Spectral distribution of resonant localized impurity vibrations at finite temperatures

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The spectrum of local and quasilocal vibrations of impurities is studied in the case where the frequency of local vibrations and the electron transition frequency are in resonance. The case of resonance in a system of three local vibration modes, two of which are high-frequency modes, is also considered. A system of linear equations governing the spectral distribution of local vibrations is obtained and analyzed. Such a system of equations converges rapidly (exponentially), which makes it possible to obtain the spectrum for an arbitrary ratio of the resonance interaction parameter to the broadening of the levels and at arbitrary temperatures. When the resonance splitting of the levels is much larger than their width, a fine structure of the spectrum may appear in a well-defined range of temperatures. An operator equation is derived which can be used to study the spectral distribution of arbitrary interacting local vibrations (including the symmetry-degenerate vibrations) provided the energies of several lowest levels of the system are found analytically or numerically.

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When the spectrum of the infrared absorption and the Raman scattering of light by impurity centers in a crystal is studied, the frequency of vibrations localized in the vicinity of an impurity (local or quasilocal vibrations) is sometimes close to the frequency of the impurity electron transition or to the combined frequency of other local vibrations.[1,2] The resonance interaction gives rise to a splitting of the levels of local vibrations which is analogous to the Fermi resonance.[3,4] The resonance splitting of local vibrations was studied by one of the present authors[5,6] at low temperatures. In particular, it has been shown that, when only the occupation of the first excited level of local vibrations is taken into account, additional fine structure lines can occur in the spectrum.

At higher temperatures, a large number of excited states participate in the formation of the spectrum and, therefore, the number of fine structure lines increases, different lines begin to overlap, and at high temperatures, a unique nearly continuous distribution of lines is created (in the classical limit, the fine structure disappears completely). Therefore, it is of interest to develop a unified theory which could describe the spectrum in a wide range of temperatures taking into account the fine structure and the broadening of individual lines.

A new method was proposed in refs. 7 and 8 for the microscopic description of the spectral distribution of an anharmonic oscillator interacting with a thermostat. This method is applicable in a wide temperature range and to a wide range of parameters of the system. We shall generalize the method of refs. 7 and 8 to arbitrary systems whose spectrum in the absence of interaction with the thermostat is known and represents a set of groups of levels such that the energy gap between individual groups is approximately constant and much larger than the separation of the lines within each group (for example, the levels of an oscillator which are interaction-split exhibit such a spectrum). The proposed method holds at arbitrary temperatures and for an arbitrary ratio of the relaxation linewidth to the separation of the levels within a group (provided the width is much smaller than the gap between the groups).

We shall study the spectral distribution of resonance local vibrations in the following cases: 1) The local vibration frequency is close to the energy of a transition in a two-level electron system; 2) the frequency of a local vibration is close to the sum of the frequencies of high-frequency and low-frequency local vibrations.

1. CORRELATION FUNCTIONS AND THE HAMILTONIAN OF THE SYSTEM

The form of the spectrum of the infrared absorption and of the Raman scattering in the approximation linear in the displacements of local vibrations is governed by the correlation function

$$Q_\varkappa(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle c_\varkappa(t)\,c_\varkappa(0)\rangle e^{i\omega t}dt$$

$$\approx\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty\langle a_\varkappa(t)\,a_\varkappa^+(0)\rangle e^{i\omega t}dt,\quad \omega\sim\omega_\varkappa;\ c_\varkappa=a_\varkappa+a_\varkappa^+. \tag{1}$$

Here, $a_\varkappa^+$, $a_\varkappa$ are the creation and annihilation operators of local vibrations $\varkappa$ with a frequency $\omega_\varkappa$. The second equality holds with the accuracy up to terms $\sim\Gamma_\varkappa/\omega_\varkappa$, where $\Gamma_\varkappa$ is the damping of local vibrations and $\Gamma_\varkappa\ll\omega_\varkappa$.

The Hamiltonian of the system under study is given by

$$H=H_0+H_1, \tag{2}$$

where the term H_0 describes the energy of resonant local excitations neglecting the interaction with the vibrations of the continuous spectrum of the crystal. When the local vibrations with $\varkappa=1$ are in resonance with a two-level electron system, the Hamiltonian H_0 has the form

$$H_0=\left(\omega_1 a_1^+a_1+\frac{1}{2}\omega_B\right)\hat{J}+\frac{1}{2}\omega_B\sigma_3+V(a_1^+\sigma^-+a_1\sigma^+), \tag{3}$$

where σ are the Pauli matrices. $\hat{J}$ is a unit matrix. ω_B is

the electron transition frequency. V is the resonance interaction parameter, and $|\omega_B - \omega_1|$, $|V| \ll \omega_1$.

When the resonance interaction of three local vibration modes takes place, the Hamiltonian H_0 is given by

$$H_0 = \tilde{H}_0 = \sum_{\varkappa=1,2,3} \omega_\varkappa a_\varkappa^+ a_\varkappa + \tilde{V}(a_1 a_2^+ a_3^+ + a_1^+ a_2 a_3). \tag{4}$$

We shall assume that $\omega_{1,2} \gg \omega_3$ and $|\omega_1 - \omega_2 - \omega_3|$, $|\tilde{V}| \ll \omega_3$. The nonresonance and higher-order terms with respect to the intrinsic anharmonicity of local vibrations are neglected in H_0 and $\tilde{H}_0$.

The Hamiltonian H_i describes the vibrations belonging to the continuous spectrum of the crystal and their interaction with local vibrations:

$$\left.\begin{aligned} H_1 &= H_0^{ph} + H_i; \quad H_0^{ph} = \sum_q \omega_q a_q^+ a_q; \\ H_i &= \frac{1}{2}\sum_{\varkappa q q_1} V_{\varkappa q q_1} c_\varkappa c_q c_{q_1} + \sum_{\varkappa\varkappa' q} V_{\varkappa\varkappa' q} c_\varkappa c_{\varkappa'} c_q + \sum_{\varkappa q q_1} V_{\varkappa\varkappa q q_1} a_\varkappa^+ a_\varkappa a_q^+ a_{q_1}, \end{aligned}\right\} \tag{5}$$

where a_q^+ and a_q are the creation and annihilation operators of vibrations belonging to the continuous spectrum of the crystal and having the wave vector q and the frequency ω_q.

The index $\varkappa$ may also label weakly coupled quasilocal vibrations. In this case, q labels the vibrations of an imperfect crystal from which an impurity has been removed. The Hamiltonian H_i should then be supplemented by the term

$$H_i' = \sum_{\varkappa q} V_{\varkappa q} c_\varkappa c_q. \tag{5a}$$

The parameters V_q which appear in H_i are assumed to be small so that the damping of local vibrations satisfies $\Gamma_\varkappa \ll \omega_\varkappa$ and $|d\Gamma_\varkappa/d\omega_\varkappa| \ll 1$. For simplicity, the intrinsic relaxation of electron states is neglected.

In the calculation of the correlation function $\langle R(t)Q(0)\rangle$, where R and Q are the operators of a subsystem under study, it is convenient to average first over the vibrations of the continuous spectrum and then over the states of the Hamiltonian H_0.

We shall now introduce the interaction representation by means of the operator $U(t) = \exp(iH_0t)\exp(-iHt)$. The correlation function $\langle R(t)Q(0)\rangle$ is given by

$$\left.\begin{aligned} \langle R(t)Q(0)\rangle &= \mathrm{Tr}_0\,[\exp(iH_0t)\,R\exp(-iH_0t)\,G_Q(t)]; \\ G_Q(t) &= Z^{-1}\,\mathrm{Tr}_{ph}[U(t)\,Q\exp(-\lambda H)\,U^{-1}(t)]; \\ Z &= \mathrm{Sp}_0\,\mathrm{Tr}_{ph}\exp(-\lambda H), \end{aligned}\right\} \tag{6}$$

where Tr_0 and Tr_{ph} are taken over the wave functions of H_0 and H_0^{ph}, $\lambda = T^{-1}$ ($k = \hbar = 1$).

It follows from Eq. (1) that the calculation of the line profile of the spectral distribution requires the knowledge of the correlation function at times $t \sim \Gamma_\varkappa^{-1}$. We can obtain this correlation function by the asymptotic method developed in refs. 7 and 8. Using this method, we can carry out the averaging over phonons, which yields an operator equation for the function $G_Q(t)$ which is given in the Appendix.

2. RESONANCE OF LOCAL VIBRATIONS WITH AN ELECTRON TRANSITION

The exact eigenvalues $\omega_j(n)$ and the eigenfunctions $|n)_j$ (j = 1, 2; n = 0, 1, 2, ...) of the Hamiltonian H_0 defined by Eq. (3), which describes the resonance interaction of local vibrations ($\varkappa = 1$) with an electron transition, are given by

$$\left.\begin{aligned} &\omega_j(n) = \omega_1 n + \frac{\delta}{2} - (-1)^j\Delta_n, \quad n \geqslant 1, \quad j = 1, 2; \quad \omega(0) = 0; \quad \delta = \omega_B - \omega_1; \\ &\Delta_n^2 = V^2 n + \frac{\delta^2}{4}; \end{aligned}\right\} \tag{7}$$

$$\left.\begin{aligned} &|n)_j = \begin{vmatrix} \alpha_j(n)\,|\,n-1\rangle \\ \beta_j(n)\,|\,n\rangle \end{vmatrix}, \quad n \geqslant 1; \quad |0) = \begin{vmatrix} 0 \\ |\,0\rangle \end{vmatrix}; \\ &\alpha_j(n) = \frac{V\sqrt{n}}{c_j(n)}, \quad \beta_j(n) = -\frac{(-1)^j\Delta_n + \delta/2}{c_j(n)}, \\ &c_j^2(n) = 2\Delta_n^2 + (-1)^j\delta\Delta_n. \end{aligned}\right\} \tag{8}$$

The structure of the energy spectrum defined by Eq. (7) is similar to the spectrum of an oscillator whose levels n (with the exception of the lowest level n = 0) are split in a doublet. The separation of the levels in a doublet satisfies the inequality $2\Delta_n \ll \omega_1, \omega_B$. The quantity $|n\rangle$ in Eq. (8) is the wave function of a harmonic vibration of type 1 in the second-quantization representation.

The nonzero matrix elements of the operators corresponding to the oscillator of type 1 between the wave functions defined by Eq. (8) are given by

$$\left.\begin{aligned} A_{jk}(n) &= {}_j(n\,|\,a_1\,|\,n+1)_k \\ &= \alpha_j(n)\,\alpha_k(n+1)\sqrt{n} + \beta_j(n)\,\beta_k(n+1)\sqrt{n+1}; \\ N_{jk}(n) &= {}_j(n\,|\,a_1^+a_1\,|\,n)_k = n\delta_{jk} - \alpha_j(n)\,\alpha_k(n); \quad j, k = 1, 2. \end{aligned}\right\} \tag{9}$$

Without loss of generality, we can assume in Eq. (9) and in our further discussion that $n \geq 0$. We shall set $\alpha_{1,2}(0) = \beta_1(0) = 0$; $\beta_2(0) = -1$.

We shall consider the correlation function of local vibration $Q_1(\omega)$ defined by Eq. (1). Setting $R = a_1$, $Q = a_1^+$, and taking Tr_0 in Eq. (6) over the wave functions defined by Eq. (8), we obtain

$$Q_1(\omega) = \frac{1}{\pi}\,\mathrm{Re}\sum_{n=0}^{\infty}\sum_{j,\,k=1,2} A_{kj}(n)\,\varphi_{jk}(n,\,\Omega), \quad \Omega = \omega - \omega_1. \tag{10}$$

$$\varphi_{jk}(n,\,\Omega) = \int_0^\infty dt\;{}_j(n+1\,|\,G_{a_1^+}(t)\,|\,n)_k$$

$$\times \exp\{it[\Omega - (-1)^k\Delta_n + (-1)^j\Delta_{n+1}]\}. \tag{11}$$

Equation (10) represents the spectral distribution of local vibrations, which consists of a set of partial spectra $\varphi_{jk}(n, \Omega)$ corresponding to transition between the states $|n)_k \to |n+1)_j$. Since the frequencies of these transitions are close to one another, they are mutually coupled because of the relaxation effects and, therefore, all these transitions contribute to the function $\mathrm{Re}\,\varphi_{jk}(n, \Omega)$.

Using the operator equation (A.1) and Eq. (A.4), we obtain the following set of linear equations for the function $\varphi_{jk}(n, \Omega)$:

$$\left.\begin{aligned} &\sum_{j_1,\,k_1=1,2}\{-i[\Omega + (-1)^j\Delta_{n+1} - (-1)^k\Delta_n]\delta_{jj_1}\delta_{kk_1} \\ &\qquad + D_{jkj_1k_1}(n)\}\,\varphi_{j_1k_1}(n,\,\Omega) \\ &+\sum_{l=\pm1}\sum_{j_1,\,k_1=1,2} F_{jkj_1k_1}(n,\,l)\,\varphi_{j_1k_1}(n+l,\,\Omega) = A_{kj}(n)\,\frac{\exp(-\lambda\omega_1 n)}{2\bar{n}_1+1}; \\ &\bar{n}_1 = [\exp(\lambda\omega_1) - 1]^{-1}, \end{aligned}\right\} \tag{12}$$

where

$$
\left.\begin{aligned}
&D_{jkj_1k_1}(n)=\Gamma_{jj_1}(n+1)\,\delta_{kk_1}+\Gamma_{k_1k}(n)\,\delta_{jj_1}\\
&+\Gamma_{M1}\sum_{k_2=1,2}[N_{jk_2}(n+1)\,N_{k_2j_1}(n+1)\,\delta_{kk_1}\\
&+N_{k_1k_2}(n)\,N_{k_2k}(n)\,\delta_{jj_1}-N_{jj_1}(n+1)\,N_{k_1k}(n)];\\
&\Gamma_{M1}=\pi\sum_{qq'}V^2_{11qq'}\bar{n}_q(\bar{n}_q+1)\,\delta(\omega_q-\omega_{q'});\\
&\Gamma_{jj_1}(n)=(2\bar{n}_1+1)\,\Gamma_1N_{jj_1}(n)+\Gamma_1\bar{n}_1\delta_{jj_1};\\
&F_{jkj_1k_1}(n,1)=-2(\bar{n}_1+1)\,\Gamma_1A_{jj_1}(n+1)\,A_{kk_1}(n);\\
&F_{jkj_1k_1}(n,-1)=-2\Gamma_1\bar{n}_1A_{j_1j}(n)\,A_{k_1k}(n-1).
\end{aligned}\right\}\qquad(13)
$$

As in H_0, we have omitted in Eqs. (12) and (13) all the terms related to the nonequidistant distribution of the local vibration levels which result in a dependence of the resonance detuning on the oscillator level. When the deviation from an equidistant distribution is much smaller than the electron–vibration interaction constant V, such terms can be neglected.

We shall now discuss the physical origin of the terms in Eq. (12). The diagonal terms $D_{jkjk}(n)$ describe the intrinsic line broadening $\omega_{jk}(n, \Omega)$; $\Gamma_{jj}(n)$ is the reciprocal lifetime of the state $|n\rangle_j$, and the terms containing Γ_{M_1} correspond to the modulation line broadening. The nondiagonal terms $D_{jkj_1k_1}(n)$ describe the interference of different transitions between the n-th and (n + 1)-th levels of the doublets. The terms $F_{jkj_1k_1}(n, l)$ couple the transitions $|n\rangle \to |n+1\rangle$ with the transitions between the levels of neighboring doublets $|n-1\rangle \to |n\rangle$ and $|n+1\rangle \to |n+2\rangle$.

For large n, the right-hand side of Eq. (12) is exponentially small [proportional to $\exp(-\lambda\omega_1 n)$], which represents an important special feature of the system (12). Therefore, we can truncate the system (12). The resulting finite system of linear equations can be easily resolved on a computer for arbitrary values of the parameters in a wide range of temperatures. Therefore, the system (12) yields a complete solution of the problem of the spectrum of an oscillator in resonance with the electron transitions and interacting with a thermostat (in the approximation $\Gamma_1/\omega_1, |V|/\omega_1, |\delta|/\omega_1, |d\Gamma_1/d\omega_1|, \bar{n}_1\Gamma_1/T, \bar{n}_1|V|/T \ll 1$).

An analytic solution of the system (12) can be obtained in several limiting cases. For $\omega_1/T \gg 1$, it is sufficient to consider in Eq. (12) only two equations with n = 0 describing the interference of the transitions $|0\rangle \to |1\rangle_1$ and $|0\rangle \to |1\rangle_2$. Therefore, we obtain

$$
Q_1(\omega)=\frac{1}{\pi}\,\frac{\Gamma(\Omega-\delta)^2}{[\Omega(\Omega-\delta)-V^2]^2+\Gamma^2(\Omega-\delta)^2},\qquad \Gamma=\Gamma_1+\Gamma_{M1}.\qquad(13)
$$

The distribution (14) is identical with Eq. (8) of ref. 5 for $\bar{n}_1 = 0$. For V = 0, it describes a Lorentzian curve with a half-width 2Γ. For $V \neq 0$, the curve (14) exhibits two maxima of equal height $(\pi\Gamma)^{-1}$ which are separated by a distance $2\sqrt{V^2+\delta^2/4}$. For $|\delta|, |V| \ll \Gamma$, the dependence in the minimum between the two maxima is described by

$$
\frac{1}{\pi\Gamma}\left(1-\frac{V^4/\Gamma^2}{V^4/\Gamma^2+(\Omega-\delta)^2}\right),\qquad(14)
$$

i.e., the minimum is Lorentzian with a half-width $2V^2/\Gamma$. The width of the minimum is an increasing function of $|\delta|/V$ and, for $|\delta| \gg |V|$, Γ, the spectrum exhibits two nearly Lorentzian peaks with very different half-widths and intensities (see ref. 5). For intermediate values of the parameters, the line profile $Q_1(\omega)$ is shown in Fig. 1. For $|V| \gg |\delta|$, Γ, Eq. (14) represents two nearly symmetric (with the accuracy up to terms δ/V) Lorentzian curves of half-width Γ.

When the separation of the levels of a doublet is much greater than the width of the levels,

$$
|V|\,|\sqrt{n+1}-\sqrt{n}\,|\gg|\delta|,\quad (n+1)(2\bar{n}_1+1)\,\Gamma_1,\ \Gamma_{M1},\qquad(15)
$$

the system (12) has an analytic solution at arbitrary temperatures. The solution is given by

$$
\left.\begin{aligned}
&Q_1(\omega)=\frac{1}{\pi}\sum_{n=0}^{\infty}\sum_{j,\,k=1,2}\psi_{jk}(n,\Omega)\,[\sqrt{n}+(-1)^{j-k}\sqrt{n+1}\,]^2\\
&\times\exp(-\lambda\omega_1 n)\,[4(2\bar{n}_1+1)]^{-1};\\
&\psi_{jk}(n,\Omega)=\frac{\Gamma^0_{jk}(n)}{[\Gamma^0_{jk}(n)]^2+\Omega^2_{jk}(n)};\\
&\Omega_{jk}(n)=\omega-\omega_j(n+1)+\omega_k(n)\\
&=\Omega+(-1)^j|V|\sqrt{n+1}-(-1)^k|V|\sqrt{n};\\
&\Gamma^0_{jk}(n)=2[n(2\bar{n}_1+1)+\bar{n}_1]\,\Gamma_1+\frac{3}{2}\Gamma_{M1},\quad n\geqslant 1;\\
&\psi_{11}(0,\Omega)=\psi_{21}(0,\Omega)=0;\quad \Gamma^0_{22}(0)=\Gamma^0_{12}(0)\\
&=\frac{1}{2}(6\bar{n}_1+1)\,\Gamma_1+\frac{1}{2}\Gamma_{M1}.
\end{aligned}\right\}\qquad(16)
$$

It follows from Eq. (16) that, in addition to a doublet

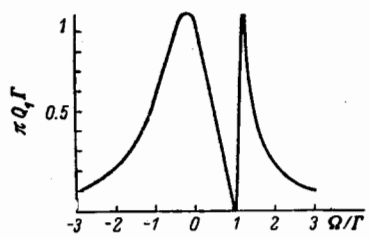

Fig. 1. Spectral distribution of local (quasilocal) vibrations which are in resonance with an electron transition for T = 0, δ/Γ = 1, V/Γ = 0.5.

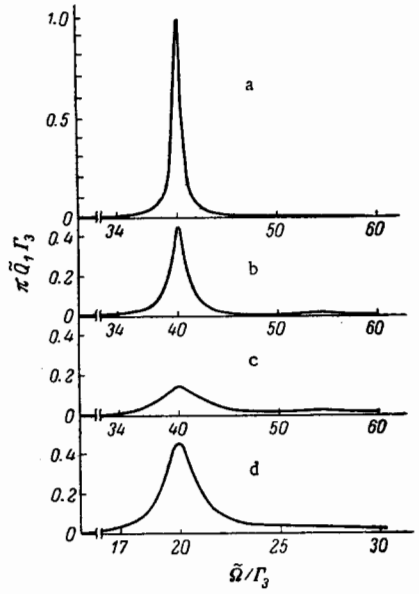

Fig. 2. Spectral distribution of $\tilde{Q}_1(\omega)$ for $\tilde{\Gamma}_{kj}(n) = \tilde{\delta} = \Gamma_{123} = 0$. a–c) $|\tilde{V}|/\Gamma_3 = 40, \omega_3/T = \infty, 2, 1$; d) $|\tilde{V}|/\Gamma_3 = 20, \omega_3/T = 2$. Only halves of the lines, which are symmetric with respect to Ω = 0, are shown.

with frequencies $\omega_1 \pm |V|$, which occurs for $\bar{n}_1 = 0$, additional quadruplets of lines occur at finite temperatures. The frequencies of such lines $\omega_j(n+1) - \omega_k(n)$ correspond to the transitions $|n)_k \to |n+1)_j$. Their intensity is proportional to $\exp(-\lambda\omega_1 n)$. The lines in question are Lorentzian with half-widths $2\Gamma^0_{jk}(n)$. When the modulation broadening is neglected, these widths are identical with the widths evaluated from the Weisskopf–Wigner theory.

The terms proportional to the dipole moment of the electron transition may also make an important contribution to the absorption cross section and the scattering of light by the system consisting of an electron and an oscillator. Such a contribution is described by the correlation function

$$Q_e(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty \langle \sigma^-(t)\, \sigma^+(0) \rangle\, e^{i\omega t} dt. \tag{17}$$

Using the wave functions defined by Eq. (8), we can write $Q_e(\omega)$ in the following form:

$$\left.\begin{aligned} Q_e(\omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{n=0}^{\infty} \sum_{j,k=1,2} \sigma_{kj}(n)\, \varphi^e_{jk}(n, \Omega_e), \quad \Omega_e = \omega - \omega_B; \\ \sigma_{kj}(n) &= {}_k(n|\sigma^-|n+1)_j = \beta_k(n)\, \alpha_j(n+1). \end{aligned}\right\} \tag{18}$$

The functions $\varphi^e_{jk}(n, \Omega_e)$ satisfy Eq. (12), in which the term $A_{kj}(n)$ which appears on the right-hand side should be replaced by $\sigma_{kj}(n)$.

When the condition of existence of a fine structure [Eq. (15)] is satisfied, the distribution $Q_e(\omega)$ is similar to that defined by Eq. (16). However, for $|V| \lesssim \Gamma_1, \Gamma_{M_1}$, the line profiles of the electron $Q_e(\omega)$ and of the vibrational $Q_1(\omega)$ transitions and also their widths can differ considerably (see ref. 5).

3. RESONANCE OF A SYSTEM OF THREE LOCAL VIBRATIONS

We shall consider a system of three local vibrations, two of which ($\varkappa = 1, 2$) are high-frequency vibrations and the third ($\varkappa = 3$) is a low-frequency vibration: $\omega_{1,2} \gg \omega_3$, where $\omega_1 - \omega_2 = \omega_3 + \tilde{\delta}$, and $|\tilde{\delta}| \ll \omega_3$. The resonance interaction in such a system is described by the Hamiltonian (4). We shall consider low temperatures $T \ll \omega_{1,2}$, when the occupation numbers of the vibrations 1 and 2 are effectively equal to zero (the occupation numbers of the vibration 3 are unbounded) and we shall study the absorption cross section corresponding to the scattering of light at frequencies $\omega \sim \omega_{1,2}$. In this case, the calculation of the averages in Eqs. (1) and (6) requires only the knowledge of the wave functions and eigenvalues of the Hamiltonian $\tilde{H}_0$ corresponding to the excitation of only one of the high-frequency vibrations

$$\left.\begin{aligned} |n)_0 &= |0, 0, n\rangle; \quad \omega_0(n) = \omega_3 n; \quad n \equiv n_3; \\ |n)_j &= \tilde{\alpha}_j(n)\,|1, 0, n-1\rangle + \tilde{\beta}_j(n)\,|0, 1, n\rangle, \quad j = 1, 2; \\ \omega_j(n) &= \omega_3 n + \omega_2 + \tilde{\delta}/2 - (-1)^j \tilde{\Delta}_n, \quad n \geqslant 1; \quad \omega_j(0) = \omega_2. \end{aligned}\right\} \tag{19}$$

where $|n_1, n_2, n_3\rangle$ is the wave function of noninteracting oscillators 1, 2, and 3 in the second-quantization representation. The parameters $\tilde{\alpha}_j(n)$, $\tilde{\beta}_j(n)$, and $\tilde{\Delta}_n$ are defined by Eqs. (7) and (8), in which V and δ should be replaced by $\tilde{V}$ and $\tilde{\delta}$ and $\tilde{\alpha}_j(0) = \tilde{\beta}_1(0) = 0$, $\tilde{\beta}_2(0) = -1$.

In the state $|n)_0$, neither of the high-frequency vibrations is excited and only one of them is excited in the state $|n)_{1,2}$. Using the representation defined by Eq. (6), we can write the spectral distribution of the correlation function $\langle a_1(t) a_1^+(0)\rangle - \tilde{Q}_1(\omega)$ at frequencies $\omega \approx \omega_1$ in the following form:

$$\left.\begin{aligned} \tilde{Q}_1(\omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{n=0}^{\infty} \sum_{k=1,2} A_k(n)\, \varphi_k(n, \tilde{\Omega}); \quad \tilde{\Omega} = \omega - \omega_1 + \delta/2; \\ \varphi_k(n, \tilde{\Omega}) &= \int_0^\infty dt\, {}_k(n+1|G_{a_1^+}(t)|n)_0 \exp\{it[\tilde{\Omega} + (-1)^k \tilde{\Delta}_{n+1}]\}; \\ A_k(n) &= \langle 1, 0, n|n+1)_k = \tilde{\alpha}_k(n+1). \end{aligned}\right\} \tag{20}$$

It follows from Eqs. (A.1)–(A.4) and (19) that the system of equations for the functions $\varphi_k(n, \tilde{\Omega})$ is given by

$$\begin{aligned} &\sum_{j=1,2} \{-i[\tilde{\Omega} + (-1)^k \tilde{\Delta}_{n+1}]\, \delta_{kj} + D_{kj}(n)\}\, \varphi_j(n, \tilde{\Omega}) \\ &+ \sum_{l=\pm 1} \sum_{j=1,2} F_{kj}(n, l)\, \varphi_j(n+l, \tilde{\Omega}) = (\bar{n}_3 + 1)^{-1} \exp(-\lambda\omega_3 n)\, \tilde{\alpha}_k(n+1), \end{aligned} \tag{21}$$

where

$$\left.\begin{aligned} D_{kj}(n) &= (2\bar{n}_3 + 1)\,\Gamma_3[\delta_{kj} n + \tilde{N}_{kj}(n+1)] + 2\Gamma_3 \bar{n}_3 \delta_{kj} \\ &+ \Gamma_{123} \sqrt{n+1}\,(2\bar{n}_3 + 1)[(\tilde{\alpha}_k(n+1)\,\tilde{\beta}_j(n \\ &+ 1) + \tilde{\alpha}_j(n+1)\,\tilde{\beta}_k(n+1)] + \tilde{\Gamma}_{kj}(n); \\ F_{kj}(n, 1) &= -2(\bar{n}_3 + 1)\sqrt{n+1}\,[\Gamma_3 \tilde{A}_{kj}(n \\ &+ 1) + \Gamma_{123} \tilde{\beta}_k(n+1)\,\tilde{\alpha}_j(n+2)]; \\ F_{kj}(n, -1) &= -2\bar{n}_3 \sqrt{n}\,[\Gamma_3 \tilde{A}_{jk}(n) + \Gamma_{123} \tilde{\alpha}_k(n+1)\,\tilde{\beta}_j(n)]; \end{aligned}\right\} \tag{22}$$

$\tilde{N}_{kj}(n)$ and $\tilde{A}_{kj}(n)$ are defined by Eq. (9), in which α_j and β_j should be replaced by $\tilde{\alpha}_j$ and $\tilde{\beta}_j$; $\tilde{\Gamma}_{kj}(n)$ describes the modulation broadening of all the local vibration branches considered and also the broadening of the vibrations 1 and 2 related to their finite lifetimes.

As in the case of Eqs. (12) and (13) for the spectrum of a resonance electron vibrational system, the diagonal terms $D_{kk}(n)$ govern the intrinsic broadening of the line $\varphi_k(n, \tilde{\Omega})$ corresponding to the transition $|n)_0 \to |n+1)_k$. The nondiagonal terms $D_{kj}(n)$ describe the interference of the lines with identical n and $F_{kj}(n, \pm 1)$ couple the lines with different n.

At low temperatures ($\omega_3/T \gg 1$), only the term $\varphi_k(n = 0, \tilde{\Omega})$ should be considered in Eq. (21). Therefore, we obtain

$$\begin{aligned} \tilde{Q}_1(\omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{k=1,2} \tilde{\alpha}_k(1)\, \varphi_k(0, \tilde{\Omega}) = \frac{1}{\pi} \\ &\times \frac{(\tilde{\Omega} + \delta/2)^2 \tilde{\Gamma}_1 + (\tilde{\Omega} + \delta/2)\, 2\tilde{V}^2 \Gamma_{123} + \tilde{\Gamma}_3 [\tilde{\Gamma}_3 \tilde{\Gamma}_1 - \Gamma^2_{123} + \tilde{V}^2]}{[\tilde{\Gamma}_3 \tilde{\Gamma}_1 - \Gamma^2_{123} - \tilde{\Omega}^2 + \tilde{\Delta}^2_n]^2 + [(\tilde{\Omega} + \delta/2)\,\tilde{\Gamma}_1 + (\tilde{\Omega} - \delta/2)\,\tilde{\Gamma}_3 + 2\tilde{V}\Gamma_{123}]^2}; \\ \tilde{\Gamma}_1 &= \Gamma_1 + \Gamma_{12} + \Gamma_{M_1}; \quad \tilde{\Gamma}_3 = \Gamma_3 + \Gamma_2 + \Gamma_{M_2}; \\ \Gamma_{M_1} &= \pi \sum_{qq'} V^2_{11qq'} \bar{n}_q (\bar{n}_q + 1)\, \delta(\omega_q - \omega_{q'}); \\ \Gamma_{M_2} &= \pi \sum_{qq'} (V_{22qq'} - V_{33qq'})^2\, \bar{n}_q (\bar{n}_q + 1)\, \delta(\omega_q - \omega_{q'}). \end{aligned} \tag{23}$$

The necessary condition for the quantity $\tilde{Q}_1(\omega)$ to be positive is the inequality $\tilde{\Gamma}_1 \tilde{\Gamma}_3 \geq \Gamma^2_{123}$. The latter inequality is always satisfied because of the Cauchy inequality, which holds because Γ_{123} corresponds to the interference of the decays resulting in a broadening of Γ_{12} and Γ_3 (the equality can occur only for $\Gamma_1 = \Gamma_2 = \Gamma_{M_{1,2}} = 0$).

Equation (23) simplifies in the following limiting cases:

a) for $V = \Gamma_{123} = 0$, Eq. (23) describes a Lorentzian curve with a half-width $2\tilde{\Gamma}_1$; b) for $\tilde{\Gamma}_1, \Gamma_{123} \ll \tilde{\Delta}_1, \Gamma_3$, we obtain

$$\tilde{Q}_1(\omega) = \frac{1}{\pi} \frac{\tilde{V}^2 \tilde{\Gamma}_3}{(\tilde{\Omega}^2 - \tilde{\Delta}_1^2)^2 + \tilde{\Gamma}_3^2 (\tilde{\Omega} - \tilde{\delta}/2)^2}; \tag{24}$$

c) $|\tilde{\delta}| \ll |\tilde{V}| \ll \tilde{\Gamma}_3$, the distribution defined by Eq. (24) is a Lorentzian curve with a half-width $2\tilde{V}^2/\Gamma_3$; d) for $|\tilde{V}| \gg |\tilde{\delta}|$, $\tilde{\Gamma}_1, \tilde{\Gamma}_3$, Eq. (23) describes two Lorentzian curves with maxima at $\tilde{\Omega} = \pm|\tilde{V}|$ and of half-width $\tilde{\Gamma}_1 + \tilde{\Gamma}_3 \pm 2\tilde{\Gamma}_{123}\tilde{V}/|\tilde{V}|$ (it should be noted that the terms Γ_{123} result in different half-widths of the two maxima).

If the following condition is satisfied for several $n = 0, 1, 2, \ldots$:

$$|\tilde{V}|(\sqrt{n+1} - \sqrt{n}) \gg |D_{kj}(n)|, \quad |F_{kj}(n, l)|, |\delta|, \tag{25}$$

the spectrum of $\tilde{Q}_1(\omega)$ exhibits at $T \sim \hbar\omega_3$ not only the two principal maxima located at $\tilde{\Omega} = \pm|\tilde{V}|$ but also additional lines and $\tilde{Q}_1(\omega)$ is described by the following asymptotic equation:

$$\left.\begin{aligned} \tilde{Q}_1(\omega) &= \frac{1}{\pi} \sum_{n=0}^{\infty} \sum_{k=1,2} \psi_k(n, \tilde{\Omega}) \exp(-\lambda\omega_3 n)/2(\bar{n}_3 + 1); \\ \psi_k(n, \tilde{\Omega}) &= \frac{\gamma_k(n)}{\gamma_k^2(n) + \Omega_k^2(n)}; \quad \Omega_k(n) = \tilde{\Omega} + (-1)^k |\tilde{V}| \sqrt{n+1}; \\ \gamma_k(n) &= \frac{1}{2}[\Gamma_1 + \Gamma_2 + \Gamma_{M1} + \Gamma_{M2} + \Gamma_{12}(2\bar{n}_3 + 1)] \\ &+ \Gamma_3\left[2n(2\bar{n}_3 + 1) + \frac{1}{2} + 3\bar{n}_3\right] + \frac{\tilde{V}}{|\tilde{V}|}(-1)^{k-1}\Gamma_{123}(2\bar{n}_3 + 1)\sqrt{n+1}. \end{aligned}\right\} \tag{26}$$

It follows from Eq. (26) that each state of the oscillator $\varkappa = 3$ corresponds to two lines whose intensity is a decreasing function of n_3, the relevant dependence being $\exp(-\lambda\omega_3 n_3)$. The separation of the lines with a given k decreases as $\sqrt{n_3+1} - \sqrt{n_3}$ and it follows from Eq. (26) that the half-widths of the lines $2\gamma_k(n_3)$ are proportional to n_3. Therefore, the condition (25) is not satisfied for lines with large n_3 and the fine structure disappears in the wings of $\tilde{Q}_1(\omega)$. Since $\gamma_k(n)$ is a rapidly increasing function of temperature, the condition (25) ceases to be satisfied at high temperatures and, for $T/\omega_3 > |\tilde{V}|/\Gamma_3$, the structure of $\tilde{Q}_1(\omega)$ disappears.

Figure 2 shows the distribution $\tilde{Q}_1(\omega)$ obtained as a result of the numerical solution of the system (21) in the case when the broadening is due only to the decay of the vibration 3 and $\tilde{\delta} = 0$. The curves **a–c** show the temperature dependence of $\tilde{Q}_1(\omega)$. The additional lines (with $n \geq 1$) are not resolved in curve d, where $|\tilde{V}|/\Gamma_3$ is half the value for the first three curves. It follows from Fig. 2 that the additional lines have only a small amplitude. For $|\tilde{V}|/\Gamma_3 \to \infty$, the maximum amplitude of the line with $n = 1$ is $\sim 0.017/\pi\Gamma_3$ and is obtained for $\omega_3/T \approx 1.4$.

The nonlinear components of the polarizability of the system[1,2,6] may also make important contribution to the absorption cross section or to the Raman scattering of light at frequencies close to ω_1. In this case, it is necessary to evaluate the correlation function $Q_\xi(t) = \langle[a_1(t) + a_2(t)a_3(t)\xi] \cdot [a_1^+(0) + a_2^+(0)a_3^+(0)\xi]\rangle$, where the parameter ξ governs the relative contribution of the nonlinear polarizability. The equation for $Q_\xi(\omega)$ is identical with Eq. (20) for $\tilde{Q}_1(\omega)$ provided $\tilde{\alpha}_k(n+1)$ in the expression for $\tilde{A}_k(n)$ which appears in Eq. (20) and on the right-hand side of the system (21) is replaced by $\tilde{\alpha}_k(n+1) + \xi\tilde{\beta}_k(n+1)\sqrt{n+1}$. It should be noted that, when the spectrum exhibits a fine structure, the intensity of the additional lines contains a coefficient $[1 - (-1)^k(\tilde{V}/|\tilde{V}|)\xi\sqrt{n+1}]^2$, which enhances the amplitude of some of the lines.

At low temperatures, $T \ll \omega_3$, the spectrum of resonance local vibrations contains a single Lorentzian peak in the vicinity of the frequency ω_2. When the temperature is raised and the condition (25) is satisfied, additional doublet lines can appear in the neighborhood of such a peak at frequencies $\omega_2 \pm |\tilde{V}|\sqrt{n}$. It should be noted that, at $T \ll \omega_{1,2}$, the fine structure and modulation broadening due to the resonance interaction with the vibrations 1, 2 do not occur in the neighborhood of the frequency ω_3.

4. CONCLUSIONS

The systems of linear equations (12) and (21) describe the spectrum of local vibrations in the case of a resonance of an oscillator with an electron transition and a resonance of high-frequency local vibrations with a low-frequency local vibration in a wide range of temperatures and for an arbitrary relationship between the broadening and resonance interaction parameters. In general, the spectra obtained are rather complex and it is difficult to deduce the theoretical parameters from the experimental curves. However, the problem simplifies considerably when the resonance splitting of the levels of the system under study is much greater than their width. At low temperatures, the spectra then exhibit two peaks (such peaks were reported, for example, in refs. 1 and 2). At higher temperatures, the spectra may exhibit an additional fine structure consisting of lines whose separation (similarly to the separation of the principal lines) is of the order of the resonance interaction constant. The observation of such lines would be of interest, especially since it would confirm the interpretation of low-temperature spectra. It should be noted that a fine structure can exist only in a limited temperature range since, at high temperatures, the individual lines overlap and a single broadened spectral distribution arises.

The thermal smearing can be avoided if the fine structure of the spectrum is studied at low temperatures and the resonant subsystem is kept in a nonequilibrium state (the spectrum can be calculated by the method of ref. 9 and from the results of the present paper).

An investigation of the absorption (scattering) of light at higher harmonics of local vibrations could yield additional information about the energy spectrum of the system since the resonance splitting is proportional to $\sqrt{n}$ (ref. 10), i.e., it increases as a function of the number of the harmonics.

Apart from the fine structure, the spectral distribution of resonant systems exhibits curves with a narrow minimum [see ref. 5 and also Eq. (14)]. For example, when the width of the electron levels is much smaller than the width of the resonant local vibration levels, the minimum in the spectrum of local vibrations can be studied either by the inelastic neutron scattering method or by optical methods (when the electron transition is forbidden).

We have studied above the spectral distribution for systems whose energy spectrum in the absence of relaxation can be obtained analytically. However, the present

method is applicable even to more complex oscillator systems. This is due to the fact that the free term in Eqs. (12) and (21) and in similar equations describing other systems decays exponentially as a function of the level n [as $\exp(-\omega_\varkappa n/T)$], which makes it possible to truncate the system of equations and consider only several excited states whose energies can be obtained numerically. The degenerate local and quasilocal vibrations of centers with a high symmetry represent an example of such systems. The anharmonicity of such systems may give rise to a splitting of the excited levels.[11] The system of three resonant local vibrations with frequencies of the same order of magnitude represents another example.[1]

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APPENDIX

Using the chronological ordering, we can eliminate the phonon operators from the expression for $G_Q(t)$ in Eq. (6). Applying further the asymptotic method[7] at $t \gg \omega_\varkappa^{-1}(\omega_\varkappa \gg \Gamma_\varkappa)$, we obtain the following equation:

$$\frac{\partial G_Q}{\partial t} = -\sum_x \Gamma_x \{(\bar{n}_x + 1)([\hat{n}_x, G_Q]_+ - 2a_x G_Q a_x^+) + \bar{n}_x [\hat{n}_x + 1, G_Q]_+ - 2a_x^+ G_Q a_x\} - \hat{\Gamma}_M G_Q + \hat{L} G_Q - i\sum_x P_x [\hat{n}_x, G_Q];$$

$$\bar{n}_x \equiv \bar{n}(\omega_x) = [\exp(\lambda\omega_x) - 1]^{-1}; \quad \hat{n}_x = a_x^+ a_x; \quad [R, Q]_+ = RQ + QR, \qquad (A.1)$$

where all the operators are taken at a time t.

The parameters of the damping due to a decay $\Gamma_\varkappa$ and a shift of local vibrations $P_\varkappa$ are quadratic functions of $V_{\varkappa q}$, $V_{\varkappa qq'}$; they are defined, for example, by Eqs. (9) and (20) of ref. 7. The term $\hat{\Gamma}_M G_Q$ in Eq. (A.1) is related to the fourth-order anharmonic terms in H_i and describes the modulation broadening of local vibrations[12]:

$$\left.\begin{aligned} \hat{\Gamma}_M G_Q = \pi \sum_{qq'} \bar{n}_q (\bar{n}_q + 1)\, \delta(\omega_q - \omega_{q'}) \{[\hat{a}^2_{qq'}, G_Q]_+ - 2\hat{a}_{qq'} G_Q \hat{a}_{qq'}\}, \\ \hat{a}_{qq'} = \sum_x V_{xxqq'} \hat{n}_x. \end{aligned}\right\} \qquad (A.2)$$

The operator $\hat{L}G_Q$ is due to terms containing $V_{\varkappa\varkappa' q}$ which appear in H_i and describes the renormalization of the frequencies of local vibrations and the broadening due to the effects with the participation of several local vibrations:

$$\begin{aligned} \hat{L}G_Q = &-i\sum_{xx'} V_{xx'} [\hat{n}_x \hat{n}_{x'}, G_Q] - iP_{123}[a_1^+ a_2 a_3 + a_1 a_2^+ a_3^+, G_Q] \\ &- \Gamma_{12}\{(\bar{n}_3 + 1)([\hat{n}_1(\hat{n}_2 + 1), G_Q]_+ - 2a_1 a_2^+ G_Q a_1^+ a_2) \\ &+ \bar{n}_3([(\hat{n}_1 + 1)\hat{n}_2, G_Q]_+ \\ &- 2a_1^+ a_2 G_Q a_1 a_2^+)\} - \Gamma_{123}\{(2\bar{n}_3 + 1)[a_1^+ a_2 a_3 + a_1 a_2^+ a_3^+, G_Q]_+ \\ &- 2(\bar{n}_3 + 1)(a_1 a_2^+ G_Q a_3^+ + a_3 G_Q a_1^+ a_2) - 2\bar{n}_3(a_1^+ a_2 G_Q a_3 + a_3^+ G_Q a_1 a_2^+)\}; \end{aligned}$$

$$\Gamma_{12} = \pi \sum_q V^2_{12q} \delta(\omega_3 - \omega_q);$$

$$i\Gamma_{123} + P_{123} = \sum_q V_{12q} V_{3q} \frac{2\omega_q}{(\omega_3 - i0)^2 - \omega_q^2}. \qquad (A.3)$$

The parameters $V_{\varkappa\varkappa'}$ and the renormalization of $P_\varkappa$ due to the terms $V_{\varkappa\varkappa' q}$ are given by Eq. (26) of ref. 7. We shall also assume that $2\omega_\varkappa$ does not lie in the continuous spectrum. The resonance of local vibrations with an electron transition is described only by the first term in Eq. (A.3). In the derivation of Eq. (A.1), we have retained the terms of the type Γt, Δt and neglected the corrections proportional to $\Gamma/\omega_\varkappa$, $\Gamma\lambda\bar{n}_\varkappa$, $\Delta/\omega_\varkappa$, $|d\Gamma/d\omega_\varkappa| \ll 1$ (Δ is the maximum gap between the levels belonging to a single group). Moreover, we have neglected the decay broadening due to transitions between the levels within each multiplet. On the other hand, the ratio Γ/Δ has been assumed to be arbitrary.

It follows from Eq. (6) that, when Q is a unit operator, $G_Q(t)$ represents the density matrix of a selected resonant system. It should be noted that the first term on the right-hand side of Eq. (A.1) has the same form as the right-hand side of the transport equation for the density matrix of a harmonic oscillator which was studied in ref. 13. However, the time dependence of the operators $a_\varkappa(t)$ in Eq. (A.1) is rather complex [it is not given by $\exp(-i\omega_\varkappa t)$]. Moreover, our consistent quantum-statistical derivation of Eq. (A.1) yields additional (compared with ref. 13) terms, which describe the renormalization of the spectrum, the modulation broadening, etc.

For $\bar{n}\Gamma/T \ll 1$, the initial condition to Eq. (A.1) has the form

$$G_Q(0) = Q\exp(-\lambda H_0)(\mathrm{Tr}\, e^{-\lambda H_0})^{-1}. \qquad (A.4)$$

We can write formally Eq. (A.1) in the following form:

$$\frac{\partial G_Q}{\partial t} = -\hat{\Gamma}(t) G_Q - i[\hat{P}(t), G_Q]. \qquad (A.5)$$

where $\hat{\Gamma}$ and $\hat{P}$ are Hermitian operators, evaluated (similarly to G_Q) in the interaction representation with the Hamiltonian H_0. The second term in Eq. (A.5) can be eliminated by the transformation to the interaction representation with the Hamiltonian $H_0 + \hat{P}(0)$. Therefore, the shift terms $\hat{P}$ in Eqs. (A.1) and (A.3) lead only to a renormalization of the corresponding parameters in H_0, which has been assumed to be carried out.

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