

# Time dependent spectra of resonant secondary radiation

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A theory is proposed of the time dependent (transient) spectra of resonant secondary radiation (RSR) of luminescence centers. The spectra in question are emitted in the course of vibrational relaxation in an excited electronic state. Analytic formulas are obtained for the transient spectrum recorded in the experiment. The time dependence of the smoothed transient spectra is investigated in detail for the case of large Stokes losses. It is shown that the changes in the positions of the maxima and in the widths of such spectra with time have the character of damped oscillations with periods in the picosecond and subpicosecond bands. The results of the theory are illustrated with computer calculations.

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## 1. INTRODUCTION

The investigation of vibrational relaxation processes is at present one of the pressing problems in the physics of crystals and molecules. The development of laser systems with picosecond and subpicosecond pulses makes it possible to set up experiments aimed at a direct observation of the time evolution of such processes. This makes it urgent to develop a theory of the time dependences of those physical phenomena in which vibrational relaxation can be observed directly. One such phenomenon is resonant secondary radiation (RSR).

A number of workers<sup>[1,2]</sup> (see also the review<sup>[3]</sup>) have previously developed a theory of stationary spectra of RSR of luminescence spectra. It was established that the basis of a theory that describes all the RSR phenomena can be a formula, of second-order in the interaction between light and matter, for the resonant-scattering cross section (the Heisenberg-Kramers formula). In those cases when the vibrational relaxation in the excited electronic state of the center is much faster than the damping of this state (this is precisely the property possessed by the known centers), the main part of the RSR intensity is ordinary luminescence (OL). This formula contains also resonant scattering (RS), both Rayleigh and Raman, and in many cases also hot luminescence (HL). Whereas the OL is emitted following vibrational relaxation in the excited electronic state, the scattering and the HL take place either before or during this relaxation, the HL being emitted after the phase relaxation but during the energy relaxation, while the scattering occurs after the end of the phase relaxation (a criterion of phase relaxation for discrimination between resonant scattering and hot luminescence was proposed by Tekhver and one of us<sup>[4]</sup>; a more detailed discussion of the roles of energy and phase relaxation in the classification of the RSR is contained in<sup>[3]</sup>).

In stationary RSR spectra all the relaxation processes manifest themselves in averaged form. In the case of pulsed excitation, as demonstrated by experiment,<sup>[5]</sup> they can be investigated in much greater detail by using the time dependence of the RSR. This has attracted great interest to the theory of time-dependent (tran-

sient) RSR spectra (see, e.g.,<sup>[6-11]</sup>). In particular formulas were derived for the time dependence of the moments of the RSR spectra, and studies were made of the time dependence of the moments of the shape of the envelope, of the time separation between the scattering and luminescence, and of many other problems. At the same time, there were not enough studies of questions such as the connection between the photon-emission rates and the directly measured transient spectrum, or of the role of the spectral apparatus. In the present paper we consider these questions. We obtain a general formula for the transient spectra directly recorded in experiments under various registration conditions and show in which cases this spectrum reduces to the photon emission rate, and in which to the emission probability. On the basis of these formulas, we investigate in detail the changes of the envelope of the HL+OL spectra in the course of vibrational relaxation and perform numerical calculations of these spectra in some concrete models of the luminescence center.

## 2. THE TRANSIENT SPECTRUM

We consider the process of the measurement of the transient (i.e., dependent on the registration time) spectrum of the RSR using a very simple system consisting of a spectral instrument and a pointlike photon counter. The latter is assumed to have a wide spectral sensitivity band (such a counter can be turned on and off practically instantaneously). The transient spectrum  $I(\Omega, t)$  is defined as the photon counting rate at the instant of time  $t$  when the spectral instrument is tuned to the frequency  $\Omega$ . In this case  $I(\Omega, t)$  is determined by the average (over the ensemble) value of the normal products of the field-intensity operators  $E^+$  and  $E^-$  at the instant of time  $t$  at the point where the counter is located<sup>[12]</sup>:

$$I(\Omega, t) \sim \langle E^+(t)E^-(t) \rangle.$$

In the absence of the spectral instrument, then the indicated mean value would be determined in the case of a sufficiently small emitter only by the amplitudes  $C_{1\Omega_j}(t)$  of the transitions in which one photon is produced and another annihilated, and its value would be

$$I(t) \sim \iint d\Omega' d\Omega'' \sum_j \langle C_{i\omega_j}(t) C_{i\omega_j}^*(t) \rangle$$

( $j$  numbers the states of the spectrum and  $\langle \dots \rangle$  denotes averaging over the ensemble).

The spectral instrument influences mainly only the amplitude of the waves that pass through it, and this influence is different for different frequencies. This influence can be described by adding under the integral signs with respect to  $\Omega'$  and  $\Omega''$  the spectral transmission function  $f_\Omega(\Omega', \Omega'')$ :

$$I(\Omega, t') = \iint d\Omega' d\Omega'' f_\Omega(\Omega', \Omega'') \sum_j \langle C_{i\omega_j}(t) C_{i\omega_j}^*(t) \rangle, \quad (1)$$

$t' = t + \tau_0$ , where  $\tau_0$  is the time of flight of the photons from the emitter to the counter. The function  $f_\Omega(\Omega', \Omega'')$  in (1) differs noticeably from zero in the region  $|\Omega' - \Omega| \sim |\Omega'' - \Omega| \sim \Delta\Omega$ , where  $\Omega$  is the frequency to which the spectral instrument is tuned, and  $\Delta\Omega$  is the employed spectral resolution. The probability amplitudes in (1) take for the considered two-photon process the values

$$C_{i\omega_j} = - \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \sum_{j_1, j_2} \langle j_1 | v_\omega | j_1 \rangle \langle j_2 | v_\omega | j_2 \rangle \times \exp[-i(\Omega + E_j)(t - t_1) - i(E_{j_1} - i\gamma_{j_1})(t_1 - t_2) - iE_{j_2} t_2] e(t_2) b_{j_2} \quad (2)$$

Here  $b_{j_2}$  is the amplitude of the probability of finding the center at the initial instant of time  $t = -\infty$  in the eigenstate  $|j\rangle$  of the Hamiltonian  $H$ ,  $E_j$  is the energy of the state  $|j\rangle$ ,  $\gamma_j$  is the constant of the radiative damping of this state,  $\omega$  is the average excitation frequency,

$$v_\omega = \langle N-1_\omega | H' | N \rangle, \quad v_\omega = \langle N-1_\omega - 1_\omega | H' | N-1_\omega \rangle$$

are the single-photon matrix elements of the Hamiltonian  $H'$  of the interaction of the field with the medium, and describe respectively the annihilation of a photon of frequency  $\omega$  and production of a photon of frequency  $\Omega$ ,  $|N\rangle$  is the initial state of the field, and  $\epsilon(t)$  is the time dependence of the perturbation of the center by the exciting light. (In the dipole approximation,  $\epsilon(t)$  is determined by the intensity of the electric field acting on the center at the instant of time  $t$ .) It is assumed in (2) that the excitation is quasimonochromatic, i.e.,  $\epsilon(t) = e^{i\omega t} \bar{\epsilon}(t)$ , where  $\bar{\epsilon}(t)$  is function of  $t$  that varies slowly compared with  $e^{i\omega t}$ . In addition, it is assumed in (2), as is customary in problems of the scattering type, that there is no interaction between the exciting light and the medium at  $t = \pm\infty$ .

We substitute (2) in (1) and recognize that under thermal-equilibrium conditions

$$\langle b_{j_2} b_{j_2} \rangle = \delta_{j_2 j_2} \exp(-E_{j_2}/kT) z^{-1}$$

( $z$  is the partition function and  $T$  the temperature). Then

$$I(\Omega, t') = \iint_{-\infty}^t dt_1 dt_1' \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2'} dt_2' \exp\{i\Omega(t_1' - t)\} \times a(t_1' - t_1, t_1' - t_2', t_1 - t_2) C(t - t_1, t - t_1') S(t_2, t_2'), \quad (3a)$$

or, using the variables  $\tau = t_1' - t_2'$ ,  $\tau' = t_1 - t_2$ ,  $\mu = t_1' - t_1$ ,  $\nu = t - \frac{1}{2}(t_1 + t_1')$ ,

$$I(\Omega, t') = \int_{-\infty}^t d\mu \int_0^{\mu} d\tau d\tau' \int_{|\mu|/2}^{\mu} d\nu e^{i\Omega\nu} a(\mu, \tau, \tau') \times C\left(\nu + \frac{\mu}{2}, \nu - \frac{\mu}{2}\right) S\left(t - \nu - \tau' - \frac{\mu}{2}, t - \nu - \tau + \frac{\mu}{2}\right). \quad (3b)$$

Here  $S(t, t') = \langle \epsilon^*(t) \epsilon(t') \rangle$  is the correlation function of the exciting field

$$C(\nu, \nu') = \iint dx dx' e^{i\nu x - i\nu' x'} f_\Omega(\Omega + x, \Omega + x')$$

is the registration correlation function and differs noticeably from zero in the region  $|\nu| \sim |\nu'| \sim t_0 \sim 1/\Delta\Omega$ , and

$$a(\mu, \tau, \tau') = \langle v_{\omega_1}^+ e^{i(H+\tau)v_1} v_{\omega_1}^+ e^{-iHv_1} v_{\omega_2} e^{-i(H-\tau')v_2} v_{\omega_2} e^{-iH(\mu+\tau'-\tau)} \rangle_0$$

is the three-time correlation function of the medium.

It is of interest to consider the following two limiting cases: 1) measurement with high spectral resolution  $\Delta\Omega \ll 1/\tau_1$ , and 2) measurement with slow spectral resolution  $\Delta\Omega \gg 1/\tau_1$  ( $\tau_1$  is the characteristic time of the variation of  $I(\Omega, t)$ ).

In the former case we can assume in (3a)  $C(t - t_1, t - t_1') \approx \text{const}$ . Then

$$I(\Omega, t') \sim W(\Omega, t) = \iint_{-\infty}^t dt_1 dt_1' \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2'} dt_2' \times e^{i\Omega(t_1' - t_1)} a(t_1' - t_1, t_1' - t_2', t_1 - t_2) S(t_2, t_2'), \quad (4)$$

i.e., in this case the transient spectrum reduces, apart from a constant factor, to the probability  $W(\Omega, t)$  of emission of a photon of frequency  $\Omega$  at the instant of time  $t$ . In the latter case  $C(t - t_1, t - t_1') \equiv C(\nu + \mu/2, \nu - \mu/2)$  differs noticeably from zero in the region  $|\nu| \sim |\mu| \sim 1/\Delta\Omega \ll 1/\tau_1$ . We can therefore neglect in (3b) the dependence of  $S$  on  $\nu$  and  $\mu$ . If we assume furthermore that the line widths  $\delta\Omega$  in the spectrum exceed  $\Delta\Omega$  substantially, then we can neglect in (3b) also the dependence of  $C$  on  $\mu$ .

As a result we have

$$I(\Omega, t') \approx \Pi(\Omega, t) \int_0^{\mu} d\nu C(\nu, \nu) \sim \Pi(\Omega, t), \quad (5)$$

where

$$\Pi(\Omega, t) = \frac{dW(\Omega, t)}{dt} = 2 \text{Re} \int_0^{\mu} \int_0^{\mu} d\mu d\tau d\tau' e^{i\Omega\mu} a(\mu, \tau, \tau') S(t - \mu - \tau', t - \tau) \quad (6)$$

is the rate of emission of photons of frequency  $\Omega$  at the instant of time  $t$ . This is precisely the quantity previously taken to be  $^{[6-11]}$  the transient spectrum. We see that this holds true only in those cases when the line width of the transient spectrum greatly exceeds the limiting width  $1/\tau_1$  determined by the Heisenberg uncertainty relation. We note also that in the latter case  $\Pi(\Omega, t) > 0$ .

The physical meaning of formulas (4) and (5) is the

following: At a spectral resolution  $\Delta\Omega$ , the spectral instrument passes photons with coherence length  $L \sim c/\Delta\Omega$ . These photons traverse the aperture of the counter during a time of the order of the coherence time  $t_0 = 1/\Delta\Omega$ . If  $t_0 \gg t$ , it is possible to register at the instant of time  $t'$  any photon emitted prior to the instant  $t = t' - \tau_0$ . (The time is reckoned here and hereafter from the value of  $t$  at the maximum of the exciting signal at the center.) Therefore the photon counting rate is determined directly by the probability  $W(\Omega, t)$ . On the other hand if  $t_0 \ll t$ , then at the instant of time one can register only the photons emitted in the short time interval between  $t - t_0$  and  $t$ . Hence the photon counting rate is determined by the difference  $W(\Omega, t) - W(\Omega, t - t_0)$ . If furthermore the condition  $t_0 \ll \tau_1$  is also satisfied, then  $W(\Omega, t) - W(\Omega, t - t_0) \sim t_0 dW(\Omega, t)/dt \sim \Pi(\Omega, t)$ .

Under stationary excitation conditions, the RSR does not depend on the registration time (in this case the function  $S_{gt}(t, t') = S_{gt}(t - t')$  depends only on the time difference). Therefore the condition of the applicability of formula (5) is satisfied only for arbitrarily small  $\Delta\Omega$ , so that the measured stationary spectrum is determined by the emission rate  $\Pi(\Omega, t)$ .

It was assumed above that the photon counter is actuated only for an instant. If the photon counting extends over a finite period, the measured spectrum is determined, in the case of a spectrally insensitive counter, by the integral of  $|E(t)|^2$  with respect to the registration time.<sup>[12]</sup> In this case

$$I(\Omega, t, \Delta t) = \int \chi_{\Delta t}(t - t_1) I(\Omega, t_1) dt_1, \quad (7)$$

where  $\chi_{\Delta t}(t - t_1)$  is the counter switching-on-and-off function, which differs from zero substantially in the region  $|t - t_1| \sim \Delta t$ . If at the same time  $\Delta t \gg 1/\Delta\Omega$  (the registration time is much longer than the coherence-loss time of the photon passed by the spectral instrument), and also if the spectral resolution is sufficient for the investigated structure of the spectrum  $\Delta\Omega \ll \delta\Omega$ , then  $I(\Omega, t_1)$  in (7) can be replaced by the emission rate  $\Pi(\Omega, t_1 - \tau_0)$ . In the simplest case of a rectangular function  $\chi_{\Delta t}(t - t')$ , and under the conditions  $\Delta\Omega \ll \delta\Omega$  and  $\Delta\Omega \ll 1/\Delta t$ , the spectrum registered in the interval  $(t, t + \Delta t)$  is given by

$$I(\Omega, t, \Delta t) = \int_{t-\Delta t}^t \Pi(\Omega, t+x) dx. \quad (8)$$

### 3. LUMINESCENCE

On the basis of the general formulas obtained above, we consider the transient spectra in the following model: there are two nondegenerate electron levels—ground and excited, the adiabatic approximation and the Condon approximation are valid, and the excited electron level remains empty under conditions of thermal equilibrium. In this case

$$a(\mu, \tau, \tau') = |M_1 M_2|^2 e^{-\tau(\tau+\tau')} A(\mu, \tau, \tau').$$

Here (and below)

$$A(\mu, \tau, \tau') = \langle e^{i\tau' H_0} e^{i\mu H_0} e^{-i\tau H_0} e^{-i(\mu+\tau-\tau') H_0} \rangle_0, \quad (9)$$

$H_0$  and  $H_1$  are the vibrational Hamiltonians of the ground and excited electronic states,  $M_1$  and  $M_2$  are the electronic matrix elements for the absorption and emission,  $\langle \dots \rangle_{0,1} \equiv \text{Sp}(\dots \rho_{0,1})$  is the symbol of quantum-mechanical averaging over the oscillations, while

$$\rho_{0,1} = \exp(-H_{0,1}/kT) / \text{Sp}[\exp(-H_{0,1}/kT)]$$

is the vibrational density matrix in the ground (0) or excited (1) electronic state, and  $\gamma$  is the radiative-damping constant of the excited state.

We consider first the RSR in the region of long times  $t \geq 1/\gamma \gg \delta t$  ( $\delta t$  is the characteristic excitation duration). In this case the excitation can be regarded as instantaneous:

$$S(t - \mu - \tau', t - \tau) = S_0 \delta(t - \mu - \tau') \delta(t - \tau) = S_0 \delta(t - \tau) \delta(\mu + \tau' - \tau). \quad (10)$$

We obtain first the emission rate  $\Pi(\Omega, t)$ . Substituting (9) and (10) in (6) we get

$$\begin{aligned} \Pi(\Omega, t) &= 2 B e^{-2\gamma t} \text{Re} \int_0^t d\mu e^{i\Omega\mu + i\mu} \langle e^{-i\mu H_1} e^{i\mu H_0} \rangle_1, \\ B &= S_0 |M_1 M_2|^2, \quad \langle \dots \rangle_1 = \text{Sp}(\dots \rho(t)_1), \end{aligned} \quad (11)$$

where

$$\rho(t)_1 = \exp(-itH_1) \rho_0 \exp(itH_1)$$

is the vibrational density matrix in the excited electronic state at the instant of time  $t$ . The dependence of  $\rho(t)_1$  on  $t$  describes the vibrational relaxation in the excited electronic state, and the dependence of  $\Pi(\Omega, t)$  on  $t$  describes the change of the rate of emission of photons of frequency  $\Omega$  in the course of this relaxation.

We recognize that according to the ergodic theorem we have  $\langle \hat{F} \rangle_t = \langle \hat{F} \rangle_1$  if  $t \rightarrow \infty$  ( $\hat{F}$  is a certain operator). Consequently we have in (11)  $\rho(t)_1 \rightarrow \rho_1$  as  $t \rightarrow \infty$ . The time domain  $t$  in which  $\rho(t)_1$  differs noticeably from  $\rho_1$  determines the characteristic time  $\Gamma_1^{-1}$  of the total (energy vibrational relaxation in the excited state. This time is usually much shorter than the radiative lifetime  $\gamma^{-1}$ . Therefore at  $t \sim \gamma^{-1} \gg \Gamma_1^{-1}$  we can assume in (11) that  $\rho(t)_1 = \rho_1$ . If furthermore we replace the integration limits in this formula by  $\pm\infty$  and neglect the factor  $e^{\gamma|\mu|}$ , then  $\Pi(\Omega, t)$  reduces to the well-known formula for the spectrum of the OL whose intensity attenuates at the decay rate of the excited level:

$$\Pi(\Omega, t) \approx B e^{-2\gamma t} \int_{-\infty}^{\infty} d\mu e^{i\Omega\mu} \langle e^{-i\mu H_1} e^{i\mu H_0} \rangle_1. \quad (12)$$

At a spectral resolution  $\Delta\Omega \gg 1/t \sim \gamma^{-1}$  these approximations are justified. This resolution is as a rule sufficient, since ordinarily  $\delta\Omega \gg \gamma$ . In such cases, as noted above  $\Pi(\Omega, t)$  actually determines the spectrum determined in the experiment. An exception is the spectrum in the region of zero-phonon lines, whose width can be very small at low temperatures. To find the

measured spectrum in the last case we must use the general formulas (3). If we choose then the registration correlation function in the exponential form  $C(t-t_1, t-t'_1) = C_0 \exp[-\Gamma(2t-t_1-t'_1)]$ , then we have in the considered case of the instantaneous excitation in the region of the zero-phonon line

$$I(\Omega, t') \sim \frac{e^{-2\Gamma_1 \gamma_1 / \bar{\gamma}}}{x^2 + \gamma_1^2} + \frac{e^{-2\Gamma_1 \gamma_2 / \bar{\gamma}}}{x^2 + \gamma_2^2} - 2e^{-(\Gamma_1 + \Gamma_2 + \Gamma)t} \frac{(x^2 + \gamma_1 \gamma_2) \cos xt + 2\gamma_1 x \sin xt}{(x^2 + \gamma_1^2)(x^2 + \gamma_2^2)}, \quad (13)$$

where  $\gamma_1 = \gamma - \gamma_v - \Gamma$ ,  $\gamma_2 = \gamma + \gamma_v - \Gamma$ ,  $\bar{\gamma} = \gamma - \Gamma$ . We see that with increasing distance from the center the spectrum  $I(\Omega, t')$  undergoes damped oscillations. The distance between neighboring oscillation maxima is  $xt$ , and the oscillation amplitude is larger the smaller  $\gamma$  and  $\Gamma$ .

It is of interest to note that the width of the individual oscillation maxima can be smaller than the spectral resolution  $\Gamma$ , but in accord with the Heisenberg uncertainty relation it is always  $\geq 1/t$ . We note also that, in accord with the general theory developed above, we have at  $\Gamma = 0$

$$I(\Omega, t') \sim W(\Omega, t),$$

and at  $\gamma_1 \gg \Gamma \gg 1/t$

$$I(\Omega, t') \sim \Pi(\Omega, t).$$

In the case  $\gamma_v = 0$  and  $\Gamma = \gamma$  formula goes over into the known formula<sup>[13]</sup> that describes the time dependence of a zero-phonon line in the Mössbauer effect.

#### 4. SMOOTHED TRANSIENT SPECTRUM IN STRONG ELECTRON-PHONON INTERACTION

In the region  $t \lesssim \Gamma_1^{-1}$  the transient spectrum depends essentially on the excitation and registration characteristics determined by the functions  $S$  and  $C$ . We select below these functions in the following simple form:

$$S(t, t') = S_0 \exp\{i\omega_0(t-t') - 1/2\sigma^2[(t-t')^2 + (t+t')^2]\}, \\ C(t, t') = C_0 \exp\{-1/2\beta^2[(t-t')^2 + (t+t')^2]\}. \quad (14)$$

Here  $\sigma$  determines the spectral width of the exciting light (and the excitation duration:  $\delta t \sim \sigma^{-1}$ ), and  $\beta$  determines the employed spectral resolution:  $\beta \sim \Delta\Omega$ .

Assume that the interaction between the optical electrons and the phonons is strong, i.e., the Stokes losses and the widths of the absorption and luminescence spectra are large compared with the average oscillation frequency  $\bar{\omega}$ . Then the total width of the transient spectrum  $\sigma_t$  is large compared with  $\bar{\omega}$ . In this case it is of interest to find the transient spectrum in the time region  $t \geq \bar{T} = 2\pi/\bar{\omega}$  ( $\bar{T}$  is the average period of the oscillations) in the case of poor spectral resolution  $\Delta\Omega \sim \beta \gg \bar{\omega}$ , since this spectral resolution, on the one hand, is sufficient for the investigation of the smoothed spectrum ( $\beta \ll \sigma_t$ ), and on the other hand it makes it possible to obtain fast changes of  $I(\Omega, t')$  with time in view of the "good" temporal localization of the registration function  $C$ . Naturally, the smoothed spectrum  $I(\Omega, t')$  can change

significantly in the time region  $t \sim \bar{T}$  only if the excitation duration  $\sigma^{-1}$  is also small enough. We assume therefore not only  $\beta \gg \bar{\omega}$ , but also  $\sigma \gg \bar{\omega}$ . We note that in this case we are dealing in the considered region  $t \geq T \gg \delta t$  with afterglow, i.e., with HL+OL.

We change over in (3b) from the integration variables  $\tau$  and  $\tau'$  to  $z = \mu + \tau' - \tau$  and  $y = \tau + \tau' - 2(t - \nu)$ . We recognize that when  $\Delta\Omega \gg \omega$  and  $1/\delta t \gg \bar{\omega}$  in (3b) the actual values of  $|\mu|$  and  $|z|$  are small compared with  $\bar{\omega}^{-1}$ . In this case we can use the approximations

$$e^{i\mu H_0} \approx e^{-i\mu V(\mu/z)}, e^{i\mu H_1} \approx e^{i\mu H_0}, e^{iz H_1} \approx e^{iz V(z/z)}, e^{iz H_0}$$

where  $V(x)_{0,1} = e^{ix H_{0,1}} V e^{-ix H_{0,1}}$ . Under these approximations

$$A \approx A^0 = \langle \exp[-i\mu V(t - \nu + (y+z)/2)] e^{iz V(z/z)} \rangle_0. \quad (15)$$

In addition, at  $t \geq \bar{T}$  the actual values of  $|\nu|$ ,  $|y|$ , and  $|z|$  are much less than  $t$ . Therefore the limits of integration with respect to  $y$  and  $z$  can be assumed equal to  $\pm\infty$ . We recognize also that if  $\beta \ll \sigma_t$  we have  $|\mu| \ll \nu$ . Then

$$I(\Omega, t') \approx \frac{B_1}{2} e^{-2\Gamma t} \int_0^{\bar{\omega}} dv \iiint_{-\infty}^{\infty} dy dz d\mu \\ \times \exp\left[-\frac{\beta^2}{2}(4v^2 + \mu^2) + i\Omega\mu - i\omega_0 z - \frac{\sigma^2}{2}(y^2 + z^2)\right] A^0. \quad (16)$$

where  $B_1 = S_0 C_0 |M_1 M_2|^2$ .

Further calculation of the spectrum  $I(\Omega, t')$  calls for specifying more concretely the model of the electron-vibrational system. We assume in this paper that the vibrations are harmonic and that the difference of the adiabatic potentials  $V$  is linear in the displacements of the nuclei:

$$H_0 = \frac{1}{2} \sum_j \left( -\frac{\partial^2}{\partial x_j^2} + \omega_j^2 x_j^2 \right), \quad V = V_0 + q = V_0 + \sum_j e_j x_j. \quad (17)$$

Here  $\omega_j$  is the frequency of the normal oscillation  $j$ , and  $x_j$  is its coordinate. In this case

$$V(x)_1 = V_0 + q(x)_1 = \omega_L + l_x + q(x)_0, \quad (18)$$

where

$$l_x = \langle q(x)_1 \rangle_0 = \sum_j \left( \frac{e_j}{\omega_j} \right)^2 \cos \omega_j x,$$

$x = t - \nu + (y+z)/2$ ,  $\omega_L = V_0 - l$  is the frequency of the maximum of the OL spectrum, and  $l \equiv l_0$  is the Stokes loss.

We substitute (18) in (15) and use the Bloch theorem on pair correlations.<sup>[14]</sup>

Then

$$A^0 = \langle \exp[-i\mu(\omega_L + l_x) + izV_0 + \mu z \bar{m}_x - m(\mu^2 + z^2)/2] \rangle, \quad (19)$$

where

$$x' = x - z/2, \quad \bar{m}_x = m_x + il_x'/2, \quad l_x' = dl_x/dx,$$

$$m_x = \sum_j \frac{e_j^2}{2\omega_j} \cos(\omega_j x) \operatorname{cth} \frac{\omega_j}{2kT},$$

$m \equiv m_0$  is the second central moment of the absorption band. Inasmuch as the essential region of integration in (16) is with respect to  $|\nu|$ ,  $|\mu|$ ,  $|y|$ ,  $|z| \ll \bar{T} \lesssim t$ ,

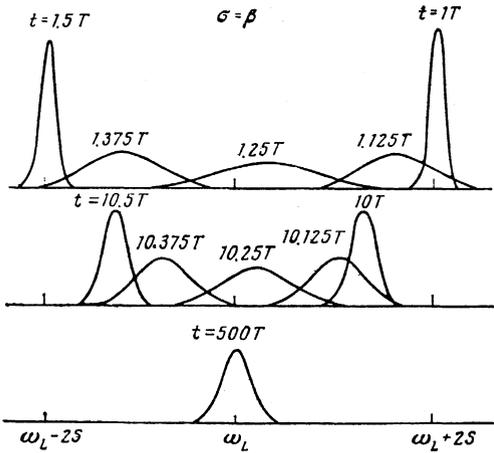


FIG. 1. The spectrum  $I(\Omega, t)$  with account taken of one damped local vibrations; the Stokes loss is  $S_{loc} = 55$ , the damping constant is  $\Gamma^{-1} = 20 T_{loc}$ ;  $\beta = \sigma$ ,  $\sigma^2 = 0.111 m_0$ .

we can put henceforth

$$\bar{m}_i \approx m_i, \quad l_i \approx l_i' (y+z-2v)/2.$$

Therefore

$$I(\Omega, t) = B_i e^{-2\gamma t} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mu dy dz \exp\{-2\beta^2 v^2 + i(\Omega - \omega_i) \mu - \mu^2(m + \beta^2)/2 + i\mu l_i'(v - y/2) - \sigma^2 y^2/2 - i\omega z - z^2(m + \sigma^2)/2 + \mu z m_i\}. \quad (20)$$

The integrals with respect to  $z$ ,  $y$ , and  $\mu$  are calculated in elementary fashion, and the remaining integral with respect to  $v$  is expressed in terms of the error function. As a result we have

$$I(\Omega, t) = (B/\sigma_i) (1 - \text{erf } \epsilon_i) \exp[-2\gamma t - (\Omega - \omega_i)^2/2\sigma_i^2], \quad (21)$$

where

$$B = (2\pi^2 B_i / \beta \sigma (m + \sigma^2)^{3/2}) \exp[-(\omega - V_0)^2/2(m + \sigma^2)], \\ \omega_i = \omega_L + l_i + (\omega - V_0) m_i / (m + \sigma^2), \\ \sigma_i^2 = m + \beta^2 + l_i'^2/4\sigma^2 + l_i'^2/4\beta^2 - m_i^2 / (m + \sigma^2), \\ \epsilon_i = l_i' (\Omega - \omega_i) / 2^{3/2} \beta \sigma_i, \quad \sigma_i^2 = \sigma_i^2 - l_i'^2/4\beta^2.$$

Thus, in the model considered here, the time dependence of the smoothed transient spectrum is determined by the functions  $l_i$  and  $m_i$ . The time dependence of the position of the maximum of the spectrum is determined only by the function  $l_i$ , which is described by the dependence of the configuration coordinate on the time in the excited electronic state. This dependence has the character of damping of almost periodic (if the phonon dispersion  $\Gamma$  is small compared with  $\bar{\omega}$ ) or aperiodic (if  $\Gamma \approx \bar{\omega}$ ) oscillations.<sup>11</sup> In the region  $t \lesssim \Gamma^{-1}$  the shift of the spectrum during one-half oscillation period is quite large, of the order of the Stokes loss  $l$  (or even  $\sim 2l$ ), and can amount to several electron volts.

The variation of the width of the spectrum with time in the region  $t \lesssim \Gamma^{-1}$  is also appreciable and takes the form of damped oscillations (see Figs. 1 and 2). The spectrum  $I(\Omega, t)$  has the largest peak intensity and the smallest width in the region of the classical turning points of the configuration coordinate  $q(t)_1$ , which are reached at instants of time  $t = t_n \approx nT/2$  ( $n = 0, 1, 2, \dots$ ), satisfying the condition  $l_i' = 0$ . In the region of these points its shape is approximately described by the

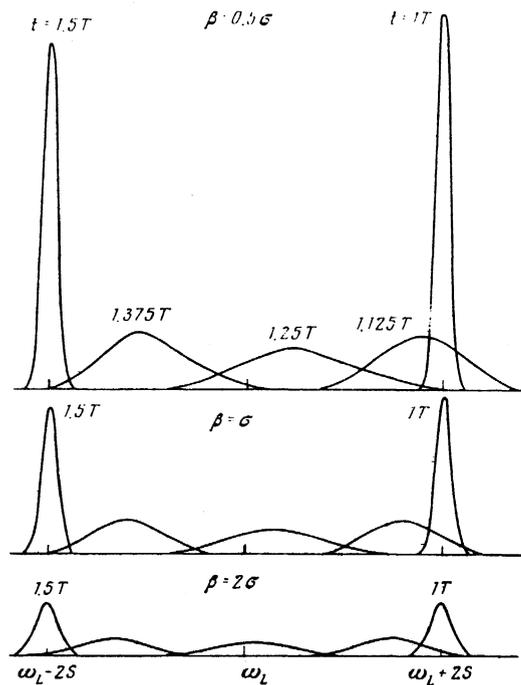


FIG. 2. The spectrum  $I(\Omega, t)$  for different ratios of  $\beta$  and  $\sigma$ . The remaining parameters are the same as in Fig. 1.

normal distribution

$$I(\Omega, t_n) \approx \frac{B}{\sigma_n} \exp\left[\frac{-(\Omega - \omega_n)^2}{2\sigma_n^2}\right], \quad (22)$$

where  $\omega_n = \omega_{tn}$ ,  $\sigma_n = \sigma_{tn}$ . In the limit of large  $t \gg \Gamma^{-1}$  we have  $l_i \approx 0$ ,  $l_i' \approx m_i \approx 0$ . As a result the transient spectrum reduces to OL, as it should.

## 5. THE SPECTRA $I(\Omega, t, \Delta t)$

The "instantaneous" transient spectrum (21) obtained above can be measured in experiment only if the registration duration  $\Delta t$  can be made substantially shorter than the characteristic time  $\tau_1$  of the variation of the transient spectrum. It follows from (21) that during the initial stages of the relaxation we have  $(l\bar{\omega}^3)^{1/4} \lesssim \tau_1 \lesssim (l\bar{\omega})^{1/2}$ , i.e., usually in the range  $10^{-13} - 10^{-14}$  sec (we assume that  $\beta \lesssim \sigma \sim m^{1/2} \sim (l\bar{\omega})^{1/2}$ ). At the present time, however, the experimentally attainable registration time is  $\Delta t \gtrsim 10^{-12}$  sec. It is therefore of interest to calculate the spectrum  $I(\Omega, t, \Delta t)$ , defined by (8), averaged over the registration time  $\Delta t$ . Since we are interested here in the case  $\Delta t \gtrsim T$ , it is not obligatory to use in the integral (7) the exact value of  $\Pi(\Omega, t)$ ; it suffices to use the correct value of the spectrum width only in the region of the extreme positions of the spectrum, which correspond to the classical turning points of the configuration coordinate  $q$ . We can therefore assume at  $\Delta T \gtrsim T$

$$I(\Omega, t', \Delta t) = \text{const} \int_{t'}^{t'+\Delta t} dt_i \exp\left[\frac{-(\Omega - \omega_i)^2}{2\sigma_i^2}\right], \quad (23)$$

that determines  $m_{1t}$  and  $m_{2t}$ . We have chosen this function in the form

$$\varphi(\omega) = \theta(\omega) S_{\kappa} \left( \frac{2\omega}{\omega_{\kappa}} \right)^2 \exp\left( \frac{-2\omega}{\omega_{\kappa}} \right) + S_{\lambda} \omega_{\kappa} \frac{\Gamma_1/\pi}{(\omega - \omega_{\kappa})^2 + \Gamma_1^2}, \quad (24)$$

where  $S$  are the dimensionless Stokes losses. The first term in this formula takes into account the crystal vibrations, and the second and local (pseudolocal) vibration. We note that such a function  $\varphi(\omega)$  results in a qualitatively correct asymptotic behavior of  $m_{1t}$  and  $m_{2t}$  at small and large times  $t$ . The numerical calculations were performed with an M-4030 computer. In all cases, the summary dimensionless Stokes losses were chosen to be the same:  $S_{\kappa} + S_{\lambda} = 55$ . The calculation results are shown in Figs. 3 and 4.

Figure 3 shows the spectra  $I(\Omega, t, \Delta t)$  with only the slowly damped local vibration taken into account. It is seen that during the initial relaxation stages the spectrum has a two-mode shape, the maxima being due to radiation from the classical turning point. This result agrees with the conclusion of [15] based on an analysis of the Franck-Condon factors. Figure 4 describes the transient spectra in the case when the vibrational relaxation has two stages—short and long. The maxima in the spectra are due as before by radiation from the regions of the classical turning points.

We note in conclusion that we have investigated in detail above only the time dependence of the smoothed RSR spectrum. In many cases the exact spectrum should contain sufficiently narrow lines of the vibrational spectrum. In such cases the smoothed spectrum yields only some information on the redistribution of the spectra among the lines in the course of time. On the other hand, the detailed behavior of the position, width, and shape of each such line calls for a special investigation.

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<sup>1</sup>In the considered model the cause of the relaxation is the dephasing of the phonons with increasing  $t$ . In those cases when there are phonon branches of small dispersion or else local oscillations, a correct description of the relaxation, and by the same token, of the time dependence of the transient spectrum calls for allowance for the anharmonic decay of the oscillations. The obtained first-order approximations remain in force if the oscillation frequencies  $\omega_j$  are replaced by  $\omega_j \pm i\Gamma_j$ , where  $\Gamma_j$  is the anharmonic-damping constant of the normal oscillation  $j$  (see [1]).

<sup>1</sup>I. Yu. Tekhver and V. V. Khizhnyakov, *Izv. Akad. Nauk Est. SSR Ser. Fiz.-Mat. Tekh. Nauk* 15, 9 (1966); V. Hizhnyakov and I. Tehver, *Phys. Status Solidi* 21, 755 (1967); V. Hizhnyakov, K. Rebane, and I. Tehver, in: *Light Scattering Spectra of Solids*, ed. G. B. Wright, Springer-Verlag, New York, 1969, p. 513; K. Peuker and E. D. Trifonov, *Phys. Status Solidi* 30, 479 (1968); D. L. Huber, *Phys. Rev.* 170, 418 (1968).

<sup>2</sup>Y. R. Shen, *Phys. Rev. B* 9, 622 (1974); Y. Toyozawa, *J. Phys. Soc. Jpn.* 41, 400 (1976); R. Kubo, T. Takagahara, and

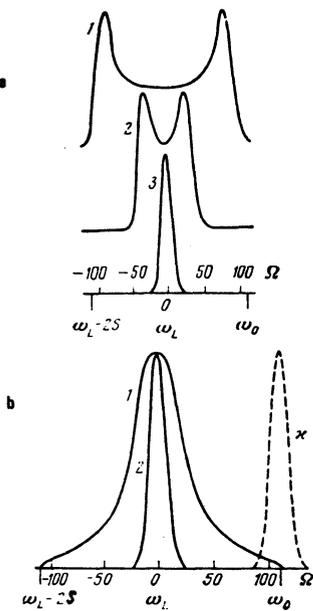


FIG. 3. The spectra  $I(\Omega, t, \Delta t)$  with account taken of only local (pseudolocal) vibration,  $S_{loc} = 55$ ; the damping constant is  $\Gamma^{-1} = 20 T_{loc} = 40 \pi / \omega_{loc}$ . a) The registration time is  $\Delta t = 5 T_{loc}$ . Initial time: 1)  $t = T_{loc}$ , 2)  $t = 20 T_{loc}$ , 3)  $t = 400 T_{loc}$ . b) Registration time  $\Delta t = 50 T_{loc}$ . Initial time: 1)  $t = T_{loc}$ , 2)  $t = 500 T_{loc}$ ;  $\kappa$ —absorption spectrum.

where  $\sigma_{0t}^2 = m - m_0^2 / 2(m + \sigma^2)$ . In the considered case  $\Delta t \gtrsim \bar{T}$  the spectrum (22) can be calculated only numerically. It is then necessary to specify the function

$$\varphi(\omega) = \sum_j \left( \frac{e_j}{\omega_j} \right)^2 \delta(\omega - \omega_j),$$

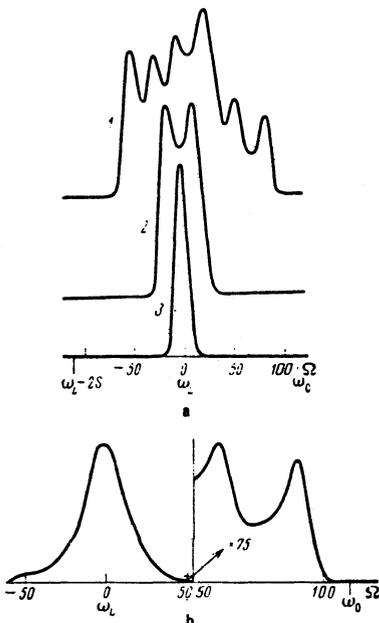


FIG. 4. Spectra  $I(\Omega, t, \Delta t)$  with account taken of both the crystal and the local vibrations;  $S_{cr} = S_{loc} = 27.5$ ; local-vibration damping time  $\Gamma_{loc} = 20 T_{loc} = 40 \pi / \omega_{loc}$ . Frequency ratio  $\omega_{loc} / \omega_{cr} = 9$ . a) Registration time  $\Delta t = 5 T_{loc}$ ; initial time: 1)  $t = T_{loc}$ , 2)  $t = 20 T_{loc}$ , 3)  $t = 400 T_{loc}$ . b) Registration time  $\Delta t = 50 T_{loc}$ ;  $\sigma^2 = 0.111 m_0$ .

- E. Hanamura, in: *Physics of Highly Excited States in Solids*, ed. M. Ueta and Y. Nishika, Springer-Verlag, 1976, p. 304.
- <sup>3</sup>I. K. Rebane, I. A. Tehver, and V. V. Hizhnyakov, in: *The Theory of Light Scattering in Solids*, eds. V. M. Agranovich and J. L. Birman, Nauka, 1976, p. 467.
- <sup>4</sup>I. Yu. Tekhver and V. V. Knizhnyakov, *Zh. Eksp. Teor. Fiz.* **69**, 599 (1975) [*Sov. Phys. JETP* **42**, 305 (1975)].
- <sup>5</sup>D. L. Rousseau and P. F. Williams, *J. Chem. Phys.* **64**, 3519 (1976); R. T. Williams, M. N. Kabler, W. Hayes, and J. P. Scott, *Phys. Rev. B* **14**, 725 (1976); R. M. Hochstrasser, *Chem. Phys.* **6**, 155 (1974); F. De Martin, G. Guiliani, and P. Mataloni, *Phys. Rev. Lett.* **35**, 1464 (1975).
- <sup>6</sup>A. P. Purga, *Tr. Inst. Fiz. Astron. Akad. Nauk Est. SSR* No. 25, 109 (1964).
- <sup>7</sup>I. Yu. Tekhver, Candidate's Dissertation, *Inst. Fiz. Astron. Est. SSR, Tartu*, 1968.
- <sup>8</sup>V. V. Knizhnyakov and I. K. Rebane, *Izv. Akad. Nauk SSSR Ser. Fiz.-Mat.* **26**, 260 (1977).
- <sup>9</sup>Y. Toyozawa, A. Kotani, and A. Sumi, *J. Phys. Soc. Jpn.* **42**, 1495 (1977).
- <sup>10</sup>S. Mukamel and J. Jortner, *J. Chem. Phys.* **62**, 3609 (1975); S. Mukamel, A. Ben-Reuven, and J. Jortner, *Phys. Rev. A* **12**, 947 (1975); *J. Chem. Phys.* **64**, 39 (1976).
- <sup>11</sup>T. Takagahara, Doctoral Thesis, University of Tokyo, 1977.
- <sup>12</sup>R. J. Glauber, *Phys. Rev.* **130**, 2529 (1963).
- <sup>13</sup>F. J. Lynch, R. E. Holland, and M. Hamermesh, *Phys. Rev.* **120**, 513 (1960).
- <sup>14</sup>C. Bloch and C. de Dominicis, *Nucl. Phys.* **7**, 459 (1958).
- <sup>15</sup>D. Dexter, *Phys. Status Solidi B* **51**, 571 (1972).

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## Charge transfer between hydrogen atoms and the nuclei of multicharged ions with allowance for the degeneracy of the final states

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The cross sections,  $\sigma$ , for charge transfer between hydrogen and the nuclei of multicharged ions are computed with allowance for the degeneracy of the final hydrogen-like ion states. Allowance for the transitions, induced by the rotation of the internuclear axis, between these states leads to a qualitative change in the  $v$  dependence of  $\sigma$  at low  $v$  (a power-law decrease of the cross sections instead of the exponential decrease found in the Landau-Zener model), as well as to a significant increase in the cross section at the peak. The solution is based on the use of the symmetry properties of the hydrogen atom; this approach makes it possible to take account of the rotation effects in a wide range of velocities. Concrete computations are carried out for the ions  $C^{+6}$  and  $O^{+8}$ .

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### §1. INTRODUCTION

Calculations of the cross sections for charge transfer between neutral hydrogen and multicharged ions are of considerable interest from both the practical and methodological points of view. The practical importance of this problem is due to its connection with the problems of high-temperature-plasma heating and diagnostics. At the same time, charge transfer between hydrogen and nuclei is the simplest type of process in which a large number of degenerate states participate, a process which is of general physical interest (see below).

Of the number of papers devoted to this problem let us note Gershtein's paper,<sup>[1]</sup> in which charge transfer between mesic hydrogen atoms and ions is computed in the Landau-Zener model. Charge transfer between a hydrogen-like ion and its nucleus has been considered by Smirnov.<sup>[2]</sup> The distinctive feature of hydrogen-like systems stems from the presence of the additional symmetry connected with the separability in the field of the two-Coulomb centers of the variables in elliptic coordi-

nates.<sup>[3]</sup> This fact was also used recently by Olson and Salop,<sup>[4,5]</sup> who undertook charge-transfer cross-section calculations within the framework of the Landau-Zener model with allowance for numerical data<sup>[6]</sup> for the electronic terms of the molecular ion  $(HZ)^{+Z}$ , composed of hydrogen, H, and the nucleus of a multicharged ion,  $X^{+Z}$ , with charge  $Z$ .

In Ref. 7, to compute the charge-transfer cross sections, Presnyakov and Ulantsev use the Landau-Zener formula for low speeds together with the Vainshtein-Presnyakov-Sobel'man formula,<sup>[8]</sup> which allows us to follow the transition to the region of high speeds of the charge-exchanging particles. An important distinctive feature of Presnyakov and Ulantsev's paper<sup>[7]</sup> is the description of the transition from the Landau-Zener model to the Brinkman-Kramers model,<sup>[9]</sup> which is valid for fast collisions.

In Ref. 10, Chibisov uses the concept of the decay of the initial "neutral atom+nucleus" term into the continuum of the final "proton+level system of multicharged ion" states. An advantage of the method is its simplicity