Interaction of a "level-band" quantum system with a quasiresonant monochromatic field

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The dynamics of excitation from a discrete state into a quasicontinuous spectrum (band of levels) under the influence of a monochromatic field is considered. Exact solutions are obtained for the Schrödinger equation in a number of particular cases. The condition under which the solutions for excitation into a discrete and into a continuous band are equivalent is obtained. The quasienergy spectrum, the structure of the quasienergy eigenstates, and the properties of the solutions are investigated. The results are used to formulate a theoretical approach to the description of the process of accumulation of energy by a polyatomic molecule over the levels of a quasicontinuum of excited vibrational states under the influence of IR radiation.

1. INTRODUCTION. FORMULATION OF THE PROBLEM

The discovery of collisionless dissociation of poly-atomic molecules under the influence of IR laser radiation[1,2] and the use of this effect for isotope separation[3,4] have stimulated theoretical investigations on the interaction of the vibrations of molecules with an IR field. The rapidly developing theory of the phenomenon covers a number of aspects. The spectroscopy of degenerate oscillations of spherical-top molecules,[5-9] the dynamics of the excitation of various multilevel systems that simulate atomic molecules,[10-27] the possibility of describing the phenomenon in quasiclassical and semiclassical language,[28-31] and the application of the theory of monomolecular reactions to the description of the dissociation stage,[32-34] are only some of the topics in question.

In view of the complexity of the problem, there is a natural justification for a stepwise approach, in which the energy spectrum of the molecule is arbitrarily broken up into at least three regions (see, e.g., the review[35]): a system of lower vibrational levels, a quasi-continuum of highly excited vibrational states, and a continuum of states lying above the dissociation boundary. To consider the excitation of the molecule over the spectrum in each of these regions, it is of interest to consider elementary model-dependent problems. In the present paper we consider the simplest of the problems for the quasi-continuum, namely the problem of the interaction of a "level-band" quantum system with a quasiresonant field; this problem admits of exact solutions in a number of interesting cases.[1)]

We consider the lower discrete state $|a\rangle$ and a set of upper discrete states $|b_n\rangle$, the characteristic energy distance between which is much shorter than the distance to the level $|a\rangle$. We also assume that the level $|a\rangle$ is connected with each state $|b_n\rangle$ by a transition with a dipole moment μ_n.

When a quasiresonant monochromatic field $\mathscr{E}\cos\Omega t$ is applied, the time evolution of the system is described by the following well known equations for the amplitudes of the states $a(t)$ and $b_n(t)$:

$$\frac{da}{dt} = i\sum_n \gamma_n b_n \exp[i(\Omega-\omega_n)t],$$

$$\frac{db_n}{dt} = i\gamma_n a \exp[i(\omega_n-\Omega)t]. \tag{1.1}$$

Here $\gamma_n = \mu_n \mathscr{E}/2\hbar$ (we assume henceforth for the sake of argument that $\gamma_n > 0$); ω_n are the frequencies of the transitions $|b_n\rangle - |a\rangle$. Obviously the analysis of the system (1.1) becomes much simpler if the discrete band is replaced by a quasi-continuous one. It can be assumed that a sufficient condition for this replacement is the inequality

$$\gamma_r \gg \delta, \tag{1.2}$$

where γ_r is the characteristic value of the matrix element of the interaction operator $\hat{\mu}\mathscr{E}/2\hbar$ near resonance, and $\hbar\delta$ is the characteristic energy distance between neighboring levels of the band. It can be shown, using an example that admits of an analytic solution, that the condition (1.2) can be replaced by a less stringent one. This is the example of a band with equal distances between neighboring levels and with a Lorentz contour for the quantity μ_n^2:

$$\mu_n^2 \propto (n^2\delta^2+\sigma^2)^{-1} \quad (-\infty<n<+\infty), \tag{1.3}$$

where δ is the distance between the levels of the band and σ is the half-width of the band at half-maximum.

The solution for the case of a discrete Lorentz band, satisfying the initial conditions

$$a(0)=1, \quad b_n(0)=0, \tag{1.4}$$

will be obtained in Sec. 2 together with the corresponding solution for the case of a continuous Lorentz band and with a comparison of the two solutions. It turns out that a perfectly sufficient condition for the equivalence of the two solutions is

$$\gamma_r \approx \delta. \tag{1.5}$$

The results of Sec. 2 serve in essence as the basis for the approximation in which the band is regarded as continuous. However, since the form of the contour of the transitions from a given excited state of the molecule is not known beforehand, it is of interest to obtain solutions also for other (non-Lorentz) continuous contours $\mu^2(\omega)$. In particular, the case of a restricted band is of interest. For this case we develop in Sec. 3

a general solution method based on the quasi-energy approach.[36] The method is used in explicit form for

$$\mu(\omega) = \begin{cases} \text{const} & \omega_1 < \omega < \omega_2, \\ 0 & \omega < \omega_1 \text{ and } \omega > \omega_2. \end{cases} \qquad (1.6)$$

In this example of a rectangular band one can discern clearly the limiting case of a strong field, when the system degenerates in fact into a two-level one. At the same time, a comparison with the solutions obtained in Sec. 2 enables us to conclude that in the case of a relatively weak field (a criterion will be given in the main text) the behavior of the amplitude of the lower level (exponential decay) is insensitive to the form of the $\mu(\omega)$ dependence and corresponds on the linear section to perturbation theory for transitions to a continuous spectrum.[37]

Section 4 deals with a particular case that corresponds as close as possible to the real situation for transitions of spherical-top molecules into the quasi-continuum. This is the case when the band has a pronounced level dipole-coupled much more strongly with the lower state than with the remaining levels of the band. This pronounced level can correspond, for example, to one of the anharmonic-splitting components[5-7] that is closest to resonance.

In the conclusion (Sec. 5) we discuss, on the basis of the results, some qualitative aspects of the development of a theory for the excitation of molecules under the influence of an IR field over the quasi-continuum levels.

2. CASES OF DISCRETE AND CONTINUOUS BANDS WITH LORENTZ CONTOUR FOR THE TRANSITION CROSS SECTIONS

We consider the equations in (1.1) for the case of a discrete band with

$$\gamma_n^2 = \frac{\sigma\delta}{\pi} \frac{\gamma^2}{n^2\delta^2+\sigma^2} \operatorname{th}\frac{\pi\sigma}{\delta}, \quad \omega_n = \omega_0 + n\delta. \qquad (2.1)$$

The normalization in (2.1) is chosen such that

$$\sum_{n=-\infty}^{+\infty} \gamma_n^2 = \gamma^2.$$

The system (1.1) with initial conditions (1.4) is equivalent to the following Volterra-type integro-differential equation:

$$\frac{da}{dt} + \int_0^t a(\tau) K(t-\tau) d\tau = 0, \quad a(0) = 1, \qquad (2.2)$$

where the integral kernel $K(z)$ is given by

$$K(z) = \sum_{n=-\infty}^{+\infty} \gamma_n^2 \exp[i(\Omega-\omega_n)z]. \qquad (2.3)$$

For the case (2.1), summation in (2.3) yields

$$K(z) = \gamma^2 \exp(isz) [\operatorname{ch} \sigma z - \operatorname{th}(\pi\sigma/\delta) \operatorname{sh} \sigma z]$$
$$\text{at } 0 \leqslant z \leqslant 2\pi/\delta, \qquad (2.4)$$
$$K(z+2\pi/\delta) = K(z) \exp(isz),$$

where s is the detuning from resonance for the transition to the center of the band ($s = \Omega - \omega_0$).

The standard method of solving equations such as (2.2) is to use Laplace transforms (see, e.g., Ref. 38).

In our case (2.4), the Laplace transform $\tilde{a}(p)$ of the function $a(t)$ is given by

$$\tilde{a}(p) = [p + \tilde{K}(p)]^{-1} = [(p-is)^2 - \sigma^2] \{p^3 - 2isp^2$$
$$+ (\gamma^2-\sigma^2-s^2)p - i\gamma^2 s - \sigma\gamma^2 \operatorname{th}(\pi\sigma/\delta)\operatorname{cth}[\pi(p-is)/\delta]\}^{-1}. \qquad (2.5)$$

Since the choice of the integration line $\operatorname{Re} p = c > 0$ for the inversion of the Laplace transformation

$$a(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \tilde{a}(p) e^{pt} dp \qquad (2.6)$$

is in a certain sense arbitrary, we can choose a line far enough from the imaginary axis, where it can be shown that the function $\tilde{a}(p)$ can be expanded in the following form:

$$\tilde{a}(p) = [(p-is)^2 - \sigma^2] \left\{ \prod_{k=1}^{3} (p-p_k)^{-1} \right.$$
$$\left. + 2\sigma\gamma^2 \operatorname{th}\frac{\pi\sigma}{\delta} \sum_{n=1}^{\infty} \exp\left[-\frac{2\pi n(p-is)}{\delta}\right] \prod_{k=1}^{3} \frac{(p+p_k^*)^{n-1}}{(p-p_k)^{n+1}} \right\}. \qquad (2.7)$$

Here p_k are the roots of the equation

$$p^3 - 2isp^2 + (\gamma^2-\sigma^2-s^2)p - i\gamma^2 s - \sigma\gamma^2 \operatorname{th}(\pi\sigma/\delta) = 0, \qquad (2.8)$$

and the asterisk denotes complex conjugation.

From (2.6) and (2.7) follows an expression that describes the time behavior of the amplitude of the lower level

$$a_d(t) = \sum_{n=0}^{\infty} c_n(t), \qquad (2.9)$$

where the function $c_0(t)$ yields the contribution for all the times and is determined by the formula

$$c_0(t) = \frac{(p_1-is)^2-\sigma^2}{(p_1-p_2)(p_1-p_3)} e^{p_1 t} +$$
$$+ \frac{(p_2-is)^2-\sigma^2}{(p_2-p_1)(p_2-p_3)} e^{p_2 t} + \frac{(p_3-is)^2-\sigma^2}{(p_3-p_1)(p_3-p_2)} e^{p_3 t}, \qquad (2.10)$$

while the remaining functions $c_n(t) (n = 1, 2, \ldots)$ are turned on in succession at the instants of time $2\pi n/\delta$:

$$c_n(t) = \begin{cases} 0 & \text{at } t < 2\pi n/\delta, \\ 2\sigma\gamma^2 \operatorname{th}\frac{\pi\sigma}{\delta} \exp\left(\frac{2\pi ins}{\delta}\right) \sum_{j=1}^{3} \operatorname*{res}_{p=p_j}\left\{ [(p-is)^2 \right. \\ \left. -\sigma^2] \exp\left[\left(t-\frac{2\pi n}{\delta}\right)p\right] \prod_{k=1}^{3} \frac{(p+p_k^*)^{n-1}}{(p-p_k)^{n+1}} \right\} & \text{at } t > 2\pi n/\delta. \end{cases} \qquad (2.11)$$

For our purposes it will be sufficient from now on to analyze mainly the behavior of $a_d(t)$ only in the first time interval $t < 2\pi/\delta$. Some results of numerical calculations by formulas (2.9)–(2.11) will be given also for larger time intervals. But at first we obtain the solution for the continuous band with a Lorentz contour

$$\gamma_\omega^2 = \frac{1}{\pi} \frac{\sigma\gamma^2}{(\omega-\omega_0)^2+\sigma^2}, \quad \int_{-\infty}^{+\infty} \gamma_\omega^2 d\omega = \gamma^2. \qquad (2.12)$$

For the case of a continuous band, the evolution of the amplitude of the lower level $a(t)$, just as for the discrete band, is described by (2.2). The integral kernel corresponding to (2.12) is

$$K(z) = \gamma^2 \exp[(is-\sigma)z]. \qquad (2.13)$$

Omitting the elementary intermediate steps of deter-

mining and inverting the Laplace transformation, we obtain

$$a_{cont}(t) = \frac{r_1 + \sigma - is}{r_1 - r_2} e^{r_1 t} + \frac{r_2 + \sigma - is}{r_2 - r_1} e^{r_2 t},$$ (2.14)

where

$$r_{1,2} = -\frac{\sigma - is}{2} \pm \left[\left(\frac{\sigma - is}{2} \right)^2 - \gamma^2 \right]^{1/2}.$$ (2.15)

We now compare the solution $a_d(t)$ for the case of a discrete band and the solution $a_{cont}(t)$ for the case of a continuous band in the time interval $0 < t < 2\pi/\delta$. It is natural to seek equivalence of the two solutions under the condition that the dipole moments of the neighboring transitions into the discrete band do not differ very strongly. By way of a criterion it suffices to require satisfaction of the inequality

$$\varepsilon = 1 - \text{th} \, (\pi\sigma/\delta) \ll 1$$

or

$$\exp(-2\pi\sigma/\delta) \ll 1,$$ (2.16)

which holes with large margin already at $\sigma \approx \delta$.

When the condition (2.16) is satisfied, there is no difficulty in obtaining an estimate for the roots of Eq. (2.8). The first two roots $p_{1,2}$, accurate to terms that are small in the parameter ε, coincide with $r_{1,2}$ which enter in the solution (2.14) for $a_{cont}(t)$. For the third root p_3 we have, accurate to terms $\sim \varepsilon$, the expression

$$p_3 \approx \sigma + is - \frac{\sigma\gamma^2}{2\sigma^2 + 2i\sigma s + \gamma^2} \varepsilon.$$ (2.17)

Consequently the solution $a_d(t)$ in the time interval $0 < t < 2\pi/\delta$ takes the following form:

$$a_d(t) \approx \frac{r_1 + \sigma - is}{r_1 - r_2} e^{p_1 t} + \frac{r_2 + \sigma - is}{r_2 - r_1} e^{p_2 t} - \frac{2\sigma^2 \gamma^2}{(2\sigma^2 + 2i\sigma s + \gamma^2)^2} \varepsilon e^{p_3 t},$$ (2.18)

where $p_1 \approx r_1, p_2 \approx r_2, r_{1,2}$ are defined in (2.15), and p_3 is approximately given by (2.17).

It follows from (2.18) that if the most substantial changes of the modulus of the amplitude of the lower level occur within times shorter than $2\pi/\delta$, then the excitation process can be described with good accuracy by the solution (2.14) for the case of the continuous band. To ascertain the conditions under which the time interval $0 < t < 2\pi/\delta$ is sufficient for the description of the main features of the excitation process, we consider the limiting relations between the parameters.

For a strong field, when the following condition is satisfied

$$\gamma \gg |\sigma - is|,$$ (2.19)

the behavior of the amplitude of the lower level is described by a damped oscillating solution

$$a(t) \sim \exp\left(-\frac{\sigma - is}{2} t\right) \cos \gamma t.$$ (2.20)

The characteristic changes of the solution, by virtue of the condition (2.16), occur in times much shorter than $2\pi/\delta$. The last statement remains valid also for intermediate fields.

The case of greatest interest is that of a weak field, when

$$\gamma \ll |\sigma - is|.$$ (2.19')

In this case the amplitude of the lower level is damped exponentially without oscillations:

$$a(t) \sim \exp\left(-i\frac{\gamma^2 s}{\sigma^2 + s^2} t\right) \exp\left(-\frac{\gamma^2 \sigma}{\sigma^2 + s^2} t\right).$$ (2.21)

At the instant of time $t = 2\pi/\delta$ the probability of finding the system on the lower level is given by

$$\left| a\left(\frac{2\pi}{\delta}\right) \right|^2 \sim \exp\left[-\frac{4\pi\gamma^2 \sigma}{\delta(\sigma^2 + s^2)} \right].$$ (2.22)

Obviously, the condition

$$\exp\left[-\frac{4\pi\gamma^2 \sigma}{\delta(\sigma^2 + s^2)} \right] \ll 1$$ (2.23)

is a sufficient criterion for the equivalence of the solutions for the cases of discrete and continuous bands.

To impart to the condition (2.23) a clear physical meaning, we introduce in it explicitly the characteristic value of the matrix element of the interaction operator γ_p near resonance. Combining (2.1) with the relation $\gamma_p \approx \gamma_n(n \approx s/\delta)$, we obtain the following criterion:

$$\exp(-4\pi^2\gamma_p^2/\delta^2) \ll 1.$$ (2.24)

It is clear therefore that the condition (1.5) is perfectly sufficient for the change from the discrete to the continuous description.

However, when comparing the two solutions (2.9) and (2.14), it must be remembered that their equivalence holds only in the time interval $0 < t < 2\pi/\delta$. Whereas in the case of the continuous band the decay of the lower level is irreversible, for the case of the discrete band the system returns at definite instants of time to the ground state. The limiting case of such a return (at $\gamma_p \ll \delta$) constitutes ordinary oscillations of the populations between the lower state and that band state to which the transition is closest to resonance. This statement is illustrated by results of a numerical calculation by means of exact formulas (2.9)–(2.11). For the calculations illustrated in Fig. 1, we chose the case of resonance at the center of the band ($s = 0$).

3. CASE OF CONTINUOUS LIMITED BAND

We consider Eqs. (1.1) for a system (see Fig. 2) consisting of a lower discrete state $|a\rangle$ and states $|b(x)\rangle$ of a continuous band; the variable x, which has the di-
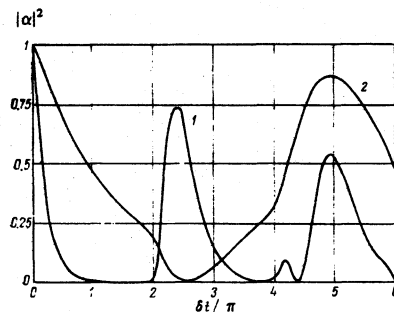

FIG. 1. Dependence of the quantity $|a|^2$ on the time for excitation into a discrete band with a Lorentz contour for the transition cross sections. The parameter values are: $s/\delta = 0$ and $\sigma/\delta = 5$; curve 1—$\gamma_0/\delta = 0.5$ ($\gamma/\delta = 1.98$); curve 2—$\gamma_0/\delta = 0.2$ ($\gamma/\delta = 0.79$).
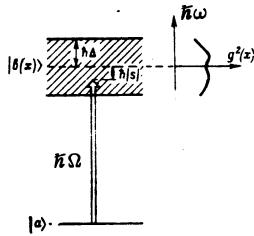
FIG. 2. Level scheme and notation for the case of excitation to a continuous limited band.

mension of frequency, is reckoned from the center of the band $(-\Delta < x < \Delta)$. It is convenient to use the following notation for the matrix element of the interaction operator:

$$\langle b(x)|\hat{\mu}\mathscr{E}/2\hbar|a\rangle = \gamma g(x). \tag{3.1}$$

Here, just as in (2.1) and (2.12), the form factor $g(x)$ of the transition cross section is normalized in such a way that

$$\int_{-\Delta}^{\Delta} g^2(x) = 1.$$

In the assumed notation, the equations in (1.1) take the form

$$\begin{aligned}
\frac{da(t)}{dt} &= i\gamma e^{ist}\int_{-\Delta}^{\Delta} g(x)b(x,t)e^{-ixt}dx, \\
\frac{db(x,t)}{dt} &= i\gamma g(x)e^{i(x-s)t}a(t),
\end{aligned} \tag{3.2}$$

where, as before, s is the deviation from resonance with the field for a transition to the center of the band.

Regarding (3.2) as equations for the determination of the quasi-energy eigenvalues, we seek the solution in the form

$$\begin{aligned}
a(t) &= A(\lambda)\exp[i(s-\lambda)t], \\
b(x,t) &= B(x,\lambda)\exp[i(x-\lambda)t],
\end{aligned} \tag{3.3}$$

where the quasi-energy $\hbar\lambda$ is reckoned from the center of the band. From this we get the following equations that connect the coefficients $A(\lambda)$ and $B(x,\lambda)$:

$$\begin{aligned}
(s-\lambda)A(\lambda) &= \gamma\int_{-\Delta}^{\Delta} g(x)B(x,\lambda)dx, \\
(x-\lambda)B(x,\lambda) &= \gamma g(x)A(\lambda).
\end{aligned} \tag{3.4}$$

The condition for the existence of a nontrivial solution of the system (3.4) obviously determine the spectrum of the eigenvalues λ_j, and the corresponding connection between $A(\lambda_j)$ and $B(x,\lambda_j)$ determines the wave functions of the quasi-energy eigenstates (QES).

An investigation of Eqs. (3.4) shows that the quasi-energy spectrum always contains a continuous segment

$$-\Delta < \lambda < \Delta, \tag{3.5}$$

which coincides with the energy spectrum of the band. In fact, considering the function $B(x,\lambda)$ in a generalized sense, we obtain from the second equation of (3.4), if the condition (3.5) is satisfied,[39]

$$B(x,\lambda) = \gamma g(x)A(\lambda)\mathscr{P}\frac{1}{x-\lambda} + C(\lambda)\delta(x-\lambda). \tag{3.6}$$

Substituting (3.6) in the first equation of (3.4) we get

$$C(\lambda) = \frac{A(\lambda)}{g(\lambda)}\left[\frac{s-\lambda}{\gamma} - \gamma\int_{-\Delta}^{\Delta}\frac{g^2(x)}{x-\lambda}dx\right]. \tag{3.7}$$

Thus, when (3.5) holds, the system (3.4) has a nontrivial solution determined by formulas (3.6) and (3.7).

In (3.6) and (3.7), $A(\lambda)$ is in essence a normalization factor. It is convenient in what follows to normalize the quasi-energy eigenstates to a δ function, putting

$$1 + \frac{1}{A(\lambda)A(\lambda_1)}\int_{-\Delta}^{\Delta}B(x,\lambda)B(x,\lambda_1)dx = \frac{\delta(\lambda-\lambda_1)}{A(\lambda)A(\lambda_1)}. \tag{3.8}$$

The possiblity of such a normalization follows from the general property of the orthogonality of the quasi-energy eigenstates,[36] and also directly from (3.4). Integrating (3.8) with respect to λ_1 over the interval $-\Delta < \lambda_1 < \Delta$ and using the Poincare–Bertrand permutation formula[40] we obtain after simple calculations the following expression for the normalization constant:

$$A(\lambda) = \left\{\frac{1}{g^2(\lambda)}\left[\frac{s-\lambda}{\gamma} - \gamma\int_{-\Delta}^{\Delta}\frac{g^2(y)}{y-\lambda}dy\right]^2 + \pi^2\gamma^2 g^2(\lambda)\right\}^{-1/2}. \tag{3.9}$$

We now obtain conditions under which discrete eigenvalues λ exist outside the interval $(-\Delta, \Delta)$. These eigenvalues, as follows from (3.4), must satisfy the transcendental equation

$$s-\lambda = \gamma^2\int_{-\Delta}^{\Delta}\frac{g^2(x)}{x-\lambda}dx \quad (|\lambda|>\Delta). \tag{3.10}$$

The simple properties of (3.10) allow us to formulate the following statements, which cover all the possible cases.

1. There exist not more than two discrete eigenvalues $(\lambda_+ > \Delta$ and $\lambda_- < -\Delta)$.

2. If the condition $\lim g(x) \neq 0$ is satisfied, a discrete eigenvalue λ_+ exists for any value of the field amplitude.

3. If the radiation frequency is lower than the frequency of the transition to the upper edge of the band $(s < \Delta)$ and if the condition

$$\lim_{x\to\Delta} g(x) = 0,$$

is satisfied, then on discrete eigenvalue λ_+ appears only at field amplitudes exceeding a certain critical value determined from the equation

$$\gamma_{cr}^2\int_{-\Delta}^{\Delta}\frac{g^2(x)}{\Delta-x}dx = \Delta-s. \tag{3.11}$$

4. If the radiation frequency lies above the frequency of the transition to the upper edge of the band $(s > \Delta)$, then a discrete eigenvalue λ_+ exists for any value of the field amplitude regardless of the value of $g(x)$ at the upper limit $x = \Delta$.

5. Statements analogous to 2–4 can be formulated also for the discrete eigenvalue λ_-.

The structure of the quasi-energy eigenstates for the discrete eigenvalues $\lambda_\pm$ is determined by the relation

$$B(x,\lambda_\pm) = \gamma g(x)A(\lambda_\pm)/(x-\lambda_\pm). \tag{3.12}$$

Therefore, normalizing the discrete quasi-energy eigenstate to unity, we obtain the following expression for the normalization constants $A(\lambda_\pm)$:

$$A(\lambda_\pm) = \left[1 + \gamma^2 \int_{-\Delta}^{\Delta} \frac{g^2(y)}{(y-\lambda_\pm)^2} dy\right]^{-1/2}. \tag{3.13}$$

We have thus obtained the quasi-energy spectrum and the wave functions of the quasi-energy eigenstates. Using the orthogonality properties of the quasi-energy eigenstates, we can obtain a solution of the system (3.2) with arbitrary initial conditions. We shall not write out the solution in general form, and confine ourselves to the case of a constant dipole moment of the transitions to the band

$$g(x) = (2\Delta)^{-1/2}, \tag{3.14}$$

with initial conditions (1.4). For this case both discrete quasi-energy states exist, and the solution takes the form

$$a(t) = e^{ist}\left\{\frac{\lambda_+^2 - \Delta^2}{\lambda_+^2 + \gamma^2 - \Delta^2} e^{-i\lambda_+ t} + \frac{\lambda_-^2 - \Delta^2}{\lambda_-^2 + \gamma^2 - \Delta^2} e^{-i\lambda_- t}\right.$$
$$\left. + \int_{-\Delta}^{\Delta} \frac{e^{-i\lambda t} d\lambda}{2\Delta F^2(\lambda) + \pi^2\gamma^2/2\Delta}\right\}, \tag{3.15}$$

$$b(x,t) = -(2\Delta)^{1/2} \frac{F(x)}{2\Delta F^2(x) + \pi^2\gamma^2/2\Delta}$$

$$+ \frac{\gamma}{(2\Delta)^{1/2}} e^{ist} \cdot \left\{\frac{\lambda_+^2 - \Delta^2}{(\lambda_+^2 + \gamma^2 - \Delta^2)(x-\lambda_+)} e^{-i\lambda_+ t} + \frac{\lambda_-^2 - \Delta^2}{(\lambda_-^2 + \gamma^2 - \Delta^2)(x-\lambda_-)} e^{-i\lambda_- t}\right.$$
$$\left. + \int_{-\Delta}^{\Delta} \frac{e^{-i\lambda t} d\lambda}{(x-\lambda)[2\Delta F^2(\lambda) + \pi^2\gamma^2/2\Delta]}\right\}. \tag{3.16}$$

The function F is determined here by the relation

$$F(\lambda) = \frac{\lambda - s}{\gamma} - \frac{\gamma}{2\Delta} \ln\frac{\Delta+\lambda}{\Delta-\lambda}, \tag{3.17}$$

and $\lambda_\pm$ are respectively the positive and the negative roots of the equation

$$\lambda - s = \frac{\gamma^2}{2\Delta} \ln\frac{\lambda+\Delta}{\lambda-\Delta}. \tag{3.18}$$

The properties of the obtained solution depend essentially on the relation between the probability W_d of finding the system in discrete quasi-energy states and the probability W_{cont} for finding the system in continuous quasi-energy states. Obviously,

$$W_d = \frac{\lambda_+^2 - \Delta^2}{\lambda_+^2 + \gamma^2 - \Delta^2} + \frac{\lambda_-^2 - \Delta^2}{\lambda_-^2 + \gamma^2 - \Delta^2}, \quad W_{cont} = 1 - W_d. \tag{3.19}$$

In the limiting case $W_d \gg W_{cont}$ the solution has in the main an oscillating character determined by the discrete quasi-energy states. In the limiting case $W_d \ll W_{cont}$ the main singularity of the solution is the damping of the amplitude of the lower level, due to the damping of the integral term in (3.15). We shall illustrate this circumstance for the particular case of resonance at the center of the band ($s = 0$). In this case $\lambda_- = -\lambda_+$.

For a strong field, when the condition

$$\gamma \gg \Delta \tag{3.20}$$

is satisfied, the roots of (3.18) can be estimated, accurate to terms $\sim(\Delta/\gamma)^2$, as follows:

$$\lambda_\pm \sim \pm\gamma(1 - \Delta^2/2\gamma^2), \tag{3.21}$$

and it follows from (3.19) that

$$W_d \sim 1 - (\Delta/\gamma)^2, \quad W_{cont} \sim (\Delta/\gamma)^2, \quad W_d \gg W_{cont}. \tag{3.22}$$

The solution oscillates, just as for a two-level system, and all the states of the bands are on the average approximately equally excited.

In the case of a weak field, when the condition $\gamma \ll \Delta$ is satisfied, the roots of (3.18) are exponentially close to the edges of the band:

$$\lambda_\pm \sim \pm\Delta[1 + 2\exp(-2\Delta^2/\gamma^2)]. \tag{3.23}$$

It then follows from (3.19) that W_d is exponentially small:

$$W_d \sim \frac{8\Delta^2}{\gamma^2} \exp\left(-\frac{2\Delta^2}{\gamma^2}\right) \ll 1. \tag{3.24}$$

Thus, the process of excitation is described by the integral damped term in (3.13). Obviously, if the condition (3.20) is satisfied the main contribution to this integral term is made by the vicinity of the point $\lambda = 0$, where $F(\lambda) \approx \lambda/\gamma$.

Neglecting the logarithmic term in Eq. (3.17) for $F(\lambda)$ and extending formally the integration to the entire infinite axis, we arrive at the expression

$$a(t) \sim \exp(-\pi\gamma^2 t/2\Delta), \tag{3.25}$$

which coincides exactly with (2.21) if the "resonant" matrix element of the interaction operator is introduced in both expressions in explicit form. As to the distribution produced in the band in the course of the excitation, a simple estimate can be obtained by integrating the equations (3.2) and using (3.25). As a result we obtain for the probabilities $|b(x)|^2$ the Lorentz distribution

$$|b(x)|^2 \infty (x^2 + \pi\gamma^4/4\Delta^2)^{-1}, \tag{3.26}$$

whose maximum corresponds to resonance, and whose characteristic width coincides with the rate of decay of the lower level. These two facts, naturally, are consequences of the energy conservation law and of the uncertainty relation.

The intermediate cases are reflected in the calculations illustrated in Fig. 3, which shows plots of W_d
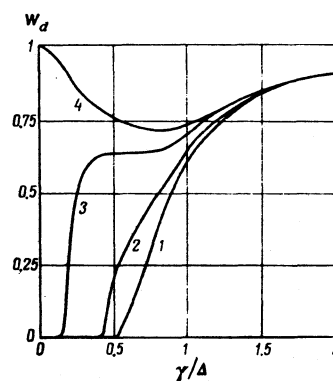

FIG. 3. Dependence of the probability W_d of finding the system in discrete quasi-energy eigenstates on the parameter γ/Δ for the case of excitation into a bounded continuous band with constant dipole moment of the transitions. The deviations of the field frequency from the frequency of the transition to the center of the band are: 1—$s/\Delta = 0$; 2—$s/\Delta = 0.5$; 3—$s/\Delta = 0.9$; 4—$s/\Delta = 1.1$ (in the last case, the field frequency exceeds the frequency of the transition to the upper edge of the band.

against the ratio γ/Δ. In addition to the case of resonance at the center of the band ($s=0$), curves were calculated also for other values of s.

4. CASE OF BAND WITH PRONOUNCED LEVEL

In the preceding sections it was shown that in a sufficiently weak field the excitation of the "level-band" level is described by exponential decay of the lower discrete level [see formulas (2.21) and (3.25)]. It is of interest to examine the change in the excitation dynamics if the band has a pronounced level $|c\rangle$ that is dipole-coupled with the lower state $|a\rangle$ much more strongly that the remaining levels $|b_n\rangle$ of the band.

The methods described in Secs. 2 and 3 for the solution of the equations of the amplitudes can be easily generalized also to this case. It turns out that all the main qualitative features can be illustrated with a simple example of a continuous Lorentz band with a pronounced level, the transition to which from the lower state is at resonance (Fig. 4a). In this case, interest attaches to the situation when the pronounced level is near the center of the band, i.e.,

$$|s| \lesssim \sigma, \tag{4.1}$$

and the field is weak enough:

$$\gamma/\sigma \lesssim 1. \tag{4.2}$$

The equations for the amplitudes of the level system shown in Fig. 4a are

$$\frac{da}{dt} = i\gamma \left(\frac{\sigma}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} \frac{b(x)}{x^2+\sigma^2} \exp[i(s-x)t]dx + i\Gamma c,$$

$$\frac{db(x)}{dt} = i\gamma \left(\frac{\sigma}{\pi}\right)^{1/2} \frac{a}{x^2+\sigma^2} \exp[i(x-s)t], \quad \frac{dc}{dt} = i\Gamma a. \tag{4.3}$$

Here $\Gamma = \langle c | \hat{\mu}\mathscr{E}/2\hbar | a \rangle$, and the criterion of "strong" coupling of the levels $|a\rangle$ and $|c\rangle$ can naturally be taken to be the inequality

$$\Gamma \gg \gamma^2/\sigma. \tag{4.4}$$

A solution satisfying the initial conditions (1.4) supplemented by the conditions $c(0) = 0$ can be obtained for Eqs. (4.3) for the amplitude of the lower level $a(t)$ in the same manner as in Sec. 2 by using the Laplace transformation. This solution takes the form

$$a(t) = \frac{q_1(q_1+\sigma-is)}{(q_1-q_2)(q_1-q_3)} e^{q_1 t} + \frac{q_2(q_2+\sigma-is)}{(q_2-q_1)(q_2-q_3)} e^{q_2 t} + \frac{q_3(q_3+\sigma-is)}{(q_3-q_1)(q_3-q_2)} e^{q_3 t}, \tag{4.5}$$

where q_k are the roots of the equation

$$q^3 + (\sigma-is)q^2 + (\Gamma^2+\gamma^2)q + \Gamma^2(\sigma-is) = 0. \tag{4.6}$$

When the conditions (4.1), (4.2), and (4.4) are satisfied, the solution (4.5) takes the approximate form

$$a(t) \sim \frac{1}{2} \exp\left[i\Gamma t - \frac{1}{2} \frac{\gamma^2\sigma t}{(s-\Gamma)^2+\sigma^2}\right]$$

$$+ \frac{1}{2} \exp\left[-i\Gamma t - \frac{1}{2} \frac{\gamma^2\sigma t}{(s+\Gamma)^2+\sigma^2}\right]. \tag{4.7}$$

We have retained in this formula the principal terms of the real and imaginary parts of the two roots $q_{1,2}$ of Eq. (4.6). The third root $q_3 \approx (is - \sigma)(1-\gamma^2/\Gamma^2)$ makes a small contribution to the solution.

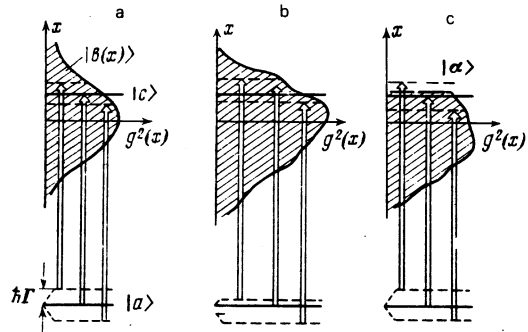The solution (4.7) has a clear meaning. For times t

FIG. 4. Process of excitation into a continuous band with a pronounced level. The dashed lines show schematically the quasi-energy states in the approximation of the two-level system $|a\rangle - |c\rangle$, and also the most effectively populated states $|b\rangle$ of the continuous spectrum.

satisfying the condition

$$1/\Gamma \ll t \ll \sigma/\gamma^2, \tag{4.8}$$

the amplitude of the lower level oscillates, just as in the case of the two-level system. The oscillations are damped at a rate corresponding approximately to the characteristic rate of transitions from the discrete lower level to the continuous band [see formula (2.21)]. A more accurate interpretation of the damping rates of each of the terms in (4.7) becomes understandable if we start from the quasi-energy approach. Indeed, because of the interaction with the level $|c\rangle$, the level $|a\rangle$ is split in the field into two quasi-energy states located at distances $\mp\hbar\Gamma$ from the exact resonance (see Fig. 4a). As a result of this splitting, the states that are "resonant" in the continuous band are now those separated from the exact resonance by the amount $\mp\hbar\Gamma$. The corresponding values of the matrix element of the interaction operator are given by the relations

$$\gamma_r = \gamma \left\{ \frac{\sigma}{\pi[(s\mp\Gamma)^2+\sigma^2]} \right\}^{1/2}. \tag{4.9}$$

It is precisely the quantities $\pi\gamma_r^2$ which characterize the decay rates of the first and second terms in (4.2) respectively. The factor $1/2$ takes into account the fact that for each of the quasi-energy states the probability of being located at the level $|a\rangle$ from which the decay to the continuum takes place is equal to $1/2$.

This interpretation of the obtained solution can be easily generalized also to include the case of an arbitrary $g(x)$ dependence [see (3.1)]. In addition, the frequency of the pronounced transition can differ from the field frequency. In the general case (see Fig. 4b) the interaction with the field is best taken into account in two steps. In the first step we obtain the quasi-energy states that interact relatively more strongly with the field of the two-level system. The second stage is essentially equivalent to calculating the probabilities of the transitions from the obtained quasi-energy states into the continuous spectrum.

Special notice should be taken of the situation when the pronounced level is near the edge of the band (Fig. 4c), so that in the case of its resonant interaction with the lower state one of the quasi-energy states $|\alpha\rangle$ is beyond the edge of the band. In this case a system in-

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itially in the lower state remains, with probability 1/2, in the state $|\alpha\rangle$ for an arbitrarily long time.

5. CONCLUSION

At the present time there is not a single concept with which to describe the process whereby a polyatomic molecule acquires energy over the levels over a quasi-continuum of excited vibrational states. We can perhaps mention only two papers[41,42] where attempts were made to compare the theoretical models with the experimental results.

The theory developed in the present paper for the interaction between a field and a "level-band" quantum system is the simplest model problem for one act of photon absorption in a quasi-continuum. At the same time, we can formulate on the basis of the results the main premises of a theoretical description of the manner in which the molecule acquires energy in the quasi-continuum. To this end, we make a few estimates on the basis of the experimental data on the excitation of the ν_3 vibrational mode of the SF_6 molecule, for which this process was most thoroughly studied.

1. It is known from experiment that at CO_2-laser pulse energy densities $E > 0.1$ J/cm^2 most of the rotational states of the SF_6 molecules take part in the excitation.[43,44] The characteristic width of the absorption band in a strong field is then $\Delta\nu_{abs} \sim 20$ cm^{-1} (Ref. 45). From these two experimental facts we can obtain the following lower bound for $\Delta\nu_{quas}$ of the widths of the transitions from a given vibrational-rotational state to vibrational quasi-continuum energies ($E_{vib} > (3\ldots5)\hbar\omega$ (Refs. 10 and 11):

$$\Delta\nu_{quas} \gtrsim \Delta\nu_{abs} \quad \text{or} \quad \Delta\nu_{quas} \gtrsim 20 \, cm^{-1}. \tag{5.1}$$

It follows from experimental results[46] that this lower-bound estimate is possibly smaller by a factor 2-3 than the real value of $\Delta\nu_{quas}$.

2. The dipole moment for an allowed vibrational-rotational transition in the ν_3 mode of the SF_6 molecule amounts to $\mu_{01} \approx 0.3$ D.[47] For an allowed transition from a specified excited level to a state with energy E_{vib}, the dipole moment in the harmonic approximation has an estimated upper bound

$$\mu \lesssim \mu_{01}(E_{vib}/\hbar\omega_3)^{1/2}. \tag{5.2}$$

Since the mixing of the states, which leads to the quasi-continuous "band" of transitions, does not change the integrated value of the square of the dipole moment, the following estimate holds true for the parameter γ (see Secs. 2 and 3) that characterizes the integral interaction of the band with the level:

$$\gamma \lesssim \frac{\mu_{01}\mathscr{E}}{2\hbar}\left(\frac{E_{vib}}{\hbar\omega_3}\right)^{1/2}. \tag{5.3}$$

Assuming a laser intensity $I = 10^7$ W/cm^2, at which the SF_6 absorbs ~ 10 photons[48] ($E_{vib}/\hbar\omega_3 \sim 10$), we estimate the upper bound of γ under typical experimental conditions at

$$\gamma < 0.6 \, cm^{-1}. \tag{5.4}$$

3. From the estimates (5.1) and (5.4) it follows that, under the experimental conditions of the energy acquisition by the SF_6 molecule over the quasi-continuum
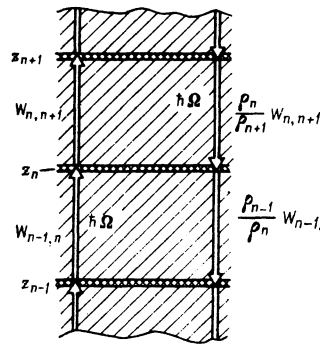

FIG. 5. Illustration of the theoretical description of the process of energy acquisition by a polyatomic molecule in the quasi-continuum region of excited vibrational states under the influence of IR radiation.

levels, the following inequality is certainly satisfied:

$$\gamma \ll \Delta\nu_{quas}. \tag{5.5}$$

This ratio of the parameters (see Secs. 2 and 3) corresponds to an exponential decay of the level into a band. This circumstance is in fact the basis of the possibility of describing the dynamics of excitation of the quasi-continuum within the framework of kinetic equations that operate with the transition rates W, as noted in a number of papers.[26,41,42,49-51]

The kinetic equations must describe the time variation of the populations z_n, summed over states lying in narrow energy intervals near the energies $n\hbar\Omega$ which are multiples of the laser-quantum energy (Fig. 5). These equations take the following form[41,50,51]:

$$\frac{dz_n}{dt} = W_{n-1,n}\left(z_{n-1} - \frac{\rho_{n-1}}{\rho_n}z_n\right) - W_{n,n+1}\left(z_n - \frac{\rho_n}{\rho_{n+1}}z_{n+1}\right). \tag{5.6}$$

Here ρ_n is the density of the vibrational states for the energy $n\hbar\Omega$. In Eqs. (5.6), the only unknown quantities are in fact the rates of the successive transitions $W_{n-1,n}$. Since the integrated cross sections of the transitions from states with energy $(n-1)\hbar\Omega$ are quite easy to determine from the known characteristics of the molecule, the only unknown parameters that necessitate a thorough comparison of theory with experiment are the form factors $g_{n-1,n}(x)$ [see formula (3.1)] of the cross sections of the successive transitions.

An interesting question (see Ref. 6) is whether an individual triplet degenerate vibrational mode of a spherical-top type molecule (e.g., the ν_3 mode of the SF_6 molecule) can form a quasi-continuum via an intrinsic anharmonic splitting without participation other modes of the molecule. It is known[52] that an anharmonic interaction leads to a splitting of the levels of a triplet degenerate mode with energy $v\hbar\omega$. The characteristic distance between the components of the anharmonic splitting, for example for the SF_6 molecule, amounts to $\delta_{anh} \sim 1$-7 cm^{-1} (Refs. 5 and 8). This quantity depends little on the number of vibrational level v, since both the width of the multiplet and the number of its components are proportional to v^2. Assume that an optimal case is realized, when transitions are possible between all the components of the level with number $v - 1$ and the level with number v, and that the dipole moment is

uniformly distributed over all the possible transitions. From this we find that the dipole moment of each individual transition does not exceed μ_{01}. Using the value of μ_{01} given above for the SF_6 molecule, we find that for typical experimental conditions ($I \sim 10^7 \ W/cm^2$) we have

$$\gamma_p \lesssim 0.2 \ cm^{-1} \quad or \quad \gamma_r \ll \delta_{anh} \ . \tag{5.7}$$

Thus, the transition density produced only on account of anharmonic splitting is patently insufficient for the formation of a quasi-continuum, since the criterion (1.5) derived in Sec. 2 is not satisfied. It was pointed out in Ref. 9, however, that a possible role can be played by the octahedral splitting of the vibrational-rotational sublevels degenerate in the projection of the angular momentum on an axis connected with the molecule. This additional splitting can substantially increase the density of the transitions and ensure satisfaction of the criterion (1.5). In addition, interest attaches to the case when certain definite (but not all) vibrations participate in the formation of the quasi-continuum in addition to the triply degenerate mode. This possibility was recently discussed in Ref. 42.

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Ionization detection of single atoms by laser radiation using Rydberg states

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Single atoms of sodium and ytterbium were detected by the electric-field ionization of atoms from high (Rydberg) states. Sodium and ytterbium atoms in a beam were stepwise excited to Rydberg states by radiation from tunable dye lasers and ionized by electric field pulses. The conditions for maximum ion yield were investigated and implemented in the excitation and ionization processes. The statistics of appearance of atoms in the detection zone was studied for low-density beams under ion counting conditions.

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1. INTRODUCTION. FORMULATION OF THE PROBLEM

Much attention has been paid recently to methods for detecting very small amounts of matter. The smallest amount of matter detectable in the atomic approach is a single atom because it carries full spectral information on matter. Consequently, the sensitivity of an ideal recording system should be capable of detecting a single atom. Among all the detection methods, the most promising is the laser excitation of resonance fluorescence and selective stepwise ionization of atoms by laser radiation.

In the resonance fluorescence method,[1] an atom emits photons repeatedly, returning to the initial state after each emission and it can be subjected once again to laser radiation. However, repeated excitation and relaxation of an atom back to the ground state require the existence of a transition close to that found in a two-level system. This seriously restricts the class of atoms that can be detected. The stepwise ionization method[2,3] is more universal than the fluorescence detection technique but it is destructive because the recorded atom is ionized and no longer interacts with the laser field. Attention has been drawn[4-6] to the possibility of using the stepwise ionization method in detecting atoms since the quantum efficiency of photoionization is close to unity if the energy density of laser pulses is high enough.[7] Modern methods for recording charged particles can detect ions and electrons with near-unity efficiency. If the transitions involved in the excitation stages are completely saturated, it is possible to use about half the atoms in the ground state. Consequently, under these conditions, one can detect every second atom. The first successful experimental detection of single atoms by the stepwise photoionization method was reported in Ref. 8. Cesium atoms in a buffer gas were excited to the $7^2P_{3/2}$ state by dye laser pulses and the same pulses were used for the subsequent ionization. The resultant electron–ion pairs were detected by a proportional counter. The system thus provided a stable means for detecting single cesium atoms.

However, the application of this method to atoms moving at thermal velocities in vacuum, which are of the greatest interest, presents the difficulty of very stringent requirements in respect of the energy of ionizing laser radiation. This is due to the relatively small photoionization cross section of the atoms ($\sigma_{\text{ion}} \approx 10^{-17} - 10^{-18}$ cm^2). When the thermal velocity is $\bar{v} = 5 \times 10^4$ cm/sec and the diameter of a laser beam is $d = 1$ cm, every atom moving at right-angles to a laser beam can be ionized if the laser pulses are repeated at a frequency of 50 kHz. Under these conditions, the average laser radiation power required for efficient ionization amounts to several kilowatt.

The energy of laser pulses needed for the ionization of an atom can be reduced by several orders of magnitude if an atom is ionized from a high state by an electric field. This ionization method was proposed, implemented, and investigated in detail by the present authors and their colleagues.[9-11] In this method, the nonresonance process of photoionization from an intermediate state is replaced by resonance excitation of an atom to a high (Rydberg) state and subsequent ionization by an electric field pulse, which ensures near 100% ion yield.

An atom can be excited to a high state in two or three stages by radiation from several pulsed dye lasers synchronized with one another. The selection of the excitation scheme depends on the actual atom. For alkali metal atoms, it is convenient to use the two-stage excitation scheme. In the case of heavy elements with