Transient quasiline spectra of resonant secondary emission

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We consider time-dependent (transient) quasiline spectra of resonant secondary emission (RSE) of luminescence centers. A quantitative investigation was made of the time-dependent conversion of resonant Rayleigh scattering and resonant Raman scattering into hot and ordinary luminescence. The characteristics of the lines of the resonant Rayleigh and Raman scattering and of the hot and ordinary luminescence are obtained as functions of the parameters of the electron-phonon interaction, of the energy and phase vibrational relaxation constants, and of the characteristics of the registration and excitation. It is shown that lines of width $\sim t^{-1}$ have wings of oscillatory form. Compensation of the registration width and of the width of the excitation (for resonant Raman scattering) or of the decay width (for hot luminescence) was observed.

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1. INTRODUCTION

The technique of ultrashort laser pulses has made it possible at present to measure time intervals $\sim 10^{-12}$ sec. This has made feasible temporal investigations of vibrational relaxation processes in condensed matter. One of the methods used for this purpose is the study of the temporal behavior of the components of resonant secondary emission (RSE), namely resonant Rayleigh Raman scattering in hot and ordinary luminescence (HL and OL). It is therefore important to develop a theory of the time dependent (transient) RSE spectra as is evidenced by the appreciable number of papers published recently on this subject.[1-17] It was shown in these papers that the decisive role in the transformation of the transient spectra of RSE of the resonant Rayleigh and Raman scattering type in HL and OL is played by both energy and phase relaxation processes in the excited state. It was established that the transient spectra can change strongly even within a time $t\sim\bar{\omega}^{-1}\sim 10^{-13}$ sec ($\bar{\omega}$ is the average oscillation frequency): the maximum of the spectrum can shift by 1–2 eV, and its width can change by one order of magnitude or more. Also considered were the dependences of the transient spectra and of their polarization on the excitation duration, on the strength of the electron–phonon interaction, on the vibrational spectrum, on the oscillation damping constants, and on other material parameters.

One of the important questions in the theory of time-dependent spectra is their definition.[18] In many papers (see Res. 1–9, 14) these spectra are defined as the rate $\Pi(\Omega, t)$ of emission of a photon of specified frequency Ω (and polarization) at the instant of time t. However, the emission rate, generally speaking, is not a positive-definite quantity; it can assume negative values in the case of spectral lines of width t^{-1} determined by the Heisenberg uncertainty relation. Therefore other definitions were presented in Refs. 12 and 13 (see also Refs. 10 and 11) for the transient spectra, with allowance for the concrete scheme for their registration from the very outset.

In the present paper we use the formulation proposed in Ref. 12 for the theory of transient spectra. Our purpose is to investigate transient spectra that have a distinct phonon (quasi-line) structure. This case is of particular interest from the point of view of studying manifestations of processes of phase and energy relaxation and the transformation of resonant Rayleigh and Raman scattering in HL and OL, since the different components of the RSE can be easily distinguished here by their spectral positions. We use a model[19,20] previously investigated in connection with the problem of the classification of stationary SRE spectra of impurity centers of crystals. In this model we consider one (resonant) electronic transition and one local (pseudolocal) oscillation, whose equilibrium position and frequency vary in the course of this transition. Account is taken of the decay of this oscillation and of the modulation of the energy of the purely electronic transition, which lead respectively to energy and phase relaxation in the excited electronic state. The rate of the phase relaxation, which occurs without loss of vibrational energy by the center, is characterized by the reciprocal relaxation time $\tau_\perp^{-1}$, and the rate of the energy relaxation is characterized by the reciprocal longitudinal relaxation time $\tau_\parallel^{-1}$. We note that allowance for $\tau_\perp$ makes it possible to obtain, besides resonant Raman scattering, also hot luminescence from the initially excited level of the local oscillation. On the other hand, allowance for $\tau_\parallel$ leads to HL and OL from lower vibrational levels of the excited electronic state, which are populated in the course of the energetic vibrational relaxation (see Fig. 1).

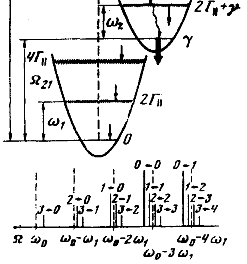

FIG. 1. Scheme of electron-vibrational transitions qualitatively illustrating the quasiline RSE spectrum produced under resonant excitation. The spectrum consists of OL lines (solid thick line), HL (solid thin line), and scattering line (resonant Raman and resonant Rayleigh; thin broken line).

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2. INITIAL FORMULAS. THE MODEL

We consider, as in Ref. 12, the process of measuring the transient RSE spectrum by means of a very simple scheme that includes a dispersing system followed by a pointlike photon detector with a broad spectral sensitivity band.[21] In this case the transient spectrum $I(\Omega, \eta, t)$, defined as the photon counting rate at the instant of time $t+\tau_0$ (τ_0 is the time of flight of the photons from the emitter to the counter), when the dispersion system is tuned to the frequency Ω with a spectral resolution η, is described by the following formula:

$$I(\Omega, \eta, t)=2\,\mathrm{Re}\iiiint_0^\infty d\mu\, d\nu\, d\tau\, d\tau' e^{i\Omega\mu} \times a(\mu, \tau, \tau')C(\mu+\nu, \nu)S(t-\mu-\nu-\tau', t-\nu-\tau). \tag{1}$$

Here $a(\mu, \tau, \tau')$ is the three-time correlation time of the medium:

$$a(\mu, \tau, \tau')=\langle v_{\omega_0}{}^+ e^{i(H+i\gamma)\tau'} v_\Omega{}^+ e^{iH\mu} v_\Omega e^{-i(H-i\gamma)\tau} v_{\omega_0} e^{-iH(\mu+\tau'-\tau)}\rangle_0, \tag{2}$$

where $v_{\omega 0}$ and v_Ω are the single-photon matrix elements that describe respectively the annihilation of a photon of frequency ω_0 and production of a photon of frequency Ω, ω_0 is the average frequency of the exciting radiation, H is Hamiltonian of the medium, and γ is the radiative damping operator; $S(\tau, \tau')$ is the correlation function of the exciting optical radiation; $C(\nu, \nu')$ is the correlation function of the registration. The function $S(\tau, \tau')$ differs noticably from zero in the region $|\tau| \sim |\tau'| \sim \Delta^{-1}$ (Δ is the spectral width of the exciting pulse), while the function $C(\nu, \nu')$ differs noticably from zero in the region $|\nu| \sim |\nu'| \sim \eta^{-1}$. We note that Δ^{-1} determines in the case of a coherently exciting pulse the pulse duration,[21] and η^{-1} is the characteristic coherence time of the waves passing through the dispersing system[12]; it indicates the time interval $(t-\eta^{-1}, t)$ in which the photons registered at the instant $t+\tau_0$ were emitted.

For the considered model, in the adiabatic approximation and in the Condon approximation, the correlation function $a(\mu, \tau, \tau')$ takes, apart from a constant factor, the form[19,20]

$$a(\mu, \tau, \tau')=\exp\{i\Omega_{21}(\tau'-\tau)-\gamma(\tau+\tau')/2\}A(\mu, \tau, \tau'). \tag{3}$$

Here

$$A(\mu, \tau, \tau')=\langle e^{iH_2\tau'} e^{iH_1\mu} e^{-iH_2\tau} e^{-iH_1(\mu+\tau'-\tau)}\rangle_1, \tag{4}$$

H_1 and H_2 are the vibrational Hamiltonians of the ground and excited electronic states,

$$\langle\ldots\rangle_1=\mathrm{Sp}\,(e^{-H_1/kT}\ldots)/\mathrm{Sp}\,(e^{-H_1/kT})$$

is the symbol of quantum-statistical averaging over the oscillations, γ is the constant of the relaxation damping of the excited state ($\gamma^{-1}=\tau_{opt}$), Ω_{21} is the frequency of the purely electronic transition, and $\hbar=1$.

If the equilibrium position of only one local oscillation λ changes in the course of the electronic transition, then

$$H_2=e^\nabla(H_1+V)e^{-\nabla}+\sum_{i,i'}\varepsilon_{ii'}(a_i{}^++a_i)(a_{i'}{}^++a_{i'}), \tag{5}$$

where i numbers all the normal oscillations with the exception of the local oscillation λ, a_i^+ and a_i are the photon creation and annihilation operators, $e^\nabla \equiv \exp[\xi(a_\lambda - a_\lambda^+)]$ is the operator of the shift of the equilibrium position of the coordinate of the local oscillation λ, ξ^2 are the dimensionless Stokes losses to this oscillation,

$$V=\Delta\omega\,(a_\lambda{}^+a_\lambda+{}^1/_2) \tag{6}$$

is an operator that takes into account the change of the frequency of the local oscillation in the electronic transition ($\Delta\omega=\omega_2-\omega_1 \ll \omega_1$; ω_1 and ω_2 are the frequencies of the local oscillation in the ground and excited electronic states, respectively).

Neglecting the second term in (5), the correlator $A(\mu, \tau, \tau')$ was calculated previously[20] under the following approximations: 1) quasi-harmonic approximation, 2) low temperature: $T \ll \omega_1/k$, 3) exponential decay of local oscillation:

$$\langle a_\lambda a_\lambda{}^+(\tau)\rangle=\exp\,(i\omega_\lambda\tau-\Gamma_\parallel|\tau|) \quad (\Gamma_\parallel \ll \omega_\lambda).$$

The damping constant $\Gamma_\parallel$ determines the characteristic time of the energy of relaxation of the n-th level of the local oscillation: $\tau_{\parallel,n}=(2n\Gamma_\parallel)^{-1}$. Allowance for the second term in (5) leads to a modulation broadening of the vibronic levels of the local oscillation in the excited electronic state. Its influence on the correlation function $A(\mu, \tau, \tau')$ was considered in Ref. 19. Using the results of the excited papers, we obtain the following formula for the correlator $A(\mu, \tau, \tau')$, which is valid in the case $\Delta\omega \gg \Gamma_\parallel$:

$$\begin{aligned}A(\mu, \tau, \tau')=\exp\{&-2\xi^2+\xi^2[\exp\{i\omega_1\mu-\Gamma_\parallel\mu\}\\&\times(\exp\{i\omega_2\tau'-\Gamma_\parallel\tau'\}-1)(\exp\{-i\omega_2\tau-\Gamma_\parallel\tau\}-1)\\&+\exp\{i\omega_2\tau'-\Gamma_\parallel\tau'\}+\exp\{-i\omega_2\tau-\Gamma_\parallel\tau\}+\exp\{i\omega_2(\mu+\tau'-\tau)\}\\&\times(\exp\{-\Gamma_\parallel|\mu+\tau'-\tau|\}-\exp\{\Gamma_\parallel(|\mu-\tau|+\tau')\})]\\&-\Gamma_\perp(\tau+|\mu+\tau'-\tau|-|\mu-\tau|)\}.\end{aligned} \tag{7}$$

Here $\Gamma_\perp$ is the modulation broadening which determines in this model the rate of phase relaxation of the vibronic levels of the local oscillation in the excited electronic state [$\Gamma_\perp=(2\tau_\perp)^{-1}$; $\Gamma_\perp \sim T^7$ as $T \to 0$]. The condition $\Delta\omega \gg \Gamma_\parallel$, and also the condition $\Delta\omega \gg \Gamma_\perp$ used later on, make it possible to distinguish spectrally the lines that start out from different vibrational levels (see Fig. 1). Assume that the center is excited by a single coherent optical pulse of the form

$$S(\tau, \tau')=S_0\exp[i\omega_0(\tau-\tau')-\Delta(|\tau|+|\tau'|)]. \tag{8}$$

The time is reckoned here from the instant of passage of the maximum of the exciting light pulse through the center. The average pulse frequency ω_0 is at resonance with the electron-vibrational transition from the zeroth vibrational level of the ground ($|1\rangle$) electronic state to the M-th vibrational level of the excited ($|2\rangle$) excited state (the transition $|1,0\rangle \to |2,M\rangle$), while the spectral width of the pulse is $\Delta \ll \omega^2$ (see Fig. 1). In this case there is initially populated in the excited electronic state only the M-th level of the local oscillation. The radiation, however, proceeds from the vibrational levels $L_2 \ll M$ of the excited electronic state to the vibrational levels $L_1=0, 1, 2, \ldots$ of the ground electronic state.

The correlation function of the registration is chosen in the form

$$C(\nu,\nu')=C_0\exp\{-\eta|\nu|-\eta|\nu'|\},\tag{9}$$

which is convenient for further integration of formula (1).

3. RESOLUTION OF THE TRANSIENT SPECTRUM INTO LINES

We substitute formulas (7)–(9) in (1), expand the correlation function $A(\mu,\tau,\tau')$ in a power series,

$$\exp[{}^1/{}_2 i\omega_{1(2)}(\mu+\tau'-\tau\pm\mu\pm\tau\pm\tau') \\ -{}^1/{}_2\Gamma_\parallel(\mu+\tau'-\tau\pm\mu\pm\tau\pm\tau')]$$

and integrate with respect to μ,τ,τ', and ν. We obtain[14]

$$I(\Omega,\eta,t)=\sum_{L_1=0}^{\infty}\sum_{L_2=0}^{M}I^{L_2L_1}(\Omega,\eta,t),\tag{10}$$

where $I^{L_2L_1}(\Omega,\eta,t)$ describes the spectral line corresponding to the transition $|2,L_2\rangle\to|1,L_1\rangle$. The spectra $I^{L_2L_1}(\Omega,\eta,t)$ are substantially different in the cases $L_2<M$ and $L_2=M$.

If $L_2<M$, then

$$\begin{aligned}I^{L_2L_1}(\Omega,\eta,t)&=S_0C_0|\langle 0|M\rangle|^2|\langle L_2|L_1\rangle|^2\binom{M}{L_2}\\ &\times\sum_{k=0}^{M-L_2}\binom{M-L_2}{k}(-1)^{M-L_2+k}\Big[\frac{e^{-2\eta t}-e^{\alpha_1 t}}{\alpha_1+2\eta}\Big(\sum_{i=1}^{4}D_i+D_4^*\Big)\\ &+\frac{e^{\alpha_1 t}-e^{\alpha_3 t}}{\alpha_1-\alpha_3}D_1+\frac{e^{\alpha_1 t}-e^{-2\Delta t}}{\alpha_1+2\Delta}D_2+\frac{e^{\alpha_1 t}}{\alpha_1-2\Delta}D_3+\frac{e^{\alpha_1 t}-e^{\alpha_2 t}}{\alpha_1-\alpha_2}D_4^*\\ &+\frac{e^{\alpha_1 t}-\exp(\alpha_2^* t)}{\alpha_1-\alpha_2^*}D_4+\text{c.c.}\Big]\end{aligned}\tag{11}$$

Here $|\langle 0|M\rangle|^2$ and $|\langle L_2|L_1\rangle|^2$ are the Franck–Condon factors respectively for the transitions $|1,0\rangle\to|2,M\rangle$ and $|2,L_2\rangle\to|1,L_1\rangle$ (for their values, see, e.g., Ref. 20),

$$\begin{gathered}\alpha_1=i(\Omega-\Omega_{21}+\omega_1L_1-\omega_2L_2)-\Gamma_\parallel(L_1+L_2)-\Gamma_\perp-\eta-\gamma/2,\\ \alpha_2=ix-\Gamma_\parallel M-\Gamma_\perp-\Delta-\gamma/2,\quad \alpha_3=-2\Gamma_\parallel(M-k)-\gamma,\\ x=\Omega_{21}+\omega_2M-\omega_0.\end{gathered}\tag{12}$$

The coefficients D_i are given by

$$\begin{gathered}D_1=\frac{8\Delta}{(\alpha_3^2-4\Delta^2)(\alpha_3+2\eta)}\operatorname{Re}\frac{ix+\Gamma_\parallel k+\Gamma_\perp+2\Delta}{\alpha_2^*(\alpha_2+2(k+\Gamma_\perp+\Delta))},\\ D_2=-\frac{\operatorname{Re}(\alpha_2+2\Delta)}{(\Delta-\eta)(\alpha_2+2\Delta)(\alpha_2^*+2\Delta)(\alpha_3+2\Delta)},\\ D_3=-\frac{\operatorname{Re}\alpha_2}{(\Delta+\eta)\alpha_2\alpha_2^*(\alpha_3-2\Delta)},\\ D_4=2\Delta\{\alpha_2^*(\alpha_2^*+2\Delta)(\alpha_2^*+2\eta)[\alpha_2+2(\Gamma_\parallel k+\Gamma_\perp+\Delta)]\}^{-1},\\ D_5=-2\Delta\{\alpha_2\alpha_2^*(\alpha_2^*+2\Delta)[\alpha_2^*+2(\Delta+\eta)]\}^{-1},\\ D_6=-2\Delta[\alpha_2(\alpha_2+2\eta)(\alpha_2+2\Delta)(\alpha_2^*+2\Delta)]^{-1},\\ D_7=[2(\Delta+\eta)\alpha_2\alpha_2^*]^{-1},\quad D_8=[2(\Delta-\eta)(\alpha_2+2\Delta)(\alpha_2^*+2\Delta)]^{-1},\\ D_9=[2\eta\alpha_2(\alpha_2^*+2\Delta)]^{-1}.\end{gathered}$$

The radiation described by formula (11) constitutes hot luminescence (if $L_2>0$) or ordinary luminescence (if $L_2=0$). The positions of the maxima and the widths of the corresponding lines depend on the oscillation frequencies and on the numbers of levels in the ground and excited electronic states, but does not depend on ω_0.

If $L_2=M$, then

$$\begin{aligned}I^{ML_1}(\Omega,\eta,t)&=S_0C_0|\langle 0|M\rangle|^2|\langle M|L_1\rangle|^2\\ &\times\Big\{\frac{e^{-2\eta t}-\exp(\bar\alpha_1t)}{\bar\alpha_1+2\eta}\Big(\sum_{i=1}^{8}D_i+D_4^*\Big)\\ &+\frac{\exp(\bar\alpha_1t)-\exp(\bar\alpha_3t)}{\bar\alpha_1-\bar\alpha_3}D_1+\frac{\exp(\bar\alpha_1t)-e^{-2\Delta t}}{\bar\alpha_1+2\Delta}(D_2+D_8)\\ &+\frac{\exp(\bar\alpha_1t)}{\bar\alpha_1-2\Delta}(D_3+D_7)-\frac{\exp(\alpha_2t)-\exp(\bar\alpha_2t)}{\alpha_2-\bar\alpha_2}D_6\\ &+\frac{[\exp(\bar\alpha_1t)-\exp(\alpha_2^*t)]D_4-[\exp(\bar\alpha_2t)-e^{-2\Delta t}]D_8}{\bar\alpha_2+2\Delta}\\ &+\frac{\exp(\bar\alpha_1t)-\exp(\alpha_2t)}{\bar\alpha_2+2\Delta-2ix}(D_4^*+D_6)+\frac{\exp(\bar\alpha_2t)-e^{-2\eta t}}{\bar\alpha_2+2\eta}(D_5+D_8+D_9)\\ &+\frac{1}{\bar\alpha_2}[e^{-2\eta t}(D_9-D_5-D_7)+\exp(\bar\alpha_1t)D_5-\exp(\bar\alpha_2t)D_9]+\text{c.c.}\Big\},\end{aligned}\tag{13}$$

where

$$\begin{gathered}\bar\alpha_1=i(\Omega-\Omega_{21}+\omega_1L_1-\omega_2M)-\Gamma_\parallel(M+L_1)-\Gamma_\perp-\eta-\gamma/2,\\ \bar\alpha_2=i(\Omega+\omega_1L_1-\omega_0)-\Gamma_\parallel L_1-\Delta-\eta,\\ \bar\alpha_3=-2\Gamma_\parallel M-\gamma/2.\end{gathered}$$

The radiation described by formula (13) contains HL lines with maxima at the frequencies $\Omega_{HL}\approx\Omega_{21}+\omega_2M-\omega_1L_1$ and the resonant Raman and Rayleigh scattering lines, the frequencies of the maxima of which are $\Omega_{RS}\approx\omega_0-\omega_1L_1$. Equation (13) takes into account also the effects of interference between the resonant Raman (Rayleigh) scattering and HL, which are particularly substantial at small t and $|x|$ (see Fig. 8 below).

The general form of the spectrum (11)–(12) is shown in Fig. 2. It is seen from this figure that at $t=0$ (first half of the exciting pulse has passed through center) the spectrum contains mainly resonant Raman and Rayleigh scattering. The HL lines ($|2,1\rangle\to|1,0\rangle$, $|2,2\rangle\to|1,1\rangle$) only begin to appear. At $t=0.5\,\Gamma^{-1}$ the spectra contain resonant Rayleigh and Raman scattering lines as well as HL lines. At $t=\Gamma_\parallel^{-1}$ there is separated in the spectrum the purely electronic line $|2,0\rangle\to|1,0\rangle$, which stays in the spectrum up to the time $t\gtrsim\tau_{opt}+\eta^{-1}$, whereas the HL lines disappear at $t>\tau_{\parallel,n}+\eta^{-1}$.

4. TIME DEPENDENCES OF THE INTENSITY, WIDTH, AND SHAPE OF THE LINES

The areas under the lines of the considered transient spectrum $I(\Omega,\eta,t)$ depend on the spectral resolution η.

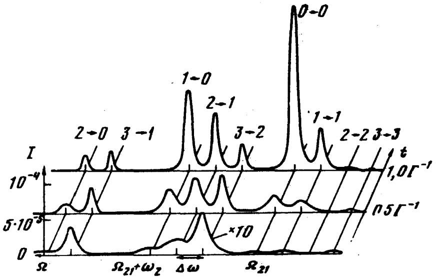

FIG. 2. Transient spectrum of RSE for times $t=0$, $0.5\,\Gamma^{-1}$, and Γ^{-1}. Excitation on vibrational level $M=3$. Phase-relaxation constant $\Gamma_\perp=0$, Stokes losses $\xi^2=0.5$, $\eta=1\,\Gamma$, $\omega_1=150\,\Gamma$, $\omega_2=120\,\Gamma$, $\Delta=5\,\Gamma$, $x=0$, $\gamma=0.002\,\Gamma$. The intensity of the Rayleigh line is too small to be shown in the figure. Here and in the remaining figures the frequency is given in units of the vibrational relaxation constant $\Gamma_\parallel\equiv\Gamma$, and the time in reciprocal units Γ^{-1}.

These dependences were considered in Ref. 22. In the present paper we present only their values at $\eta \gg \Gamma_{\parallel}$, $\Gamma_{\perp}$, Δ, corresponding to the experimentally determined total line intensity with a coarse (compared with the line width) spectral resolution. The total line intensity determined in this manner, which is equal to the rate $\Pi^{L_2L_1}(t)$ of photon emission into the given line, is shown in Fig. 3. It is seen that for sufficiently short exciting pulses ($\Delta^{-1} \ll \Gamma_{\parallel}^{-1}$) the form of the function $\Pi^{L_2L_1}(t)$ does not depend on Δ and can be used to determine the time of vibrational relaxation of the level $|2, L_2\rangle$.

Taking the foregoing into account, we calculated the time dependences of the intensity of the line $|2,1\rangle \to |1,0\rangle$ for different M in the case of a short exciting pulse. The results of the calculation are shown in Fig. 4. It is seen from this figure that with increasing M the maximum of the intensity of the considered line shifts towards larger t. This is understandable: the higher the excited level M, the more time is needed for the system to land on the level $L_2 = 1$. The difference in time between the maxima of the functions $\Pi^{10}(t)$ for M and $M-1$ is determined by the rate of vibrational relaxation of the M-th level $(2\Gamma_{\parallel}M)^{-1}$.

As noted above, emission from the level $L_2 = M$ consists of hot luminescence and resonant Raman scattering. To separate the contributions of the hot luminescence and the resonant Raman scattering to the line intensity, we have assumed the distance x between their maxima to be large compared with their widths ($x \gg \eta \gg \Gamma_{\perp}$, Δ, $\Gamma_{\parallel}$, γ) and integrated with respect to Ω both components separately. The separate intensities of the HL and resonant Raman scattering lines were the following:

$$\Pi_{\mathrm{RSR}}^{ML_1}(t) \sim e^{-2\Delta t}/2\eta x^2, \tag{14}$$

$$\Pi_{\mathrm{HL}}^{ML_1}(t) \sim \frac{\Gamma_{\perp}}{2\eta x^2}\left(\Gamma_{\parallel}M + \frac{\gamma}{2} - \Delta\right)^{-1}\Big[e^{-2\Delta t} - \Delta \exp[-(2\Gamma_{\parallel}M+\gamma)t]\left(\Gamma_{\parallel}M + \frac{\gamma}{2} + \Delta\right)^{-1}\Big]. \tag{15}$$

It is seen from (15) that the function $\Pi_{\mathrm{HL}}^{ML_1}(t)$ is proportional to the phase relaxation constant $\Gamma_{\perp}$, i.e., at $\Gamma_{\perp} = 0$ the intensity of the considered HL line vanishes. Consequently, to obtain HL from the level $L_2 = M$ it is indeed necessary to take into account its phase relaxation.

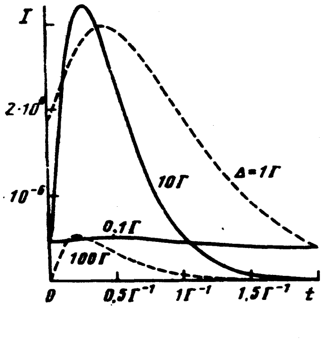

FIG. 3. Time dependence of the integral emission rate $\Pi^{20}(t)$ of the HL line $|2,2\rangle \to |1,0\rangle$ at different half-widths of the exciting pulse: $\Gamma_{\perp} = x = 0$, $\eta = 100\ \Gamma$, $\gamma = 0.002\ \Gamma$, $\xi^2 = 0.5$.

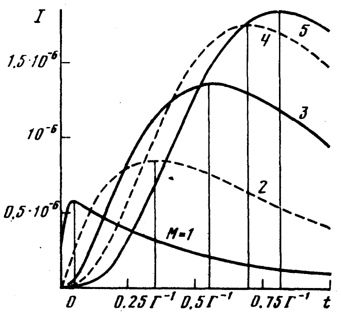

FIG. 4. Time dependence of the frequency-integrated emission rate $\Pi^{10}(t)$ of the HL line $|2,1\rangle \to |1,0\rangle$ for different numbers M of the excited vibrational level: $\Gamma_{\perp} = x = 0$, $\Delta = \eta = 100\ \Gamma$, $\xi^2 = 5.5$, $\gamma = 0.002\ \Gamma$.

We consider now the half-width $\sigma(t)$ of the transition spectrum lines. Figure 5 shows the results of computer calculations of the time dependence of $\sigma(t)$ of the OL and HL lines and of the parameters Δ and η, using formulas (11)–(13). We see that with increasing t the lines become narrower (Figs. 5a–5c). This character of the dependence of $\sigma(t)$ on t can be easily understood on the basis of the Heisenberg uncertainty relation. In fact, the larger t the smaller the energy uncertainty of the emitting centers.

In contrast to t, the dependence of $\sigma(t)$ on η and Δ is not monotonic. This is readily seen in Figs. 5e and 5f: at large t the line $|2,3\rangle \to |1,1\rangle$ has a minimal width at $\eta = 3$. A similar conclusion can be drawn also from the following analytic expressions for $\sigma(t)$ at $t = 0$ and $t \to \infty$:

$$\sigma(0) = \Gamma_{\perp} + \Gamma_{\parallel}(L_1 + L_2) + 2\Delta + \eta + \gamma/2. \tag{16}$$

$$\sigma(t) \underset{t\to\infty}{=} \begin{cases} \Gamma_{\perp} + \Gamma_{\parallel}(L_1+L_2) + \gamma/2 - \eta, & \eta \leqslant \Delta, \Gamma_{\parallel}L_2 + \gamma/2 \\ \Gamma_{\perp} + \Gamma_{\parallel}L_1 + \eta - \Gamma_{\parallel}L_2 - \gamma/2, & \Gamma_{\parallel}L_2 + \gamma/2 \leqslant \Delta, \eta. \\ \Gamma_{\perp} + \Gamma_{\parallel}(L_1+L_2) + \eta + \gamma/2 - 2\Delta, & \Delta \leqslant \eta, \Gamma_{\parallel}L_2 + \gamma/2 \end{cases} \tag{17}$$

It is seen from (17) that in the case $\eta = \Gamma_{\parallel}L_2 + \gamma/2 \leqslant \Delta$ the half-width of the lines $|2, L_2\rangle \to |1, 0\rangle$ tends with increasing t to the phase-relaxation constant $\Gamma_{\perp}$. This makes it possible to determine $\Gamma_{\perp}$. In addition, it follows from these formulas that the transient spectra can include lines with widths smaller than the natural width $\sigma_0 = \Gamma_{\perp} + \Gamma_{\parallel}(L_1 + L_2) + \gamma/2$.

This interesting effect of compensation of the decay and instrumental widths makes it possible to eliminate completely from the transition spectrum of the HL the entire decay width of the excited levels $\sigma_d = \Gamma_{\parallel}L_2 + \gamma/2$, which is due both to radiative decay and to vibrational relaxation, by choosing the spectral resolution in such

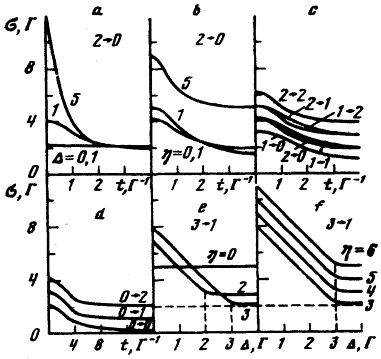

FIG. 5. Dependence of the half-width of the HL lines on the time (a–d) and on the parameters Δ and η (e, f): a) $\eta = \Gamma_{\perp} = 0$, $M = 3$; b) $\Delta = \Gamma$, $M = 3$, $\Gamma_{\perp} = 0$; c,d) $\Delta = \Gamma$, $\eta = 0.1\ \Gamma$, $\Gamma_{\perp} = 0$, $M = 3$; e,f) $\Gamma_{\perp} = \Gamma$, $t = 8\Gamma^{-1}$, $M = 4$.

a way as to satisfy the equality $\eta+\sigma_d$. In this case at $\Gamma_\perp=0$, $L_1=0$, $t\to\infty$ we can obtain arbitrarily narrow HL lines, since $\sigma(t)$ turns out to be in this case its minimum possible value t^{-1} that follows from the Heisenberg uncertainty relation.[1)] We note that the narrowing of a zero-phonon line with increasing t was observed in experiments on the Mossbauer effect.[23,24]

Figure 6 shows plots of the widths (more accurately, half-widths) of the resonant Raman scattering lines on the time and on the parameters Δ and η. At $t=0$ they are equal to the sum of the decay width of the final vibrational state and the widths of excitation and registration $x\gg\Gamma_\parallel, \Gamma_\perp, \Delta, \eta, \gamma$:

$$\sigma(0)=\Gamma_\parallel L_1+\Delta+\eta. \tag{18}$$

As should be the case, the characteristics of the levels of the excited electronic states make no contribution to $\sigma(t)$. With increasing t, the width of the resonant Raman scattering line decreases. This is understandable: the resonant Raman scattering takes place during the time of excitation. Since, on the other hand, when t is increased the excitation becomes more monochromatic (only part of the exciting packet with spectral width $\sim t^{-1}$ continues to act on the center at the instant of time $t>\Delta^{-1}$), the resonant Raman scattering lines also narrow down. However, at any t the widths of the resonant scattering lines are not smaller than the decay width of the final level:

$$\sigma(t)\geqslant\Gamma_\parallel L_1. \tag{19}$$

It follows also from Fig. 6 that the dependence of the widths of the resonant Raman scattering lines on Δ and η is not monotonic: for each pair L_1 and Δ there is a definite value of η, at which $\sigma(t)$ is minimal. This effect, which makes it possible by suitable choice of $\eta(\Delta)$, at $t\gg\Delta^{-1}$ and $t\gg\eta^{-1}$, to eliminate η and Δ from the observed width of the resonant Raman scattering lines in the transient spectrum, can be called the effect of cancellation of the spectral widths of the excitation and registration.

We consider now the line shapes. All the HL and OL lines, at all values of the parameters, are symmetrical about the maximum and all have as a rule a nearly Lorentzian contour. The purely electronic line (PEL) of the luminescence at the instant of time $t\sim\tau_\parallel\ll\tau_{opt}$ is in general the same, both in intensity and in width, as all the remaining HL and OL lines (see Fig. 2). With increasing t, besides the continuous increase of the integral intensity, a narrowing takes place accompanied by oscillations on the wings of the line contour.[12,15,17] Similar oscillations can occur also in other lines if their width is $\sim t^{-1}$ [see Fig. 7 and Eq. (17)].

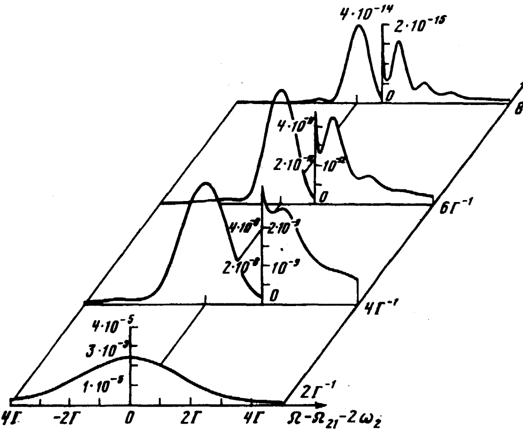

FIG. 7. Shape of the HL line $|2,2\rangle\to|1,0\rangle$; $M=3$, $\Delta=3\Gamma$, $\eta=2.001\Gamma$, $\Gamma_\perp=x=0$, $\gamma=0.002\Gamma$.

We consider now the resonant Rayleigh and Raman scattering lines and the HL lines, corresponding to the transitions $|2,M\rangle\to|1,L_1\rangle$. As noted above, if $\Gamma_\perp>0$, then the radiative transition $|2,M\rangle\to|1,L_1\rangle$ gives two spectral lines: resonant Raman scattering (Rayleigh scattering if $L_1=0$) lines and a hot luminescence line. These lines overlap at $|x|\lesssim\sigma_{\rm HL}(t)+\sigma_{\rm RRS}(t)$. In this case interference between the resonant Raman scattering (RRS) and hot luminescence lines takes place[25] and makes it impossible to separate them exactly (see Fig. 8). The resonant Rayleigh scattering line, just as the PEL, can have oscillations on the wings.

5. CONCLUSION

Using a quasi-line transition spectra of RSE luminescence centers as an example, we have followed in detail the manner in which resonant Raman and Rayleigh lines and hot and ordinarly luminescence lines appear and disappear in time. We also obtained the dependences of the properties of all these RSE components on the parameters that determine the electron-phonon interaction and on the rates of energy and phase relaxations. We have shown that not only the intensities but also the widths of the lines of the transient spectrum change substantially with time. It was also shown that by suit-

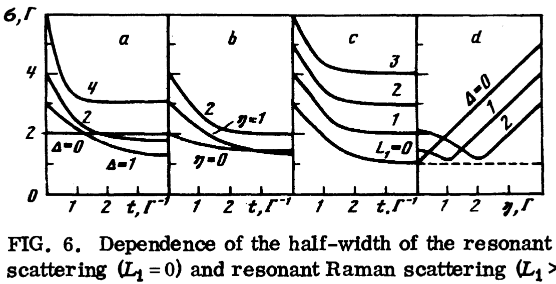

FIG. 6. Dependence of the half-width of the resonant Rayleigh scattering ($L_1=0$) and resonant Raman scattering ($L_1>0$) lines on the time and on the parameters Δ and η: a) $L_1=1$, $\eta=\Gamma$; b) $L_1=1$, $\Delta=\Gamma$; c) $\Delta=\Gamma$, $\eta=2\Gamma$; d) $L_1=1$, $t=8\Gamma^{-1}$.

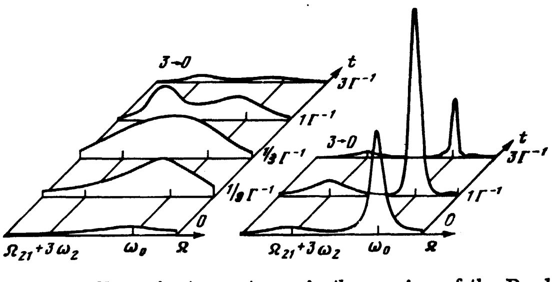

FIG. 8. Transient spectrum in the region of the Rayleigh line and the HL line $|2,3\rangle\to|1,0\rangle$ in the case of excitation to the vibrational level $M=3$; $x=20\Gamma$, $\eta=0.5\Gamma$, $\Gamma_\perp=1\Gamma$; on the left $\Delta=9\Gamma$, on the right $\Delta=\Gamma$.

able choice of the spectral resolution η it is possible to narrow down substantially the lines in the transient spectrum [effects of cancellation of the registration width and the decay width (HL) or the exciting width (resonant Raman scattering)]. In addition, we have shown that the line shape also changes greatly with time. Thus, in the region of intermediate times t there can be observed oscillations on the wings of certain lines. All this is evidence of the variety of properties of quasi-line transition spectra and the large amount of information that they contain.

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1) A similar narrowing of the emission line with increasing t was obtained in Ref. 2 for the particular case $\Gamma_{\parallel}L_2 = 0$ as applied to a purely electronic OL line.

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Excitation of molecule vibrations in resonant scattering of electrons

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A general approach is proposed for finding the cross section for vibrational excitation of molecules by slow electrons in the resonance region. The approach is based on the formalism of time-dependent perturbation theory. An expression is obtained for the cross section of vibrational excitation of diatomic molecules in the limiting case of two-atom molecules using a classical description of the motion of the nuclei in molecular particles. The calculation results obtained within the framework of various approximations are compared with one another and with the experimental data in the case of N_2 molecules.

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1. The possibility of formation of self-detached (resonant) states of an electron when scattered by molecules influences substantially the cross sections of their vibrational excitation in definite collision-energy ranges.[1] A characteristic feature of these cross sections is the peaked structure of the $\sigma(\varepsilon)$ curves in the indicated region of the incident-electron energies ε, when the cross sections at the maxima can exceed by several orders of magnitude the cross section in the region off resonance, where it varies smoothly with ε. The indicated peaks of the cross-section curves can vary greatly in shape and range from very broad ones

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