Excitation of a degenerate level + band system by radiation of varying frequency

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The ensemble-averaging method is used to consider the dynamics of resonance excitation, by radiation with linearly varying frequency, in a spectrally complex system of the degenerate level + band type. Asymptotic expressions are obtained for the populations. The action on the system by radiation with randomly varying frequency, and the influence of quantum fluctuations of the field, are also considered. The results are important for the understanding of processes that occur in complicated-structure spectral regions of polyatomic molecules under multiphoton-vibrational and vibronic excitation.

In the study of the action of intense radiation on polyatomic molecules it is necessary as a rule to take into account the possibility of populating a large number of different quantum states.[1] The reasons are the appreciable number of degrees of freedom that ensure a high level density, and the complicated stochastic character of the internal motion of the molecules, which permits dipole transitions even between states with greatly differing quantum numbers.

To understand the physical processes that occur in polyatomic molecules located in an intense field at resonance with their transitions, it is therefore necessary to have a clear idea of the rules of behavior of complicated multilevel quantum systems. This behavior can, of course, be described only "in the mean," i.e., one can find those features which are not sensitive to the microstructure of the spectrum. In this approach it is expedient to describe the system by a distribution function of its parameters.

Good results in problems of excitation of complicated systems were obtained by an approach based on the use of the Wigner distribution function[2] for the matrix elements of the dipole-moment operator. It described the "stepwise" excitation of a quasi-continuum,[3] excitation of multiphoton resonances in the presence of a fine structure,[4] the behavior of a spectrally complicated system in a bichromatic field,[5] collisional redistribution of the populations of strongly excited molecules,[6] and others. It is proposed to use this method in this paper to consider no less important a problem, that of the influence of the radiation-line broadening due to frequency beats on the effectiveness of resonance excitation in spectrally complicated systems.

As applied to excitation of high-order vibrational resonances in molecules, the problem is the following. When multiphoton transitions are excited the frequency-variation amplitude increases with increasing number of photons in the resonance. At the same time, for transitions that proceed without intermediate resonances, the composite matrix element of the transition[7] decreases. Consequently the characteristic width of the Stark trapping also decreases, although the number of levels in it may continue to remain large because of the increasing density of states. It is known from the solution of the problem of excitation of vibrational-rotational multiphoton resonance from a lower (resonant) level[4] that when an external field is turned on the ratio of the stationary populations of the lower (degenerate) level and of the band is proportional to their statistical weights, the role of the latter being assumed by the number of states that land in the Stark width of the resonance.

If the radiation frequency fluctuates in time, the resonant value of the energy shifts over the band, and the levels that determine the effective statistical weight of the band change continuously. If some fraction of the population is left on the levels that have gone out of resonance with changing frequency, the total population of the multiphoton-resonance band may turn out to be larger than in the case of monochromatic excitation.

It is proposed to describe here this phenomenon in the simplest case that lends itself to an analytic solution, that of frequency variation linear in time. Similar problems, which arise in connection with the study of collisions, were considered in Refs. 8–10 for single level + continuum or single level + band systems.[1)] Their solution could be physically generalized to include the case of a nonmonotonic change of the level position. Such a generalization is expected also for the case of a degenerate level + band system. It must be borne in mind, however, that the present problem differs somewhat in its formulation from those in Refs. 8–10, since it is aimed mainly at investigating the asymptotic behavior of the populations as $t\to\infty$ in the case when the interaction is not turned off.

The Schrödinger equation for the system in question takes in the resonance approximation the form ($\hbar\equiv 1$)

$$i\dot{\psi}_n=(\Delta_n-\Delta(t))\psi_n+V_{nk}\psi_k,\quad i\dot{\psi}_k=V_{kn}\psi_n, \tag{1}$$

where n and k number respectivley the states of the band and of the degenerate levels, respectively, V_{kn} is the composite matrix element of the interaction, Δ_n is the detuning of the nth level from a fixed position in the band, and $\Delta(t)$ is the detuning of the resonance from this position at the instant of time t.

We take the Fourier transforms of the system (1) and of its complex conjugate. Using the method of generalized functions, we take into consideration the initial conditions[12] for $\psi_n(0)$; $\psi_k(0)$; $\psi_n{}^*(0)$; $\psi_k{}^*(0)$. As a result we get

$$\varepsilon\psi_n(\varepsilon)+\frac{i}{2\pi}\psi_n(0)$$

$$=\Delta_n\psi_n(\varepsilon)-\frac{1}{2\pi}\int\Delta(\varepsilon-\varepsilon')\psi_n(\varepsilon')d\varepsilon'+V_{nk}\psi_k(\varepsilon), \tag{2}$$

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$$\varepsilon\psi_k(\varepsilon)+\frac{i}{2\pi}\psi_k(0)=V_{kn}\psi_n(\varepsilon),$$

and

$$\xi\psi_n(\xi)-\frac{i}{2\pi}\psi_n{}^*(0)$$
$$=\Delta_n\psi_n(\xi)-\frac{1}{2\pi}\int\Delta(\xi'-\xi)\psi_n(\xi')d\xi'+V_{nk}\psi_k(\xi),$$
$$\xi\psi_k(\xi)-\frac{i}{2\pi}\psi_k{}^*(0)=V_{kn}\psi_n(\xi), \tag{3}$$

where

$$\Delta(x)=\int_0^\infty\Delta(t)e^{ixt}dt. \tag{4}$$

We consider a situation wherein only one of the states of the lower degenerate level is populated at the initial instant. In other words, the initial conditions are of the form

$$\psi_k(0)=\delta_{k,0},\quad \psi_k{}^*(0)=\delta_{k,0},\quad \psi_n(0)=\psi_n{}^*(0)=0.$$

Denoting the integral operator in Eq. (2) by $\hat{\Delta}$ and in (3) by Δ, the solutions of (2) and (3) can be represented as series in powers of the operator $\hat{V}$. Introducing the notation

$$\Sigma_0=\sum_k\psi_k(\varepsilon)\psi_k(\xi),\quad \Sigma_1=\sum_n\psi_n(\varepsilon)\psi_n(\xi), \tag{5}$$

representing the functions in them as series in powers of $\hat{V}$, multiplying the series, using the assumption that the operator $\hat{V}$ is complex and the ensuing procedure for selecting the terms of the series, and then summing, we obtain expressions for Σ_0 and Σ_1:

$$\Sigma_1=\sum_n\hat{X}_n(\varepsilon)\hat{\bar{X}}_n(\xi)V^2\Sigma_0,$$
$$\Sigma_0=V^2\sum_k\hat{X}_k(\varepsilon)\hat{\bar{X}}_k(\xi)\Sigma_1+{}^1/_4\pi^2, \tag{6}$$

where V is the mean squared matrix element of the transition operator, and quantities $\hat{V}$ and $\bar{X}$ (the polarization operators) satisfy the equations

$$\hat{X}_n(\varepsilon)=\Big[\varepsilon-\Delta_n+\hat{\Delta}-V^2\sum_k\hat{X}_k(\varepsilon)\Big]^{-1},$$
$$\hat{X}_k(\varepsilon)=\Big[\varepsilon-V^2\sum_n\hat{X}_n(\varepsilon)\Big]^{-1},$$
$$\hat{\bar{X}}_n(\xi)=\Big[\xi-\Delta_n+\hat{\bar{\Delta}}-V^2\sum_k\hat{\bar{X}}_k(\xi)\Big]^{-1},$$
$$\hat{\bar{X}}_k(\xi)=\Big[\xi-V^2\sum_n\hat{\bar{X}}_n(\xi)\Big]^{-1}. \tag{7}$$

For further calculations we use the model of equidistant band levels, $\Delta_n=\pi\delta n$. It has already been noted that this restriction is immaterial if $V\gg\delta$ (Ref. 3). Then

$$\sum_n\hat{X}_n(\varepsilon)=\frac{1}{\delta}\operatorname{ctg}\Big(\frac{\varepsilon}{\delta}-\frac{V^2}{\delta}\sum_k\hat{X}_k(\varepsilon)\Big),$$
$$\sum_n\hat{\bar{X}}_n(\xi)=\frac{1}{\delta}\operatorname{ctg}\Big(\frac{\xi}{\delta}-\frac{V^2}{\delta}\sum_k\hat{\bar{X}}_k(\xi)\Big). \tag{8}$$

Since the ratio V/δ is assumed large and the sums of the polarization operators of the degenerate-level states should have an imaginary part, the arguments of the cotangents have a large imaginary part and the cotangents take on the values $\pm i$, depending on the sign of the imaginary part of their argument. These signs can be determined from the causality principle, after which Eqs. (7) take the form

$$\hat{X}_k(\varepsilon)=(\varepsilon+iV^2/\delta)^{-1},\quad \hat{X}_n(\varepsilon)=[\varepsilon-(\Delta_n-\hat{\Delta})-V^2N\hat{X}_k]^{-1},$$
$$\bar{X}_k(\xi)=(\xi-iV^2/\delta)^{-1},\quad \hat{\bar{X}}_n(\xi)=[\xi-(\Delta_n-\hat{\bar{\Delta}})-V^2N\bar{X}_k]^{-1}, \tag{9}$$

where N denotes the degeneracy of the lower level. We note that X_k does not depend on k, and designate this operator simply as X. Taking into account the relations

$$\sum_n\hat{\bar{X}}_n(\xi)\hat{X}_n(\varepsilon)=\sum_n[\hat{\bar{X}}_n{}^{-1}-\hat{X}_n{}^{-1}]^{-1}(\hat{X}_n-\hat{\bar{X}}_n)$$
$$=-\frac{2i}{\delta}[\xi-\varepsilon-(\hat{\bar{\Delta}}-\hat{\Delta})-V^2N(\hat{\bar{X}}-\hat{X})]^{-1} \tag{10}$$

and substituting in the first equation of (6) the value of Σ_0 expressed in terms of Σ_1, the system (6) becomes

$$[\xi-\varepsilon-(\hat{\bar{\Delta}}-\hat{\Delta})-V^2N(\varepsilon-\xi)\hat{\bar{X}}(\xi)\hat{X}(\varepsilon)]\Sigma_1$$
$$=-\frac{iV^2}{2\pi^2\delta}\hat{\bar{X}}(\xi)\hat{X}(\varepsilon), \tag{11}$$
$$\Big(\varepsilon+i\frac{V^2}{\delta}\Big)\Big(\xi-i\frac{V^2}{\delta}\Big)\Sigma_0=NV^2\Sigma_1+\frac{1}{4\pi^2}.$$

If the detuning varies linearly with the time, $\Delta(t)=\alpha t$, then

$$\Delta(\varepsilon-\varepsilon')=i\alpha\delta'(\varepsilon-\varepsilon'),\quad \Delta(\xi'-\xi)=-i\alpha\delta'(\xi-\xi'),$$

and

$$\hat{\bar{\Delta}}=-i\alpha\frac{\partial}{\partial\xi},\quad \hat{\Delta}=i\alpha\frac{\partial}{\partial\varepsilon}. \tag{12}$$

Substituting (12) in (11) and introducing the notation $u=\varepsilon+\xi$, $v=\xi-\varepsilon$, we obtain for Σ_1 the equation

$$2i\alpha\frac{\partial}{\partial u}\Sigma_1-v\Big(1+\frac{4V^2N}{u^2-(v-2iV^2\delta^{-1})^2}\Big)\Sigma_1$$
$$=-\frac{2iV^2}{\pi^2\delta}\frac{1}{u^2-(v-2iV^2\delta^{-1})^2}. \tag{13}$$

Equation (13) is linear, of first order, and with right-hand-side coefficients that depend on the variable. It can be solved by the method of variation of the constant

$$\Sigma_1=\frac{V^2}{\pi^2\alpha\delta}(v+u-i\Gamma)^{-1}(v-u-i\Gamma)^{-1}$$
$$\times\int e^{i\beta\lambda}\Big(1+\frac{\lambda}{v+u-i\Gamma}\Big)^{-1-a}\Big(1-\frac{\lambda}{v-u-i\Gamma}\Big)^{a-1}d\lambda, \tag{14}$$

where

$$\Gamma=\frac{V^2}{\delta},\quad a=\frac{v}{i\alpha}\frac{V^2N}{(v-i\Gamma)},\quad \beta=\frac{v}{2\alpha},$$

and the integration is along a ray that passes through zero and is directed such that the integral converges at infinity.

To integrate with respect to $d\lambda$ it is convenient to use the relation

$$(1+x)^{a-1}=\frac{1}{2i\sin(\pi a)\Gamma(1-a)}\int\limits_{C_\Gamma}(-\tau)^{-a}e^{-(1+x)\tau}d\tau, \qquad (15)$$

where C_Γ is the contour of the integral representation of the Γ function.

After integrating with respect to $d\lambda$, we integrate Σ_1 with respect to $(2\pi)^{-1}du$. As a result we get

$$\Sigma_1=\frac{V^2}{\pi\alpha\delta}\frac{1}{4\pi a\sin(\pi a)}\int\limits_{C_\Gamma}\int\limits_{C_\Gamma}d\tau\,d\theta\left(\frac{\tau}{\theta}\right)^{\alpha}e^{-\tau-\theta}$$
$$\times[(\theta+\tau)^2-4\beta^2(v-\tau\Gamma)^2+4i\beta(v-i\Gamma)(\tau-\theta)]^{-1/2}. \qquad (16)$$

If the times considered are much longer than the duration of the transient when the field is turned off, it can be assumed that $v\ll\Gamma$. Measuring v in units of α/Γ and t in units of Γ/α, and putting $B=V^2N\Gamma^{-2}$, we obtain for $\Sigma_1(t)$ the expression

$$\Sigma_1(t)=\frac{1}{2\pi}\int\limits_{C_\Gamma}\int\limits_{C_\Gamma}d\tau\,d\theta\int dv\frac{\exp(-\tau-\theta-ivt)}{4\pi vB\sin\pi vB}\left(\frac{\tau}{\theta}\right)^{Bv}$$
$$\times[(\theta+\tau)^2+v^2+2v(\tau-\theta)]^{-1/2}. \qquad (17)$$

We note that the integral is not changed by the substitutions $\tau+\theta$, $\theta\to\tau$, $v\to v$, so that only its real part differs from zero. We introduce the notation

$$Y=v(\tau-\theta),\quad \varphi=\operatorname{arcth}\frac{\theta+\tau}{\tau-\theta};$$

then

$$\Sigma_1=\frac{1}{4\pi}\operatorname{Re}\int\limits_{C_v}\frac{(-i)\,dv}{4\pi B\sin(\pi vB)}\int\limits_{C_Y}Y\,dY\int\limits_{C_\varphi}d\varphi\,\operatorname{ch}^{-2}\varphi$$
$$\times\exp\{-vY\operatorname{th}\varphi-ivt+i\pi vB-2\varphi vB\}(Y^2\operatorname{th}^2\varphi+2Y+1)^{-1/2}, \qquad (18)$$

where the integration contour C_v encircles the points m/B ($m=1,2,3...$) on the real axis, the contour C_Y comes from $+\infty$ above the real axis, circles around the origin, and returns to infinity below the real axis. The integration contour C_φ is shown in Fig. 1.

The integration with respect to dv yields the expression

$$\Sigma_1=\frac{1}{8\pi^2B^2}\operatorname{Re}\int\limits_{C_Y}\int\limits_{C_\varphi}Y\,dY\,d\varphi\,(Y^2\operatorname{th}^2\varphi+2Y+1)^{1/2}\operatorname{ch}^{-2}\varphi$$
$$\times\left[\exp\left(-2\varphi+\frac{it}{B}+\frac{Y}{B}\operatorname{th}\varphi\right)-1\right]^{-1}. \qquad (19)$$

The integration with respect to dY in (19) calls for determining the residue at the point $Y=(2\varphi-it)B\coth\varphi$. As a result of this integration we get

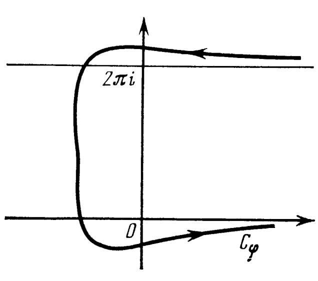

FIG. 1.

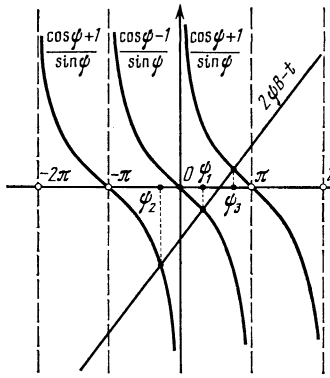

FIG. 2. The intersection of the straight line $2B\psi-t$ with the function $(\cos\psi\mp1)/\sin\psi$ determines the zeros of the denominator of the integrand in (22).

$$\Sigma_1=\frac{1}{4\pi B}\operatorname{Re}\int\frac{(-i)\,d\varphi}{\operatorname{sh}^2\varphi}$$
$$\times\frac{2\varphi B-it}{[(2\varphi B-it)^2+2\operatorname{cth}\varphi(2\varphi B-it)+1)]^{1/2}}. \qquad (20)$$

The limit $\alpha\to0$ corresponds asymptotically to $t\to0$. In this case the main contribution to the integral is made by the point $\varphi=0$:

$$\Sigma_1=(4B+1)^{-1/2}, \qquad (21)$$

which coincides with the expression for the stationary population of the degenerate level + band system in a monochromatic field.[4]

We make the change of variable $\varphi+i\psi$. Then

$$\Sigma_1=\frac{1}{4\pi B}\operatorname{Re}\int\limits_{C_\psi}\frac{(it-2iB\psi)\sin^{-2}\psi\,d\psi}{[1-(2\psi B-t)^2+2\operatorname{ctg}\psi(2\psi B-t)]^{1/2}}; \qquad (22)$$

at $t\neq0$ the integrand has four branch points: $\psi=0$, $\psi=\psi_1$, $\psi=\psi_2$, $\psi=\psi_3$ (see Fig. 2). With account taken the signs of the imaginary parts, the integration contour C_ψ encircles the points 0 and ψ_1. Making the change of variable $\cot\psi=x$, the integral takes the form

$$\int\limits_{C_1}[1+2x(t-2B\operatorname{arctg}x)^{-1}-(t-2B\operatorname{arctg}x)^{-2}]^{-1/2}dx \qquad (23)$$

and should be taken along a contour that passes over two sheets of the Riemann surface, as shown in Fig. 3. The main contribution to the integral is made by the points x_1 and x_2. The difference between the contributions from these points as $t\to\infty$ plays a decisive role and is equal to unity, i.e., $\Sigma_1\to1$ as $t\to\infty$. The contributions from the branch points are exponentially small and are of the order of $\exp(-t/B)$.

After a long time, thus, the system goes completely over asymptotically to the upper band. In other words, just as in the problem considered in Ref. 8, a situation is realized in which the stationary population is distributed over the levels in proportion to their statistical weights. In the problem considered above, the total statistical weight of the band was assumed to be infinite, therefore only this band turned out to be populated as $t\to\infty$.

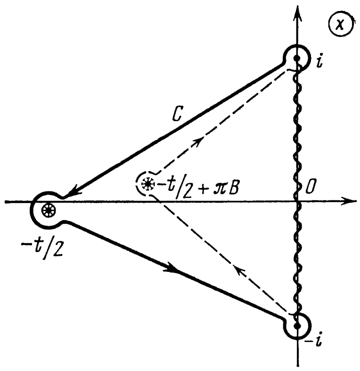

FIG. 3. The integral in (23) is taken along a contour lying on two sheets of the Riemann surface. The singularities $x_1 = -t/2$ and $x_2 = -t/2 + \pi B$ of the integrand are located on different sheets.

We determine now the asymptotic time dependence of the approach to the stationary population distribution. To this end we must retain the first nonzero term in the expansion of the integrand of (20) in the powers of t^{-1}. By making the change of variable $x = tu$ in the integral of (23) and expanding the integrand in powers of t^{-1} in the vicinity of the branch point located near $u = 1$, we find that

$$(1-\Sigma_1)=\Sigma_0=O(B/t^2). \tag{24}$$

If we return to the initial notation, the population of the degenerate level Σ_0, which decreases quadratically with time, turns out to be proportional to the square of the ratio of the Stark-trapping region to the size of the energy band negotiated during the time t:

$$\Sigma_0\sim V^2N/\alpha^2t^2. \tag{25}$$

This model problem can be used to describe the excitation dynamics of a degenerate level + band system in the case when the time derivative of the field frequency does not change substantially over times of the order of $V^{-1}N^{-1/2}$; δV^{-2}. In the opposite limiting case, when the external field variations are fast compared with the characteristic Rabi frequencies and the transition rates, a different approach is needed, based on assumptions substantially different from the linearity, proposed in (12), of the time dependence of the detuning and used to transform from the system (11) to expression (13). We assume thus in particular that $\Delta(t)$ is a random function with a rapidly decreasing correlation $\int \Delta(t)\Delta(t+\tau)dt \to 0$ at $\tau\to\infty$, and denote by $\Delta^{(2)}(x)$ the Fourier transform of the correlation function. We next carry out transformations that include representing the first equation of (11) as a formal series in powers of the operator $(\overline{\Delta}-\widetilde{\Delta})$, assume also randomness of the function $\Delta(t)$ and hence that the series terms odd in $(\overline{\Delta}-\widehat{\Delta})$ can be discarded, sum the series, rewrite the equation in the initial form with allowance for the fact that the operator $2i\alpha\partial/\partial u$ in (13) is replaced after the foregoing transformation by the operator

$$(\hat{\Delta}-\hat{\Delta})\,[\xi-\varepsilon-V^2N(\hat{\overline{X}}-\hat{X})]^{-1}(\hat{\Delta}-\Delta), \tag{26}$$

averaged over the realizations of $\Delta(t)$ with allowance for correlation, and take the limit as $v=(\xi-\varepsilon)\to 0$. We then obtain

$$4\pi i\Delta^{(2)}(0)\,v\frac{\partial\Sigma_1}{\partial u}-v\left(1+\frac{4V^2N}{u^2+\Gamma^2}\right)^2\Sigma_1 =\frac{-2i\Gamma(u^2+\Gamma^2+4V^2N)}{\pi^2(u^2+\Gamma^2)^2}; \tag{27}$$

as $t\to\infty$ the value of Σ_1 tends to a limit determined by the integral with respect to u, from $-\infty$ to $+\infty$, of the solution of the equation

$$4\pi i\Delta^{(2)}(0)\frac{\partial\Sigma_1}{\partial u}-\left(1+\frac{4V^2N}{u^2+\Gamma^2}\right)^2\Sigma_1 =-\frac{2i\Gamma}{\pi^2}\frac{1}{u^2+\Gamma^2}\left(1+\frac{4V^2N}{u^2+\Gamma^2}\right). \tag{28}$$

When the solution of (28) is integrated with respect to u in the case

$$\Gamma(4V^2N/\Gamma^2)^2\gg\Delta^{(2)}(0)\gg\Gamma, \tag{29}$$

we obtain

$$\Sigma_1\approx\Delta^{(2)}(0)/2B\Gamma=\Delta^{(2)}(0)/2N\delta, \tag{30}$$

where $B = V^2N\Gamma^{-2}$. In other words, if the emission-spectrum width exceeds the Stark trapping width, the effective statistical weight of the band begins to be determined by the number of levels spanned by the spectral width of the resonance. The stationary distribution of the population ceases then to depend on the external field. We note that allowance for the width of the emission spectrum does not change expression (21) for the stationary population at $\Delta^{(2)}\ll\Gamma$.

At very large values of $\Delta^{(2)}$, when $\Delta^{(2)}\gg B^2\Gamma$, the solution obtained for (28) by variation of the constants in analogy with (14) is determined by the behavior near the singularities of the integrand. In this case the stationary population of the band approaches unity like

$$\Sigma_1(t=\infty)=\exp\{-B^2\Gamma/8\Delta^{(2)}\}.$$

We note that if fluctuations of the frequency are superimposed on its linear time variation, the system-excitation dynamics can be described by Eq. (13) with an additional term added in the left hand side, viz., the operator (2b) acting on Σ_1.

We emphasize, however, that the approach based on the solution of (27) is not valid when the photon statistics does not permit the quantum field to be set in correspondence with the classical field even if the frequency of the latter has a complicated time variation, i.e., when the quantum state of the field deviates substantially from coherence. This means that the dispersion of the operator corresponding to the phase in the classical case exceeds 2π substantially, meaning that the phase is not at all descriptive of the field, since it is subject to strong quantum fluctuations. This takes place when the characteristic spacing Ω/n of the photon frequencies (Ω is the width of the spectrum of the radiation incident on the particle in question, and n is the number of photons it contains) becomes comparable with or much larger than the reciprocal of the radiation-pulse duration, $\tau_p\Omega/n\gg 1$, i.e., (in the case of focusing)

$$\Omega\hbar\omega W^{-1}\lambda^{-2}\gg 1, \tag{31}$$

where W is the radiation power density and λ is the wavelength. At wavelengths on the order of 10 μm the inequality (31) begins to be satisfied when the density of the radiation power becomes less than 1 W/cm^2 if the relative linewidth Ω/ω is 10^{-6}. The threshold power at a fixed relative linewidth increases in proportion to the fourth power of the frequency and reaches values 10^8 W/cm^2 at a wavelength 100 nm.

The condition (31) calls for a quantum treatment of the radiation field. The approach that must be used to describe the dynamics of the system excitation when this condition is satisfied must be based on consideration of the quantum photon variables. The asymptotic ratio of the level and band populations depends in this case on the radiation mode content and statistics. Without going into details, we consider only some of the possible limiting cases that admit of a lucid interpretation. We assume that the number of radiation modes participating in the system-excitation process is estimated by the total number $n \sim \tau_p W\lambda^2/\hbar\omega$ of the photons incident of the particles, and that the phases of these photons are random, since $\tau_p \Omega / n \gg 1$ by virtue of (31). We can therefore describe the process by using the two-band model with random matrix elements of the interaction operator.

The combined spectrum of the system and of the photons is shown in Fig. 4. On the left and right are shown respectively the energy levels corresponding to the lower state and to the upper band of the system. If the width of the radiation spectrum exceeds the width of the band, transitions are possible to any of the upper states, and the ratios of the stationary level and band populations are equal to those of the statistical weights. In the other case when the radiation spectrum is strictly limited, transitions are possible only to those bands that enter into resonance, so that only a fraction of the bands shown in Fig. 4 participate in the formation of the spectral density of the quantum states of the band and of the radiation, and only that part of the band that is at resonance with the radiation determines the statistical weight.

In both cited limiting cases the quantum treatment of the radiation field leads to the same conclusions as the classical approach based on Eq. (28). Differences can appear when the spectral radiation line has slowly decreasing wings. In the ensuring situation the transitions induced by the radiation frequencies located on the wings of the spectral line cause the density of the final quantum states to increase, and the corresponding matrix element of the transition operator decreases. This problem is similar to that considered in Ref. 13 and requires a special analysis that includes a study of the behavior of the parameter $W\lambda^2\tau_p V^2/\hbar\omega\Omega^2$ when the radiation frequency is shifted away from the line center.

Our analysis demonstrates thus that when resonances are excited in complex multilevel systems the role of the emission spectrum width can be quite important. Its influence depends substantially on the character of those processes that cause broadening of the spectral line. Thus, in particular, if the field frequency changes little during the time necessary to excite the system, the result of the slow motion of the resonance over the states of the upper band is total excitation of the system. This stationary distribution is approached in power-law fashion, and the population of the band approaches unit following a t^{-2} law. When the change of the radiation frequency is fast compared with the system excitation rates, the stationary distribution of the populations is determined by the ratio of the number of states of the lower level and the band states that enter into resonance with the radiation. The steady state is reached in this case exponentially. If the relations between the pulse duration and its energy, frequency, and spectral widths are such that a quantum treatment of the radiation is necessary, a special analysis, with account taken of the radiation line shape, is needed to determine the steady-state populations.

It seems that the results of this paper should be taken into account when considering questions such as excitation of multiquantum transitions in polyatomic molecules[14–16] and excitation of electronic transitions that have a complicated vibrational-rotational structure.[17–19] Allowance for the radiation-field statistics in the experimental study of these phenomena can offer additional possibilities of analyzing the spectra and, in particular, permit the features of the density of states to be distinguished from the features of the transition cross sections.

Indeed, in weak fields whose interaction with molecules is too weak to saturate a transition during the pulse time, the degree of absorption of the radiation is determined by the cross section for the transition, i.e., by a kinetic coefficient proportional to the mean squared matrix element of the di-

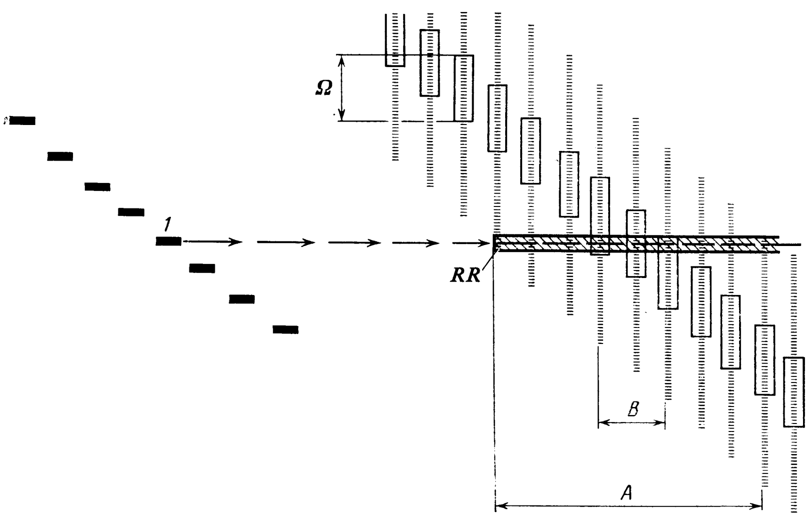

FIG. 4. State spectrum of a system consisting of a degenerate level or band plus a quantum radiation field. The levels (left) and bands (right) correspond to the states of the system at different states of the field (RR—resonance region). If the radiation-frequency spectrum is broader than the band, all the bands from among those landing in A have resonant levels corresponding to different excited states of the system. When the band is broader than the radiation-frequency spectrum (its width is marked), only the bands in the assembly B are at resonance.

pole-moment operator of the resonant levels, to the square field amplitude, and to the spectral density of the quantum states. Investigation of the spectral dependence of the transition cross section is in fact, as a rule, the subject of the spectroscopy of high vibrational states of a molecule. At the same time the transition cross ection, being an invariant according to the optical theorem, cannot determine the total number of levels that participate in the radiation absorption. In other words, the determination of the molecule properties of interest, such as the degree and limit of stochasticity of its vibrational motion, the values of the dipole moments, the inactive modes shifted to the infrared, remains beyond the capabilities of the traditional methods of this science.

Measurement of the absorbed radiation energy over times substantially longer than the reciprical width of its spectrum, when the kinetic coefficient of the transition is less than this width, makes it possible in principle to determine the statistical weight of the resonant levels and find the energy-space regions where the mixing of the mode levels is stronger. From the degree of mixing it is possible to assess in turn the degree of stochasticity of the motion and the value of the phase volume occupied by this motion.

The problem dealt with this paper can be apparently also of interest when considering radiative collisions in spectrally complicated molecular systems, when the change of the number of levels in a band that is at resonance with radiation is due to the change of the level positions in the process of pair collisions of excited particles.

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