Nonlinear magnetooptical resonances of hyperfine structure in radiative transitions

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A theory is proposed for nonlinear magnetooptical resonances of absorption (or amplification) of coherent radiation at transitions having a hyperfine structure. The solutions obtained for the quantum transport equation with exact allowance for the Zeeman effect under hyperfine splitting conditions provide a continuous description of the nonlinear absorption as a function of the magnetic field, both for weak energy-level Zeeman splitting comparable with the hyperfine-structure interval, and for strong splitting of the order of the homogeneous width. With a gas of particles having a nuclear spin $I = 1/2$ as an example, the forms of the nonlinear magnetooptic resonances that result from hyperfine splitting of atomic and molecular terms are analyzed.

§1. INTRODUCTION

Recent experiments aimed at observing nonlinear magnetooptical phenomena due to the hyperfine structures of atoms and molecules have revealed quite narrow nonlinear magnetooptical resonances (NMOR), much narrower than the Doppler line widths or the resonance-level widths.[1–5] The NMOR were produced in these experiments on aggregates of radiative transitions between hyperfine components of terms split by the magnetic field, i.e., under nuclear magnetic resonance conditions. Until recently, all theoretical papers on NMOR dealt with systems whose energy spectra had no hyperfine structure (see, e.g., Refs. 6–10). We develop here a theory of NMOR in absorption (or amplification) of coherent laser radiation on transitions with hyperfine structure.

A quantum transport equation is derived for the density matrix of particles having nuclear spins $I = 1/2$ and 1, with the Zeeman effect taken accurately into account, when hyperfine splitting of the atomic and molecular terms is present. The profiles of the NMOR due to the radiative transitions between the hyperfine structure components are analyzed. The solutions obtained for the transport equation permit a continuous description of the magnetic-field dependence of the nonlinear absorption both for weak Zeeman level splitting comparable with the hyperfine-structure spacing, and for strong splitting on the order of the homogeneous linewidth. To analyze the absorption resonances on vibrational-rotational transitions we use a quasiclassical description of the orientational states of the rotational and total angular momenta of the molecules.

We explain a number of facts that seem paradoxical from the standpoint of the Zeeman-laser theory that takes no account of the hyperfine splitting. According to that theory, in particular, there is no NMOR at all for circular polarization of the radiation in an axial magnetic field. In the theory we have developed, the circularly polarized radiation experimentally in an axial magnetic field[3,4] is attributed to collisions between the molecules in the gas; these collisions cause disorientation and intermixing of the hyperfine structure components split by the magnetic field. A process wherein nuclear magnetic resonance is induced by collisions sets in. The simplest mechanism for inducing NMOR by collisions was considered earlier in Ref. 11 for transitions between energy levels with electron angular momentum $J = 1$ in the anomalous Zeeman effect. This resonance, similar to the collision-induced optical double resonance, is due to collisional crossing of Bennett dips in the particle velocity distribution. In the anomalous Zeeman effect produced by the hyperfine splitting of the terms, the amplitude of the collison-induced NMOR decreased more steeply with increasing pressure than the amplitude of ordinary NMOR. This systematic behavior of the nonlinear-optics nuclear magnetic resonance can be made the basis for the development of new ultrahigh-resolution nonlinear-spectroscopy methods capable of yielding information on the properties of the nuclei and on the fine details of relaxation processes in low-density gases, details that reflect the interaction of the electron shell of an atom or a molecule with a nucleus.

§2. GENERAL RELATIONS

Consider a gas of particles with nonzero spin **I** placed in a constant uniform magnetic field and resonantly interacting with a traveling electromagnetic wave. The interaction of the particle electron shell with the magnetic dipole and electric quadrupole moments of the nucleus causes hyperfine splitting of the energy levels into components, each of which corresponds to a specific total particle angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$. The total system Hamiltonian $\mathscr{H}$, whose eigenvalues are determined by the energy levels in the absence of interaction with the perturbing particles, can be represented as the sum

$$\mathscr{H} = \mathscr{H}_0 + \hbar(U + V + W), \tag{2.1}$$

where the $\mathscr{H}_0$ term corresponds to the energy of the unperturbed electron shell: U is the hyperfine structure Hamiltonian; the V and W operators take into account the interaction with the electromagnetic radiation and with the external electromagnetic field.

When a method which depends nonlinearly on the intensity is used to record absorption on an m-n transition, the

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behavior of the gas is described with allowance for relaxation and excitation, by the equation for the Wigner density matrix elements $\rho_{ij}(\mathbf{r}, \mathbf{v}, t)$ in the interaction representation:

$$(\partial/\partial t+\mathbf{v}\nabla_{\mathbf{r}})\rho_{ij}=q_j\delta_{ij}-i[U+V+W,\ \rho]_{ij}+(R+S)_{ij}, \quad (2.2)$$
$$i, j=m, n.$$

Here R is the radiative-decay operator, S is the collison integral, q_j is the Maxwell excitation function,

$$q_j=Q_jF_M(\mathbf{v}), \quad F_M(\mathbf{v})=(\pi^{1/2}\bar{v})^{-3}\exp(-v^2/\bar{v}^2), \quad (2.3)$$

and $\bar{v}$ is the mean thermal velocity of the particles. The operator of the interaction with the electromagnetic radiation has an irreducible-tensor expansion with coefficients that satisfy the relation[13]

$$V_{1\sigma}(F_mF_n)=[(2F_m+1)(2F_n+1)]^{1/2}\begin{Bmatrix} I & J_n & F_n \\ 1 & F_m & J_m \end{Bmatrix} G_\sigma e^{-i(\Omega t-\mathbf{kr})},$$
$$G_\sigma=E_\sigma d_{mn}/2\hbar, \quad (2.4)$$

where $\Omega=\omega-\omega_{mn}$ is the shift of the frequency $\omega=kc$ from the transition frquency ω_{mn}, d_{mn} is the reduced matrix element of the transition dipole moment, and E_σ are the spherical component of the light-wave electric vector.

As usual, collisions accompanied by a change of the component M of the total angular momentum, i.e., disorienting collisions, are treated by using the isotropic-perturbation model. It is assumed also that the state of the nuclei remains unchanged during the collision time τ_c. Since the characteristic hyperfine splitting of the level is $\Delta\omega_F \ll \tau_c^{-1}$, the nuclear spin does not manage to reverse during the time τ_c (Ref. 14).

For simplicity, we analyze here the role of the collisions that cause intermixing of the hyperfine structure components within the framework of the relaxation-constant model, and describe the relaxation of the electron-shell multipole polarization moments of rank $\varkappa$ by the parameters

$$\Gamma_{ij\varkappa}=\gamma_i+\gamma_j+\gamma_{ij\varkappa}, \quad (2.5)$$

where $\gamma_{i,j}$ are the radiative-decay constants of the levels, and $\gamma_{ij\varkappa}$ are the parameters of the relaxation collisions, whose connection with the operators of the elementary scattering act is indicated in Ref. 10. We note that a collision integral of this type was used earlier to analyze a ground-state nuclear-magnetic-resonance spectrum[15] linear in the microwave-field power. The relaxation-constant model was used in Refs. 12 and 16 to analyze experiments aimed at observing double optical resonance induced by disorienting molecular collisions.

§3. MAGNETOOPTICAL EFFECTS OF NONLINEAR ABSORPTION BY ATOMS WITH $I=J=1/2$

In the case of a gas of identical atoms, the interaction with a magnetic field is described by the Hamiltonian

$$W=-\mu_0 g_j\mathbf{HJ}/\hbar, \quad (3.1)$$

where μ_0 is the Bohr magneton and g_j is the Landé factor for the state j.

We assume for the sake of argument that $J_m = J_n = I = 1/2$ and that the hyperfine structure of the resonant energy levels m and n is the result of interaction with the magnetic dipole moment of the nucleus[1)]:

$$U=A_j\mathbf{IJ}_j, \quad (3.2)$$

where A_j are the level hyperfine splitting constants.

We proceed to analyze the dependence on the magnetic field strength of the work performed by a light field

$$\mathscr{P}=2\hbar\omega\,\mathrm{Im}\int \mathrm{Sp}_M\langle\rho_{mn}V_{nm}\rangle d\mathbf{v}, \quad (3.3)$$

represented by a monochromatic circularly polarized wave propagating along the vector $\mathbf{H}$.

The energy shifts E_{jFM} of the states in the magnetic field are given by the Breit and Rabi equations[17]

$$E_{j1,\pm1}=(A_j/2\mp g_j\Delta)\hbar/2, \quad \Delta=\mu_0 H/\hbar;$$
$$E_{j10}=[-A_j/2+(A_j^2+g_j^2\Delta^2)^{1/2}]\hbar/2, \quad (3.4)$$
$$E_{j00}=-[A_j/2+(A_j^2+g_j^2\Delta^2)^{1/2}]\hbar/2.$$

The subscript F designates the total angular momentum of the state in the absence of a magnetic field.

In the absence of an external magnetic field and M-splitting of the levels, it would be necessary to use for the irreducible tensor operators a representation in which the system of equations for the off-diagonal elements of the density matrix breaks up into independent equations. The level splitting, however, forces us to turn to the M_JM_I representation (in which the Hamiltonian of the interaction of the atom with the magnetic field is diagonal).

The H-dependence of the expansion coefficients of the wave functions of the $|jFM>$ states in the basis states manifests itself in the influence of the magnetic field on the electric dipole moments of the transitions, whose matrix elements, with allowance for the selection rules in the nuclear-spin projection $\Delta M_I = 0$, are of the form

$$\langle n1, -1|d_{+1}|m10\rangle=d_{mn}\cos(\beta_m/2),$$
$$\langle n1, -1|d_{+1}|m00\rangle=-d_{mn}\sin(\beta_m/2),$$
$$\langle n10|d_{+1}|m11\rangle=d_{mn}\sin(\beta_n/2), \quad (3.5)$$
$$\langle n00|d_{+1}|m11\rangle=d_{mn}\cos(\beta_n/2),$$
$$\mathrm{ctg}\,\beta_j=g_j\Delta/A_j.$$

Figure 1 shows the radiative-transition scheme. In a strong magnetic field, when $|\Delta| \gg A_j$, transitions whose dipole moments are proportional to $\sin(\beta_j/2)$ are forbidden, a situation corresponding to the approximation in which the coupling between the J and I angular momenta is destroyed.

We begin the analysis of the nonlinear magnetooptical phenomena with a model having three relaxation constants, assuming no mixing of the magnetic hyperfine structure by the collisions. Direct calculation using the procedure described in Ref. 10 shows that in the large-Doppler-broadening limit and with allowance for (3.5) the work $\mathscr{P}$ performed by the traveling-wave field is described, including a correction which is nonlinear in the intensity, by the expression ($k\bar{v} \gg A_j$):

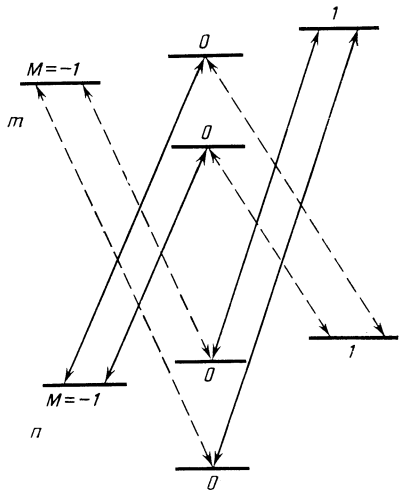

FIG. 1. Electric dipole transitions between the components, split by the magnetic field, of the hyperfine structure of the atom energy levels m and n in the case $J_m, J_n, I = 1/2$.

$$\mathcal{P} \propto \frac{\sqrt{\pi}}{k\bar{v}}|G|^2\left\{\exp\left[-\left(\frac{\Omega+\bar{\Delta}}{k\bar{v}}\right)^2\right]-\frac{|G|^2}{\Gamma}\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_n}\right)\right. \quad (3.6)$$

$$\left.+|G|^2\sum_{j=m,n}\frac{A_j^2}{A_j^2+g_j^2\Delta^2}\left[\frac{1}{2\Gamma}\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_n}\right)-Y_j(\Delta_j)\right]\right\},$$

$$\bar{\Delta}=(g_m+g_n)\Delta/2, \quad \Delta_j=(A_j^2+g_j^2\Delta^2)^{1/2};$$

$$Y_m(\Delta_m)=\mathrm{Re}\left[\left(\frac{1}{\Gamma_n}-\frac{1}{2\Gamma-\Gamma_m}\right)\frac{1}{2\Gamma-i\Delta_m}+\frac{1}{2\Gamma-\Gamma_m}\frac{1}{\Gamma_m-i\Delta_m}\right]$$

$$Y_n(\Delta_n)=\mathrm{Re}\left[\left(\frac{1}{\Gamma_m}-\frac{1}{2\Gamma-\Gamma_n}\right)\frac{1}{2\Gamma-i\Delta_n}+\frac{1}{2\Gamma-\Gamma_n}\frac{1}{\Gamma_n-i\Delta_n}\right], \quad (3.7)$$

where Γ_j are the relaxation constants of the levels $j = m$ and n, while Γ is the homogeneous linewidth.

It can be easily noted that when the condition $2\Gamma = \Gamma_m + \Gamma_n$ is met, e.g., in the spontaneous-decay approximation, the functions

$$Y_j(\Delta_j)=\frac{1}{\Gamma_m\Gamma_n}\frac{1}{1+\Delta_j^2/\Gamma_j^2}. \quad (3.8)$$

In this case

$$\mathcal{P} \propto \frac{\pi^{1/2}}{k\bar{v}}|G|^2\left\{\exp\left[-\left(\frac{\Omega+\bar{\Delta}}{k\bar{v}}\right)^2\right]\right.$$

$$\left.-\frac{|G|^2}{\Gamma_m\Gamma_n}\left[1-\sum_{j=m,n}\frac{A_j^2}{\Gamma_j^2+A_j^2+g_j^2\Delta^2}\right]\right\}, \quad (3.9)$$

and in the nonlinear absorption one can distinguish against the constant background two magnetooptic resonances with Lorentzian profiles and with widths $(\Gamma_j^2 + A_j^2)^{1/2}/g_j$; they stem from Raman scattering of the light by the split hyperfine resonant levels. It is readily noted that if the radiation is circularly polarized this multilevel system breaks up into a set of two three-level subsystems $|m00\rangle \leftrightarrow |n1, -1\rangle \leftrightarrow |m10\rangle$ and $|n00\rangle \leftrightarrow |m11\rangle \leftrightarrow |n10\rangle$. These transitions lead to resonant light scattering in which one photon vanishes and another appears. The magnetic field dependence of the probability of these processes is determined by the relations (3.5) for the electric dipole moments of these transitions. Resonant Raman scattering is described by the off-diagonal elements of the density matrix for the optically forbidden transitions $\psi_{j00} \leftrightarrow \psi_{j10}$; these elements oscillate with frequencies $\Delta_j = A_j^2 + g_j^2\Delta^2)^{1/2}$, as follows from (3.4). The relaxation constants of these density-matrix elements are the constants Γ_j of the radiative and collisional decays of the levels. Here scattering through the upper and lower levels corresponds to nonlinear-inteference resonances of widths $(\Gamma_n^2 + A_n^2)^{1/2}/g_n$ and $(\Gamma_m^2 + A_m^2)^{1/2}/g_m$, respectively.

If the Weisskopf broadening mechanism becomes appreciable, we have $2\Gamma > \Gamma_m + \Gamma_n$, and the nonlinear absorption exhibits a Lorentz profile of width $(4\Gamma^2 + A_j^2)^{1/2}/g_j$, which stands out against the background of the narrower nonlinear-interference Γ_j resonances if the width difference is large. Lorentz factors of the type $\sin^2\beta_j \neq A_j^2(A_j^2 + g_j^2\Delta^2)^{-1}$ reflect the magnetic field dependence of the probability of the Raman transitions.

In the case of a traveling wave with linear polarization, the magnetic field dependence of the resonant absorption is complicated by the nonlinear coupling of the opposite circular polarizations of the radiation:

$$\mathcal{P} \propto \frac{\pi^{1/2}}{k\bar{v}}|G|^2\left\{\sum_{\sigma=\pm1}\exp\left[-\left(\frac{\Omega+\sigma\bar{\Delta}}{k\bar{v}}\right)^2\right]\right.$$

$$-|G|^2\sum_{j=m,n}\left[\frac{2-\sin^2\beta_j}{2}\left(\frac{1}{\Gamma_m}+\frac{1}{\Gamma_n}\right)\right.$$

$$\left.\left.+\sin^2\beta_j Y_j(\Delta_j)\right]-|G|^2[\sin^2\beta_n Y_m(g_m\Delta)+\sin^2\beta_m Y_n(g_n\Delta)]\right\}. \quad (3.10)$$

The structures $Y_j(g_j\Delta)$ that appear here alongside those already described are due to resonant scattering processes in which a photon having one circular polarization vanishes and a photon with opposite polarization appears. The selection rules for the projection M of the total angular momentum have here the usual form $\Delta M = \pm 2$. These light-scattering processes are described by the off-diagonal elements of the density matrix for the forbidden transitions $|j1, -1\rangle \rightarrow |j11\rangle$ with frequencies $g_j\Delta$, and produce in the nonlinear absorption nonlinear-interference Lorentz resonances with widths Γ_j/g_j.

In the limit of large homogeneous broadening ($\Gamma \gg A_j$) the angular momenta **J** and **I** are no longer coupled and the nonlinear absorption remains dependent on the magnetic field only in the presence of disorienting collisions that provide a coupling between the oppositely directed circular components of the radiation. Since $\varkappa = 0.1$ in this case, the mixing of the Zeeman components of the level is described by the orientation constant γ_{j11}, and the profile of collision-induced NMOR is given by a Lorentzian $(\Gamma^2 + \tilde{\Delta}^2)^{-1}$ with an amplitude proportional to γ_{j11} (Ref. 10).

§4. SPLITTING OF HYPERFINE STRUCTURE OF MOLECULAR LEVELS IN A MAGNETIC FIELD

For molecules of the symmetric-top type with nuclear spin I and with component K of the angular momentum J along the symmetry axis, the locations of the hyperfine-structure levels E_F are determined by those elements of the

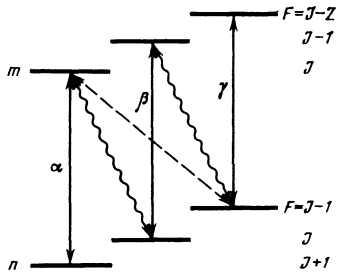

FIG. 2. Hyperfine structure of states corresponding to the $P(J)$ branch of the vibrational-rotational transition of molecules with nuclear spin $I = 1$.

operator U which are diagonal in the $IJKFM$ representation.[17,18] To determine accurately the hyperfine components of an energy level with angular momentum J in a magnetic field, we must diagonalize the submatrix $U + W$ in the $IJKM_JK$ representation, where $M = M_J + M_I$. The operator of the molecular interaction with the magnetic field $\mathbf{H}$ is of the form

$$\hbar W = -\mu_N (g_J \mathbf{HJ} + g_I \mathbf{HI}); \tag{4.1}$$

where μ_N is the nuclear magneton, and g_J and g_I are the orbital and nuclear Landé factors. Since F_Z commutes with the Hamiltonian $U + W$, the latter is diagonal in M, and it remains to diagonalize the submatrix $\langle IJKMM_J|U+W|IJKMM_J'\rangle$, recognizing that elements that are not diagonal in M_J are obtained only from the nuclear quadrupole interaction operator U:

$$\langle MM_J|U|MM_J'\rangle = \sum_F (2F+1) \begin{pmatrix} J & I & F \\ M_J & M-M_J & -M \end{pmatrix} \begin{pmatrix} J & I & F \\ M_J' & M-M_J' & -M \end{pmatrix} \times \frac{E_F}{\hbar}. \tag{4.2}$$

The order of the secular equation for the energy levels in a magnetic field of arbitrary strength depends on M. In particular, at $I = 1$, when $F = J$ or $J \pm 1$, the secular equation is linear if $|M| = J + 1$, quadratic if $|M| = 1$, and cubic if $|M| \leqslant 1$. Using the properties of the vector-addition coefficients, we can express the matrix elements $\langle M_J|U+W|M_J'\rangle$ that determine these equations in terms of the hyperfine-splitting energy E_F.

At $J \gg 1$ the hyperfine-structure spacing satisfies the relation

$$|E_{J-1} - E_{J+1}| \gg |2E_J - E_{J-1} - E_{J+1}|, \tag{4.3}$$

if the hyperfine splitting is due to magnetic dipole interaction (e.g., for CH_4 molecules, Refs. 19 and 20). Changing over for $J \gg 1$ to the quasiclassical description of the orientational states of the angular momentum, and using the indicated inequality, we can represent the roots of the secular equation for molecules with $I = 1$ in the form

$$E_1 = E_J - \mu_N g_J HJ \cos\theta, \quad \cos\theta = M/J; \tag{4.4}$$

$$E_{2,3} = (E_{J-1} + E_{J+1})/2 - \mu_N g_J HJ \cos\theta \pm [(E_{J-1} + E_{J+1})^2/4 + (E_{J-1} - E_{J+1})\mu_N g_I H \cos\theta + (\mu_N g_I H)^2]^{1/2}. \tag{4.5}$$

It follows from (4.4) and (4.5) that in a weak magnetic field we have

$$E_1 = E_J - \mu_N g_J HJ \cos\theta, \quad E_{2,3} = E_{J\pm1} - \mu_N (g_J J \pm g_I) H \cos\theta. \tag{4.6}$$

In the limit of a strong magnetic field, a state with energy E_1 corresponds to a nuclear-spin component $M_I = 0$, and states with energies $E_{2,3}$ correspond respectively to $M_I = \pm 1$. The roots of the secular equation for terms with quadrupole hyperfine structure can be obtained in similar manner in the quasiclassical approximation.[17,18]

§5. NONLINEAR MAGNETOOPTICAL ABSORPTION RESONANCES IN VIBRATIONAL-ROTATIONAL TRANSITIONS OF MOLECULES

We shall consider the magnetooptical manifestations of nonlinear absorption for hyperfine splitting of vibrational-rotational transitions using as the example the $P(J)$ branch for spherical-top molecules with magnetic hyperfine structure, assuming that $J \gg 1$ and $I = 1$. It follows from (2.4) that in this case it suffices to take into account only three lines having approximately equal intensity and corresponding to transitions between hyperfine-structure levels with total angular momenta $F = J + 1 \to J$, $J \to J - 1$, $J - 1 \to J - 2$, since the probabilities of these transitions exceed those of the transitions $F = J \to J$, $J - 1 \to J - 1$, by a factor J^2 and the probability of the transition $F = J - 1 \to J - 1$ by a factor $4J^2$. The transition scheme is shown in Fig. 2.

To describe radiative processes in transitions with large values of the quantum number J it is very effective to use a representation in which the density-matrix elements are identical with the classical distribution functions in the vector directions (see, e.g., Ref. 21). A transformation similar to that of Wigner for translational degrees of freedom is used to convert from the M representation to the quasiclassical one.[10] In this representation the elements of the density matrix depend parametrically on the orientation angles θ and φ of the angular momentum $\mathbf{J}$, as a result of which the transport equation is diagonal.

Labeling the transitions $F = J + 1 \to J$, $J \to J - 1$, $J - 1 \to J - 2$ and the related quantities by the respective indices α, β, and γ, the system of equations for the density-matrix elements can be written in the $\theta\varphi$ representation in

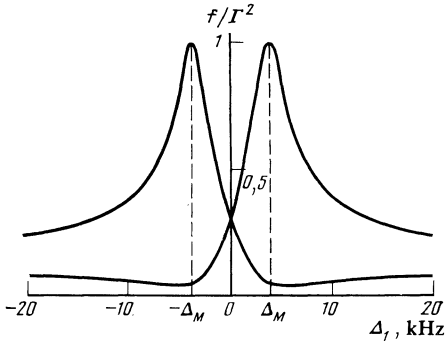

FIG. 3. Plots of the function $f(H)$ in arbitrary units: $r_m = 74.3$ kHz, $r_n = 85.3$ kHz, $g_J = 0.31$, $g_N = 18 g_J$ ($\pm \Delta_M$ are the coordinates of the resonance maxima).

the following form:

$$\left[\Gamma-i(\Omega-\mathbf{kv}-\Delta_\xi)+\frac{1}{2}(\Delta_{m\xi}+\Delta_{n\xi})\frac{\partial}{\partial\varphi}\right]\rho_\xi=iV_{mn}(\rho_{m\xi}-\rho_{n\xi}),$$

$$\xi=\alpha,\beta,\gamma; \tag{5.1}$$

$$\left(\Gamma_j+\Delta_{j\xi}\frac{\partial}{\partial\varphi}\right)\rho_{j\xi}=q_j\pm 2\,\mathrm{Re}[iV_{mn}{}^*\rho_\xi]+S_{j\xi},\quad j=m,n.$$

$\rho_\xi(\theta,\varphi)$ are density-matrix elements which are nondiagonal in the indices m and n of the resonance levels and characterize the polarization of the optical transitions $\xi=\alpha,\beta,\gamma$; $\rho_{j\xi}(\theta,\varphi)$ is the level population of the hyperfine component ξ of the absorption line. The splitting of the structure resonant frequencies are determined by parameters Δ_ξ that in the case of an axial magnetic field take the form

$$\Delta_\alpha=(a_m+b_m-a_n-b_n)/2+(r_m{}^2+2r_m\delta\cos\theta+\delta^2)^{1/2}-(r_n{}^2+2r_n\delta\cos\theta+\delta^2)^{1/2}; \tag{5.2}$$

$$\Delta_\beta=0,\quad \Delta_\gamma=a_m+b_m-a_n-b_n-\Delta_\alpha,$$

$$\delta=\mu_N g_I H/\hbar, \tag{5.3}$$

$$a_j=(E_{J_j+1}-E_{J_j})/\hbar,\quad b_j=(E_{J_j-1}-E_{J_j})/\hbar,\quad r_j=(b_j-a_j)/2,$$

where E_{F_j} is the energy shift of the j-level component having a total angular momentum $F_j=J_j=\pm 1$, as a result of the hyperfine splitting. The Zeeman splitting of the neighboring M sublevels of the state on the transition ξ is given by the parameters

$$\Delta_{j\alpha}=-\Delta_1+(r_j{}^2+2r_j\delta\cos\theta+\delta^2)^{1/2}-[r_j{}^2+2r_j\delta(\cos\theta+J^{-1})+\delta^2]^{1/2}, \tag{5.4}$$

$$\Delta_{j\beta}=-\Delta_1,\quad \Delta_{j\gamma}=-2\Delta_1-\Delta_{j\alpha},\quad \Delta_1=\mu_N g_J H/\hbar.$$

In the derivation of (5.2)–(5.4) we used the solution (4.4) and (4.5) of the secular equation.

We examine how disorientation affects elastic collisions, using as an example the model of strong collisions[10] that ensure an equilibrium distribution over the FM states of the excited levels. The model chosen corresponds to collision integrals of the type

$$S_{j\xi}(\theta,\varphi)=-\nu_j\rho_{j\xi}(\theta,\varphi)+\frac{\tilde\nu_j}{4\pi(2I+1)}\int_0^{2\pi}d\varphi_1\int_0^{\pi}\sin\theta_1\,d\theta_1\sum_{\xi_1}\rho_{j\xi_1}(\theta_1,\varphi_1), \tag{5.5}$$

where ν_j and $\tilde\nu_j$ are the collisional-disorientation constants for the level j. As shown in Refs. 12, 16, and 22, the change of the molecule velocities can be neglected in a classical description of the effects due to disorienting collisions in a low-pressure molecular gas.

Using the asymptotic values of the $3J$ symbols at $J\gg 1$, we obtain from (2.2) an expression for the matrix element of the interaction with an electromagnetic wave:

$$V_{mn}=-\frac{1}{2J}\sum_{\sigma=\pm1}G_\sigma D^{1*}_{\sigma,\Delta F}(\varphi\theta 0), \tag{5.6}$$

where the dependence on the angles θ and φ is given by Wigner D functions with $\Delta F=F_m-F_n$.

We calculate the work peformed by the traveling wave

$$\mathscr{P}=\frac{\hbar\omega}{6\pi}\,\mathrm{Im}\sum_\xi\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta\,d\theta\langle\rho_\xi(\theta,\varphi)V_{mn}{}^*(\theta,\varphi)\rangle_v \tag{5.7}$$

first for the case of circular polarization, including the first-order corrections for saturation. In addition, we confine ourselves to an approximation in which the Doppler broadening is large, i.e., $k\bar v\gg|\Omega|$, $|\Delta_1|$, Γ, r_j:

$$\mathscr{P}\propto\frac{\sqrt\pi}{k\bar v}\frac{|G|^2}{J}\left\{\exp\left[-\left(\frac{\Omega+\Delta_1}{k\bar v}\right)^2\right]-\frac{3|G|^2}{10J\Gamma}\sum_{j=m,n}\frac{1}{2\gamma_j+\nu_j}\left[1+\frac{5\tilde\nu_j}{9\Gamma_j}L(H)\right]\right\}; \tag{5.8}$$

$$L=\sum_{\xi\xi_1}L_{\xi\xi_1},\quad L_{\xi\xi_1}=2^{-6}\int_0^{\pi}(1-\cos\theta)^2\sin\theta\,d\theta\int_0^{\pi}(1-\cos\theta_1)^2 \tag{5.9}$$

$$\times\sin\theta_1\,d\theta_1\,\mathrm{Re}\{1+i[\Delta_\xi'(\theta)-\Delta_{\xi_1}'(\theta_1)]/2\Gamma\}^{-1},\quad \xi,\xi_1=\alpha,\beta,\gamma;$$

$$\Gamma_j=2\gamma_j+\nu_j-\tilde\nu_j,\quad \Delta_\xi'=\Delta_\xi+(\Delta_{m\xi}+\Delta_{n\xi})/2. \tag{5.10}$$

The dependence of the nonlinear correction to $\mathscr{P}$ for the magnetic field is complicated in form and is determined entirely by the collisional crossing of the Bennett dips in the molecule velocity distribution. The coordinates of the Bennett dips reflect the frequency structure of the resonant optical transitions in a magnetic field with allowance for the hyperfine splitting, and are given by the relations

$$\mathbf{kv}=\Omega-\Delta_\xi'(\theta,H). \tag{5.11}$$

We emphasize that in the absence of collisional disorientation that ensures a coupling between different states of working levels m and n, the nonlinear absorption does not depend on the magnetic field.

The profile of the NMOR induced by molecule collisions is determined by superposition of all possible structures of type $L_{\xi\xi_1}(H)$. It is asymmetric and its shift from the point $H=0$ reverses sign when the direction of the circular polarization of the radiation is reversed. At $\Gamma\gg|a_j|$, $|b_j|$ its parameters are determined by the hyperfine-splitting constants and have a weak pressure dependence. In this case the NMOR profile can be described qualitatively by the relation

$$L(H)=1-f(\delta)/8\Gamma^2;\quad f(\delta)=\mathrm{Re}\int_0^1 b^2(y)\,y^2\,dy, \tag{5.12}$$

$$b(y)=0{,}5\{[(r_n+\delta)^2-4r_n\delta y]^{1/2}-3[(r_m+\delta)^2-4r_m\delta y]^{1/2}+[(r_n+\delta)^2-4r_n\delta y+2r_n\delta/J]^{1/2}+[(r_m+\delta)^2-4r_m\delta y+2r_m\delta/J]^{1/2}\},\quad j=m,n.$$

The sign of the NMOR due to the presence of the hyperfine structure depends on the hyperfine-splitting constants r_j. In particular, for the $P(7)$ branch of the vibrational-rotational transitions of spherical-top molecules the relations (5.9) and (5.12) determine a resonance whose sign differs from that of the usual NMOR.[6–10] In the scale of δ its width and shift are of the same order as those of r_j. The shapes of these resonances are qualitatively similar to the plots of Fig. 3,

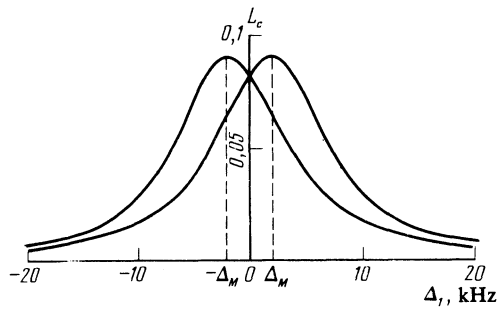

FIG. 4. Nonlinear-interference profiles $L_c(H)$: $r_m = 74.3$ kHz, $r_n = 85.3$ kHz, $\Gamma = 65$ kHz, $g_J = 0.31$, $g_N = 18\,g_J$, $a_j + b_j = -30$ kHz.

calculated from Eq. (5.12) for nonlinar absorption of opposite σ components of radiation in the $F_2^{(2)}$ transition of methane [line $P(7)$ of the ν_3 band]. In this case $r_m = 74.3$ kHz, $r_n = 85.3$ kHz, $g_j = 0.31$, and $g_N = 18 g_J$ (Ref. 19). It follows from (5.11) that the scale $\Delta_1 = \mu_N g_J H/\hbar$ used in the diagrams coincides with the frequency scale.

We now determine the contribution made to the total profile of the NMOR resonant-light-scattering processes due to the presence of two radiative transitions, with selection rule $\Delta F = 0$ in a zero magnetic field; the probabilities of these transitions are smaller by a factor J^2 than the probabilities of the strong lines corresponding to the selection rules $\Delta F = -1$. In the approximation in which the relaxation constants are equal ($2\gamma_j + \nu_j \approx \Gamma$) the profile of the nonlinear resonances due to the indicated processes is of the form

$$L_c(H) = \int_0^1 y^3(1-y)\,dy \sum_{j=m,n} \left(\frac{1}{1+\Delta_{j+}^2/\Gamma^2} + \frac{1}{1+\Delta_{j-}^2/\Gamma^2} \right), \tag{5.13}$$

$$\Delta_{j\pm}(y) = \pm [(r_j+\delta)^2 - 4r_j y\delta]^{1/2} + (a_j+b_j)/2. \tag{5.14}$$

At $\Gamma \sim r_j$ the amplitude of this form is approximately J^2 times smaller than that of ordinary NMOR; in the δ scale, the shift of such a resonance relative to the point $\delta = 0$ is of the order of the parameter r_j, and the approximate width is max (Γ, r_j). Figure 4 shows plots of the $L_c(H)$ contours associated with resonant absorption of oppositely circularly polarized radiation components in the methane transition at $\Gamma = 65$ kHz mentioned above. The amplitude

$$\tilde{\nu}_j (r_m - r_n)^2/6\Gamma_j\Gamma^2 \gg J^{-2} \tag{5.15}$$

of the NMOR induced by collisional mixing of the components of the magnetic hyperfine structure of the levels substantially exceeds the amplitude of the nonlinear-interference resonance. If the absorbed radiation is linearly polarized and $\Gamma \gg |r_m - r_n|$, the NMOR is given by two shapes of different widths. The profile of the narrow component is described at $\delta \sim r_j$ mainly by a superposition of structures of types (5.9). The broad component is approximated at $\Delta \sim \Gamma$ by a superposition of the Lorentzians $(\Gamma^2 + \Delta_1^2)^{-1}$ and $[(\gamma_j + \nu_j/2)^2 + \Delta_1^2]^{-1}$. This is in accord with the NMOR theory that does not take hyperfine splitting into account.[7,10] Just as in linear absorption of light by atoms, the ratio of the amplitudes of the narrow and broad resonances decreases in proportion to Γ^{-2} when the pressure is increased, provided that the level spontaneous decay constants are small compared with the parameters of the collisional relaxation. The widths of the collision-induced narrow magnetooptical resonances produced by absorption of circularly or linearly polarized radiation are determined by the inverse time of interaction between the nuclear spin and the electron shell. In the scale of δ, this inverse time is of the order of the hyperfine splitting interval r_j.

The numerically calculated NMOR profiles shown in Figs. 3 and 4 permit our theory to be compared with experiment, by using the experimental data of Refs. 3 and 4 on the magnetic-field dependence of resonant absorption of circularly or linearly polarized He-Ne laser emission by CH_4 molecules [transition $F_2^{(2)}$, $P(7)$ branch of the ν_3 band]. Modulating the magnetic field strength made is possible to record the first derivative of the function that describes the NMOR profile. Since the methane pressure was varied in the range 3–6 mTorr, the relations $\gamma_j \gg \nu_j \approx \Gamma$ and (5.12) were satisfied for the relaxation constants. In this situation, the final calculated contour is well approximated by the plots of Fig. 3.

In accordance with the present theory, when the radiation was circularly polarized the measured nonlinear-absorption magnetooptic resonance was of opposite sign relative to usual nonlinear spectral structures such as the Lamb dip, and its shift was $\pm\Delta_M$ relative to the point $\Delta_1 = 0$. Without changing absolute value, the shift reversed sign when the polarization of the circular components of the radiation was reversed. The asymmetries of the experimental and calculated profiles are qualitatively the same. In the course of the measurements, the width and shift of the NMOR depended little on pressure, and their recorded values, about 5 kHz, were approximately a factor of ten lower than the homogeneous line width Γ and were quite close to the corresponding parameters of the profiles of Fig. 3. The NMOR deformation due to the change of the gas pressure is described by Eqs. (5.8) and (5.13). For linearly polarized radiation, we observed superposition of the usual broad Lorentz structures $(\nu_j^2/4 + \Delta_1^2)^{-1}$ and the narrow resonances due to the presence of a hyperfine structure in the molecular terms.[4] The previously mentioned decrease of the amplitude ratio of the narrow and broad components was observed with increase of pressure.

The experimental and calculation data are thus qualitatively in agreement within the framework of the model considered.

§6. CONCLUSION

The present results are essentially a generalization of the theory of nonlinear magnetooptical resonances to include transitions having a hyperfine structure. We note that capabilities of the method of inducing hyperfine-structure NMOR, considered in this paper and based on an analysis of the magnetic-field dependence of nonlinear absorption of cw radiation, can be expanded by using trains of synchronized ultrashort laser pulses. This leads to greater narrowing of the nonlinear magnetooptical structures via synchronized flipping of the nuclear spins.[1,2] A similar process is induced in

linear nuclear magnetic resonance by rf pulses.[23] The analysis of the NMOR due to the presence of hyperfine structure in the radiative transitions, can serve as a theoretical basis for new methods of ultrahigh-resolution laser-spectroscopy methods based on the use of nonlinear-optics nuclear magnetic resonance effects.

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