Dynamics of excitation of multilevel band-type systems in a bichromatic laser field

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An analysis is made of the problem encountered in investigations of the dynamics of excitation of multilevel molecules in a two-frequency field. The solution of this problem can also be used to investigate the influence of the width of the radiation spectrum and of the time dependence of the field amplitude on the process of excitation by a monochromatic field. An exact solution of the problem is found assuming a total absence of correlations between the matrix elements of the dipole moment operator for an interband transition. It is shown that a suitable selection of the frequencies of a bichromatic field can accelerate greatly the rate of excitation of molecules. This acceleration is due to a change in the nature of the process, which can be regarded as a one-dimensional random walk in the monochromatic case and as a two-dimensional walk in the bichromatic case. A study is made of the additional opportunities provided by a bichromatic field in investigations of the spectral charcteristics of the process of excitation of molecules.

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§1. INTRODUCTION

In investigations of the effects of high-power laser radiation on molecules[1-4] it is necessary to tackle the problem of the dynamics of excitation of complex multilevel quantum systems in an intense electromagnetic field. Knowledge of the exact solutions of model problems in which an allowance is made for the main features of the process of excitation of spectrally complex systems gives the correct overview of the mechanism of filling of vibrational–rotational states of complex molecules. Several theoretical papers have been devoted to such problems (see, for example, Refs. 5–11). However, in these theoretical treatments the dynamics of excitation is usually considered for a monochromatic field.

In describing the excitation of molecules by a monochromatic field it is convenient to use a band-type model of a multilevel system[10] when a study is made of the dynamics of filling of groups of levels (bands) located near resonance values of the energy. The band populations then obey the balance equation. The kinetic coefficients of the interband transitions are products of three quantities: the square of the intensity of the laser field, rms value of the matrix element of the dipole moment operator, and density of the quantum states in the vicinity of a resonance. The distributions of the populations within the bands are Lorentzian and localized near a resonance value of the energy; the width of a distribution is equal to the kinetic coefficient of a transition from a given band. In other words, laser radiation causes one-dimensional diffusion of populations within narrow regions near resonances. In view of the one-dimensional nature of this process, the rate of energy acquisition by a molecule is governed by that minimum value of the kinetic coefficient which is encountered in a stage of the process as a result of a regular or irregular change in the rms value of the matrix element of the transition and in the level density considered as functions of the band number and of the frequency of the field (bottleneck effect).

The investigation reported below is concerned with the excitation of a complex band-type multilevel system[10] in a bichromatic field. Solution of the problem of such excitation should give answers to the following questions: 1) How does the excitation dynamics change when the amplitude of the electromagnetic field becomes a function of time? 2) How does the width of the incident radiation spectrum affect the excitation process? 3) How the distribution of the populations between the levels in a band changes in a bichromatic field, compared with a monochromatic field? 4) What are the opportunities provided by a bichromatic laser field for increasing the efficiency of the excitation of molecules and for investigating in greater detail their structure?

§2. TWO BANDS IN A BICHROMATIC FIELD

The main features of the behavior of complex systems in a bichromatic field are manifested fully in the excitation of a two-band system. We shall now tackle this problem. As before,[10,11] we shall consider a two-band system assuming that the matrix elements of the dipole moment operator are completely uncorrelated; this will allow us to use the ensemble averaging method.[12,13] One should also point out that we shall consider times much shorter than the values of the density of levels in a band multiplied by the Planck constant for which the separate levels in a band cannot be resolved spectrally. We shall also assume that the level densities are the same in the upper and lower bands of the system. We shall generalize this problem to the case of arbitrary level densities in the bands in §4.

The dynamics of a system comprising two bands and two types of photons can be described in the basis of ψ functions $\psi_{p m \tilde{n} \tilde{n}'}$, where the first index ($p=0$ or 1) labels the band, the second index ($m=0, \pm 1, \pm 2, \ldots$) labels a level in a band, the index $\tilde{n}$ denotes the number of photons of the first type (of frequency ω) and $\tilde{n}'$ denotes the number of photons of the second type (of frequency ω'); $\tilde{n}, \tilde{n}' \gg 1$. We shall select the units so that

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the Planck constant is $\hbar \equiv 1$. The characteristic densities of levels g_1 and g_2 in the two bands, the band width Γ, and the frequencies ω and ω' satisfy the following inequality:

$$\omega;\ \omega' \gg \Gamma \gg |\omega-\omega'| \gg g_1^{-1};\ g_2^{-1}. \tag{1}$$

The numbers of photons $\tilde{n}$ and $\tilde{n}'$ are such that the corresponding amplitudes of the fields E and E' (assumed to be the same, $|E-E'| \ll E$) satisfy the following inequality which ensures the existence of a quasicontinuum:

$$E^2\mu^2 g_{1,2}^2 \gg 1, \tag{2}$$

where $\mu \equiv \langle \mu^2 \rangle^{1/2}$ is the rms value of the matrix element of the dipole moment operator.

We shall assume that initially the system is in the lower band $p=0$ in a state with $m=0$. The numbers of photons are initially $\tilde{n}_0$ and $\tilde{n}_0'$, respectively. We shall measure the energy from a level whose energy is $E_{00}+\omega\tilde{n}_0+\omega'\tilde{n}_0'$. Then, the Schrödinger equation of this two-band system is

$$i\dot{\psi}_{0,m,N,n} = [E_{0,m}-E_{00}+{}^1/_2\omega(N+n-N_0-n_0)+{}^1/_2\omega'(N-n-N_0+n_0)]\psi_{0,m,N,n} + \sum_{m'} E(\mu_{0m}^{1m'}\psi_{1,m',N-1,n-1}+\mu_{0m}^{1m'}\psi_{1,m',N-1,n+1}),$$

$$i\dot{\psi}_{1,m,N-1,n} = [E_{1,m}-E_{00}+{}^1/_2\omega(N-1+n-N_0-n_0) + {}^1/_2\omega'(N-1-n-N_0+n_0)]\psi_{1,m,N-1,n} + \sum_{m'} E(\mu_{1m}^{0m'}\psi_{0,m',N,n+1}+\mu_{1,m}^{0,m'}\psi_{0,m',N,n-1});$$

$$N_0=\tilde{n}_0+\tilde{n}_0',\ n_0=\tilde{n}_0-\tilde{n}_0',\ N=\tilde{n}+\tilde{n}',\ n=\tilde{n}-\tilde{n}'. \tag{3}$$

We note that for the zeroth band ($p=0$) we have $N=N_0$, whereas for $p=1$, we have $N=N_0-1$. The even values of n correspond to the lower band, and the odd values of n to the upper band. We shall introduce the notation

$$\psi_{p,m,N_0,n} \equiv \psi_{p,m,n},\ \omega-\omega' \equiv \alpha,\ E_{0,m}-E_{00} \equiv \Delta_{0,m},\ E_{1,m}-E_{00}-{}^1/_2(\omega+\omega') \equiv \Delta_{1,m},$$
$$\mu_{0,m}^{1,m'} \equiv \mu_{mm'}.$$

We shall write the equations of the system (3) in the form

$$i\dot{\psi}_{0,m,n} = \sum_{n',m'} [(\Delta_{0,m}+\alpha n)\delta_{nn'}\delta_{mm'}\psi_{0,m',n'}+E\mu_{mm'}(\delta_{n,n'+1}+\delta_{n,n'-1})\psi_{1,n',m'}],$$
$$i\dot{\psi}_{1,m,n} = \sum_{n',m'} [(\Delta_{1,m}+\alpha n)\delta_{nn'}\delta_{mm'}\psi_{1,m',n'}+E\mu_{mm'}(\delta_{n,n'+1}+\delta_{n,n'-1})\psi_{0,n',m'}] \tag{4}$$

or in the equivalent matrix form

$$i\dot{\psi}_{0,m} = (\Delta_{0,m}\mathbf{I}+\alpha\mathbf{B})\psi_{0,m} + \sum_{m'}\mu_{mm'}\mathbf{E}\psi_{1,m'},$$

$$i\dot{\psi}_{1,m} = (\Delta_{1,m}\mathbf{I}+\alpha\mathbf{B})\psi_{1,m} + \sum_{m'}\mu_{mm'}\mathbf{E}\psi_{0,m'}; \tag{5}$$

$$\mathbf{I}_{n,n'} \equiv \delta_{nn'},\quad \mathbf{B}_{nn'} = \alpha n\delta_{nn'},\quad \mathbf{E}_{nn'} = E(\delta_{n,n'+1}+\delta_{n,n'-1}),$$

where $\psi_{0,m}$ is the vector $\{\psi_{0,m,n}\}$.

If initially we have

$$\psi_{1,m} \equiv 0,\quad \psi_{0,mn} = \delta_{0m}\delta_{n_0,n},$$

then Fourier transformation $t \to \varepsilon$ of Eq. (5) gives

$$\mathbf{H}_{0,m}(\varepsilon)\psi_{0,m} - \sum_{m'}\mu_{mm'}\mathbf{E}\psi_{1,m} = \delta_{0,m}\delta_{n,n_0},$$

$$\mathbf{H}_{1,m}(\varepsilon)\psi_{1,m} - \sum_{m'}\mu_{mm'}\mathbf{E}\psi_{0,m} = 0;$$

$$\mathbf{H}_{p,m}(\varepsilon) = (\varepsilon-\Delta_{p,m})\mathbf{I}-\alpha\mathbf{B}. \tag{6}$$

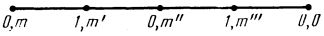
The solution of the system (6) can be represented as a series:

$$\psi_{0,m} = \mathbf{H}_{0,m}^{-1}\delta_{0,m}\delta_{n,n_0} + \mathbf{H}_{0,m}^{-1}\mathbf{E}\mu_{m,m'}\mathbf{H}_{1,m'}^{-1}\mathbf{E}\mu_{m',m''}\mathbf{H}_{0,m''}^{-1}\delta_{m'',0}\delta_{n,n_0} + \mathbf{H}_{0,m}^{-1}\mathbf{E}\mu_{m,m'}\mathbf{H}_{1,m'}^{-1}\mathbf{E}\mu_{m',m''}\mathbf{H}_{0,m''}^{-1}\mathbf{E}\mu_{m'',m'''} \times \mathbf{H}_{1,m'''}^{-1}\mathbf{E}\mu_{m''',m''''}\mathbf{H}_{0,m''''}^{-1}\delta_{m'''',0}\delta_{n,n_0}+\ldots, \tag{7}$$

$$\psi_{1,m} = \mathbf{H}_{1,m}^{-1}\mathbf{E}\mu_{m,m}\mathbf{H}_{0,m'}^{-1}\delta_{m',0}\delta_{n,n_0} + \mathbf{H}_{1,m}^{-1}\mathbf{E}\mu_{mm'}\mathbf{H}_{0,m'}^{-1}\mathbf{E}\mu_{m',m''}\mathbf{H}_{1,m''}^{-1}\mathbf{E}\mu_{m'',m'''}\mathbf{H}_{0,m'''}^{-1}\delta_{m''',0}\delta_{n,n_0}+\ldots,$$

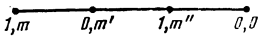
where repeated indices represent summation. Similar series are obtained also for the Fourier transforms $t \to \xi$ of the complex-conjugate ψ functions $\psi^*(t)$. We shall indicate the photon indices of $\psi^*(t)$ and $\psi(\xi) \equiv F[\psi^*(t)]$ by superscripts.

It is convenient to represent each term of the series (7) graphically. For example, the third term of the series representing $\psi_{0,m}(\varepsilon)$ can be described by



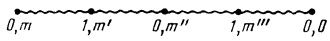
(8a)

whereas the second term of the series representing $\psi_{1,m}(\varepsilon)$ becomes

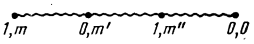


(8b)

In the case of $\psi(\xi)$ the corresponding terms of the series are described by



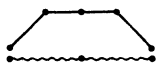
(9a)



(9b)

Each point on a straight line corresponds to a matrix factor $\mathbf{H}_{p,m}^{-1}(\varepsilon)$ and a point on a wavy line to $\bar{\mathbf{H}}_{p,m}^{-1}(\xi)$. The lines joining points $(1,m)$ and $(0,m')$ correspond to the matrix factors $\mathbf{E}\mu_{mm'}$ for a straight line and $\mathbf{E}\bar{\mu}_{mm'}$ for a wavy line. A bar above an operator means that it acts on the left side. The photon indices of the matrix elements of the operators with a bar will be denoted by superscripts.

We shall be interested in the populations of the various states. Each term of the series for the populations, obtained by multiplying the series (7) by the corresponding series for the complex-conjugate ψ functions can be represented by a diagram containing straight and wavy lines, for example:


(10)

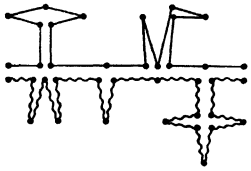
Before summing the series for the populations, we shall use the hypothesis that the matrix elements of the dipole moment operators are uncorrelated and we shall average each term of the series using the Wigner distribution function[12,13]:

$$w(\mu_{m,m'};\ \mu_{m',m''};\ \ldots) = \pi^{-N^2/2}\exp\Big\{-\sum_{m,m'}(\mu_{mm'})^2\mu^{-2}\Big\}. \tag{11}$$

Then, the sum in the series representing the populations contains only those diagrams in which each matrix element occurs twice. For the terms of the series

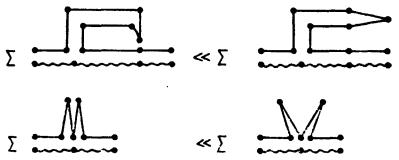
(10) these are the diagrams

For terms of higher order, we can also have more complex diagrams



(12)

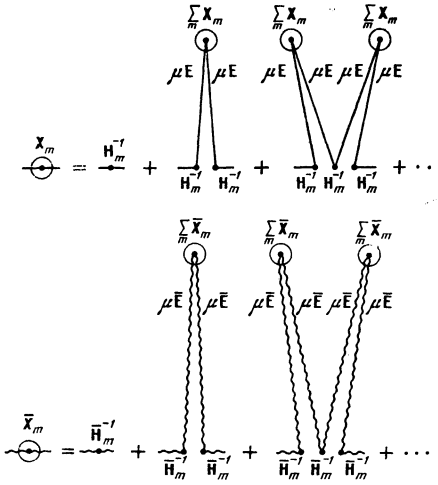
We can show that for times $t<g$ the influence of an increase in the statistical weight of the diagrams in the case of their self-intersections due to various possible types of transition is unimportant, and we can consider only the pairwise coalescence of diagrams, neglecting the coalescence of the fourth and higher orders. In other words, the following inequality satisfied:



(13)

The reason for this behavior is the small number of the diagrams on the left compared with the number on the right.

In the summation of the series for the populations we note that the coalescence of diagrams allows us to renormalize the operators corresponding to points on the straight and wavy lines:



(14)

Substituting $\mathbf{H}$ and $\bar{\mathbf{H}}$ explicitly and summing the operator geometric progressions (14), we obtain

$$\mathbf{X}_{p,m}=\left[(\varepsilon-\Delta_{p,m})\mathbf{I}-\alpha\mathbf{B}-\mathbf{E}\mu^2\sum_{m'}\mathbf{X}_{p',m'}\mathbf{E}\right]^{-1}$$

$$\bar{\mathbf{X}}_{p,m}=\left[(\xi-\Delta_{p,m})\bar{\mathbf{I}}-\alpha\bar{\mathbf{B}}-\bar{\mathbf{E}}\mu^2\sum_{m'}\bar{\mathbf{X}}_{p',m'}\bar{\mathbf{E}}\right]^{-1};\quad p'\neq p. \tag{15}$$

If we assume that $\Delta_{p,m}=\delta\pi m$ (if $t<g$ and $g_1=g_2$, this assumption does not restrict the generality of our treatment) and if we sum the system (15) with respect to m, we obtain the following expressions

$$\mathbf{Q}\equiv\sum_m\mathbf{X}_{0,m}\equiv\sum_m\mathbf{X}_{1,m}=\sum_m\mathbf{X}_m=\delta^{-1}\operatorname{ctg}\left(\frac{\varepsilon}{\delta}\mathbf{I}-\frac{\alpha}{\delta}\mathbf{B}-\frac{\mu^2}{\delta}\mathbf{EQE}\right),$$

$$\bar{\mathbf{Q}}\equiv\sum_m\bar{\mathbf{X}}_{0,m}\equiv\sum_m\bar{\mathbf{X}}_{1,m}=\sum_m\bar{\mathbf{X}}_m=\delta^{-1}\operatorname{ctg}\left(\frac{\xi}{\delta}\bar{\mathbf{I}}-\frac{\alpha}{\delta}\bar{\mathbf{B}}-\frac{\mu^2}{\delta}\bar{\mathbf{E}}\bar{\mathbf{Q}}\bar{\mathbf{E}}\right). \tag{16}$$

It follows from the inequality (2) that the quantity $E^2\mu^2\delta^{-2}\gg1$, which gives two exponentially accurate solutions of the system (16) and these have the following form if allowance is made for the signs of the imaginary parts ε and ξ:

$$\mathbf{Q}=i\mathbf{I}/\delta,\quad \bar{\mathbf{Q}}=-i\bar{\mathbf{I}}/\delta. \tag{17}$$

Substituting Eq. (17) into the system (15) and using the definition of the inverse matrix, we obtain

$$\left.\begin{aligned}&\left[(\varepsilon-\Delta_{p,m})\mathbf{I}-\alpha\mathbf{B}-i\frac{\mu^2}{\delta}\mathbf{EE}\right]\mathbf{X}_{p,m}=\mathbf{I},\\&\left[\left(\xi-\Delta_{p,m}\right)\bar{\mathbf{I}}-\alpha\bar{\mathbf{B}}+i\frac{\mu^2}{\delta}\bar{\mathbf{E}}\bar{\mathbf{E}}\right]\bar{\mathbf{X}}_{p,m}=\bar{\mathbf{I}}.\end{aligned}\right\} \tag{18}$$

Rewriting the system (18) in tensor notation and omitting the indices p and m (the dependences on these indices occur only in Δ), we obtain

$$\left.\begin{aligned}&\left(\varepsilon-\Delta-i\frac{2E^2\mu^2}{\delta}\right)X_{nn'}-i\frac{E^2\mu^2}{\delta}(X_{n+2,n'}+X_{n-2,n'})=\delta_{nn'},\\&\left(\xi-\Delta+i\frac{2E^2\mu^2}{\delta}\right)X^{kk'}+i\frac{E^2\mu^2}{\delta}(X^{k+2,k'}+X^{k-2,k'})=\delta^{kk'}.\end{aligned}\right\} \tag{19}$$

The solutions of the system (19) are

$$\left.\begin{aligned}X_{nn'}&=\sum_{s=-\infty}^{\infty}J_{[n/2]-s}\left(i\frac{E^2\mu^2}{\alpha\delta}\right)J_{[n'/2]-s}\left(i\frac{E^2\mu^2}{\alpha\delta}\right)\\&\times\left(\varepsilon-\Delta-i\frac{2E^2\mu^2}{\delta}-\left\{\frac{n}{2}\right\}2\alpha-2\alpha s\right)^{-1}\\X^{kk'}&=\sum_{s=-\infty}^{\infty}J_{s-[k/2]}\left(i\frac{E^2\mu^2}{\alpha\delta}\right)J_{s-[k'/2]}\left(i\frac{E^2\mu^2}{\alpha\delta}\right)\\&\times\left(\xi-\Delta+i\frac{2E^2\mu^2}{\delta}-\left\{\frac{k}{2}\right\}2\alpha-2\alpha s\right)^{-1},\end{aligned}\right\} \tag{20}$$

where J is a Bessel function ($[\ldots]$ is the integer part of a number and $\{\ldots\}$ is the fractional part).

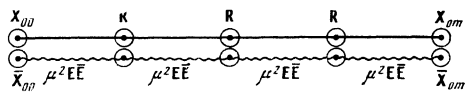
We note the validity of the expression

$$\mathbf{R}\equiv\sum_m\mathbf{X}_{p,m}\bar{\mathbf{X}}_{p,m}=-\frac{2i}{\delta}\left[(\varepsilon-\xi)\mathbf{I}\bar{\mathbf{I}}-\alpha(\mathbf{B}\bar{\mathbf{I}}-\bar{\mathbf{B}}\mathbf{I})-\frac{i\mu^2}{\delta}(\mathbf{E}^2\bar{\mathbf{I}}+\mathbf{I}\bar{\mathbf{E}}^2)\right]^{-1}, \tag{21}$$

which can be obtained from the system (15) allowing for Eq. (17) and for

$$\sum_m(\mathbf{A}-\pi m\delta\mathbf{I})^{-1}(\bar{\mathbf{A}}-\pi m\delta\bar{\mathbf{I}})^{-1}=(\bar{\mathbf{A}}\mathbf{I}-\bar{\mathbf{I}}\mathbf{A})^{-1}\delta^{-1}(\operatorname{ctg}\mathbf{A}\bar{\mathbf{I}}-\operatorname{ctg}\mathbf{I}\bar{\mathbf{A}}). \tag{22}$$

The use of Eq. (21) permits us to sum the series for the populations. The terms in this series (which are still the operators of photon variables) can be described by the following characteristic diagram:



(23)

which consists of an even number of links for the lower band and of an odd number of links for the upper band. The population of the lower band is expressed in terms of a sum of all the diagrams of the (23) type containing an even number of links and the population of the upper band contains an odd number of links.

It is convenient to introduce constant-sign **C** and variable-sign **P** sums of all the terms in the series, which represent the sum and difference between the populations of the lower and upper bands. We shall calculate these sums. We shall do this by summing each term of the population series (23) with respect to the index m of the final point. Next, we shall introduce new variables $\zeta = \varepsilon - \xi$ and $\eta = \varepsilon + \xi$, integrate the only η-dependent factor $\mathbf{X}_{00}\bar{\mathbf{X}}_{00}$ with respect to $d\eta$, and sum the geometric progression for **C** and **P**. This gives

$$\mathbf{C}=2\pi i\left[\mathbf{R}+\frac{2i}{\delta}\mu^2\mathbf{E}\bar{\mathbf{E}}\right]^{-1}, \tag{24}$$

$$\mathbf{P}=2\pi i\left[\mathbf{R}-\frac{2i}{\delta}\mu^2\mathbf{E}\bar{\mathbf{E}}\right]^{-1}. \tag{25}$$

The sum and difference of the total populations of the lower and upper bands ρ_C and ρ_P can be found using Eqs. (24) and (25) as follows:

$$\left.\begin{aligned}\rho_C(t)&=\int_{-\infty}^{\infty}\sum_{n,k,n',k'}\rho_n{}^k\mathbf{C}_{nn'}^{kk'}(\zeta)\delta_n^{k'}e^{-i\zeta t}\frac{d\zeta}{2\pi},\\ \rho_P(t)&=\int_{-\infty}^{\infty}\sum_{n,k,n',k'}\rho_n{}^k\mathbf{P}_{nn'}^{kk'}(\zeta)\delta_n^{k'}e^{-i\zeta t}\frac{d\zeta}{2\pi},\end{aligned}\right\} \tag{26}$$

where ρ_n^k is the initial value of the density matrix of the laser radiation.

We shall obtain the explicit forms of the operators **C** and **P**, which are fourth-rank tensors, by noting that they satisfy equations following from Eqs. (24) and (25):

$$\left.\begin{aligned}&\left[\zeta-\alpha(n-k)-i\frac{4E^2\mu^2}{\delta}\right]\mathbf{C}_{n,n'}^{k,k'}-i\frac{\mu^2E^2}{\delta}[\mathbf{C}_{n+2,n'}^{kk}+\mathbf{C}_{n,n'}^{k+2,k'}+\mathbf{C}_{n-2,n'}^{k,k'}+\mathbf{C}_{n,n'}^{k-2,k'}]\\&\quad+\frac{2iE^2\mu^2}{\delta}[\mathbf{C}_{n-1,n'}^{k-1,k'}+\mathbf{C}_{n+1,n'}^{k+1,k'}+\mathbf{C}_{n-1,n'}^{k+1,k'}+\mathbf{C}_{n+1,n'}^{k-1,k'}]=2\pi i\delta_{nn'}\delta^{kk'},\\&\left[\zeta-\alpha(n-k)-i\frac{4E^2\mu^2}{\delta}\right]\mathbf{P}_{n,n'}^{k,k'}-i\frac{\mu^2E^2}{\delta}[\mathbf{P}_{n+2,n'}^{k,k'}+\mathbf{P}_{n,n'}^{k+2,k'}+\mathbf{P}_{n-2,n'}^{k,k'}+\mathbf{P}_{n,n'}^{k-2,k'}]\\&\quad-\frac{2iE^2\mu^2}{\delta}[\mathbf{P}_{n-1,n'}^{k-1,k'}+\mathbf{P}_{n+1,n'}^{k+1,k'}+\mathbf{P}_{n-1,n'}^{k+1,k'}+\mathbf{P}_{n+1,n'}^{k-1,k'}]=2\pi i\delta_{nn'}\delta^{kk'}.\end{aligned}\right\} \tag{27}$$

The solutions of the system (27) are described by

$$i\int_{-\pi}^{\pi}d\lambda\exp\left[-i\frac{\lambda}{2}(n+k-n'-k')\right]\sum_r J_{r-n+k}\left(i\frac{2E^2\mu^2}{\alpha\delta}(\cos\lambda\pm1)\right)$$
$$\times J_{r-n'+k'}\left(i\frac{2E^2\mu^2}{\alpha\delta}(\cos\lambda\pm1)\right)\left\{\zeta-4i\frac{\mu^2E^2}{\delta}(1\pm\cos\lambda)-2\alpha r\right\}^{-1}, \tag{28}$$

where the plus sign corresponds to **P** and the minus sign corresponds to **C**.

We shall now consider two types of the initial density matrix of the laser radiation:

$$\rho_n{}^k=\delta_n{}^k\delta_{n,n_0}, \tag{29}$$

$$\rho_n{}^k=Ae^{-i(n-k)q}, \tag{30}$$

where A is the normalization factor. The density matrix (29) corresponds to the initial state of the field with a fixed number of photons, and the density matrix (30) corresponds to a fixed value of the field intensity

$$\langle E\rangle|_{t=0}=2E\cos q.$$

Substituting Eqs. (28), (29), and (30) into Eq. (26) and then performing the necessary summations and integrations, we obtain

$$\rho_C(t)=1,\quad \rho_P(t)=\exp\left\{-8\frac{E^2\mu^2}{\delta}t\right\}I_0\left(8\frac{E^2\mu^2}{\alpha\delta}\sin\alpha t\right) \tag{31}$$

for the density matrix (29) and

$$\rho_C(t)=1,\quad \rho_P(t)=\exp\left\{-8\frac{E^2\mu^2}{\delta}\left[t+\frac{\sin\alpha t}{\alpha}\cos(2q-\alpha t)\right]\right\} \tag{32}$$

for the density matrix (30); here, I_0 is a modified Bessel function.

The expression (32) shows that in the case of a bichromatic field the exact solution of the problem is identical with the solution obtained on the assumption of a slowly varying field, where the distribution of the populations between the bands is governed by the integral of the square of the field intensity with respect to time. This conclusion is the answer to the first of the questions formulated in §1. Moreover, the above analysis gives the answer to the question of the dependence of the dynamics of excitation of a system on the correlation between the photon phases. In the case of small values of the parameters $\mu^2E^2/\alpha\delta \ll 1$ the excitation dynamics is independent of the correlation of the photon phases, whereas in the $\mu^2E^2/\alpha\delta \gg 1$ case the excitation of the system is faster in a phase-uncorrelated field. Averaging of the expression (32) with respect to q can be used to find the dependences $\rho_P(t)$ for some other statistics.

§3. INTERNAL POPULATION DISTRIBUTIONS IN BANDS

We shall now find the distributions of the populations between the band levels. We shall be interested in the distributions at times longer than that required for one transition, when the difference between the populations of the lower and upper bands is small. In finding the distribution function we have to sum the series for the populations without summing with respect to the index m [see Eq. (23)] labeling the final level. The level populations can be expressed in terms of the operators **C** and **P** (for times longer than the time needed for one transition only the operator **C** is important) as well as in terms of the operators **X** and $\bar{\mathbf{X}}$:

$$\rho_C(t,\Delta)=(2\pi)^{-2}\int_{-\infty}^{\infty}d\varepsilon\int_{-\infty}^{\infty}d\xi\sum_{(n)(k)}\rho_n{}^k(\delta_{nn'}X^{kk'}(\xi,0)$$
$$-X_{n,n'}(\varepsilon,0)\delta^{kk'})\mathbf{C}_{n',n''}^{k',k''}(\varepsilon-\xi)(\delta_{n'',n'''}X^{k'',k'''}(\xi,\Delta)$$
$$-\delta^{k'',k'''}X_{n'',n'''}(\varepsilon,\Delta))\delta_n^{k'''}\exp[i(\xi-\varepsilon)t]. \tag{33}$$

We shall investigate Eq. (33) in the case $\mu^2E^2 \ll \alpha\delta$. In this limiting case the expressions for **X** and $\bar{\mathbf{X}}$ simplify greatly. It follows from the system (20) that

$$\left.\begin{aligned}X_{n,n'}(\varepsilon,\Delta)&=\delta_{n,n'}\left(\varepsilon-\Delta-2i\frac{E^2\mu^2}{\delta}-\alpha n\right)^{-1},\\ X^{k,k'}(\xi,\Delta)&=\delta^{k,k'}\left(\xi-\Delta+2i\frac{E^2\mu^2}{\delta}-\alpha k\right)^{-1},\end{aligned}\right\} \tag{34}$$

where the even values of n and k correspond to the lower band, and the odd values to the upper band. It follows from Eq. (28) that

$$\left.\begin{aligned} \mathbf{C}_{nn'}^{kk'} &= i\int_{-\pi}^{\pi} d\lambda \exp\left[-i\frac{\lambda}{2}(n+k-n'-k')\right]\delta_{k-n,k'-n'}\Big[\zeta \\ &\quad -4i\frac{E^2\mu^2}{\delta}(1-\cos\lambda)-2\alpha(n-k)\Big]^{-1}, \\ \mathbf{P}_{nn'}^{kk'} &= i\int_{-\pi}^{\pi} d\lambda \exp\left[-i\frac{\lambda}{2}(n+k-n'-k')\right]\delta_{k-n,k'-n'}\Big[\zeta \\ &\quad -4i\frac{E^2\mu^2}{\delta}(1+\cos\lambda)-2\alpha(n-k)\Big]^{-1}. \end{aligned}\right\} \tag{35}$$

Substituting Eqs. (35) and (34) into Eq. (33) and normalizing the density matrix ρ_n^k, we find that the level populations are localized within narrow ($\sim 2E^2\mu^2/\delta$) regions in the vicinity of resonances $n\alpha$ (the distributions within these regions are Lorentzian), and the total populations ρ_n in the vicinity of these $n\alpha$ resonances obey the following kinetic equation

$$\dot{\rho}_n = 2\frac{E^2\mu^2}{\delta}(\rho_{n+1}+\rho_{n-1}-2\rho_n), \tag{36}$$

where—as before—the even values of n correspond to the lower band, and the odd values of n correspond to the upper band.

It is much more cumbersome to study the opposite limiting case $\mu^2E^2 \gg \alpha\delta$ at times $t \gtrsim \alpha^{-1} \gg \delta E^{-2}\mu^{-2}$. In this case we need consider only the operator $\mathbf{C}$ because at such times the difference between the band populations is small. We note also that since the poles $\mathbf{X}$ and $\bar{\mathbf{X}}$ and the functions $\eta = \varepsilon + \xi$ lie on opposite sides of the real axis, we can restrict Eq. (33) to just one of the four terms:

$$\rho(\Delta,t) = \mathrm{Re}\,\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int d\varepsilon\, d\xi \sum_{\{n\}\{k\}} \rho_n^k X^{kk'}(\xi,0)\mathbf{C}_{nn'}^{k'n''} X_{n'n''}(\varepsilon,\Delta)e^{-i(\varepsilon-\xi)t}. \tag{37}$$

Substituting Eqs. (20), (28), and (30) into Eq. (37), and using the integral representation of the Bessel functions, we obtain

$$\begin{aligned} \rho(\Delta,\xi) &\sim \mathrm{Im}\int_{-\pi}^{\pi}\int d\lambda\, d\sigma\, d\sigma' \sum_{m,m',m''} (\xi-2iq_1-2\alpha m)^{-1}(\varepsilon-\Delta-2iq_1-2\alpha m')^{-1} \\ &\times[\xi-4iq_1(1-\cos\lambda)-2\alpha m'']^{-1}\exp\left\{-\frac{2q_1}{\alpha}(\cos\lambda-1)(\sin\sigma+\sin\sigma')\right\} \\ &\times \sum_{K,K',K''}\sum_{N,N'',N'''} J_{m-K}\left(\frac{iq_1}{\alpha}\right)J_{m-K'}\left(\frac{iq_1}{\alpha}\right)J_{N'''-m}\left(\frac{iq_1}{\alpha}\right)J_{N'''-m'}\left(\frac{iq_1}{\alpha}\right)\delta_{N''',K''} \\ &\times \exp\Big\{-2iq(N-K)-i\sigma(m''-N+K')-i\sigma'(m''-N''+K'') \\ &\quad +i\frac{\lambda}{2}(N+K'-N''-K'')\Big\}, \qquad q_1 = E^2\mu^2\delta^{-1}. \end{aligned} \tag{38}$$

Using the relationships

$$\left.\begin{aligned} &\sum_N \exp i(\sigma-2q+\lambda)N = 2\pi\delta(\sigma-2q+\lambda), \\ &\sum_N J_N(a)e^{-iNb} = \exp(ia\sin b) \end{aligned}\right\} \tag{39}$$

and integrating with respect to $d\eta$ and $d\zeta$, we can reduce Eq. (38) to

$$\begin{aligned} \rho(\Delta,t) &\sim \mathrm{Re}\,\frac{1}{\alpha}\int_{-\pi}^{\pi}\int d\lambda\, d\sigma\, d\sigma'\,\delta(\sigma-2q+\lambda)\,\delta(2\alpha t-2\lambda-\sigma+\sigma')\exp\Big\{i\lambda\frac{4iq_1+\Delta}{\alpha} \\ &\quad +i\frac{\sigma-\sigma'}{2\alpha}4iq_1(1-\cos\lambda) \\ &\quad +\frac{4q_1}{\alpha}\cos\frac{\sigma-\sigma'}{2}\Big[\sin\lambda\cos\frac{\sigma+\sigma'}{2}-(\cos\lambda-1)\sin\frac{\sigma+\sigma'}{2}\Big]\Big\}, \end{aligned} \tag{40}$$

and then we find that in the case $\Delta \gg E^2\mu^2/\delta$, and $\alpha t \gg 1$

$$\rho(\Delta,t) \approx \left(2\frac{E^2\mu^2}{\delta}t\right)^{-1/2}\exp\left\{-\frac{\Delta^2\delta}{32E^2\mu^2\alpha^2 t}\right\}. \tag{41}$$

It follows from Eq. (41) that the populations diffuse within the bands and the process is characterized by a diffusion coefficient $8E^2\mu^2\alpha^2\delta^{-1}$. Consequently, in a time corresponding to one transition $\delta E^{-2}\mu^{-2}$ the diffusional broadening of the distribution is of the order of α. It also follows from the expression (38) that in a single field period the width of the distribution does not become greater than $8E^2\mu^2\delta^{-1}$.

The analysis in the present section answers the second and third questions formulated in the first section. The influence of the width of the radiation spectrum on the distribution of the level populations in a band reduces to an increase (with time) of the size of the region in which all the significantly populated levels are located in accordance with the diffusion law: the characteristic width of this region is equal to the characteristic width of the radiation spectrum multiplied by the square root of the number of transitions $(E^2\mu^2t/\delta)^{1/2}$.

A bichromatic field with a large difference between the frequencies populated narrow ($\sim E^2\mu^2/\delta$) regions in the vicinity of multiphoton resonances of various orders $n\alpha$. When the difference between the frequencies is small $\alpha \ll E^2\mu^2\delta^{-1}$, these regions overlap. In this case there is no significant broadening of the distribution during one field period, so that the distribution remains narrow ($\sim E^2\mu^2\delta^{-1}$). We may therefore conclude that the excitation of a system by a laser pulse with a smooth envelope and of finite duration $\tau > \delta E^{-2}\mu^{-2}$ can be described using a monochromatic field model. The width of the distribution inside the band begins to increase only after times representing many field periods.

§4. CASE OF A LARGE NUMBER OF BANDS

In this section we shall consider the dynamics of filling of a multilevel system subjected to a bichromatic field. We shall confine ourselves to the case of a large frequency difference $\alpha \gg E^2\mu^2\delta^{-1}$, when only narrow regions in the vicinity of all possible resonances become filled. Then, the kinetic equation (36) can be generalized rigorously to the case when the density of levels and the rms value of the matrix element of the dipole moment operator vary within a band, and also to the case of arbitrary field intensities and arbitrary number of bands:

$$\begin{aligned} \dot{\rho}_{M,n} &= D_{M,n}^{M+1,n+1}\rho_{M+1,n+1}+D_{M,n}^{M+1,n-1}\rho_{M+1,n-1}+D_{M,n}^{M-1,n+1}\rho_{M-1,n+1} \\ &\quad +D_{M,n}^{M-1,n-1}\rho_{M-1,n-1}-(D_{M+1,n+1}^{M,n}+D_{M+1,n-1}^{M,n}+D_{M-1,n+1}^{M,n}+D_{M-1,n-1}^{M,n})\rho_{M,n}, \end{aligned} \tag{42}$$

where the index M labels the bands and n—the number of

a resonance in a band;

$$D_{M,n}^{M+1,n+1}=\frac{2\pi}{\hbar}E^2\langle\mu^2\rangle_{M,n}^{M+1,n+1}g_{M+1,n+1};$$

$$D_{M,n}^{M+1,n-1}=\frac{2\pi}{\hbar}E'^2\langle\mu^2\rangle_{M,n}^{M+1,n-1}g_{M+1,n-1},$$

where $\langle\mu^2\rangle_{M,n}^{M+1,n+1}$ is the rms value of the matrix element of the dipole moment between the n-th resonance in the M-th band and the $(n+1)$-th resonance in the $(M+1)$-th band.

Equation (42) describes the diffusion of the populations between the bands and within each band. If the difference between the frequencies of the fields E and E' ($\alpha=\omega-\omega'$) is such that a typical number of resonances in the bands is of the order of the characteristic number of bands of a molecule, the process of energy acquisition occurs automatically in the most efficient channel. The influence of a regular dependence of the kinetic coefficient on the band number and field frequency, which results in a considerable slowing down of the rate of excitation in the monochromatic case, is now weak. It has been shown experimentally[14] that illumination of a gas with two consecutive laser pulses increases the excitation efficiency when the frequency of the second pulse is shifted considerably in the direction of longer wavelengths. When the two laser pulses act simultaneously, the same effect can be achieved for a much lower frequency shift.

The essence of the effect is as follows. According to the current ideas, the process of laser excitation of molecules results in a strongly nonequilibrium distribution of the vibrational energy between the degrees of freedom.[15] In particular, it may happen that the action of a field with a frequency corresponding to the main transition ω_{01} populates the states which correspond to small kinetic coefficients $D(\omega_{01})$. A considerable frequency shift of the monochromatic field during the second stage makes it possible to tune the field to the maximum of the absorption band of these states. In the case of bichromatic interaction, the degree of excitation of molecules can increase considerably for a different reason: due to the diffusion of populations within a band, which fills a considerably wider range of states, including those corresponding to large kinetic coefficients at the frequencies of the field harmonics $D(\omega\pm\alpha)$.

Moreover, a bichromatic laser field provides additional opportunities for investigating certain spectral characteristics of molecules. This is due to the fact that the determination of the dynamics of excitation of a multilevel system does not represent a complete solution of the problem of the excitation of a molecule by a laser field. We have to find also the kinetic coefficients. This requires determination of the molecular vibration dynamics. This determination is possible only if a number of simplifying assumptions is made.[15,16] In view of the complexity of the vibrational dynamics of multilevel molecules we cannot expect to be able to determine in detail the kinetic coefficients. Therefore, we are faced with the important question whether an experimental study of the excitation of molecules by a bichromatic field can provide any information on the structure of the kinetic coefficients.

In strong fields the kinetic coefficients describing the excitation of a molecule become automatically averaged over the whole region in the vicinity of a resonance (locking region). The question remains as to whether the coefficients obtained in this way are regular functions of the position in a band or whether one can expect complex irregular behavior? The answer to this question can be obtained by experiments involving bichromatic excitation of molecules. We shall ignore, for the time being, the regular variation of the band parameters on increase in the energy discussed above and we shall consider only the irregular changes. Such a situation is encountered when a field is applied to previously excited molecules. If irregular changes in the kinetic coefficients are small, then the excitation of a molecule by a bichromatic field does not give any information additional to that which can be obtained using a monochromatic field. However, if there are strong irregular changes, the situation is different. Let us assume that σ is the correlation size of such irregular changes:

$$\Gamma\gg\sigma\gg E^2\mu^2\delta^{-1}\gg\delta. \tag{43}$$

In the case of multistate monochromatic excitation one must necessarily encounter a transition with a small kinetic coefficient, which reduces the energy acquisition rate. A similar situation also occurs in a bichromatic field if the difference between the frequencies of the two fields is small. The nature of the excitation changes in a radical manner if the difference between the frequencies becomes greater than the correlation size. The diffusion of the population between the bands then becomes two-dimensional and the question of the rate of excitation of the system reduces to solution of the problem of the effective conductivity of a randomly inhomogeneous two-dimensional medium. A complete solution of the problem is not yet known for an arbitrary change in the conductivity. However, we can say that because of an increase in its dimensionality, the problem of energy acquisition becomes less subject to the influence of fluctuations and the rate of molecular excitation increases.

We shall explain this by considering two examples.

1) We shall assume that the kinetic coefficient can assume zero values. Then, the question of the possibility of a strong excitation of a molecule reduces to the familiar problem of percolation.[17] There is no excitation in the one-dimensional case. In the two-dimensional case there is some critical fraction of transitions with zero values of the kinetic coefficient for which the energy acquisition ceases.

2) If the kinetic coefficient can assume two values D_1 and D_2 for statistically equivalent regions, the effective kinetic coefficient is then equal to the geometric mean[17] of D_1 and D_2, $D_{eff}=(D_1D_2)^{1/2}$, so that if $D_1\ll D_2$, which is much greater than in the one-dimensional case when $D_{eff}=D_1D_2(D_1+D_2)^{-1}$.

We can thus see that when the difference between the frequencies of two fields is of the order of magnitude of the correlation size of the change in the kinetic

coefficient, the dimensionality of the process of excitation by diffusion changes and this reduces greatly the threshold values of the laser pulse energy and increases the efficiency of the energy acquisition process. Consequently, the experimentally observed dependence of the efficiency of excitation of molecules on the relative difference between the frequencies of the two fields can be used to determine the characteristic correlation size of the frequency dependence of the kinetic coefficient.

In an experimental investigation carried out at high rotational temperatures we encounter the kinetic coefficients not of purely vibrational transitions but of vibrational–rotational transitions. The occurrence of absorption bands corresponding to different changes in the total angular momentum $\Delta J = 0, \pm 1$ complicates greatly the behavior not only in the case of the lower levels, where this effect can be allowed for because of the rigidity of the molecules, but also at the higher levels, when the molecules can no longer be regarded as rigid tops and the rotational degrees of freedom participate partially in the formation of a quasicontinuum. Additional degrees of freedom may flatten greatly the correlation function of the kinetic coefficients or change the correlation size. Therefore, it would be desirable to carry out experiments not only at high but also at low rotational temperatures, when a suitable selection of the field polarization can suppress the influence of the rotational absorption bands. In principle, one can formulate a suitable program and study theoretically in greater detail the influence of an irregular structure of the kinetic coefficients on the energy acquisition process, but the desirability of investigations of this kind depends directly on whether the above very simple irregularity is observed experimentally.

§5. CONCLUSIONS

We shall now formulate the main conclusions.

1. Solutions of the problem of the excitation of a band system by an external time-dependent field obtained on the assumption of slow variation of the amplitudes of a bichromatic field are identical with the exact solution.

2. The rate of excitation of a band system depends on the statistics of the phases of photons of the exciting radiation.

3. The width of the radiation spectrum results in diffusion broadening of the distribution of the populations between the band levels.

4. A bichromatic field with a large difference between the two frequencies populates only narrow regions near all possible multiphoton resonances. In fields with a small frequency difference these regions overlap.

5. A bichromatic interaction with a suitably selected frequency difference may reduce considerably the threshold values of the energy of the exciting laser pulses and may increase the efficiency of the excitation of molecules for a relative small shift of the field frequencies from the frequency of the main transition.

6. Determination of the dependence of the efficiency of the excitation of molecules on the difference between the frequencies of a bichromatic field can give valuable information on the correlation size of the kinetic coefficients which provides effectively some form of "integral spectroscopy" of multilevel molecules.

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