbar^{-1}|\kappa_{12}|^2 I_p R(\delta,\Delta), \tag{26}$$

where $I_p=|\mathscr{E}_p|^2$ is the pump intensity, and the frequency-dependent factor

$$\begin{aligned} R(\delta,\Delta)&=\text{Re}[\Gamma(\delta-\Delta)-\Gamma(\delta+\Delta)]\\ &=4\delta\Delta[1+(\delta-\Delta)^2]^{-1}[1+(\delta+\Delta)^2]^{-1} \end{aligned} \tag{27}$$

is depicted as a function of $\delta$ and $\Delta$ in Fig. 3. The result for polar and nonpolar molecules is the same.

Equations (26) and (27) imply that amplification of the Stokes field ($\text{Im}\chi_s>0$) can occur only when the pump frequency is higher than the transition frequency ($\delta>0$). If $\omega_s=0$, there is no amplification of the Stokes field. For fixed $\delta$, the maximum value of the imaginary part of the Raman susceptibility is reached at the frequency

$$\omega_s=T^{-1}3^{-1/2}[\delta^2-1+2(1+\delta^2+\delta^4)^{1/2}]^{1/2}, \tag{28}$$

with $\omega_s$ being closer to $1/T\sqrt{3}$ at small values of $\delta$ and tending to infinity as $\omega_p-\omega$ when $\delta\rightarrow\infty$. The maximum value of $\text{Im}\chi_s$ corresponding to this frequency monotonically increases with $\delta$ in proportion to the factor $R(\delta,\Delta)$, which increases for small values of $\delta$ as $3^{3/2}4^{-1}\delta(1-0.75\delta^2)$ and approaches 1 as $\delta\rightarrow\infty$. The passage to the limit of ordinary Raman scattering in the optical range can be obtained from (26) and (27) by increasing $\delta$ and $\Delta$ with constant Raman shift $\delta-\Delta$. Here with $\Gamma(\delta+\Delta)\rightarrow 0$ the frequency dependences are determined as usual by the Raman shift $\delta-\Delta$ and the frequency dependence of the Raman susceptibility. For the sake of comparison, the corresponding expression is

$$\text{Im}\ \chi_s=\eta_0 T_{12}\hbar^{-1}|\kappa_{12}|^2 I_p[1+(\delta-\Delta)^2]^{-1}. \tag{29}$$

Here the maximum value of the imaginary part of the Raman susceptibility is attained at $\omega_s=\omega_p-\omega_{21}$. If this condition is met, the asymptotic behavior of the imaginary part of the Raman susceptibility as $\omega_s\rightarrow 0$ differs in our case from the usual behavior by a factor of $\omega_s^2$ the asymptotic behavior of the maximum value of the imaginary part of the Raman susceptibility differs by a factor of $\delta\propto\omega_p-\omega_{21}$.

## 6. RAMAN SUSCEPTIBILITY OF TRANSITIONS WITH ALLOWED ONE-PHOTON ABSORPTION

In the case of nonpolar molecules the condition $d_{21}\neq 0$ implies, owing to alternative exclusion, that $\kappa=0$ and hence $u_+=u_-=0$. Moreover, $l_+=0$ in such molecules. Therefore, for nonpolar molecules we have $\eta_s=0$, $S_{tpa}=S^*_{Rs}=0$, and, finally, $\text{Im}\chi_s=0$.

In a randomly nonpolar transition of a polar molecule, the diagonal matrix elements are finite but equal, so that $l_+=0$. Hence, if $\kappa=0$, we arrive at the same result: the Stokes field is not amplified. But if $\kappa\neq 0$, the susceptibility is finite. When $I_p$ is moderate and the stationary population difference is far from saturation, $\text{Im}\chi_s$ can be approximately described by Eqs. (26) and (27). As $I_p$ increases, there appears a correction, which for real $d_{12}=d$ and $\kappa_{12}=\kappa$ can be described by the factor

$$\begin{aligned} &1-2\tau T_{12}\hbar^{-2}d^2 I_p\Gamma(\Theta\Delta)[\Gamma(\delta+\Delta)+\Gamma(\delta)\\ &\quad+\Gamma^*(\delta)+\Gamma^*(\delta-\Delta)] \end{aligned} \tag{30}$$

under the real-part sign in (27). Calculations show that if we take $R(\delta,\Delta)$ in the form of the right-hand side of (27), the correction retains its form but $\Gamma(\Theta\Delta)[\cdots]$ is replaced by a function of $\delta$ and $\Delta$ that is positive for moderate values of $\delta$ and $\Delta$. This suggests that in such cases the increase in $\text{Im}\ \chi_s$ with pump intensity slows down, with a tendency to vanish. A similar result (albeit with another coefficient of $I_p$ in the correction factor) is obtained if $d\kappa^*$ is imaginary.

Now let us consider the opposite limiting case, where the pump intensity is much higher than the saturation pump intensity, so that $|1+i\Theta\Delta|$ in the denominator of (23) is much smaller than $0.5|u_0|^2|\Gamma(\delta+\Delta)+\Gamma^*(\delta-\Delta)|$. For all values of $d$ and $\kappa$ the imaginary part of the Raman susceptibility reaches a plateau. The value is zero when the product $d\kappa^*$ is imaginary and is

$$\text{Im}\ \chi_s\approx-\eta_0\hbar\kappa^2/2\tau d^2[\delta\Delta/(1+\Delta^2)] \tag{31}$$

when both $d$ and $\kappa$ are real (here we discard a cumbersome factor of order unity). From Eq. (31) follows the possibility of the Stokes field being amplified by intense pumping at a frequency below the transition frequency ($\text{Im}\chi_s>0$ for $\delta<0$). Thus, the phase of the product $d\kappa^*$ plays an important role here, just as it does in resonant parametric interactions.[6] To clarify this we notice that when (23)–(25) are substituted into (22), a noticeable contribution to the susceptibility under intense pumping is provided by terms related to the time-synchronism conditions of the type $(\omega_p)-(\omega_p+\omega_s)+(\omega_p)-(\omega_p-\omega_s)\equiv 0$, which can be obtained, by passing to the limit as $\varepsilon\rightarrow 0$, from the conditions characteristic of parametric interactions schematically depicted in Fig. 4; for example, $(\omega_1)-(\omega_2+\omega_3)+(\omega_4)$

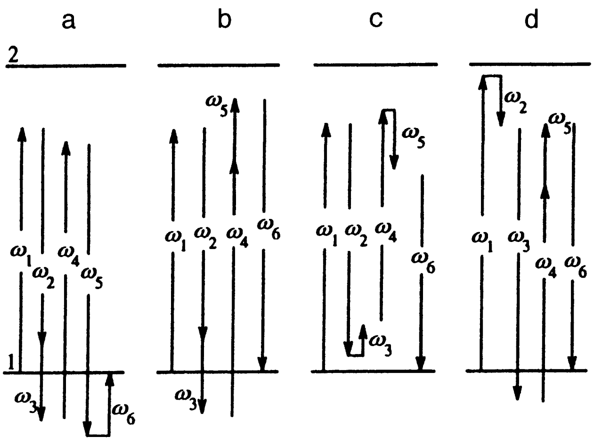

FIG. 4. Examples of parametric processes transforming, as (a) $\omega_{1,2},\omega_{4,5}\rightarrow\omega_p$ and $\omega_{3,6}\rightarrow\omega_s$, (b) $\omega_{1,2,4,6}\rightarrow\omega_p$ and $\omega_{3,5}\rightarrow\omega_s$, (c) $\omega_{1,2,4,6}\rightarrow\omega_p$ and $\omega_{3,5}\rightarrow\omega_s$, and (d) $\omega_{1,3,4,6}\rightarrow\omega_p$ and $\omega_{2,5}\rightarrow\omega_s$, into resonant processes, which markedly contribute to $\mathrm{Im}\chi_s$ under conditions of saturation.

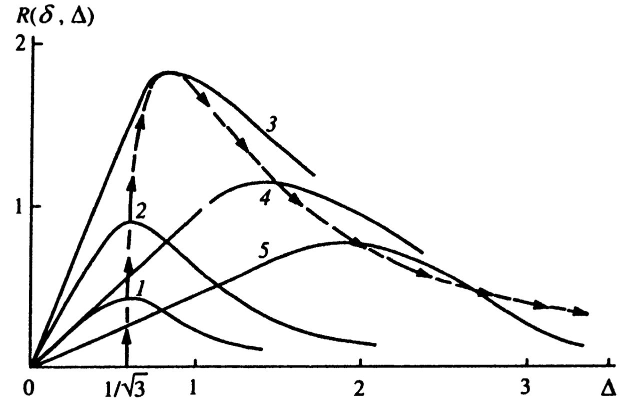

FIG. 5. The evolution of the spectrum of the imaginary part of the Raman susceptibility of a polar transition with an allowed one-photon process and a forbidden nonresonant two-photon process (see Eq. (32)) as the shift $\delta$ increases for the case where $T=2\tau$. Curves *1–5* correspond to the values $\delta_1<\delta_2<\delta_3\approx 0.7<\delta_4<\delta_5$.

$-(\omega_5-\omega_6)\equiv 0$, where $\omega_1=\omega_p+\varepsilon$, $\omega_2=\omega_p-r_1\varepsilon$, $\omega_3=\omega_s+r_1\varepsilon$, $\omega_4=\omega_p-\varepsilon$, $\omega_5=\omega_p-r_2\varepsilon$, and $\omega_6=\omega_s-r_2\varepsilon$, and in parentheses we have frequency combinations close to $\omega_{12}$.

In another special case, with the nonresonant two-photon polarizability of a polar transition with allowed one-photon absorption being zero ($\kappa=0$, $u_+=u_-=0$, $u_0\neq 0$, and $l_+\neq 0$), the imaginary part of the Raman susceptibility is

$$\mathrm{Im}\ \chi_s=\eta_{\mathrm{st}}T_{12}\hbar^{-1}|\kappa_{\mathrm{res}}|^2 I_p \times \mathrm{Re}\frac{[\Gamma^*(\delta)\Gamma^*(\delta-\Delta)-\Gamma(\delta)\Gamma(\delta+\Delta)]\Gamma(\Theta\Delta)}{1+0.5|u_0|^2[\Gamma(\delta+\Delta)+\Gamma^*(\delta-\Delta)]\Gamma(\Theta\Delta)}, \tag{32}$$

where the resonant polarizability $\kappa_{\mathrm{res}}$ is defined as

$$|\kappa_{\mathrm{res}}|^2=|d_{12}^p|^2(d_{11}^s-d_{22}^s)^2\tau^2\hbar^{-2}. \tag{33}$$

Equation (32) shows that for a pump intensity much higher than the saturation pump intensity, as $I_p$ increases the imaginary part of the Raman susceptibility decreases for all values of $\delta$ and $\Delta$. If the pump is weaker than that needed for saturation, (32) is transformed into an expression similar to (26) but with $R(\delta,\Delta)$ differing from (27) by a factor

$$[(1-(2\Theta)^{-1})+2(1+(\Delta/2)^2)\Theta^{-1}(1+\delta^2)^{-1}] \times(1+\Theta^2\Delta^2)^{-1}. \tag{34}$$

Clearly, as in the previous cases, amplification of the Stokes field ($\mathrm{Im}\ \chi_s>0$) can occur only if $\delta>0$. The shape of the Raman susceptibility spectrum, which for fixed $\delta$ is determined by the dependence of $R$ on $\Delta$, is fairly complicated for arbitrary values of $\Theta$ and $\delta$. We restrict our discussions to two limits: $\Theta=\frac{1}{2}$ (Fig. 5) and $\Theta\gg 1$ (Fig. 6). At $\Theta=\frac{1}{2}$ the factor (34) becomes $4(1+\delta^2)^{-1}$, and the imaginary part of the Raman susceptibility peaks at the frequency $\omega_s$ from (28), as in the case of transitions forbidden in one-photon absorption. Here the behavior of the maximum value of the imaginary part of the Raman susceptibility as $\delta$ increases is different: $R(\delta,\Delta)$ decreases as $1/\delta^2$, and $\mathrm{Im}\ \chi_s$ approaches the contribution of the $1\rightarrow 2$ transition to $\mathrm{Im}\ \chi_s$ in the case of ordinary Raman scattering in the optical range. As $\delta\rightarrow 0$, the imaginary part of the Raman susceptibility decreases in proportion to $\omega_s^2$ if $\omega_s=\omega_p-\omega_{21}$ and in proportion to $\omega_p-\omega_{21}$ if we consider its peak value, at $\omega_s$ from (28).

When $\Theta\gg 1$, the $\Delta$-dependence of the imaginary part of the Raman susceptibility is represented by a unimodal curve at $\delta<\delta_a=[3.5+(3.5^2-1)^{1/2}]^{1/2}\approx 2.6$ and a bimodal curve at $\delta>\delta_a$. The frequency of the first (or the only) peak is

$$\omega_1=\Delta_1 T_{12}^{-1}=\tau^{-1}(1-(1-\delta^2)/(1+\delta^2)^2\Theta^2), \tag{35}$$

with the corresponding value of $R$ being

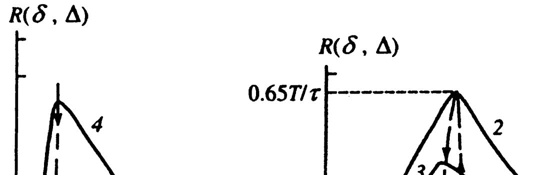

FIG. 6. The same as in Fig. 5 but with $T\ll\tau$. Curves *1–8* correspond to the following values: $\delta_1<\delta_2=1/\sqrt{3}<\delta_3<\delta_4<\delta_5=\delta_a\approx 2.6<\delta_6<\delta_7=\delta_b\approx 2\tau/T<\delta_8$. The dashed line with arrows designates the line along which the maximum shifts as $\delta$ grows.

$$R(\delta,\Delta_1)\approx 2\delta/(1+\delta^2)^2\Theta\,. \qquad (36)$$

The value of $\Delta_1$ changes little with $\delta$: from $1/\Theta(1-\Theta^{-2})$ at $\delta=0$ to $1/\Theta$ at $\delta=1$ to $1/\Theta(1+1/8\Theta^2)$ at $\delta=\sqrt{3}$, and back to $1/\Theta$ as $\delta\rightarrow\infty$. Here $R(\delta,\Delta_1)$ increases from zero at $\delta=0$ to $3\sqrt{3}/8\Theta\approx 0.65/\Theta$ at $\delta=1/\sqrt{3}$, after which it decreases to zero at $1/\delta^3$. The maximum value of the imaginary part of the Raman susceptibility is

$$\text{Im}\ \chi_s=0.65\,\eta_0|d^p_{12}|^2(d^s_{11}-d^s_{22})^2\tau T^2_{12}\hbar^{-3}I_p\,. \qquad (37)$$

As in all previous cases, as $\omega_p-\omega_{21}\rightarrow 0$ the value of Im $\chi_s$ tends to zero as $\omega_s^2$ if $\omega_s=\omega_p-\omega_{21}$ and as $\omega_p-\omega_{21}$ if the observations are conducted at the frequency $\omega_1$ where Im $\chi_s$ peaks.

Near $\delta=\delta_a$ there emerge a minimum and a maximum with $\Delta_2=\Delta_3=[0.6(\delta^2-1)]^{1/2}$ and $R(\delta_a,\Delta_2=\Delta_3)\approx 0.17/\Theta^2\ll R(\delta_a,\Delta_1)$. As $\delta$ grows, so do $\Delta_2$ and $\Delta_3$ ($\Delta_2^2$ and $\Delta_3^2$ are the roots of the equation $5x^2+6(1-\delta^2)x+(1+\delta^2)^2=0$). For $\delta$ large,

$$\Delta_2\approx\sqrt{0.2}\,\delta\left(1+\frac{2}{\delta^2}\right),\quad \Delta_3\approx\delta-\frac{1}{\delta}, \qquad (38)$$

$$R(\delta,\Delta_2)\approx\frac{14}{\Theta^2\delta^4},\quad R(\delta,\Delta_3)\approx\frac{1}{\Theta^2\delta^2}. \qquad (39)$$

When $\delta>\delta_b\approx 2\Theta$, the first peak becomes lower than the second, and the maximum value of the imaginary part of the Raman susceptibility approaches the contribution provided by the $1\rightarrow 2$ transition into Im $\chi_s$ in the case of ordinary Raman scattering in the optical range:

$$\text{Im}\ \chi_s\rightarrow\ \eta_0|d^p_{12}|^2(d^s_{11}-d^s_{22})^2\hbar^{-3}(\omega_p-\omega_{21})^2\,. \qquad (40)$$

The position of this maximum approaches $\omega_s=\omega_p-\omega_{21}$, as in ordinary Raman scattering in the optical range.

Generally $l_+$ and all the $u_j$ are finite. If the pump intensity is much higher than the saturation pump intensity, the Raman susceptibility tends to a constant value as $I_p\rightarrow\infty$, as in the case with $l_+=0$. Since the saturation pump intensity at high values of $\delta$ grows almost as $\delta^2$, the passage to the optical-range limit at fixed pump intensity cannot be traced. Let us consider in greater detail the case where the pump intensity is much lower than the saturation pump intensity. Here the imaginary part of the Raman susceptibility is the sum of three terms: the resonant term (Eq. (32) without the term proportional to $|u_0|^2$ and responsible for saturation, in the denominator), the nonresonant term (26), and the "mixed" term equal to

$$I_p\eta_0T_{12}\hbar^{-1}[R_r(\delta,\Delta)\text{Re}\ (d^p_{12}(d^s_{22}-d^2_{11})T_{12}\hbar^{-1}\kappa^*_{12})$$
$$+R_i(\delta,\Delta)\text{Im}\ (d^p_{12}(d^s_{22}-d^s_{11})T_{12}\hbar^{-1}\kappa^*_{12})], \qquad (41)$$

where

$$R_r(\delta,\Delta)=\frac{2\Delta\{1-\Theta-\Theta^2-\delta^2(3+4\Theta^2)+\delta^4(\Theta-2\Theta^2)+\Delta^2[1-\Theta-2\Theta^2-\delta^2(\Theta+2\Theta^2)]\}}{(1+\delta^2)(1+\Theta^2\Delta^2)[1+(\delta-\Delta)^2][1+(\delta+\Delta)^2]},$$

$$R_i(\delta,\Delta)=\frac{2\delta\Delta[3+2\Theta+\delta^2(1-2\Theta)+\Delta^2]}{(1+\delta^2)(1+\Theta^2\Delta^2)[1+(\delta-\Delta)^2][1+(\delta+\Delta)^2]}. \qquad (42)$$

We again examine the cases where $\Theta=0.5$ and $\Theta\gg 1$. Clearly, at $\Theta=0.5$ the imaginary part of the Raman susceptibility can be written in the form (26), where the factor $R(\delta,\Delta)$ coincides with (27) and instead of $\kappa_{12}$ we must take the quantity

$$K_{12}=\kappa_{12}+d^p_{12}(d^s_{11}-d^s_{22})T_{12}\hbar^{-1}(1+\delta^2)^{-1/2}$$
$$\times\exp\{i\sin^{-1}(1+\delta^2)^{-1/2})\}. \qquad (43)$$

Note that here the $\Delta$-dependence of Im $\chi_s$ is the same as in the earlier cases, which are described by Eq. (26) with $R(\delta,\Delta)$ in the form (27). In view of the fact that $K_{12}$ remains, Im $\chi_s\rightarrow 0$ as $\delta\rightarrow 0$ like $\omega_s^2$ if $\omega_s=\omega_p-\omega_{21}$ and like $\omega_p-\omega_{21}$ if the Stokes frequency coincides with the peak in the spectrum, Eq. (28). Note that for small $\delta$ the leading addition to $\kappa_{12}$ in Eq. (43) is related to $\text{Re}[d^p_{12}(d^s_{11}-d^s_{22})T_{12}\hbar^{-1}]$, while for large $\delta$ the leading addition is related to the imaginary part of this quantity.

When $\Theta\gg 1$, it is impossible to write Im $\chi_s$ in a form similar to (26). For small values of $\delta$ the dominant term can be shown to be the mixed term (41), which is approximately

$$4I_p\eta_0T_{12}\hbar^{-1}\Theta^2\Delta(1+\Delta^2)^{-1}(1+\Theta^2\Delta^2)^{-1}$$
$$\times\text{Re}(d^p_{12}(d^s_{11}-d^s_{22})T_{12}\hbar^{-1}\kappa^*_{12})\,.$$

Its extremum, attained at $\omega_s\approx 1/\tau$, is equal at $\delta=0$ to

$$2I_p\eta_0\hbar^{-1}\tau\text{Re}(d^p_{12}(d^s_{11}-d^s_{22})T_{12}\hbar^{-1}\kappa^*_{12}). \qquad (44)$$

Increasing $\delta$ leads to increasing the contributions of the resonant and nonresonant terms and the mixed term, which contains the imaginary part of $d^p_{12}(d^s_{22}-d^s_{11})T_{12}\hbar^{-1}\kappa^*_{12}$. Hence measurements of Im $\chi_s$ as functions of $\delta$ and $\Delta$ can provide information about the relationship between the real and imaginary parts of $d^p_{12}\kappa^*_{12}$

Concluding this section, we note that for all values of $\Theta$ the transition to large $\delta$ and $\Delta$ with $|\delta-\Delta|\ll\delta$, $\Delta$ leads to the expression (29) for the imaginary part of the Raman susceptibility characteristic of ordinary Raman scattering in the optical range, where for the polarizability $\kappa_{12}$ we must take the well-known expression obtained from (14) by discarding the last term and going over to summation over all the intermediate states (the index $m$ is taken without exclusions).

## 7. CONCLUSION

We close with some estimates. First, for ordinary Raman scattering in the optical range we have $\text{Im}\chi_s\approx 10^{-29}I_p$ for pumping at a frequency $\omega_p \gg \omega_{21}$ of the nonpolar transition with the typical values $T_{12}=10^{-8}$ s and $\kappa=10^{-24}$ (here and below all the quantities except the radiation flux are given in the esu system), $\eta_0=1$, and $\nu_{Rs}=0$.

If the pump frequency is moved closer to the transition frequency in such a way that $\omega_p-\omega_{21}=1/2T_{21}$ ($\delta=0.5$), the peak of Im$\chi_s$ is at $\omega_s \approx 0.7/T_{12}$ (see Eq. (28)) and its value is approximately three times smaller than in Raman scattering in the optical range: Im$\chi_s \approx 3.4\times 10^{-30} I_p$ (see (26) and (27)). Note that here, as in the previous case, the pump intensity $I_p$ is restricted only by optical breakdown.

For two cases of quasiresonant pumping of a polar transition with allowed one-photon absorption, (1) $\tau=0.5\times 10^{-8}\text{s}^{-1}$ and $T_{12}=10^{-8}$s for $\Theta=\frac{1}{2}$ and (2) $\tau=10^{-7}\text{s}^{-1}$ and $T_{12}=10^{-8}$s for $\Theta \gg 1$.

In the first case far from saturation the optimum shift of the pump frequency from the transition frequency is $0.7\times 10^{8}\text{s}^{-1}$, and the largest imaginary part of the Raman susceptibility is at the Stokes frequency $\omega_s \approx 0.8\times 10^{8}$s (see Fig. 5). Here Im $\chi_s \approx 4.5\times 10^{-16} I_p$, which is a factor of $4.5\times 10^{13}$ greater than in Raman scattering in the optical range with the same pump intensity. But because of saturation the increase of pump intensity above the saturation pump intensity leads to a decrease in the imaginary part of the Raman susceptibility. The optimum intensity in our first example is $I_p^{\text{opt}}=0.5\times 10^{-2}$ (obtained by the numerical study of (32)). In gases this corresponds to a pump flux of $2\text{ W cm}^{-2}$ (the refractive index of gases is close to unity). The maximum value of Im$\chi_s$ amounts to $7\times 10^{-19}$. Reaching such a value in the case of Raman scattering in the optical range requires a pump flux of roughly 30 TW cm$^{-2}$. Note that current theory predicts unlimited growth in the imaginary part of the Raman susceptibility of the polar transition as $\omega_p \to \omega_{21}$.

In the second example ($\Theta \gg 1$) in the unsaturated mode, the shift $\omega_p-\omega_{21}=0.6/T_{12}$ is optimal, and the Stokes frequency at which Im $\chi_s$ peaks is $\omega_s=1/\tau$ (see Fig. 6). For these parameter values, Im $\chi_s \approx 7\times 10^{-15} I_p$, i.e., the increase in Raman susceptibility with pump intensity proves to be even faster than at $\Theta=\frac{1}{2}$. However, the restriction due to saturation comes into play at lower intensities ($I_p^{\text{opt}} \approx 2.3\times 10^{-4}$, which corresponds to an intensity flux of 100 mW cm$^{-2}$), and the greatest value of the imaginary part of the Raman susceptibility must be somewhat lower than in the previous case: Im $\chi_s \approx 5\times 10^{-19}$.

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