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Kinetics of Doppler-spectrum saturation

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The influence of spectral migration on the saturation kinetics is investigated. It is assumed that the radiation is monochromatic and that its interaction with the medium can be described in the balance approximation. A dependence of the spectral migration and of the method of realizing the latter on the frequency ν is observed at not too large and not too small field powers and of ν (migration-accelerated stage). The width of the saturation-induced dip in the population spectrum is either constant in time if the frequency jumps are comparable with the width of the spectrum, or else increases monotonically if the jumps are so small that they result additively in spectral diffusion.

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1. INTRODUCTION

It is known that when a powerful coherent field interacts with an ensemble of inhomogeneously broadened two-level systems the first to be saturated are those transitions whose frequency detunings are within the limits of the homogeneous width. This leads to the appearance of a dip in the density of the distribution of the population difference of the two-level systems with respect to the transition frequencies—a phenomenon which serves as the basis of numerous nonlinear spectroscopy effects.[1,2] On account of absorption on the wing of the inhomogeneous line, and also because of spectral migration in the course of time, the transitions farther away from resonance become successively saturated in the course of time. The width of the resultant dip increases until the interaction with the medium, which tends to produce an equilibrium distribution of the populations over the frequencies, establishes a stationary form of the dip.

Nonlinear spectroscopy methods can be used to study all the factors on which the shape of the dip depends: the characteristics of the saturating field itself, as well as the processes of spectral migration and relaxation due to the interaction with the medium. The study of the latter is important not only from the point of view of population of quantum generators, but also because they yield valuable information on the irradiated sample, information difficult or impossible to obtain by other methods.

However, whereas the influence of relaxation on the formation of a dip can in most cases of practical importance be adequately described by introducing into the theory the relaxation constants, the role of the spectral migration is a much more difficult to evaluate.

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It is possible to advance farthest in this direction by regarding the spectral migration as a Markov random process. In this case the problem can be reduced to a solution of a system of integro-differential equations or partial differential equations.[3,4] Even in this form the problem still remains quite complicated. For an arbitrary strong interaction with the field, only a stationary solution could be studied so far, and that only in the case when the step of the spectral migration is commensurate with the width of the contour (uncorrelated process).[3,5-8] It is not excluded, however, that the migration is affected via small jumps of frequency and adds up to form a spectral diffusion (correlated process). Judging from precedents,[9,10] these cases are kinetically distinguishable, i.e., one should expect the formation of the dip in uncorrelated and correlated migrations of the frequency to be qualitative quite different.

To investigate this question to full extent, we consider it in the so-called balance approximation. The latter greatly simplifies the problem and makes it possible to describe the process in terms of transition probabilities. This simplification is legitimate if the homogeneous broadening of the spectral components is larger than the migration rate. It makes it possible to go far beyond the limits of the linear (in the interaction with light) theory. It becomes possible to investigate the kinetics of saturation of an ensemble of inhomogeneously broadened two-level systems in a powerful monochromatic field, both in the uncorrelated and the correlated case. It turns out that not only the kinetics of formation of the dip in the distribution of the populations in frequency, but also the time variation of the integral population of the states depends substantially on the degree of correlation of the frequency migration.

Since the line shape of luminescence or absorption (amplification) of a weak field is not very sensitive to the type of spectral migration,[11] it was already proposed many times to investigate this process by means of nonlinear spectroscopy. Experimental and theoretical studies were made of the manner in which the dip (peak) smears out, after the field is turned off, in inhomogeneous EPR lines,[12,13] in the optical spectra of activated glasses, and in gas lines broadened as a result of the Doppler effect[9,17-19] and of the rotational structure.[20] A study was also made of the distributions of populations during the time of the action in the field, but within the framework of perturbation theory[13,21,22] or in the boundary-condition approximation.[13,23,24]

It is shown in the present paper that the same information can be obtained by observing optically induced relaxation of the integral populations of levels, which is an easier procedure.

It must be emphasized that the theory developed here describes the interaction of a powerful field with an inhomogeneously broadened contour both in the optical and in the microwave bands, regardless of the origin of the broadening. The results obtained for the integral populations are equally applicable also to the description of the relaxation of a homogeneously broadened two-level system under the influence of frequency-modulated radiation, which is considered in Ref. 3. However, for the sake of argument, we shall consider henceforth and throughout the interaction of monochromatic light with a line inhomogeneously broadened as a result of the Doppler effect.

2. FORMULATION OF PROBLEM

The equations for the density matrix of a gas molecule[25-28] situated in an external monochromatic field resonant to the transition 1–2 can be reduced in the spatially homogeneous case to the form

$$\frac{\partial n(v,t)}{\partial t}=-4\,\mathrm{Im}\,V\sigma(v,t)+L_v n-\Gamma_1[n(v,t)-n_0\varphi(v)], \tag{2.1a}$$

$$\frac{\partial \sigma(v,t)}{\partial t}=[i(kv-\Omega)-\Gamma]\sigma(v,t)+iVn(v,t)+L_v\sigma. \tag{2.1b}$$

Here Γ_1 and Γ are respectively the rates of the longitudinal and transverse relaxation of the transition 1–2, $\Omega=\omega-\omega_0$ is the detuning of the frequency ω of the external field from the transition frequency $\omega_0=(E_2-E_1)/\hbar>0$ of the immobile atom, v is the projection of the velocity of the atom in the wave vector of the field $k=\omega_0/c$ is the wave number, c is the speed of light, $n=\rho_{11}-\rho_{22}$, $\sigma=\rho_{12}e^{-i\omega t}$, and ρ_{ik} are the elements of the density matrix. As usual, the nonresonant component of the field is neglected, i.e., the off-diagonal element of the Hamiltonian is of the form $H_{12}=Ve^{i\omega t}$, where $V=d_{12}E/\hbar$, while E is the complex amplitude of the field. To simplify the notation, the phase shift of the dipole moment of the transition d_{12} is chosen such that the interaction amplitude V is real.

The collision term is

$$L_v n=-\frac{1}{\tau_0(v)}n(v,t)+\int\frac{1}{\tau_0(v')}f(v',v)n(v',t)\,dv'. \tag{2.2}$$

Here $\tau_0(v)$ is the mean free path time and depends, generally speaking, on the velocity of the molecule, and $f(v',v)$ is the distribution in the velocities v acquired as a result of the collision by the particles that had prior to the collision a velocity v'. The width δ of the kernel $f(v',v)$ of the integral operator L_v is a measure of the change of the velocity in one collision. The kernel $f(v',v)$ is normalized:

$$\int f(v',v)\,dv=1. \tag{2.3}$$

At equilibrium the collision term (2.2) should be equal to zero, therefore the kernel $f(v',v)$ satisfies the stationarity condition

$$\int\frac{\varphi(v')}{\tau_0(v')}f(v',v)\,dv'=\frac{\varphi(v)}{\tau_0(v)}, \tag{2.4}$$

where

$$\varphi(v)=\frac{1}{(2\pi)^{1/2}\bar{v}}\exp\left(-\frac{v^2}{2\bar{v}^2}\right) \tag{2.5}$$

is the one-dimensional Maxwell distribution. We define similarly the operator $\tilde{L}_v$, the free path time $\tilde{\tau}_0(v)$, and the collision kernel $\tilde{f}(v',v)$ for the off-diagonal element σ. For simplicity we assume here that the parameters Γ_1 and Γ are independent of velocity.

Equation (2.1a) implies that the collision operators L_v are the same for both levels. This means that we are dealing here more readily with vibrational-rota-

tional than with electronic transitions.[28] If the two-levels are excited, then the depletion rates Γ_1 of the two levels are assumed to be equal. In the optical band, the stationary population difference $n_0 = \rho_{11}^0 - \rho_{22}^0$ is maintained because of the equilibrium form of the pump which populates the levels 1 and 2 at respective rates $\Gamma_1\rho_{11}^0$ and $\Gamma_1\rho_{22}^0$. Since the external resonance field does not change the total number of molecules in the 1–2 transition, it follows that

$$\rho_{11}(v,t)+\rho_{22}(v,t)=(\rho_{11}^0+\rho_{22}^0)\varphi(v).$$

Using this equality and the definition of n, we can express the populations of levels 1 and 2 in terms of the population difference

$$\begin{aligned}\rho_{11}(v,t)&=\tfrac{1}{2}[(\rho_{11}^0+\rho_{22}^0)\varphi(v)+n(v,t)],\\ \rho_{22}(v,t)&=\tfrac{1}{2}[(\rho_{11}^0+\rho_{22}^0)\varphi(v)-n(v,t)].\end{aligned}\tag{2.6}$$

Equations (2.1) are valid not only in the case $\Gamma_1=\Gamma_2$, which we shall call problem 1, but also in the case when the rate of depletion Γ_1 of one of the excited levels (for example, level 1) is much less than the rate of deactivation Γ_2 of the second level (for example, level 2) and the field is not so strong as to populate noticeably the second level (problem 2). In the last case $n\approx\rho_{11}$, and the first term in the right-hand side of (2.1a) should be decreased by one-half. Finally, we note that Eqs. (2.1) and (2.6) remain in force also for a two-level system[3] in which the levels 1 and 2 are relaxationally coupled only with each other.

It is possible to measure the populations of the transition 1–2 by observing, either along or opposite to the direction of propagation of the powerful field, the absorption (amplification) of the weak field or the luminescence on the same or adjacent transition. The optical characteristics of these processes are proportional to the integral populations

$$\bar{\rho}_{ii}(t)=\int\rho_{ii}(v,t)\,dv,\tag{2.7}$$

and the spectral characteristics yield information on the distribution on the populations in velocity. Since the powerful field distorts substantially the absorption (amplification) and luminescence spectra,[21] the latter are easiest to analyze directly after the termination of the action of the powerful field, when they are simply proportional to the convolution of the form functions of the homogeneous component of the transition with the distribution of the populations in velocity.

In addition to the populations, interest attaches also to the energy absorbed by the molecule per unit time,

$$I(t)=2\hbar\omega\,\mathrm{Im}\,V\int\sigma(v,t)\,dv.\tag{2.8}$$

In the integration of Eq. (2.1a) with respect to v, the collision term vanishes because of (2.3), and we find that the result

$$I(t)=\frac{\hbar\omega}{2}\{\Gamma_1[n_0-\bar{n}(t)]-\dot{\bar{n}}(t)\},\tag{2.9}$$

previously obtained for the case when there is no spectral migration,[3,29] is valid also in the presence of migration.

Equations (2.1) can be used to describe an ensemble of inhomogeneously broadened two-level systems independently of causes of the inhomogeneous broadening and of the spectral migration, and also to describe transitions in a homogeneously broadened two-level system under the influence of a frequency-modulated wave.[3] For this purpose it is necessary only to put in (2.1) $k=1$ and $L_v=\tilde{L}_v$, and the purely discontinuous Markov variable $v(t)$ should be regarded as a deviation of the frequency with respect to ω_0.

3. RELAXATION OF POPULATIONS

If the rate of transverse relaxation Γ greatly exceeds the rate $\tilde{\Gamma}$ of the phase relaxation induced by the spectral migration, then in Eq. (2.1b) we can neglect the collision term, i.e., we can assume the variation of v in this term to be slow. Solving the thus-simplified equation for the phase element $\sigma(v,t)$ and substituting the latter in (2.1a), we get at $\sigma(v,0)=0$

$$\begin{aligned}\frac{\partial n(v,t)}{\partial t}=-4V^2\,\mathrm{Re}\int_0^t\exp\{[i(kv-\Omega)-\Gamma]t'\}n(v,t-t')\,dt'\\ +L_v n-\Gamma_1[n(v,t)-n_0\varphi(v)]\end{aligned}\tag{3.1}$$

with initial condition $n(v,0)=n(0)\varphi(v)$.

The rate $\tilde{\Gamma}$ of the phase relaxation due to the spectral migration is measured by determining the falloff of the signals of the spin[30] and photon[31] echo. Analysis shows that if $\tilde{\tau}_0(v)$ and $\tilde{f}(v',v)$ are real and the kernel $\tilde{f}(v',v)$ has a second moment as a function of v, then the result obtained in Refs. 8 and 31 in the Keilson-Storer model[32] is valid for $\tilde{\Gamma}$. Taking this result into account, the criterion for the applicability of (3.1) becomes

$$\Gamma\gg\tilde{\Gamma}=\min\{\bar{\tau}_0^{-1},[(k\tilde{\delta})^2/\bar{\tau}_0]^{1/3}\},\tag{3.2}$$

where $\bar{\tau}_0$ is the characteristic value of the function $\tilde{\tau}_0(v)$ at $|v|\lesssim\bar{v}$, and $\tilde{\delta}$ is the width of the kernel $\tilde{f}(v',v)$. In addition, in order for the problem considered here to be meaningful, conditions must be satisfied such that the spectrum remains inhomogeneous:

$$\text{a)}\ \Gamma\ll k\bar{v},\ \text{b)}\ \nu\ll k\bar{v}.\tag{3.3}$$

Here ν is the frequency of the collisions that change the velocity.

According to (3.2) the rate of randomiation of the phase Γ should be sufficiently large. For this purpose it is necessary that the amplitudes of the scattering of the molecules in the states 1 and 2 be substantially different.[26-28] The collision operators for the populations can then remain approximately equal to one another, as is assumed in (2.1). The latter condition is not assumed satisfied in problem 2, in which the operator L_v pertains only to the level 1.

As $t\to\infty$, Eq. (3.1) goes over into the equation for the stationary population difference[21] $n_s(v)=\lim n(v,t)$, $t\to\infty$

$$-2w(v-u)n_s(v)+L_v n_s-\Gamma_1[n_s(v)-n_0\varphi(v)]=0,\tag{3.4}$$

where $u=\Omega/k$ is the frequency detuning in velocity units. It differs from the equation of the elementary probabilistic particle-balance scheme only in that the probability of the transition per unit time

$$w(v)=2V^2\Gamma/[(kv)^2+\Gamma^2]\tag{3.5}$$

is a function of the random variable v whose time vari-

ation takes into account the collision term $L_v n$.

Comparing the Laplace transform of (3.1) with (3.4), we find that the connection between the stationary population difference $n_s(v)$ and the Laplace transform of the the kinetics

$$\hat{n}(v)=\int_0^\infty n(v,t)e^{-pt}dt.$$

Namely, the change of variables $\Gamma\to\Gamma+p$, $\Gamma_1\to\Gamma_1+p$ transforms the quantity $n_s(v)/n_0\Gamma_1$ into $pn(v)/[pn(0)+n_0\Gamma_1]$. This connection makes it possible in principle to reconstruct, from the now stationary solution of (3.1), the kinetics of the process $n(v,t)$.

The balance approximation. If the characteristic rate of the population relaxation induced by the medium (Γ_1) and by the field (β) is such that

$$\text{a) } \Gamma_1\ll\Gamma,\ \text{b) } \beta\ll\Gamma, \tag{3.6}$$

then we can assume in the expression for $n(v)$ that $\Gamma+p\approx\Gamma$. This means that in Eq. (3.1) at $t\gg\Gamma^{-1}$ we can take $n(v,t-t')\approx n(v,t)$ outside the integral sign and let the upper limit of integration go to infinity. As a result we get for the kinetics the balance equation

$$\frac{\partial n(v,t)}{\partial t}=-2w(v-u)n(v,t)+L_v n-\Gamma_1[n(v,t)-n_0\varphi(v)]. \tag{3.7}$$

The longitudinal relaxation (Γ_1) can be excluded from consideration with the aid of a change of variable[33,34]

$$n(v,t)=n(0)m(v,t)e^{-\Gamma_1 t}+n_0\Gamma_1\int_0^t m(v,t')e^{-\Gamma_1 t'}dt'. \tag{3.8}$$

The new variable $m(v,t)$ describes only the optically induced relaxation and satisfies the equation

$$\frac{\partial m(v,t)}{\partial t}=-2w(v-u)m(v,t)+L_v m \tag{3.9}$$

with the initial condition $m(v,0)=\varphi(v)$. It must be emphasized that Eqs. (3.7) and (3.9) were obtained under much more limiting assumptions than (3.1). As to the stationary solution of Eq. (3.7), which is connected with $m(v,t)$ in accordance with (3.8) by the equation

$$n_s(v)=n_0\Gamma_1\int_0^\infty m(v,t)e^{-\Gamma_1 t}dt, \tag{3.10}$$

it is restricted only by the condition (3.2). This follows from the identity of Eqs. (3.7) and (3.4) as $t\to\infty$.

When account is taken of the foregoing correspondence between $n_s(v)$ and $\hat{n}(p)$, this remark enables us in principle to obtain the solution of (3.1) from the solution of (3.9) or (3.4).

Integrating (3.8) with respect to v, we obtain the connection between $\bar{m}(t)=\int m(v,t)dv$ and the integral population difference $\bar{n}(t)$:

$$\bar{n}(t)=n(0)\bar{m}(t)e^{-\Gamma_1 t}+n_0\Gamma_1\int_0^t \bar{m}(t')e^{-\Gamma_1 t'}dt'. \tag{3.11}$$

The kinetics of $\bar{m}(t)$ is generally speaking not exponential, but the average rate of the optically induced relaxation can be characterized by a generalized probability w_s, introduced in accordance with the equation[3,35]

$$\bar{n}_s=\lim_{t\to\infty}\bar{n}(t)=n_0\Gamma_1\int_0^\infty \bar{m}(t)e^{-\Gamma_1 t}dt=\frac{n_0\Gamma_1}{\Gamma_1+2w_s}. \tag{3.12}$$

According to (2.9) and (3.12), the rate of absorption of the light in the stationary regime is

$$I_s=\hbar\omega w_s n_s, \tag{3.13}$$

i.e., the generalized probability w_s determines the level not only of the stationary saturation but also of the absorption.[3,35]

For problem 2 we can obtain equations that agree with (3.1) and (3.7) accurate to the substitution $2V^2\to V^2$. For these equations to be valid it is necessary to satisfy, besides the conditions (3.2), (3.3), and (3.6), also the inequality $\beta\ll\Gamma_2$ [cf. the remark following formulas (2.6)]. Thus, all the results obtained below for the case $\Gamma_1=\Gamma_2$ pertain, with accuracy to the indicated substitution also to the problem 2.

We proceed now to find the function $m(v,t)$, which determines in accordance with (3.8), (3.11), and (2.9) the kinetics of the saturation and absorption of light.

4. STATIC LIMIT

Nonstationary saturation. If the frequency of the collisions is low enough, then we can neglect in (3.9) the collision term. This yields

$$m(v,t)=\exp[-2w(v-u)t]\varphi(v). \tag{4.1}$$

Thus, in the static limit ($\tau_0\to\infty$) the function $m(v,t)$ contains a dip whose width at large t is of the order of $(2V/k)(\Gamma t)^{1/2}$. We now estimate the limits of the region where the optically induced relaxation of most particles is described by formula (4.1) (quasistatic stage). In the indicated region the saturation process should practically terminate in the interval $0<t\ll\nu^{-1}$, i.e., before the position of the frequencies in the spectrum changes. In other words, it is necessary to satisfy the inequality $(2V/k)(\Gamma\nu)^{1/2}\gg\bar{v}+|u|$ or

$$[2w(\bar{v}+|u|)]^{1/2}\gg\nu^{1/2}. \tag{4.2}$$

The integral kinetics of the optically induced relaxation $m(t)$ in the static limit is obtained by integrating (4.1) with respect to v. Although this integral cannot be evaluated in analytic form, it is possible to obtain simple results for the majority of the important particular cases.

a) Short times. At $2w(0)t=(2V)^2t/\Gamma\ll 1$ the exponential in (4.1) can be expanded in a series, from which we get

$$\bar{m}(t)\approx 1-2\bar{w}t. \tag{4.3}$$

The average transition probability is here

$$\bar{w}=\int w(v-u)\varphi(v)dv=\frac{2\pi V^2}{k}H\left(\frac{\Gamma}{k},u\right), \tag{4.4}$$

where

$$H\left(\frac{\Gamma}{k},u\right)=\frac{1}{(2\pi)^{1/2}\bar{v}}\operatorname{Re}\exp\left[\left(\frac{\Gamma+iku}{\sqrt{2}\,k\bar{v}}\right)^2\right]\operatorname{erfc}\left(\frac{\Gamma+iku}{\sqrt{2}\,k\bar{v}}\right) \tag{4.5a}$$

$$\approx\begin{cases}\varphi(u), & |u|\ll u_{1\mathrm{im}}\\ \Gamma/\pi ku^2, & |u|\gg u_{1\mathrm{im}}\end{cases} \tag{4.5b}$$

is the known convolution of the dispersion and Doppler contours. In (4.5) the limiting value $u_{1\mathrm{im}}$ is the larger root of the equation $\pi k u_{1\mathrm{im}}^2\varphi(u_{1\mathrm{im}})=\Gamma$. According to (4.5), the quantity w has the following asymptotic forms:

$$\bar{w}=\begin{cases}(2\pi V^2/k)\varphi(u), & |u|\ll u_{1\,1\mathrm{m}} \quad (4.6a)\\ w(u), & |u|\gg u_{1\,1\mathrm{m}} \quad (4.6b)\end{cases}$$

We see from this that at $|u|\gg u_{11\mathrm{m}}$ the integral kinetics of the saturation is the same as in the case of a homogeneously broadened line with width Γ and with a center at the frequency ω_0. It will be shown below that this statement is valid at all t and ν. In other words, at $|u|\gg u_{11\mathrm{m}}$, regardless of the frequency ν of the spectral migration, we have $\bar{m}(t)=e^{-2w(u)t}$. This agrees with the known fact that at $|u|\gg u_{11\mathrm{m}}$, as seen from (4.5b), the wings of the Doppler contour are determined exclusively by the homogeneous broadening.

This does not mean, however, that in this case the Doppler contour does not differ in any way from the homogeneously broadened line. According to (4.1), a high-power field produces a dip in the velocity distribution of the populations at all values of u. However, for large frequency detunings, the details of the process whereby the dip is formed, and even the very fact of its formation, may not influence the kinetics of the saturation of most atoms. This explains also the fact that when $|u|\gg\bar{v}$ the region of quasi-static stage for the integral populations is generally speaking broader than the region of the quasi-static stage (4.2) for the partial populations (see Sec. 6).

An estimate for $m(t)$ in a larger time interval can be obtained not only at $|u|\gg u_{11\mathrm{m}}$ but also at $|u|\ll u_{11\mathrm{m}}$. In the latter case, so long as the width of the dip in the function (4.1) is not too large it can be assumed in the integration of (4.1) with respect to v that $\varphi(v)\approx\varphi(u)$, whence

$$\frac{d\bar{m}}{dt}=-2\bar{w}\exp\left(-\frac{2V^2t}{\Gamma}\right)I_0\left(\frac{2V^2t}{\Gamma}\right), \quad (4.7)$$

where $I_0(z)$ is a modified Bessel function. From this follows at $t\ll\Gamma/(2V)^2$ the equality (4.3), and at $t\gg\Gamma/(2V)^2$ we have

$$\bar{m}(t)\approx 1-\frac{4\sqrt{\pi}V}{k}\varphi(u)\sqrt{\Gamma t}. \quad (4.8)$$

b) Long times. At $u=0$ the function $\bar{m}(t)$ can be obtained for times $t\gg\Gamma/(2V)^2$, when the central component of the spectrum is practically completely saturated and the integral of (4.1) with respect to v remains practically unchanged. If the function $w(v)$ (3.5) is increased by putting $\Gamma=0$ in its denominator. Proceeding in this way, we find that at $t\gg\Gamma/(2V)^2$ we have

$$\bar{m}(t)\approx\exp(-\sqrt{qt}), \quad q=2V^2\Gamma/(k\bar{v})^2\approx w(\bar{v}). \quad (4.9)$$

At small t this expression coincides with (4.8), thus demonstrating the intersection of the asymptotic estimates (4.7) and (4.9).

At large t, the function $\bar{m}(t)$ can also be obtained for $|u|\gg v$. The quantity $\bar{n}_s$, which is obtained by substituting (4.1) in (3.10) and by integrating the subsequent expression with respect to v, is proportional according to (3.12) to the Laplace transform of the function $\bar{m}(t)$. An analysis of this transform has shown that when at large t satisfying the condition $2w(u)t\ll u^2/\bar{v}^2$ we have

$$\bar{m}(t)\approx\exp[-2w(u)t]. \quad (4.10)$$

The limiting time $t_{1\,1\mathrm{m}}$ at which this expression replaces formula (4.8) can be estimated by equating (4.8) with (4.10). As a result we find that

$$t_{1\,1\mathrm{m}}=\frac{\pi}{\Gamma}\left[\frac{ku^2\varphi(u)}{V}\right]^2.$$

The exponential kinetics of (4.10) is explained by the fact that at $|u|\gg\bar{v}$ the saturation rates for a tremendous majority of atoms with $|v|\ll|u|$ practically coincide and are equal to $2w(u)$.

Stationary saturation. We shall not present here the well known expression[3,5-8] for $n_s(v)$ and $\bar{n}_s$. We indicate only that in the static limit

$$2w_s\approx\begin{cases}\dfrac{4\pi V^2\Gamma}{k^2\Delta_h}H(\Delta_h,u), & [2w(\bar{v}+|u|)]^{1/2}\ll\Gamma_1^{1/2} \quad (4.11a)\\ \bar{t}^{-1}\approx\left(\dfrac{2V}{k}\right)^2\dfrac{\Gamma}{u^2+\bar{v}^2}, & [2w(\bar{v}+|u|)]^{1/2}\gg\Gamma_1^{1/2} \quad (4.11b)\end{cases}$$

Here

$$\Delta_h=\frac{\Gamma}{k}\left(1+\frac{(2V)^2}{\Gamma\Gamma_1}\right)^{1/2}$$

is a width of the dip in $n_s(v)$, and

$$\bar{t}=-\int_0^\infty t\frac{d\bar{m}}{dt}dt=\int_0^\infty\bar{m}(t)\,dt=\frac{1}{2w_s}\Big|_{\Gamma_1=0}=\int\frac{\varphi(v)\,dv}{2w(v-u)} \quad (4.12)$$

is the average time of the saturation at $\Gamma_1=0$. Expression (4.11a) can be simplified with the aid of (4.5). Thus, at $\sqrt{q}\ll\sqrt{\Gamma_1}$,

$$2w_s\approx\begin{cases}2\bar{w}[1+(2V)^2(\Gamma\Gamma_1)^{-1}]^{-1/2}, & |u|\ll u_{1\,1\mathrm{lim}}' \quad (4.13a)\\ 2w(u), & |u|\gg u_{1\,1\mathrm{lim}}' \quad (4.13b)\end{cases}$$

where $u_{1\,1\mathrm{m}}'$ is the larger root of the equation $\pi u_{1\,1\mathrm{m}}'^2\varphi(u_{1\,1\mathrm{m}}')=\Delta_h$.

We recall that in accordance with the statement made in Sec. 3, the applicability of the results (4.11) and (4.13) is limited only by the condition (3.2) and consequently does not depend on the ratio of the relaxation constants Γ and Γ_1. For $\Gamma=\Gamma_1$, in particular, expression (4.13a) was obtained for the first time in Ref. 7.

5. KINETIC LIMIT

The case directly opposite to the static limit is that of ultrafast migration (the kinetic limit), when the spectral migration prevents the formation of a dip and causes exponential equalization of the populations:

$$\text{a) } m(v,t)=\exp(-2\bar{w}t)\varphi(v), \quad \text{b) } \bar{m}(t)=\exp(-2\bar{w}t). \quad (5.1)$$

Substituting these equations in (3.10) and (3.12), we find find that in the kinetic limit

$$\text{a) } n_s(v)=\frac{n_0\Gamma_1\varphi(v)}{\Gamma_1+2\bar{w}}, \quad \text{b) } \bar{n}_s=\frac{n_0\Gamma_1}{\Gamma_1+2\bar{w}}. \quad (5.2)$$

As small t, the kinetics of (4.4) and (5.1), obtained respectively in the static and in the kinetic limits, coincide. But with increasing t, the rate of the process in the static limit slows down, and the average velocity of the process (4.8b) during the quasi-static stage is much less (at least at $|u|\ll u_{11\mathrm{m}}$) than the average rate of saturation $2\bar{w}$ in the kinetic stage.[1)]

In the transition region the average rate of the process should be an increasing function of ν. This stage of the process can be called the migration-accelerated stage, in analogy with the diffusion-accelerated stage of the reactions in ordinary space.[36] In this region, the saturation depends substantially on the type of ran-

dom migration, and this makes it possible in principle to obtain rather complete information on the latter. This is demonstrated below with an example of two types of Markov spectral migration: uncorrelated and Gaussian-Markov processes.

6. UNCORRELATED PROCESS

Strong collisions change the velocity of the atom by an amount $\delta \sim \bar{v}$. Exaggerating this situation, we can assume that in each collision the molecule "forgets" its initial velocity, i.e., the function $f(v', v)$ does not depend on v (uncorrelated process or model of strong collisions). If furthermore $\tau_0(v) = \tau_0 = \text{const.}$, then in the strong-collision model[11] we obtain from the stationarity condition (2.4) that $f(v', v) = \varphi(v)$. The process of spectral migration of this type can be classified as an uncorrelated Markov process.[3] Another physical example of the realization of such a process is the frequency migration in EPR spectra.[5]

Solving Eq. (3.7a) in the case of an uncorrelated process, we obtain the known expressions for $n_s(v)$ and $\bar{n}_s$.[5,6] With the aid of (3.4) we can obtain also an expression for w_s. It turned out that it coincides with the static result (4.8), accurate to the substitution $\Gamma_1 \to \Gamma_1 + \nu$. In this case the reciprocal spectral-migration time is $\nu = \tau_0^{-1}$.

Starting from the expressions obtained for $n_s(v)$ and $\bar{n}_s$, we can determine in accordance with (3.10) and (3.12) the kinetics of the saturation with the aid of the inverse Laplace transform. Analysis shows that under the condition (4.2) the results of Sec. 4 are approximately valid for nonstationary saturation. When the inequality (4.2) is reversed, it can be shown that at $t \ll \tau_0$ the kinetics is purely static, and at $t \gg \tau_0$

$$\text{a) } m(v,t) \approx \frac{\nu\varphi(v)e^{-at}}{2w(v-u)+\nu}, \quad \text{b) } \bar{m}(t) \approx e^{-at}. \tag{6.1}$$

Here $a \approx 2w_s|_{\Gamma_1=0} = \bar{t}^{-1}$, i.e., according to the foregoing the parameter is determined by expression (4.11) or (4.13), where Γ_1 must be replaced by ν.

In this case (4.13) takes the form

$$a \approx \begin{cases} 2\bar{w}[1+(2V)^2(\Gamma\nu)^{-1}]^{-1/2}, & |u| \ll u_{1\text{lim}}'' \quad (6.2a) \\ 2w(u), & |u| \gg u_{1\text{lim}}'' \quad (6.2b) \end{cases}$$

where $u_{1\text{lim}}''$ is obtained from $u_{1\text{lim}}'$ by the substitution $\Gamma_1 \to \nu$. Formulas (6.1) describe the saturation of practically all the atoms, since it can be shown that in the region $t \leq \tau_0$, where they are valid, we have $\bar{m}(t) \approx 1$.

Starting with formula (6.2a), it can be shown that for not too large values and not too small values of v, the saturation rate is proportional to $\sqrt{\nu}$:

$$a \approx 2\pi V(\Gamma\nu)^{1/2}\varphi(u)/k, \quad \nu_{\text{lim}} \ll \nu \ll (2V)^2/\Gamma, \tag{6.3}$$

where $v_{1\text{lim}} = 2w(\bar{v})$ at $|u| \lesssim \bar{v}$ and $v_{1\text{lim}} = 2w(u)/[\pi u\varphi(u)]^2$ at $|u| \gg \bar{v}$. Consequently, the saturation process is accelerated by the frequency migration.

The result (6.3) has a simple physical meaning. It is seen from it that $a \sim \nu\varphi(u)\Delta_v$, where $\Delta_v = (2V/k)(\Gamma/\nu)^{1/2}$ is the half-width of the dip in the populations, in accordance with (6.1a) and (3.5). In other words, the saturation rate a is equal to the product of the frequency ν of the hops over the spectrum by the probability $\Delta_v\varphi(u)$ of landing in the region of the dip. During the stay in this region, the atom is almost certainly saturated.

This picture of the saturation process recalls the hopping mechanism of energy transfer in a solid.[37-39] Moreover, at $u = 0$, expression (6.1a), with suitable change of rotation, it is identical with the result obtained in Ref. 37. This analogy enables us to use $u = 0$, also other results obtained in Refs. 37–39 for dipole-dipole transfer. In particular, the kinetics in the region of the transition from the quasi-static to the migration-accelerated stage was numerically calculated in Ref. 38, while the initial section of the kinetics on the migration-accelerated stage, which was omitted from (6.1b), was obtained in Ref. 39.

Remark. We note that at $|u| \gg \bar{v}$ the region of the quasi-static stage for the integral populations is much wider than the same region (4.2) for the velocity distribution. In fact, according to (6.1) and (6.2b), the result (4.10) of the static limit is approximately valid under the condition $\nu \ll 2w(u)/[\pi u\varphi(u)]^2$, which is much less stringent than (4.2).

We point out finally that the kinetic stage is reached at uncorrelated spectral migration, as seen from (6.2), when $\nu \gg (2V)^2/\Gamma$ (see Fig. 1).

7. GAUSSIAN-MARKOV PROCESS

If the change δ of the velocity in the collisions is small, and the kernel $f(v', v)$ is a function if (v) has a second moment, then the spectral migration has the character of diffusion.[9,18,21] In particular, if we assume the Keilson-Storer model,[32] then $f(v', v) = f(v - \gamma v')$; in the diffusion limit, however, $\gamma \to 1$, $\tau_0 \to 0$, $\nu = (1-\gamma)/\tau_0 = \text{const}$), Eq. (3.9) takes the form[2)] (Ref. 32)

$$\frac{\partial m}{\partial t} = -2w(v-u)m + \nu\left(m + v\frac{\partial m}{\partial v} + \bar{v}^2\frac{\partial^2 m}{\partial v^2}\right). \tag{7.1}$$

For this equation to be valid at all values of v and at positive t, it is necessary that the mean squared change of the velocity in the collision, $\delta = [2(1-\gamma)]^{1/2}\bar{v}$, be much less than the width Γ/k of the function $w(v)$. Equation (7.1) is valid also to $|v-u| \gg \Gamma/k$ and $t \gg \tau_0$ if $\Gamma/k \lesssim \delta \ll \bar{v}$.

Analysis has shown that in this case the kinetic stage

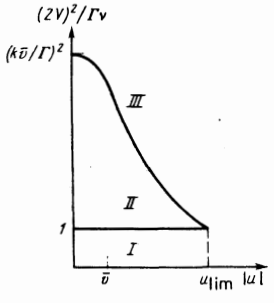

FIG. 1. Separation of the situations for the integral populations in uncorrelated spectral migration. Solid lines—boundaries between the kinetic (I), migration-accelerated (II), and quasi-static (III) stages.

sets in at

$$2\bar{w} \ll \nu. \tag{7.2}$$

On this inequality is inverted, i.e., during the migration-accelerated and static stages, it is possible, as above, to neglect the term Γ^2 in the denominator of (3.5) for $w(v)$. It is unnecessary to impose the following boundary condition on $m(v, t)$:

$$m(u, t)=0. \tag{7.3}$$

Proceeding in this manner, we exclude from consideration only a small initial section (4.3) of the integral kinetics and the integral $|v-u| \lesssim 1$ in the partial function $m(v, t)$.

If we solve Eq. (7.1) under these assumptions by the method of separation of variables, then at $u=0$ it reduces, by making the change of variable

$$m(v, t)=v \exp(-v^2/4\bar{v}^2)\,\Psi(v, t)$$

to an equation whose eigenfunctions and eigenvalues are known (see Ref. 41). The coefficients of the expansion of the initial condition in the eigenfunctions of this equation are obtained from formulas of Sec. f of the mathematical supplements of Ref. 41. The series obtained for $m(v, t)$ with the aid of the method of separation of variables is summed in accordance with formula (5) of Sec. 6.2 of the Bateman and Erdelyi book,[42] and the result is

$$m(v, t)=\varphi(v)\frac{\Gamma(s+1)}{\Gamma(2s+3/2)}z^{s+1/2}\Phi\left(s+\frac{1}{2}, 2s+\frac{3}{2}; -z\right), \qquad s=\frac{1}{4}\left(\left(\frac{2q}{\nu}+1\right)^{1/2}-1\right), \quad z=\frac{1}{2}\left(\frac{v}{\bar{v}}\right)^2\frac{1}{e^{2\nu t}-1}. \tag{7.4}$$

Here $\Gamma(x)$ is the gamma function and $\Phi(a, c; x)$ is a confluent hypergeometric function.[42]

As seen from (7.4), the function $m(v, t)/\varphi(v)$ is self-similar. In other words, the dips at different instants of time all have the same shape and only the characteristic width of the dip $\bar{v}(e^{2\nu t}-1)^{1/2}$ changes. This property can be used to derive the result (7.4) by another method.[43] It can be shown that the self-similarity property of the function (7.4) is in a certain sense "accidental," i.e., it is connected with the specific form of the operator L_v and the function $w(v)$ in Eq. (7.1). Thus, for the functions $w(v-u)$ with non-Lorentz shape or for a Lorentz function $w(v-u)$ at $u \neq 0$, the solution of (7.1) is not self-similar.

In the quasi-static region (4.2), where $s \approx (q/8\nu)^{1/2} \gg 1$, expression (7.4) can be reduced with the aid of Eq. (33) of Sec. 6.13 of the book[42] (where a factor $\nu^{-1/2}$ has been left out from its right-hand side) and with the aid of the asymptotic expression for the gamma function (Ref. 42, Sec. 1.18), to the form

$$\frac{m(v, t)}{\varphi(v)}=\left(\frac{(1+y^2)^{1/2}+1-y}{2(1+y^2)^{1/2}}\right)^{1/2}\exp\left\{s\left[\frac{(1+y^2)^{1/2}-1}{y}+\ln\left[(1+y^2)^{1/2}-y\right]\right]\right\}, \tag{7.5}$$

where $y=(2q/\nu)^{1/2}(e^{2\nu t}-1)(\bar{v}/v)^2$. With the exception of the vicinity of the point $v=0$, inside of which $m(v, t) \approx 0$, we can confine ourselves in the argument of the exponential and in the pre-exponential factor of (7.5) to the lowest terms of the expansion in powers of y

$$\frac{m(v, t)}{\varphi(v)} \approx \exp\left[-\frac{w(v)}{\nu}(e^{2\nu t}-1)\right].$$

The result (4.1) of the static limit follows from this at $t \ll \nu^{-1}$.

If the field power decreases to such an extent that $2s \approx p/2\nu \ll 1$, we obtain from (6.4)

$$\frac{m(v, t)}{\varphi(v)} \approx \begin{cases} \operatorname{erf}\left(\dfrac{|v|}{\bar{v}[2(e^{2\nu t}-1)]^{1/2}}\right), & |v| \ll v_{1\mathrm{lim}} \qquad (7.6a) \\ 1-\dfrac{w(v)}{\nu}(e^{2\nu t}-1), & |v| \gg v_{1\mathrm{lim}} \qquad (7.6b) \end{cases}$$

Here $v_{1\mathrm{lim}}=\bar{v}[2(e^{2\nu t}-1)z_{1\mathrm{lim}}]^{1/2}$, and $z_{1\mathrm{lim}}$ is the larger root of the equation $z_{1\mathrm{lim}}^{1/2}\exp(-z_{1\mathrm{lim}})=\sqrt{\pi}q/2\nu$. The result (7.6) describes the kinetics of the formation of dip of the diffusion-accelerated stage of the saturation. If we disregard the far wings of (7.6b), the shape of the dip does not depend on the field power.

It should be noted that the function (7.6a), which describes the shape of the main part of the dip, can be obtained by solving Eq. (7.4) without the first term in the right-side, but using the boundary condition (7.3). This means that during the migration-accelerated stage the saturation process is monitored by the diffusion of the atoms in velocity space towards the point $v=0$, where the interaction with the field is maximal.

The function $\bar{m}(t)$ can be obtained by integrating (7.4) with respect to v. The result for $\bar{m}(t)$ is given and analyzed in Ref. 10. It is shown there, in particular, that the characteristic time of saturation on the migration-accelerated stage is of the order of the time ν^{-1}, during which the atom migrates over the spectrum: $\nu^{-1}=\bar{v}^2/D$, where the diffusion coefficient D in velocity space, as seen from (7.1) is $\nu\bar{v}^2$.

CONCLUSION

Comparison of the partial kinetics (6.1a), (6.3), and (7.6) obtained for the migration-accelerated stage in the cases of uncorrelated and Gaussian-Markov processes demonstrates the substantial difference between the two. Whereas in the first case the process is for the most part quasistationary, i.e., no change occurs in the shape and width of the dip of the velocity distribution, in the second case the width of the dip increases without limit. There are also other substantial differences between these cases: the form and the rate of relaxation of the function (6.1a) depends on the field intensity, but (7.6) is practically independent of this intensity. The shapes of the dips of (6.1a) and (7.6) as well as the criteria for the applicability of the kinetic limit and other factors are also different.

Thus, the distinguishing features of the spectral migration process manifest themselves in the migration-accelerated stage of saturation of an inhomogeneously broadened contour.

We consider in conclusion the condition (3.6b) for the applicability of the balance approximation, which can be determined only after solving Eq. (3.7) or (3.9). According to the results obtained above, optically induced

relaxation of the integral population proceeds at the highest rate, equal to $2\bar{w}$, during the initial stage of the process [cf. Eq. (4.3)]. For the integral kinetics obtained in the balance approximation to be valid we must therefore put $\beta = 2\bar{w}$ on the entire time axis in (3.6b). According to (4.1), the highest saturation rate for the partial populations is equal to $2w(0) = (2V)^2/\Gamma \gg 2\bar{w}$, so that if the results obtained above are to be valid for $m(v,t)$ at all t we must put $\beta = (2V)2/\Gamma$ in (3.6b). But if we require that the expressions obtained in the balance approximation describe correctly the saturation of most atoms, with the possible exception of those which are saturated during the initial stage of the process, then the condition (3.6b) can be made much weaker, assuming β to be equal to the average saturation rate during the lifetime Γ_1^{-1}, i.e., to $2w_s$.

[1)]At $|u| \gg u_{1\text{lim}}$ a comparison of (4.1) and (5.1b), with (4.6b) taken into account, shows that the kinetics of the saturation is practically unchanged with increasing ν and remains equal to $\bar{m}(t) \approx \exp[-2w(u)t]$ [cf. the remark made after formulas (4.6)].

[2)]It can be shown that the random process $v(t)$ is in this case not only a Markov process but also a Gaussian process.[40]

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