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Translated by J. G. Adashko

Nonlinear resonances of accelerated atoms and molecules

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(Submitted 16 September 1977)
Zh. Eksp. Teor. Fiz. 74, 1295–1306 (April 1978)

An exact kinetic equation is obtained for the density matrix, suitable for any interaction of a particle with an external field, is obtained. It is used to analyze the singularities of the broadening of various nonlinear resonances under conditions when the excited particles move with constant acceleration over the mean free path in a gas or in a plasma. It is established that resonances of various origins react differently to the accelerated motion of the emitter. Under definite conditions the acceleration can lead to splitting or narrowing of nonlinear spectral structures.

PACS numbers: 32.70.Jz, 33.70.Jg, 41.70.+t

1. INTRODUCTION

In the solution of numerous problems of nonlinear spectroscopy one uses various nonlinear resonances: resonances with saturation of absorption by independent waves, the nonlinear Zeeman effect, and others. Under real conditions active particles are acted upon as a rule by various external forces (the Lorentz force, gravitation, etc.) and the acceleration they produce can alter the shape of the narrow resonances.[1,2] For the indicated effect to be noted, the Doppler frequency shift due to the acceleration **a**,

$$\Delta\omega \sim \mathbf{a}\mathbf{k}\tau \tag{1}$$

(τ is the emission time and **k** is the wave vector) must be comparable with the width of the corresponding nonlinear resonance γ[1]:

$$\Delta\omega \gtrsim \gamma. \tag{2}$$

These situations are encountered in ultrahigh-resolution spectroscopy quite frequently. There is therefore a distinct need for an investigation of the singularities of the broadening under the indicated conditions. This is important in order to obtain exact spectroscopic information on the physical properties in active media, and also for an effective control of the results of the acceleration.

Resonances of various origins react differently to the acceleration of the emitter. In this article we consider the singularities of this transformation for the most promising methods of obtaining ultranarrow nonlinear resonances: a) independent waves interacting with two- and three-level systems, b) the nonlinear Zeeman effect, c) competing resonances in a ring laser.

2. KINETIC EQUATION. GENERAL FORMALISM

In the quantum-mechanical treatment, the energy of the atom (or molecule) is determined by the eigenvalues of the Hamiltonian

$$H = \frac{p^2}{2m} + U(\eta, \xi) + H'(\mathbf{p}, \mathbf{r}; \eta, \xi), \tag{3}$$

where **r** is the coordinate of the mass center, ξ denotes the aggregate of the internal coordinates, and **p** and η are the corresponding momenta:

$$\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}, \quad \eta = -i\hbar\frac{\partial}{\partial\xi}. \tag{4}$$

The first term in (3) takes into account the kinetic energy of the mass center of the atom (whose mass is m); U is the operator of the interaction of the component parts of the atom, and H' describes the action of the external fields and depends on both the translational and the internal coordinates of the atom.

 0038-5646/78/040678-07$02.40

In the coordinate representation, the dynamic evolution of the system is described by the equation for the density matrix $\rho(\mathbf{r},\mathbf{r}';\xi,\xi')$:

$$i\hbar\frac{\partial}{\partial t}\rho(\mathbf{r},\mathbf{r}';\xi,\xi')=[H(\mathbf{p},\mathbf{r};\eta,\xi)-H^{*}(\mathbf{p}',\mathbf{r}';\eta',\xi')]\rho(\mathbf{r},\mathbf{r}';\xi,\xi'). \quad (5)$$

Remaining within the framework of the ξ coordinate representation, we change over for the translational degree of freedom to the Wigner representation, which is mixed with respect to the coordinate and momentum spaces. The Wigner function $\rho(\mathbf{q},\mathbf{r})$ is connected with $\rho(\mathbf{r},\mathbf{r}')$ by the relations

$$\rho(\mathbf{q},\mathbf{r})=\frac{1}{(2\pi\hbar)^3}\int\rho\left(\mathbf{r}+\frac{\boldsymbol{\varkappa}}{2},\ \mathbf{r}-\frac{\boldsymbol{\varkappa}}{2}\right)\exp\left(-\frac{i}{\hbar}\mathbf{q}\boldsymbol{\varkappa}\right)d\boldsymbol{\varkappa}, \quad (6)$$

$$\rho(\mathbf{r},\mathbf{r}')=\int\rho\left(\mathbf{q},\frac{\mathbf{r}+\mathbf{r}'}{2}\right)\exp\left[\frac{i}{\hbar}(\mathbf{r}-\mathbf{r}')\mathbf{q}\right]d\mathbf{q}. \quad (7)$$

Using (6) and (7), we can show that the density matrix in the Wigner representation satisfies the equation

$$i\hbar\frac{\partial}{\partial t}\rho(\mathbf{q},\mathbf{r};\xi,\xi')=\frac{1}{(2\pi\hbar)^6}\int\left[H\left(\mathbf{q}_1-\frac{\boldsymbol{\theta}}{2},\ \mathbf{r}_1+\frac{\boldsymbol{\varkappa}}{2};\eta,\xi\right)-H\left(\mathbf{q}_1+\frac{\boldsymbol{\theta}}{2},\ \mathbf{r}_1-\frac{\boldsymbol{\varkappa}}{2};\eta',\xi'\right)\right]\rho(\mathbf{q}_1,\mathbf{r}_1;\xi,\xi') \quad (8)$$
$$\times\exp\left\{-\frac{i}{\hbar}[(\mathbf{q}-\mathbf{q}_1)\boldsymbol{\varkappa}+(\mathbf{r}-\mathbf{r}_1)\boldsymbol{\theta}]\right\}d\boldsymbol{\varkappa}\,d\boldsymbol{\theta}\,d\mathbf{q}_1\,d\mathbf{r}_1.$$

Substituting in (8) the expression (3) and integrating the terms $p^2/2m$ and $U(\eta,\xi)$, we obtain ultimately

$$i\hbar\left(\frac{\partial}{\partial t}+\frac{\mathbf{q}}{m}\nabla_{\mathbf{r}}\right)\rho(\mathbf{q},\mathbf{r};\xi,\xi')=[U(\eta,\xi)-U(\eta',\xi')]\rho(\mathbf{q},\mathbf{r};\xi,\xi')$$
$$+\frac{1}{(2\pi\hbar)^6}\int\left[H'\left(\mathbf{q}_1-\frac{\boldsymbol{\theta}}{2},\ \mathbf{r}_1+\frac{\boldsymbol{\varkappa}}{2};\eta,\xi\right)-H'\left(\mathbf{q}_1+\frac{\boldsymbol{\theta}}{2},\ \mathbf{r}_1-\frac{\boldsymbol{\varkappa}}{2};\eta',\xi'\right)\right]$$
$$\times\rho(\mathbf{q}_1,\mathbf{r}_1;\xi,\xi')\exp\left\{-\frac{i}{\hbar}[(\mathbf{q}-\mathbf{q}_1)\boldsymbol{\varkappa}+(\mathbf{r}-\mathbf{r}_1)\boldsymbol{\theta}]\right\}d\boldsymbol{\varkappa}\,d\boldsymbol{\theta}\,d\mathbf{q}_1\,d\mathbf{r}_1. \quad (9)$$

Equation (9) is the exact equation of motion is suitable for any interaction H' of the atom with the external field.

In the approximation that is quasiclassical in the translational motion, H' is represented in the form of a series in powers of $\varkappa$ and θ and confined to the linear terms of the expansion:

$$H'\left(\mathbf{q}_1\mp\frac{\boldsymbol{\theta}}{2},\ \mathbf{r}_1\pm\frac{\boldsymbol{\varkappa}}{2};\eta,\xi\right)=H'(\mathbf{q}_1,\mathbf{r}_1;\eta,\xi)$$
$$\pm\frac{\boldsymbol{\varkappa}}{2}\nabla_{\mathbf{r}_1}H'(\mathbf{q}_1,\mathbf{r}_1;\eta,\xi)\mp\frac{\boldsymbol{\theta}}{2}\nabla_{\mathbf{q}_1}H'(\mathbf{q}_1,\mathbf{r}_1;\eta,\xi). \quad (10)$$

Substituting (10) in (9) and integrating with respect to $\varkappa$ and θ, we get

$$i\hbar\left\{\frac{\partial}{\partial t}+\frac{\mathbf{q}}{m}\nabla_{\mathbf{r}}+\frac{1}{2}\nabla_{\mathbf{q}}[H'(\mathbf{q},\mathbf{r};\eta,\xi)+H'(\mathbf{q},\mathbf{r};\eta',\xi')]\nabla_{\mathbf{r}}\right.$$
$$-\frac{1}{2}\nabla_{\mathbf{r}}[H'(\mathbf{q},\mathbf{r};\eta,\xi)+H'(\mathbf{q},\mathbf{r};\eta',\xi')]\nabla_{\mathbf{q}}$$
$$\left.-\frac{1}{i\hbar}[U(\eta,\xi)+H'(\mathbf{q},\mathbf{r};\eta,\xi)-U(\eta',\xi')-H'(\mathbf{q},\mathbf{r};\eta',\xi')]\right\}\rho(\mathbf{q},\mathbf{r};\xi,\xi')=0. \quad (11)$$

If the interaction H' does not depend on ξ (i.e., is the same for all stationary states), then the zeroth terms in the kinetic expansion of H' cancel each other, but the linear terms are additive.

After changing to the energy representation with respect to the internal variables, the kinetic equation can be written in the form

$$i\hbar\left(\frac{\partial}{\partial t}+\frac{\mathbf{q}}{m}\nabla_{\mathbf{r}}+i\omega_{mn}\right)\rho_{mn}$$
$$=\sum_{l}\left[H_{ml}'\rho_{ln}-\rho_{ml}H_{ln}'-\frac{i\hbar}{2}(\nabla_{\mathbf{q}}H_{ml}'\nabla_{\mathbf{r}}\rho_{ln}+\nabla_{\mathbf{r}}\rho_{ml}\nabla_{\mathbf{q}}H_{ln}')\right.$$
$$\left.+\frac{i\hbar}{2}(\nabla_{\mathbf{r}}H_{ml}'\nabla_{\mathbf{q}}\rho_{ln}+\nabla_{\mathbf{q}}\rho_{ml}\nabla_{\mathbf{r}}H_{ln}')\right], \quad (12)$$

where l, m, and n are the indices of the states; ω_{mn} is the frequency of the transitions between the levels m and n.

For an interaction operator H' that is independent of the internal variables we obtain

$$i\hbar\left\{\frac{\partial}{\partial t}+\left[\frac{\mathbf{q}}{m}+\nabla_{\mathbf{q}}H'(\mathbf{q},\mathbf{r})\right]\nabla_{\mathbf{r}}-\nabla_{\mathbf{r}}H'(\mathbf{q},\mathbf{r})\nabla_{\mathbf{q}}+i\omega_{mn}\right\}\rho_{mn}(\mathbf{q},\mathbf{r})=0. \quad (13)$$

This case corresponds to the action of an external field on an atom (molecule) as a whole. It can be realized when a gravitational field acts on the particle, and also when an electric or magnetic field acts on the charge of an ion (Lorentz) force, on the dipole moment of a molecule, and on moments of different multiplicity.

If H' is diagonal in the internal degrees of freedom, then

$$i\hbar\left\{\frac{\partial}{\partial t}+\left[\frac{\mathbf{q}}{m}+\frac{1}{2}\nabla_{\mathbf{q}}(H_{mm}'+H_{nn}')\right]\nabla_{\mathbf{r}}-\frac{1}{2}\nabla_{\mathbf{r}}(H_{mm}'+H_{nn}')\nabla_{\mathbf{q}}\right.$$
$$\left.+i\omega_{mn}+\frac{i}{\hbar}(H_{mm}'-H_{nn}')\right\}\rho_{mn}(\mathbf{q},\mathbf{r})=0. \quad (14)$$

Here the equation contains the arithmetic mean value of the forces and momenta in the states m and n. The case of H' diagonal in ξ and ξ' can correspond, for example, to the action of an external field on the quadrupole moment of a neutral atom.

Interaction with an electromagnetic field corresponds to the operator $\Delta_{\mathbf{r}}H_{ij}'$ which is not diagonal in the internal coordinates. The terms

$$\sum_{l}\frac{1}{i\hbar}(H_{ml}'\rho_{ln}-\rho_{ml}H_{ln}')$$

describe the induced transition when the recoil effect is neglected,[3] whereas allowance for this effect corresponds to the derivatives $\Delta_{\mathbf{r}}H_{ij}'$.[3,4] In this particular case the kinetic equation for the Wigner function (12) reduces to the equation considered by Kazentsev.[4] As shown in [3], the recoil effect in weak fields is important at $\hbar k^2/m>\Gamma$, where Γ is the homogeneous line width.

We analyze next the shape of the spectral resonances for the case of accelerations a produced by quasistationary fields and independent of the internal variables. In this case the density matrix elements satisfy the equation

$$(\partial/\partial t+\mathbf{v}\nabla_{\mathbf{r}}+\mathbf{a}\nabla_{\mathbf{v}}+\Gamma_{ij})\rho_{ij}=\delta_{ij}q_j+i[V,\ \rho]_{ij}. \quad (15)$$

The operator $V(\mathbf{r},t)$ takes into account here the interaction of the particles with the light field. Γ_{ij} are the decay fields, and q_j are the Maxwellian level-excitation functions. In the analysis that follows we use the con-

dition $|\mathbf{a}\cdot\mathbf{k}|\sim\Gamma\Gamma_j \ll k\bar{v}\Gamma$, when the frequency shift due to the acceleration distorts only the shapes of the nonlinear structure, and the characteristics of the system remain unchanged when the nonlinear phenomena are neglected.

3. RESONANT SCATTERING OF LIGHT

We place a resonantly absorbing (amplifying) medium in an electromagnetic field made up of one strong and one weak electromagnetic plane wave with respective amplitudes $\mathbf{E}_0$ and $\mathbf{E}_\mu$. In this section we are interested in the spectral contour of the response to a weak signal $\mathbf{E}_\mu$, which in contrast to the strong one does not give rise to nonlinear effects. In analogy with [1], we seek the solution of Eq. (15) by perturbation theory and express it in terms of Green's functions

$$f_0(\mathbf{r}, \mathbf{v}, t|\mathbf{r}', \mathbf{v}', 0)=\theta(t)\exp(-\Gamma_i t)\delta(\mathbf{v}-\mathbf{v}'-\mathbf{a}t)\delta(\mathbf{r}-\mathbf{r}'-\mathbf{v}'t-\mathbf{a}t^2/2), \quad (16)$$

that take into account the acceleration of the emitter over the mean free path in a gas or a plasma. The nonlinear increments added to the work of the weak field by the action of the strong wave are calculated for two- and three-level systems (the resonance-fluorescence and Raman-scattering schemes).

A. Two-level problem. If the sounding field and the strong wave are at resonance with one transition of frequency ω_{mn}, then the interaction operator is of the form

$$V=G\exp[-i(\Omega t-\mathbf{kr})]+G_\mu\exp[-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})];\quad G=\mathbf{E}_0\mathbf{d}_{mn}/2\hbar,\quad G_\mu=\mathbf{E}_\mu\mathbf{d}_{mn}/2\hbar,\quad \Omega=\omega-\omega_{mn},\quad \Omega_\mu=\omega_\mu-\omega_{mn}, \quad (17)$$

where $\mathbf{d}_{mn}$ is the dipole-moment matrix element. In this problem, calculation of the spectral profile requires knowledge of the functions

$$\rho_{jj}=R_j+2\,\mathrm{Re}\{r_j\exp[-i(\varepsilon t-\mathbf{q}\mathbf{r})]\},\quad j=m,\ n; \quad (18)$$

$$\rho_{mn}=R\exp[-i(\Omega t-\mathbf{kr})]+r\exp[-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})], \quad (19)$$

where

$$\varepsilon=\omega_\mu-\omega,\quad \mathbf{q}=\mathbf{k}_\mu-\mathbf{k}.$$

Direct calculation shows that in the case of waves having the same direction ($\mathbf{k}\uparrow\uparrow\mathbf{k}_\mu$) the work of the weak field $\mathcal{P}_\mu$ is given, accurate to the first-order nonlinear correction in the intensity, by the expression

$$\mathcal{P}_\mu\propto\Delta N\exp\left\{-\frac{\Omega_\mu^2}{(k\bar{v})^2}\right\}|G_\mu|^2\left\{1-\frac{|G|^2}{\Gamma}\sum_{j=m,n}\frac{1}{\Gamma_j}[K_j'(\varepsilon)+K_j''(\varepsilon)]\right\}, \quad (20)$$

where

$$K_j'(\varepsilon)=2\,\mathrm{Re}\int_0^\infty\frac{\Gamma\Gamma_j\,dt}{\Gamma_j+i\mathbf{akt}}\exp[-(2\Gamma-i\varepsilon)t-i\mathbf{akt}^2], \quad (21)$$

$$K_j''(\varepsilon)=2\,\mathrm{Re}\int_0^\infty\frac{\Gamma\Gamma_j\,dt}{\Gamma_j-i(\varepsilon-\mathbf{akt})}\exp[-(2\Gamma-i\varepsilon)t-i\mathbf{akt}^2]. \quad (22)$$

Here ΔN characterizes the difference between the populations in the states m and n; $\bar{v}$ is the average thermal velocity.

Formula (20) is valid when the Doppler broadening exceeds the other characteristic widths:

$$k\bar{v}\gg\Gamma_i,\ |\mathbf{a},\mathbf{k}|/\Gamma_i. \quad (23)$$

In this case the acceleration influences only the shape of the nonlinear structures that emerge against the background of the Doppler contour. The terms containing the functions $K_j'(\epsilon)$ take into account the change produced in the populations R_j by the strong field, whereas the nonlinear interference effects (NIE) are described by the functions $K_j''(\epsilon)$. Computer-derived plots of the functions $K_j'(\epsilon)$ and $K_j''(\epsilon)$ are shown in Figs. 1 and 2. At $ak=0$ these curves are Lorentzians with half-widths 2Γ and Γ_j [5]:

$$K_j'(\varepsilon)=(1+\varepsilon^2/4\Gamma^2)^{-1}, \quad (21a)$$

$$K_j''(\varepsilon)=(1-\Theta)^{-1}[(1+\varepsilon^2/\Gamma_j^2)^{-1}-\Theta(1+\varepsilon^2/4\Gamma^2)^{-1}],\ \Theta=\Gamma_j/2\Gamma. \quad (22a)$$

The acceleration acting on the phase of the radiation, and the populations that oscillate with frequency $\epsilon=\omega_\mu-\omega$, influence the shapes of the spectral resonances, which become asymmetrical

$$K_j'(\varepsilon,\mathbf{a})=K_j'(-\varepsilon,-\mathbf{a}),\quad K_j''(\varepsilon,\mathbf{a})=K_j''(-\varepsilon,-\mathbf{a}). \quad (24)$$

As shown in Figs. 1 and 2, the shifts of the resonances $K_j'(\epsilon)$ and $K_j''(\epsilon)$, due to the acceleration, is commensurate under certain conditions ($|\mathbf{a}\cdot\mathbf{k}|\gtrsim\Gamma\Gamma_j$) with the broadening. If $\Gamma\Gamma_j<|\mathbf{a}\cdot\mathbf{k}|\ll\Gamma^2$, then the principal role is played in the deformation by the change of the velocity distribution, and the resonance contours are described by the integral exponential functions $\mathrm{Ei}(z)$ of complex argument:

$$K_j'(\varepsilon)=-\frac{2\Gamma\Gamma_j}{|\mathbf{ak}|}\mathrm{Im}[e^{z'}\mathrm{Ei}(z')],\quad z'=\frac{\Gamma_j(\varepsilon+i2\Gamma)}{|\mathbf{ak}|}, \quad (21b)$$

$$K_j''(\varepsilon)=-\frac{2\Gamma\Gamma_j}{|\mathbf{ak}|}\mathrm{Im}[e^{z''}\mathrm{Ei}(z'')],\quad z''=\frac{2\Gamma\varepsilon+i(2\Gamma\Gamma_j-\varepsilon^2)}{|\mathbf{ak}|}, \quad (22b)$$

here

$$\mathrm{Ei}(z)=\int_z^\infty\frac{e^{-u}\,du}{u}.$$

For oppositely traveling waves ($\mathbf{k}\uparrow\downarrow\mathbf{k}_\mu$), when the NIE are suppressed by the Doppler broadening, the weak-field spectrum takes the form

$$\mathcal{P}_\mu\propto\Delta N\exp\left[-\frac{\Omega_\mu^2}{(k\bar{v})^2}\right]|G_\mu|^2\left\{1-\frac{|G|^2}{\Gamma}\sum_{j=m,n}\frac{1}{\Gamma_j}K_j'[-(\Omega+\Omega_\mu)]\right\}. \quad (25)$$

The nonlinear resonance is also asymmetric in this case. Its shape does not coincide with that of the Lamb dip[1] as it would at $\mathbf{a}\cdot\mathbf{k}=0$. The frequency dependence of this resonance does not differ from the frequency dependence of the Bennett dip, a fact that can be used to obtain direct information on the effect of the acceleration on the velocity distribution of the excited particles.

The simplest situation for spectral analysis is when the decay constants of the combining states differ strongly from each other. In this case the maxima of the functions K_m' and K_n' are shifted differently under the

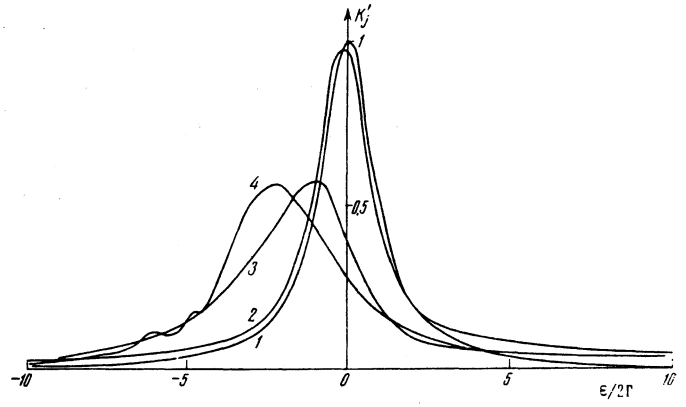

FIG. 1. Plots of the function $K_j'(\epsilon)$ at $\mathbf{a}\cdot\mathbf{k}\leq 0$; curve 1—at $\mathbf{a}\cdot\mathbf{k}=0$; curve 2—at $|\mathbf{a}\cdot\mathbf{k}| = 0.3\Gamma\Gamma_j$, $\Gamma = 10\Gamma_j$; curve 3—$|\mathbf{a}\cdot\mathbf{k}| = 4\Gamma\Gamma_j$, $\Gamma = 10\Gamma_j$; curve 4—at $|\mathbf{a}\cdot\mathbf{k}| = 4\Gamma\Gamma_j$, $\Gamma = \Gamma_j$.

action of the acceleration, and this can lead to the splitting of the combined resonance into two components corresponding to the action of the strong field on the upper and lower levels.

B. Three-level problem. In the Raman-scattering scheme, the NIE manifests itself somewhat differently than in resonance fluorescence. Here the fields E_0 and E_μ act on neighboring transitions $m \to n$ and $m \to l$, so that Eqs. (15) must be solved with interaction matrix elements in the form

$$V_{mn}=G\exp[-i(\Omega t-\mathbf{kr})],\quad V_{ml}=G_\mu\exp[-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})],$$
$$G_\mu=E_\mu d_{ml}/2\hbar,\quad \Omega_\mu=\omega_\mu-\omega_{ml}. \tag{26}$$

An essential role in the calculation of the spectral characteristics is played by the density-matrix elements

$$\rho_{ml}=r\exp[-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})],\quad \rho_{nl}=r'\exp[-i(\varepsilon t-\mathbf{qr})],$$
$$\varepsilon=\Omega_\mu-\Omega=\omega_\mu-\omega_{ml}-\omega+\omega_{mn}. \tag{27}$$

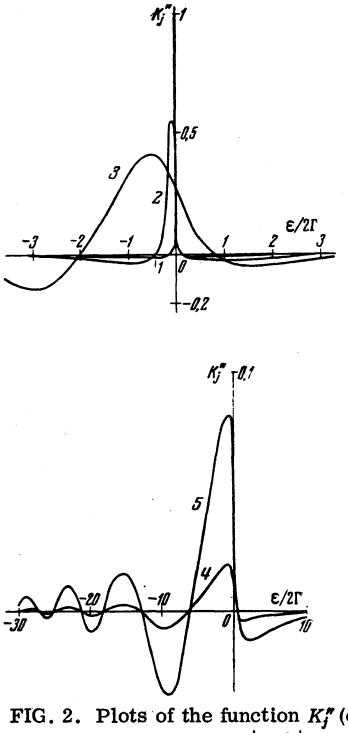

FIG. 2. Plots of the function $K_j''(\epsilon)$ at $\mathbf{a}\cdot\mathbf{k}\leq 0$; curve 1—$\mathbf{a}\cdot\mathbf{k} = 0$, $\Gamma = 10\Gamma_j$; curve 2—$|\mathbf{a}\cdot\mathbf{k}| = 4\Gamma\Gamma_j$, $\Gamma = 10\Gamma_j$; curve 3—$|\mathbf{a}\cdot\mathbf{k}| = 4\Gamma\Gamma_j$, $\Gamma = \Gamma_j$, curve 4—$|\mathbf{a}\cdot\mathbf{k}| = 40\Gamma\Gamma_j$, $\Gamma = \Gamma_j$; curve 5—$|\mathbf{a}\cdot\mathbf{k}| = 200\Gamma\Gamma_j$, $\Gamma = 5\Gamma_j$.

If the moduli of the wave vectors k and k_μ are close to ($|k - k_\mu|\bar{v} \ll \Gamma_{ij}$), then the following relation is valid for the work of the weak field

$$\mathcal{P}_\mu \infty \exp[-\Omega_\mu^2/(k\bar{v})^2]\,|G_\mu|^2(\Delta N_\mu - \Delta N\varphi_{1,2}), \tag{28}$$

where

$$\varphi_1=2\,\mathrm{Re}\int_0^\infty\left[\frac{1}{\Gamma_m+iakt}+\frac{1}{\Gamma_{ml}-i(\varepsilon-akt)}\right]\exp[-(\Gamma_{mn}+\Gamma_{ml}-i\varepsilon)t-iakt^2]\,dt, \tag{29}$$

$$\varphi_2=2\,\mathrm{Re}\int_0^\infty\frac{dt}{\Gamma_m-iakt}\exp[-(\Gamma_{mn}+\Gamma_{ml}-i\Omega-i\Omega_\mu)t+iakt^2]. \tag{30}$$

The subscripts 1 and 2 correspond to parallel and antiparallel vectors k and k_μ. If $\mathbf{k} \uparrow\uparrow \mathbf{k}_\mu$, there is present a combination of population and interference dips, whose shapes are described by functions analogous to the functions K_i' and K_j'' considered above. On the other hand if $\mathbf{k} \uparrow\downarrow \mathbf{k}_\mu$, then there is only a dip of interference origin.

The broadening action of the accelerated motion on the nonlinearly interfering resonances can in principle manifest itself under conditions that are typical of ionic lasers. The acceleration of ions over the mean free path in the plasma is caused by the electric field of the discharge. It must be noted, however, that the experimental material on NIE in the emission of ionic lasers is so far extremely scanty and reduced principally to the data of Korolev *et al.*[6], where the spectrum of the amplification of the weak field on the $4p^4D_{5/2} - 4s^2P_{3/2}$ transition (wavelength $\lambda = 5145$ Å) of an argon laser was observed in the presence of a strong field resonant to the adjacent transition $4p^2D_{5/2} - 4s^2P_{3/2}$ ($\lambda = 4880$ Å). The nonlinear resonance measured in [6] turned out to be much broader than the ordinary nonlinear-interference dip.[7] Unfortunately, the absence from [6] of data on the radiation power and on the gas discharge (electric field intensity, electron temperature and density) does not permit a quantitative comparison of the developed theory with experiment and a conclusive identification of the nature of the registered broadening anomalies.

4. NONLINEAR ZEEMAN EFFECT

Among the highly effective methods of obtaining narrow spectral resonance is the magnetic scanning method based on measuring the dependence of the coefficient of resonant absorption (amplification) on the external-

magnetic-field intensity. In the analysis of the nonlinear Zeeman effect it is necessary to take into account the state degeneracy, which had heretofore been neglected for simplicity. In the case of degenerate states, the interaction of the medium with a traveling wave of any polarization is described by the matrix elements

$$V_{mM,nM'}=\sum_{\alpha}G_{-\alpha}e^{-i(\Omega t-\mathbf{kr})}\begin{pmatrix} J_m & 1 & J_n \\ -M & \alpha & M'\end{pmatrix}(-1)^{J_m-M+\alpha},$$
$$G_\alpha=E_\alpha d_{mn}/2\hbar;\ \alpha=0,\pm1, \tag{31}$$

where E_α are the circular components of the electromagnetic field, J_j is the total angular momentum of the level j, and M is the projection of the angular momentum.

In the normal Zeeman effect, when the Landé g-factors of the levels m and n are equal, it is convenient to seek the solution of (15) in the form

$$\rho_{jM,jM'}=R_{jM,jM'}\exp(i\Delta_{MM'}t),\quad j=m,n;$$
$$\rho_{mM,nM'}=R_{mM,nM'}\exp[-i(\Omega-\Delta_{MM'})t],$$
$$\Delta_{MM'}=\Delta(M-M'),\quad \Delta=\mu_0 gH/\hbar. \tag{32}$$

The parameter Δ describes the Zeeman splitting of the levels in a magnetic field of intensity H.

In the case of an axial magnetic field ($\mathbf{k}\uparrow\downarrow\mathbf{H}$) the work $\mathcal{P}$ of the electromagnetic wave depends on Δ in the following manner:

$$\mathcal{P}(\Delta)\propto\Delta N\sum_{\alpha=\pm1}|G_\alpha|^2\exp\left[-\frac{(\Omega+\alpha\Delta)^2}{(k\bar v)^2}\right]\left\{1-\frac{A_0}{2\Gamma}\left[|G_\alpha|^2\sum_{j=m,n}\frac{K_j'(0)}{\Gamma_j}\right.\right.$$
$$+|G_{-\alpha}|^2\left(\frac{A_1K_n'(2\alpha\Delta)}{\Gamma_n}+\frac{A_2K_m'(2\alpha\Delta)}{\Gamma_m}\right.$$
$$\left.\left.\left.+\frac{A_1K_m''(2\alpha\Delta)}{\Gamma_m}+\frac{A_2K_n''(2\alpha\Delta)}{\Gamma_n}\right)\right]\right\}. \tag{33}$$

The dependence of the nonlinear increment on the total angular momenta of the levels is determined by the coefficients A_0, A_1, A_2 given in [8].

In the formula for $\mathcal{P}$, each term containing the functions $K_j'(2\alpha\Delta)$ and $K_j''(2\alpha\Delta)$ produces structures similar to those considered in the preceding section. The amplitudes of these structures depend on the degree of degeneracy of the levels and on the polarization of the radiation. At $\mathbf{a}\cdot\mathbf{k}=0$, formula (33) reduces to the result of D'yakonov and Perel'.[9,10]

If the light wave is linearly polarized, then the shape of the interference resonances is described by the function

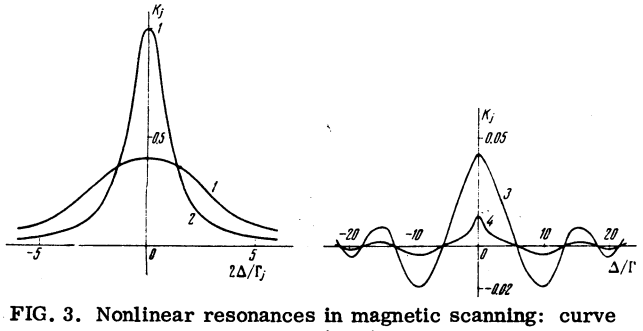

FIG. 3. Nonlinear resonances in magnetic scanning: curve 1—$\mathbf{a}\cdot\mathbf{k}=0$, $\Gamma=10\Gamma_j$; curve 2—$|\mathbf{a}\cdot\mathbf{k}|=4\Gamma\Gamma_j$, $\Gamma=10\Gamma_j$; curve 3—$|\mathbf{a}\cdot\mathbf{k}|=40\Gamma\Gamma_j$, $\Gamma=\Gamma_j$; curve 4—$|\mathbf{a}\cdot\mathbf{k}|=200\Gamma\Gamma_j$, $\Gamma=5\Gamma_j$.

$$K_j(2\Delta)=[K_j''(2\Delta)+K_j''(-2\Delta)]/2, \tag{34}$$

plots of which, calculated for different values of $|\mathbf{a}\cdot\mathbf{k}|$, are shown in Fig. 3. At sufficiently large accelerations, when $|\mathbf{a}\cdot\mathbf{k}|\gtrsim\Gamma^2$ and $|\mathbf{a}\cdot\mathbf{k}|\gtrsim\Gamma_j\Gamma$, the interference dip, while remaining symmetrical, can broaden greatly and split into two individual structures. Oscillations can appear on the edges of the dip.

For the $\lambda=4880$ Å line of the argon laser (transition $J_m=5/2\to J_n=3/2$) we have

$$A_2/A_1=3/28. \tag{35}$$

In as much as in this case there is also a very large difference between the decay constants of the levels ($\Gamma_n\gg\Gamma_m$), the nonlinear (in intensity) increment to the work of the field

$$\Delta\mathcal{P}\propto\Delta N\sum_{\alpha}|G_\alpha|^2[|G_\alpha|^2K_m'(0)+A_1K_m''(2\alpha\Delta)|G_{-\alpha}|^2]/2\Gamma\Gamma_m \tag{36}$$

contains only narrow resonances of the type $K_m''(2\alpha\Delta)$, which carry information on the relaxation processes on the upper level $4p^2D_{5/2}$. The acceleration due to the electric field of the discharge satisfies the condition $|\mathbf{a}\cdot\mathbf{k}|/\Gamma_m\sim\Gamma$ at $\Gamma_m\ll\Gamma$, and therefore the contour of $K_m''(2\alpha\Delta)$ can be described by formula (22b) with the substitution $\epsilon\to2\alpha\Delta$. If $|\mathbf{a}\cdot\mathbf{k}|/\Gamma_j\ll\Gamma$, then the effect of the acceleration on the characteristics of the Zeeman laser reduces to the "drift" effects considered in [11].

5. NARROWING OF NONLINEAR RESONANCES BY CONSTANT ACCELERATION

The idea of using acceleration of excited particles to reduce the width of nonlinear resonances was first proposed by Letokhov.[12] It was based on the localization of the atoms or molecules with low velocities in a standing electromagnetic wave. The practical realization of this method, however, calls for surmounting considerable experimental difficulties, since the fraction of localized particles in a gas at thermal equilibrium is quite small, and the untranarrow peak produced by them has low contrast. We discuss below, with a ring laser as the example, the possibility of narrowing high-contrast nonlinear resonances by the acceleration produced by constant external fields.

The presence of narrow resonances in the power of a ring laser is due not only the Bennett dips in the population velocity distribution, but also to the spatial inhomogeneity of the medium, and this leads to competition between the lasing regimes near the center of the gain or of the absorption line. Depending on the frequency detuning, standing- and traveling-wave regimes are realized. Considering henceforth a ring laser with nonlinear absorption, we assume the following conditions to be satisfied:

$$\Gamma_-\ll\Gamma_+,\quad |\mathbf{ak}|/\Gamma_j\sim\Gamma, \tag{37}$$

where the plus and minus sign distinguish between the relaxation constants of an amplifying (+) and an absorbing (−) medium. The conditions (37) mean that the acceleration acts only on the shape of the peak due to non-

linear absorption, and leaves the Lamb dip unchanged. When account is taken of the spatial inhomogeneity due to the standing wave, and the acceleration is neglected, the gains in the different regimes are the following[13,14]: for a standing wave

$$\alpha_+^{ст}=\alpha_+^0\left\{1-\frac{\varkappa_+}{2}\left[1+\frac{1}{1+\Omega_+^2/\Gamma_+^2}-\left(\frac{\Gamma_+}{k\bar{v}_+}\right)^2+\mu_+\right]\right\} \tag{38}$$

and for a traveling wave

$$\alpha_+^{б}=\alpha_+^0\left\{1-\varkappa_+\left[1-\frac{1}{2}\left(\frac{\Gamma_+}{k\bar{v}_+}\right)^2\right]\right\}. \tag{39}$$

Here

$$\varkappa_+=\frac{|G_+|^2}{\gamma_+\Gamma_+},\quad \mu_+=\frac{\Gamma_+\gamma_+}{(k\bar{v}_+)^2},\quad \gamma_+=\frac{\Gamma_m^+\Gamma_n^+}{2(\Gamma_m^++\Gamma_n^+)};$$

$\Omega_+=\omega-\omega_+$ is the detuning of the radiation frequency from the center of the gain line, and μ_+ is the spatial-inhomogeneity parameter. At $\mathbf{a}\cdot\mathbf{k}=0$, a nonlinearly absorbing medium can be described by relations (38) and (39) in which the plus sign is replaced by a minus sign. The change of the generation regimes in a ring laser with nonlinear absorption at $\mathbf{a}\cdot\mathbf{k}=0$ was considered in [15,16].

If account is taken of the acceleration, $\mathbf{a}\cdot\mathbf{k}\neq 0$, then we have for the coefficients of the resonant absorption in the standing- and traveling-wave regimes

$$\alpha_-^{ст}=\alpha_-^0\left\{1-\frac{1}{2}\varkappa_-[Y_1(0)+Y_1(\Omega_-)]\right\},\quad \alpha_-^{б}=\alpha_-^0[1-\varkappa_-Y_1(0)], \tag{40}$$

where

$$Y_1(\Omega_-)=\frac{\Gamma_m^--\Gamma_n^-}{\Gamma_m^-+\Gamma_n^-}\sum_{j=m,n}\frac{1}{2\Gamma_j}[K_j'(2\Omega)+K_j'(-2\Omega)].$$

The function $Y(\Omega_-)$, whose properties were analyzed in [1], describes an acceleration-deformed Lamb dip in the absorption line.

With the aid of (38)–(40) it is easy to show that the stability regions of the standing wave regime are determined by the inequality

$$F(\omega)=1-\frac{1}{1+\Omega_+^2/\Gamma_+^2}-\mu_+-\beta[Y_1(0)+Y_1(\Omega_-)]>0, \tag{41}$$

where

$$\beta=\alpha_-^0\varkappa_-/\alpha_+^0\varkappa_+\leqslant 1. \tag{42}$$

When an inequality inverse to (41) is satisfied, a traveling wave is generated.

The boundaries between the stability regions of the different generation regimes are the roots of the equation $F(\omega)=0$. Figure 4 shows plots of the function $F(\omega)$ at $\mathbf{a}\cdot\mathbf{k}\neq 0$ (solid curve) and $\mathbf{a}\cdot\mathbf{k}=0$ (dashed). The most interesting situation is when the acceleration splits the absorption peak due to nonlinear absorption into two structures with widths $\Gamma_-'>\Gamma_-$, symmetrically placed relative to ω_- at distances

$$\Delta_0\sim ak/\Gamma_-. \tag{43}$$

One of these structure shifts towards the center ω_+ of the gain line, as a result of which the competing resonance produced when the generation regime changes can become effectively narrower. In fact, the width of the competing resonances located near this structure is determined by the relation

$$\Delta\Omega\sim\frac{\Gamma_-'}{\sqrt{\beta}}\left[\left(\frac{\omega_--\omega_+-\Delta_0}{\Gamma_+}\right)^2-\mu_+-\theta_-\right]^{1/2}. \tag{44}$$

It is seen from (44) that $\Delta\Omega$ depends essentially on the detuning $|\omega_--\omega_+-\Delta_0|$ of the gain and absorption line centers, decreased on account of the shift Δ_0, the parameter μ_+ of the spatial modulation of the populations, and the constant θ_-, which is positive at not too large accelerations ($\Delta_0\lesssim 2^{-1/2}\Gamma_-'$) and is of the order of

$$\theta_-\sim 0{,}1\left(\frac{\Delta_0}{\Gamma_-'}\right)^2\left[1-2\left(\frac{\Delta_0}{\Gamma_-'}\right)^2\right]. \tag{45}$$

By varying the acceleration near the values $|\mathbf{a}\cdot\mathbf{k}|\lesssim\Gamma_-\Gamma_-'$, we can decrease without limit the expression in the square brackets of (44), thus greatly reducing the width of the competing resonance.

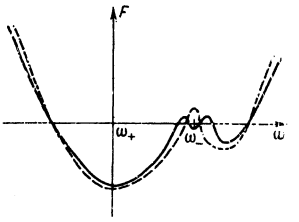

FIG. 4. Difference between the gains of a two-component medium in the standing- and traveling-wave lasing regimes.

Among the sufficiently contrasty resonances that can be narrowed down by the acceleration, mention should be made also of the nonlinear Ramsay resonance fringes produced when spatially separated standing waves interact.[17–19] It is known [17] that the width of the Ramsey fringe is determined to a considerable degree by the reciprocal transit time of the system $T^{-1}=\bar{v}/L$, where L is the distance between the light beams. Naturally, therefore, the increase of the transit time by the deceleration will contribute to the narrowing of this resonance.

The authors thank V. I. Donin and A. P. Kol'chenko for useful discussions, and V. F. Shmakov for the numerical calculations.

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Translated by J. G. Adashko

Mechanisms of activation of heterogeneous reactions by laser radiation

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(Submitted 21 September 1977)
Zh. Eksp. Teor. Fiz. **74**, 1307–1317 (April 1978)

We investigate theoretically the mechanisms whereby heterogeneous reactions are activated by IR laser radiation via selective pumping of the vibrational degrees of freedom of adsorbed molecules, and also via stimulation of electron migration between surface groups. The latter mechanism is used to explain the increased rate of decomposition of NH_2 groups on an aerosil [SiO_2] surface in the radiation field of a CO_2 laser.

PACS numbers: 82.65.Jv

1. Problems connected with the action of laser radiation on physico-chemical processes are presently attracting considerable attention for perfectly understandable reasons.[1-4] One of the timely concomitant problems is the selective activation of adsorption and catalytic processes; a solution of this problem would provide the chemical industry and the material sciences with entirely new possibilities. Direct stimulation of surface reactions by laser radiation can be effected in two ways.[1)] The first is to activate gas-phase molecules that subsequently enter in surface reactions (see, e.g.,[5]). The second is activation of molecules adsorbed on a surface.[6] This method has certain distinguishing features worthy of a more detailed examination. Adsorption (and especially chemosorption) shifts the frequencies of the molecule absorption bands and gives rise to new IR spectral bands as a result of the change in the symmetry of the force field.[7,8] For the same reason, the isotopic shift of the frequency increases in a number of cases. This extends the possibilities of laser action.

At the same time, chemosorption is connected with the formation of chemical compounds of a new type, which do not exist in the gas phase and whose reactivity and mechanisms of interaction with other molecules differ from the analogous properties of the gas phase. We note also that by using adsorbents with developed surfaces it is possible effect chemical transformations at an appreciable density of the medium, something difficult to do in the gas phase in view of the collision line broadening and other factors.

Recent theoretical investigations of energy-exchange processes in an adsorbent + adsorbate system can be of partial help in the choice of the system or of the particular type of interaction,[4,9-11] although the complexity of heterogeneous systems makes rigorous deductions impossible. At the same time, it can be concluded from the results of these theoretical papers that in the case of excitation of vibrational degrees of freedom the activation of adsorbed molecules via buildup of a definite chemical bound by IR laser radiation is possible only if the relaxation of this vibration has low probability, since the effectiveness of the activation becomes noticeable at a pumping rate exceeding the relaxation rate. In the case of chemosorption at a radiation density ~100 W/cm^2 this condition imposes considerable limitations on the type of the activated surface structures; this will be discussed separately later on.

It should also be noted here that in many cases the obvious mechanisms of activation of surface reactions by laser radiation, such as acceleration of the molecule in the course of absorption, weakening of the chemical bond by vibrational pumping or by excitation of surface migration, and others, are insufficient in a number of cases for the understanding of the surface phenomena. One must not, for example, lose sight of processes connected with electron transfer between surface

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