Contribution of weak and multiphoton transitions to the excitation of lower levels of polyatomic molecules in an intense laser field

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The excitation of a level + band quantum system in the field of a monochromatic electromagnetic wave is considered in the case when the density of the levels that are weakly coupled to the bound state is high. The asymptotic behavior at low intensity and long time is investigated in detail. It is shown that even in the case of an infinite total level density a situation is possible in which the population of the ground state assumes a nonzero value. The time dependence of the relaxation to the stationary state is determined. The relations derived are used to discuss the influence of multiphoton and forbidden rotational transitions on the excitation of lower levels of polyatomic molecules and on the formation of a "cold ensemble" of molecules.

The collisionless dissociation of polyatomic molecules by high-power resonant IR laser field[1–3] was intensively investigated during the last decade. The presently known experimental facts and theoretical models have been gathered and expounded in a large number of reviews and monographs.[4–9] At the same time, a number of questions still remain unanswered. These include the question of how an aggregate of many lower levels of molecules is excited, and what is the contribution of multiphoton[10–12] and weak (forbidden)[13–14] transitions to the process of molecule excitation up to the boundary of the quasicontinuum[1,3,15] and to the formation of the "cold ensemble,"[16] meaning that fraction of molecules which are not excited in the laser field above the first to the fourth levels. To understand these processes we must find rigorous criteria under which a system having a complicated spectrum and acomplicated structure of the operator of the interaction with the field is not excited in the field of an electromagnetic wave of a definite intensity.

Let us recall the main laws governing the formation of molecular spectra. By way of example we choose a molecule with octahedral symmetry, such as SF_6. The Hamiltonian of a molecule in the electronic ground state and situated in an external electromagnetic field having a frequency on the order of its natural vibrational frequencies can be represented in the form

$$\hat{H} = \hat{H}_{\mathrm{h}} + \hat{H}_{\mathrm{anh}} + \hat{H}_{\mathrm{rot}} + \hat{H}_{\mathrm{v.r}} + \hat{H}_{\mathrm{w}} + \hat{V}_{\mathrm{dip}} + \hat{V}_{\mathrm{m}} + \hat{V}_{\mathrm{n.o}} + \hat{H}_{\mathrm{na}} \quad \text{(a)}$$

where $\hat{H}_{\mathrm{h}}$ is the Hamiltonian of the harmonic oscillations, $\hat{H}_{\mathrm{anh}}$ is the Hamiltonian of the tensor anharmonic corrections, $\hat{H}_{\mathrm{rot}}$ is the rotational Hamiltonian, $\hat{H}_{\mathrm{v.r}}$ is the Hamiltonian that describes the interaction of the vibrations and rotations, $\hat{H}_{\mathrm{w}}$ is the weak-interaction Hamiltonian and includes the interaction of the vibrational momenta and the angular momenta of the molecule as a whole with the orbital motion of the electrons and their spins, $\hat{V}_{\mathrm{dip}}$ and $\hat{V}_{\mathrm{m}}$ are the operators of the dipole and multipole transitions, $\hat{V}_{\mathrm{n.o}}$ is the operator of the transitions due to the nonlinear dependence of the dipole moment on the displacements of the nuclei, and H_{na} are nonadiabatic increments. The first five terms of the expression for the Hamiltonian form an hierarchic spectrum of the molecule. The first rank of the hierachy is given by $\hat{H}_{\mathrm{h}}$, which ensures formation of the vibrational levels. In the case of symmetric molecules the eigenvalues of the operator $\hat{H}_{\mathrm{h}}$ are as a rule multiply degenerate. In the next rank of the hierarchy, the operator $\hat{H}_{\mathrm{anh}}$ leads to partial lifting of the degeneracy, to splitting of the levels, and to formation of groups of levels located in the vicinities of harmonic positions, i.e., to the formation of the so-called band structure of the vibrational spectrum. The third rank, $\hat{H}_{\mathrm{rot}}$, ensures the appearance of a rotational structure of the spectrum. The Hamiltonian of the vibrational-rotational interaction causes a weaker splitting of some of the states that remain degenerate, to which a nonzero vibrational angular momentum J_{vib} can be assigned. The very same interaction leads in the higher perturbation-theory orders to an even weaker (fine, or octahedral) splitting due to the lifting of the degeneracy with respect to the projections of the angular momentum on the molecule axis. Finally, the Hamiltonian $\hat{H}_{\mathrm{w}}$ ensures the finest splitting of the levels.

The description of such a complicated hierarchic spectrum is carried out with the aid of a large set of quantum numbers, most of which correspond to not strictly conserved integrals of motion. An additional hierarchy is therefore produced in the spectra of the possible transitions, and is due to the possible existence of transitions that are forbidden in zeroth order of perturbation theory. Thus, for the SF_6 molecule in particular, the possibility was discussed of transitions with violation of the selection rule with respect to the quantum number corresponding to the vector $\mathbf{R} = \mathbf{J} - \mathbf{J}_{\mathrm{vib}}$. The vector $\mathbf{R}$, in contrast to the total angular momentum vector $\mathbf{J} = \mathbf{R} + \zeta \mathbf{J}_{\mathrm{vib}}$ (ζ is the tensor of the Coriolis constants) is not a conserved quantity, but the weakness of the interaction $\hat{H}_{\mathrm{v.r}}$ compared with $\hat{H}_{\mathrm{h}}$ brings about satisfaction of the selection rule $\Delta R = 0$ with good accuracy, and the cross sections for transitions from the ground state with violation of this rule are small.

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When describing the interaction of high-power laser radiation with a molecule, not all the features of its spectrum are used to the fullest extent. Thus, when considering multiphoton transitions in the SF_6 molecule, a large number of the results can be obtained by considering only diople transitions in one triply degenerate IR active vibrational mode ν_3. In fields of fixed intensity, there exists a molecule energy above which the Stark linewidths overlap. This region has been named the vibrational quasicontinuum. Below the quasicontinuum boundary are located levels to which transitions from the ground state can proceed via the multiphoton mechanism. The number of such transitions increases rapidly with increasing degree of "photonicity" n, while the composite matrix elements of the multiphoton transitions, being quantities of n-th order perturbation theory in $\hat{V}_{\text{dip}}$, decrease rapidly.

In another question dealing with the contribution of forbidden transitions with $\Delta R \neq 0$, on the contrary, the vibrational structure of the molecule is ignored and attention is focused on transitions between states with different R under conditions when a definite vibrational moment corresponds to the upper level.

The theory of interaction of laser radiation with spectrally complicated systems was developed in a large number of papers. Investigations were made of systems of the band type,[17,18] of systems of single almost resonant levels,[19,20] and of level + band systems.[21,22] However, the dynamics of the excitation of such systems was studied for times much shorter than the level densities in the bands (Planck's constant $\hbar = 1$), under the condition that the Stark broadening of the levels exceeded considerably the characteristic distance between the level or was of its order of magnitude. Such models are not suitable for the situation typical of multiphoton and weak transitions to lower levels of polyatomic molecules, when the level densities $g(V)$, which correspond to definite values of the transition matrix elements V, can differ substantially for different values of V. Indeed, the density of the levels capable of two- and three-photon resonances with the vibrational ground state is considerably larger than for single-photon transitions,[10] but the latter transitions correspond to small composition matrix elements.

A similar situation obtains for forbidden rotational transitions,[13] namely, the number of transitions with violation of the selection rule with respect to the rotational quantum number R, $\Delta R = 0$, is much larger than the number of transitions for which this rule holds, and the corresponding matrix elements of the dipole-moment operator are considerably smaller. To describe the excitation of the lower levels and the formation of the cold ensemble it is therefore necessary to know exactly how the level + band system is excited at any dependence of the level density on the value transition-operator matrix element.

Naturally, to determine whether a given system with a specified spectrum is excited in a field of given frequency and intensity we must know exactly the positions of its levels and the matrix elements of the corresponding transitions. However, even when high-resolution laser-spectroscopy data are used, there is no hope of finding all these quantities. Moreover, the determination of a large number of quantities that differ by many orders of magnitude still does not mean that the problem can be numerically analyzed, in view of the limits on the accuracy and on a reasonable computation time. We shall therefore investigate not some definite system having a concrete spectrum, but an averaged system characterized by a level-density distribution function in the transition matrix elements V, implying thereby that owing to the thermal motion of the molecules that starting levels are different, the spectra of the transitions from them vary greatly, and averaging over the starting states is equivalent to the averaging to population of one system over the positions of the levels in the band and over the values of the transition matrix elements corresponding to these levels.

We shall also assume that the averagings over the spectrum and over the matrix elements of the transitions are statistically independent. This assumption excludes immediately the possibility of investigating the decay of a level into a real continumm,[13,14] where, by virtue of the smooth variation of the eigenfunctions of the infinite-motion Hamiltonian with change of energy, a correlation exists between the values of the energy and the values of the transition matrix, elements.

Assume that we have a single level whose population $\rho_0(t) = 1$ at $t = 0$. After turning on the external field E, this level turns out to be coupled to a larger number of levels by the transition matrix elements V_{0k}, where the subscript k labels these levels. We assume for the sake of argument that all the transitions are single-phonon and dipole, that $V_{0k} = E\mu_{0k}$, where μ_{0k} is the matrix element of the dipole-moment operator, and the levels $\{k\}$ form a band located a distance equal to the laser quantum from the starting state. The band width Γ is much less than the laser quantum, but much larger than all the possible matrix elements V_{0k}. To describe the dynamics of the system excitation we can use in this case the Schrödinger equation in the quasienergy representation and in the resonance approximation:

$$i\dot{\psi}_0 = \sum_k V_{0k}\psi_k, \quad i\dot{\psi}_k = \Delta_k\psi_k + V_{k0}\psi_0, \tag{1}$$

where Δ_k is the detuning of the k-th level from exact resonance, and the operator V_{0k} is real, $V_{0k} = V_{k0}$.

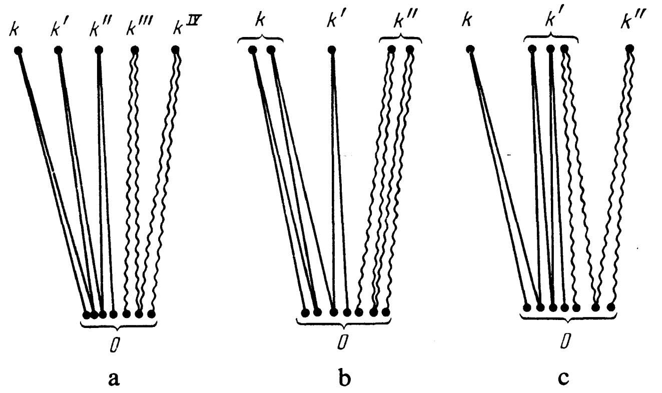
We take the Fourier transforms with respect to the time $t \to \varepsilon$; $\psi_k(t) \to \psi_k(\varepsilon)$ of the system of equations (1) and of the analogous system of equations for the complex-conjugate amplitudes, $t \to -\xi$; $\psi_k^*(t) \to \psi_k(\xi)$:

$$\begin{gathered}\varepsilon\psi_0(\varepsilon) + \sum_k V_{0k}\psi_k(\varepsilon) = i; \quad \varepsilon\psi_k(\varepsilon) + \Delta_k\psi_k(\varepsilon) + V_{0k}\psi_0(\varepsilon) = 0; \\ \xi\psi_0(\xi) + \sum_k V_{0k}\psi_k(\xi) = -i; \quad \xi\psi_k(\xi) + \Delta_k\psi_k(\xi) + V_{0k}\psi_0(\xi) = 0.\end{gathered} \tag{2}$$

The population of the ground state $\psi_0(\varepsilon)\ \psi_0(\xi)$ can be expressed as a product of series

$$\rho_0(\varepsilon,\xi)\equiv\psi_0(\varepsilon)\psi_0(\xi)=\Big(\varepsilon^{-1}+\varepsilon^{-1}\sum_{k}V_{0k}^2(\varepsilon+\Delta_k)^{-1}\varepsilon^{-1}$$
$$+\varepsilon^{-1}\sum_{k}V_{0k}^2(\varepsilon+\Delta_k)^{-1}\varepsilon^{-1}\sum_{k'}V_{0k'}(\varepsilon+\Delta_{k'})^{-1}\varepsilon^{-1}+\ldots\Big)$$
$$\times\Big(\xi^{-1}+\xi^{-1}\sum_{k}V_{0k}^2(\xi+\Delta_k)^{-1}\xi^{-1}$$
$$+\xi^{-1}\sum_{k}V_{0k}^2(\xi+\Delta_k)^{-1}\xi^{-1}\sum_{k'}V_{0k'}^2(\xi+\Delta_{k'})^{-1}\xi^{-1}+\ldots\Big).\qquad(3)$$

It is convenient to represent each term of the series for $\psi_0(\varepsilon)$ and $\psi_0(\xi)$ graphically.[17] Each factor V_{0k} contained in the terms of the series for $\psi_0(0)$ is represented by a straight line joining the points 0 and k, with the points 0 corresponding to the factor ε^{-1} and the points k to the factor $(\varepsilon+\Delta_k)^{-1}$. For $\psi_0(\xi)$ the factors V_{0k} are represented by wavy lines, and to the corresponding points, are ascribed the multipliers ξ^{-1} and $(\xi+\Delta_k)^{-1}$. Each term of the series, obtained after term-by-term multiplication of the series for $\psi_0(\varepsilon)$ and $\psi_0(\xi)$, can then by represented graphically in the form



(4)

Among the terms of series we encounter some in which each $0\leftrightarrow k$ transition has with both a right-hand and a left-hand bracket (4b, c). It is just these terms that make the main contribution to the series for the populations at long times. Assuming that in some term of the series each of the points k is encountered on a straight line n_k times and on a wavy line m_k times. Corresponding to this term is then the factor

$$\varepsilon^{-1}\xi^{-1}\prod_{k}\{[V_{0k}^2\varepsilon^{-1}(\varepsilon+\Delta_k)^{-1}]^{n_k}[V_{0k}^2\xi^{-1}(\xi+\Delta_k)^{-1}]^{m_k}\}.\qquad(5)$$

The number of series terms to which the factor (5) corresponds is equal to the number of different dispositions of the set $\{n_k\}$ of points on straight lines and the set $\{m_k\}$ of points on the wavy lines

$$\frac{\Big(\sum\limits_{k}m_k\Big)!\,\Big(\sum\limits_{k}n_k\Big)!}{\prod\limits_{k}m_k!\;\prod\limits_{k}n_k!}.\qquad(6)$$

The total population of the ground state of the system can therefore be represented in the form

$$\rho_0(\varepsilon,\xi)=\frac{1}{\varepsilon,\xi}\sum_{\substack{\{n_k\}\\\{m_k\}}}\int_0^\infty\int_0^\infty e^{-\vartheta-\varkappa}\prod_{k}\Big\{\frac{[\vartheta V_{0k}^2\varepsilon^{-1}(\varepsilon+\Delta_k)^{-1}]^{n_k}}{n_k!}$$
$$\times\frac{[\varkappa V_{0k}^2\xi^{-1}(\xi+\Delta_k)^{-1}]^{m_k}}{m_k!}\Big\}d\varkappa d\vartheta,\qquad(7)$$

where we have used the integral representations of the factorials:

$$\Big(\sum_{k}n_k\Big)!=\int_0^\infty e^{-\vartheta}\prod_{k}\vartheta^{n_k}d\vartheta,\qquad\Big(\sum_{k}m_k\Big)!=\int_0^\infty e^{-\varkappa}\prod_{k}\varkappa^{m_k}d\varkappa.\qquad(8)$$

Expression (7) contains factors of the type

$$(\varepsilon+\Delta_k)^{-n_k}(\xi+\Delta_k)^{-m_k}.\qquad(9)$$

If we average (7) over the position of each level k, assuming that the possible values of its detuning Δ_k are distributed with equal probability in the large interval from $-\Gamma/2$ to $\Gamma/2$ as $\Gamma\to\infty$ and at a fixed total number of the levels of each type per unit energy interval

$N(V)\Gamma^{-1}\equiv g(V)=\text{const}$,

then each of the factors of the type (7) will become averaged independently and its contribution to the product will be

$$\frac{1}{\Gamma}\int_{-\Gamma/2}^{\Gamma/2}\frac{d\Delta_k}{(\varepsilon+\Delta_k)^{n_k}(\xi+\Delta_k)^{m_k}}$$
$$=\frac{1}{\Gamma}\frac{(-1)^{n_k}(m_k+n_k-2)!}{(n_k-1)!(m_k-1)!}(\xi-\varepsilon)^{1-n_k-m_k}.\qquad(10)$$

After substituting (10) in (7), introducing the new variables $\zeta=\xi-\varepsilon$ and $\eta=\xi+\eta$, integrating over $(2\pi)^{-1}d\eta$, taking into account the fact that the number of levels with matrix elements in the interval $(V;\ V+dV)$ is equal to $N(V)dV=g(V)\Gamma dV$, and taking the limit as $\Gamma\to\infty$, expression (7) becomes

$$\rho_0(\zeta)=\frac{i}{\zeta}\int_0^\infty e^{-\vartheta}\exp\Big\{\int g(V)\Big[-\frac{2\pi iV^2\vartheta}{\zeta}$$
$$-2\pi i\zeta\sum_{\substack{n=1\\m=1}}^{\infty}\frac{(n+m-2)!(V^2\vartheta\zeta^{-2})^{n+m}}{n!(n-1)!m!(m-1)!}\Big]dV\Big\}d\vartheta.\qquad(11)$$

The sum in the square brackets can be represented in the form

$$\sum_{\substack{p=0\\q=0}}\frac{(p+q)!x^{p+q+2}}{p!q!(p+1)!(q+1)!}=-\frac{x^2}{4\pi^2}\int_C\int_C\frac{e^{\gamma+\chi}}{\gamma^2\chi^2}$$
$$\times\sum_{\substack{p=0\\q=0}}(p+q)!\frac{(x\gamma^{-1})^p}{p!}$$
$$\times\frac{(x\chi^{-1})^q}{q!}d\gamma d\chi,\qquad(12)$$

where the contours of integration with respect to $d\gamma$ and $d\chi$ start from $-\infty$ along the lower edge of the real axis, circle around the point 0, and go to $-\infty$ along the upper edge of the real axis. After summing the binomial expression and the geometric progression, expression (12) is reduced to

$$-\frac{x^2}{4\pi^2}\int_c\int_c \frac{e^{\gamma+\chi}d\gamma d\chi}{\chi\gamma(\chi\gamma-x\chi-x\gamma)}=-x+xe^{2x}[I_0(-2x)+I_1(-2x)]. \tag{13}$$

Expression (13) we obtained with allowance for the fact that the integrand and a function of γ has two simple poles at the points $\gamma=0$ and $\gamma=x\chi(\chi-x)^{-1}$. After calculating the contribution at the point $\gamma=0$, the integrand as a function of χ has a pole of second order at zero. The contribution from this singularity cancels out the first term in the curly brackets (11). The contribution of the pole at the point $\gamma=x\chi(\chi-x)^{-1}$ leads to an essential singularity of the integrand as a function of χ at the point $\chi=x$, which yields as a result of integration Bessel functions of zeroth and first order. In the upshot, expression (11) takes the form

$$\rho_0(\zeta)=\frac{i}{\zeta}\int_0^\infty \exp\left\{-\vartheta-2\pi i\zeta\int g(V)V^2\vartheta\zeta^{-2}\exp(2V^2\vartheta\zeta^{-2})\right.$$
$$\left.\times[I_0(-2V^2\vartheta\zeta^{-2})+I_1(-2V^2\vartheta\zeta^{-2})]dV\right\}d\vartheta. \tag{14}$$

At times of the order of $(\int g(V)V^2dV)^{-1}$ expression (14) coincides with the expressions obtained earlier[21,22] for the population of a level + band system. Indeed, when the argument of the Bessel function is small, we have

$$\rho_0(\zeta)=\frac{i}{\zeta}\int_0^\infty \exp\left(-\vartheta-2\pi i\frac{\vartheta}{\zeta}\int g(V)V^2dV\right)$$
$$d\vartheta=i\left(\zeta+2\pi i\int g(V)V^2dV\right)^{-1}, \tag{15}$$

and

$$\rho_0(t)=\frac{1}{2\pi}\int_{-\infty+i\delta}^{\infty+i\delta}\rho_0(\zeta)e^{-i\zeta t}d\zeta=\exp\left\{-2\pi t\int g(V)V^2dV\right\}, \tag{16}$$

i.e., the level decays exponentially at a characteristic rate equal to the product of the level density by the mean squared matrix element of the transition operator:

$$\int g(V)V^2dV\sim \overline{gV^2}.$$

For long times, however, the situation is different. Indeed, as $t\to\infty$ the small ζ are important, and we can deform the integration contour in the inverse Fourier transform with respect to $d\zeta$ in such a way that it goes from $-i\infty$ to the left of the imaginary axis and axis and returns, after circling around the point 0, to $-i\infty$ on the right of the imaginary axis. In this case we can assume ζ in (14) to be pure imaginary. At small negative ζ^2 we use the asymptotic expression for the Bessel function. Retaining only the first terms of the expansion, we obtain

$$\rho_0(\zeta)=\frac{i}{\zeta}\int_0^\infty \exp\left\{-\vartheta-2(\pi\vartheta)^{1/2}\int g(V)VdV\right\}d\vartheta. \tag{17}$$

It is seen from (17) that

$$\rho_0(t)|_{t\to\infty}=\int_0^\infty \exp\left\{-\vartheta-2(\pi\vartheta)^{1/2}\int g(V)VdV\right\}d\vartheta. \tag{18}$$

Denoting the dimensionless parameter by $\int g(V)VdV=N$, we obtain upon integration

$$\rho_0(t)|_{t\to\infty}=1-\pi Ne^{\pi N^2}[1-\Phi(\pi^{1/2}N)], \tag{19}$$

where Φ is the probability integral. In the asymptotic limit of small N expression (19) yields

$$\rho_0(t)|_{t\to\infty}=1-\pi N, \tag{20}$$

and a large N

$$\rho_0(t)|_{t\to\infty}=1/2\pi N^2. \tag{21}$$

The parameter N has a lucid physical meaning—it is the mathematical expectation value of the number of levels that enter into resonance with the radiation. Indeed, the levels having a transition matrix element V turn out to be at resonance if they are detuned by an amount $\Delta\lesssim V$; the probability of this event, at a uniform distribution of Δ over the wide spectral interval Γ, equals $Vg(V)dV$, and the total number of levels that become resonant is equal to the integral of this expression over all V. Consequently, at small N the resonance probability is proportional to N, meaning that this fraction of molecules will be excited. Expression (20) corresponds to this case. In the inverse limiting case (21) the physical explanation of the dependence is somewhat less clear. Indeed, if the number of levels that becomes resonant ($\Delta\lesssim V$) is $N\gg 1$, it is natural for the population to approach in the course of time the stationary value N^{-1}. But expression (21) gives an N^{-2} dependence. The reason for this difference that cooperative effects becomes substantial when a large number of levels becomes resonant simultaneously.

Let us explain this phenomenon with the following example. Assume that the level + band system consisted originally of a level and an M-fold degenerate level due to lifting of the degeneracy. The total with of the produced band is expressed in terms of the level density: $\Gamma g=M$. The transition in the level + degenerate level system corresponded to a matrix element W that became distributed, after the degeneracy was lifted, equally among all the splitting components $V\sim WM^{-1/2}$. If the matrix element of the transition is larger than the band width, $W\gtrsim\Gamma$, there is no time for the ψ functions to become dephased during one transition, the band will be perceived by the radiation as a single level, and all M of the band components will turn out to be populated. But the inequality $W\gtrsim\Gamma$ means that $M^{1/2}V\gtrsim Mg^{-1}$, i.e., $Vg\gtrsim M^{1/2}$. Consequently if $Vg\sim N$ in the level + band system, the number of levels that become resonant will be not N but N^2. In other words, the number of level that enter into resonance on account of the cooperative effect is equal to the squared mathematical expectation of the number of resonances, and the population of the ground state is of the order of N^{-2}, in accord with the exact expression (21). At small N the excitation probability is thus linear in N, and at large N the probability of staying in the ground state is quadratically small in N.

It follows from the foregoing analysis that even in the case when the level density is infinitely large and the integral $\int g(V)dV$ diverges in the region of small V, the population of the ground state assumes a nonzero stationary value if the integral $\int g(V)VdV$ is bounded.

From expression (14) we can determine the rate at which the population of the ground state approaches its stationary value. Let $g(V) \sim V^{\alpha}$ at small V. From the condition that the integral of $Vg(V)$ converge we get the requirement $\alpha > -2$. Retaining in (14) the second terms of the asymptotic expansion of the Bessel functions and expanding the exponential in a series of these functions, we obtain

$$\rho_0(t) - \rho_0(t=\infty) = \text{const} \cdot t^{-\alpha-2}. \tag{22}$$

It was recognized in the derivation of (22) that the integral of the second terms of the asymptotic expansion of the Bessel functions diverges in (14) at the lower limit and should be evaluated over the region $V^2\vartheta\zeta^{-2} \gtrsim 1$.

It follows from these results that besides the rate of the excitation of the level at short times, $\int g(V)V^2dV$, the study of such properties of the dynamics of excitation of the lower levels of polyatomic molecules as the mean values of the stationary populations and the temporal dependences of the approaches to these values can yield much information on the form of the level-density distribution as a function of the transition matrix elements and of the mathematical expectation value of the number of resonant transition. It seems however that, owing to the complexity of the spectra, these quantities can be more readily determined by experiment than by calculation.

Nevertheless, one can propose some rather general theoretical estimates that reflect the main regularities of the expected effects. It is reasonable to assume that the matrix elements of the transitions that result from weak interaction that lifts the hindrances can be represented in the form $V(s) = V\lambda^s$, where λ is a small parameter that characterizes the weakness of the interaction and s is the degree of forbiddenness of the transition. When considering multiphoton transitions, the value of λ can be estimated to be equal to the ratio $E\mu/\Delta$. In the case of forbidden rotational transitions, λ is a parameter characterized by the non-rigidity of the molecule. For the density of the levels corresponding to a definite order of forbidenness s we can expect the relation $g(s) \sim s^{\beta}K^s$, which takes into account the fact that the number of possible transition is increased by a factor K when the next hindrance is lifted, and the combinatorial increase of the number of levels, which is characterized by the parameter β. Thus, in particular, when considering the influence of multiphoton vibrational-rotational transition in a triply degenerate mode, we have $\beta = 2$, and $K = 3$ because new rotational branches are added. Expressing s in terms of V and substituting in the expression for g, we find that

$$g(V) \sim (\ln V/\ln \lambda)^{\beta} V^{\ln K/\ln \lambda}. \tag{23}$$

The main contribution to the integral for the mathematical expectation of the number of resonances on the lower level is made by the power-law dependence in (23). The condition that the integral be bounded implies that $\ln K/\ln\lambda > -2$, and consequently $K\lambda^2 > 1$. For the case of multiphoton resonances the parameter λ decreases with increasing vibrational quantum number and becomes less than unity when the quasicontinuum region is reached. In the quasicontinuum, therefore, the multiphoton resonances are capable of clear completely even those levels which do not decay as a result of single photon cascade transitions. Below the quasicontinuum boundary there are present levels that do not decay completely and whose population, according to (21), can amount to $O(1)\ln^{-2}(e^2K/\lambda)$.

We note now that by virtue of the requirement $K\lambda^2 > 1$, $K = O(1)$ the conditions imposed on the "weak"-transition strength needed for them the influence substantially the dynamics of the populations are quite stringent. The linear coefficient of absorption on forbidden transition, characterized by the parameter λ^2, can be only a few $(\sim K^{-1})$ times smaller than on the allowed transitions. It was reported in Ref. 14 that such a situation can obtain for rotational transitions, starting already with the second vibrational level of the band ν_3 of the molecules SF_6 and SiF_4. If, however, the "forbidden" transition have smaller absorption cross sections, they make no significant contribution to the excitation of the lower levels of polyatomic molecules.

In conclusion, we formulate the main conclusions of the study.

1. A feature of the population of a level decaying under the influence of laser radiation and lying above the band is that it reaches a nonzero stationary state if the mathematical expectation value of the number of resonant levels, which is defined by the expression

$$N = \int g(V)VdV,$$

is a finite quantity.

2. The stationary value of the pupulation is close to unity in the case of small N and is proportional to N^{-2} in the case of large N.

3. From the character of the power-law dependence of the rate of approach of the level population to its stationary value we can assess the form of the distribution function of the level density $g(V)$ in the region of small V.

4. The formation of the cold ensemble is due to incomplete excitation of the vibrational level of the polyatomic molecules, on account of multiphoton transitions in the region located below the quasicontinuum boundary. The reason is the existence of spectral and dynamic restrictions that exclude the possibility of total excitation of the levels even after an infinite time.

5. Forbidden rotational transitions can make a substantial contribution to the dynamics of the excitation of the lower levels only if the corresponding linear absorption coefficients differ from the linear absorption coefficients of allowed transitions by only a few times.

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