ON THE POLARIZATION DEPENDENCE OF THE CONTOUR OF A SATURATED MOLECULAR ABSORPTION LINE

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Formulas are derived for the population of the upper vibrational state of a molecule excited by a square pulse of linearly or circularly polarized laser radiation that is in resonance with a definite vibrational-rotational transition. Numerical calculations of the behavior of the shape, half-width, and maximum absorption of the line contour as a function of the intensity, width, and polarization of the radiation pulse in models with strong collisions which deorient the molecule and in the absence of deorientation were performed. The qualitative features of the nonstationary saturated absorption are compared with existing experimental facts.

Application of high-power laser pulses in high-resolution molecular spectroscopy[1] enables studying experimentally different nonlinear effects, including saturation of absorption on weak vibrational-rotational (VR) transitions of molecules.[2] Compared with simpler atomic systems, molecules have additional "degrees of freedom" — branching of the VR levels, anisotropy of polarizability, existence of permanent electric and magnetic moments, etc. This results in the appearance of qualitatively new features in the saturation, namely, the degree of saturation of a vibrational transition now depends on, apart from the collisional relaxation constants, the relative population of the rotational levels.[3–5] The characteristic features observed in VR saturated absorption spectra are caused by the nonstationary nature of the interaction of the laser pulses with the molecules.[3,4,6] In strong optical fields molecules are oriented by different physical mechanisms,[7–11] thanks to which the lineshape now depends on the polarization of the laser beam.[10,11]

Experimental investigations of the polarization dependence of the lineshape were performed in Refs. 2 and 12 with the help of the method of laser optoacoustic spectroscopy (LOAS).[13–15] In particular, in measurements of the absorption line contour for the transition $4_{-3}(000) \ldots 5_{-4}(103)$ of H_2O, $\lambda = 694.38$ nm, broadened by air and nitrogen under pressures of 200 ... 400 torr, it was found that as the intensity of the radiation of the ruby laser is increased up to $I = 35$ MW/cm^2 the contour dips by approximately 30% without a change in the case of linear polarization, while for circular polarization there is no change in the contour. At the same time, at the center of the line the absorption of circularly polarized radiation exceeded by approximately 30% the absorption of linearly polarized radiation. The absence of field-induced broadening under conditions of strong saturation of absorption on VR transitions of C_2H_2 and NH_3 molecules was recorded in Refs. 16 and 17 for linearly polarized radiation with the help of the optoacoustic technique. The experimental data cannot be understood on the basis of the standard representations of the saturation in the simplest model of a two-level system and continuous-wave radiation. At the same time, it is difficult to make even a qualitative comparison between the theory applicable to molecules and the data, since the existing theoretical works either describe stationary absorption[5,10,11] or the polarization aspect of the problem is ignored entirely.[3,4,6]

In this paper we study the polarization dependence of the lineshape for saturated absorption on vibrational transitions of molecules in application to the optoacoustic method of recording and we make a qualitative comparison of existing experimental data with the calculations performed.

Analysis of the mechanism of orientation based on the anisotropy of the polarizability of the molecules[7,8] shows that for the molecules studied a significant effect is achieved in laser fields with intensity $I \gtrsim 1$ GW/cm^2 (Ref. 18). For lower values of I this mechanism will affect predominantly the lineshift. For this reason, having in mind the experimental conditions of Refs. 2 and 12, where $I < 100$ MW/cm^2, in what follows we shall concentrate on the direct production of circularly and linearly polarized resonance radiation with different types of anisotropy in the distribution of the population of the levels over the projections of the total angular momentum.[10,11]

In order to obtain the maximum clarity of results, we shall derive the formulas for the lineshape for the case $\tau_{rot} \ll \tau \ll \tau_{VT}$, where τ is the width of the radiation pulse, which is assumed to be square, τ_{rot} is the rotational relaxation time of the molecules, assumed to be the same for the upper and lower vibrational states combining with the field, and τ_{VT} is the vibrational-translational relaxation time of the excited vibrational state. As follows from the ex-

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periment-derived theory of the LOAS method,[13–15] for pulses with this width the spectrophone signal is proportional to the population of the upper vibrational state at the moment the molecule no longer interacts with the radiation, and it is not necessary to take into account vibrational relaxation when performing relative measurements. We shall use the standard balance equations as the basis for describing the dynamics of the populations of the molecular energy levels. For them, we shall use the approximation of high angular momenta.[11] In this approximation, all orientation-dependent quantities appearing in the equations are functions of the angles, which prescribe the direction of the total angular momentum of the molecule. Under the assumptions made and for models of strong rotationally inelastic collisions the balance equations have the form

$$\left.\begin{aligned} \dot N_{2,1}/\gamma + N_{2,1} - S_{2,1} &= \pm\frac{1}{2}\kappa(n_1 - n_2) \\ \dot n_{1,2}/\gamma + n_{1,2} - qS_{1,2} &= \mp\frac{1}{2}\kappa(n_1 - n_2) \end{aligned}\right| \begin{aligned} N_1(0) &= 1, \\ n_1(0) &= q, \\ N_2(0) &= 0, \\ n_2(0) &= 0; \end{aligned} \qquad (1)$$

$$S_{1,2} = \int do' \cdot N_{1,2}(o')\, K(o, o');$$

$$\kappa = \frac{2\sigma_{abs} I}{\gamma\hbar\omega q} = \frac{1}{\gamma\Gamma}\left(d_{12}E/\hbar\right)^2/\left[1 + (\Omega/\Gamma)^2\right],$$

$$\gamma = 1/\tau_{rot},$$

$$\kappa(0) \equiv \kappa_0 = I/I_{sat}, \quad d_{12} = \bar d_{12} f(\theta)/\sqrt{2J},$$

$$f(\theta) = \begin{cases} \cos\theta, & \Delta = \sigma = 0, \\ \dfrac{1}{\sqrt2}\sin\theta, & \Delta = 0,\ \sigma = \pm1 \text{ or } \Delta = \pm1,\ \sigma = 0, \\ \dfrac{1}{2}(1 \pm \cos\theta), & \Delta\cdot\sigma = \pm1, \end{cases}$$

where $n_{1,2}$ are the populations of, respectively, the lower and upper VR levels combining with the field; $N_{1,2}$ are the populations of the vibrational states; $\gamma = 1/\tau_{rot}$ is the rotational relaxation constant, assumed to be independent of the orientation of the molecules; κ is the saturation parameter, which depends on the detuning of the frequency of the laser radiation Ω; q is the relative population of these rotational levels, assumed to be the same for the states 1 and 2; Γ is the rate of decay of the dipole moment induced in the VR transition 1–2; d_{12} is the matrix element of the dipole moment; $\bar d_{12}$ is the reduced matrix element of the dipole moment; σ_{abs} is the cross section for absorption of radiation on this transition by the molecule; ω is the frequency of the laser radiation; E is the intensity of the electric field of the light wave; J is the rotational moment of the lower state; o, o', and θ are singles which prescribe the directions of the angular momenta; Δ is the difference of the values of J for the upper and lower states; $\sigma = 0$ corresponds to linear polarization and $\sigma = \pm1$ corresponds to circular polarization. The kernel $K(o, o')$ prescribes the degree of deorientation of the molecules which absorb radiation in collisions. The form of $K(o, o')$ is simplest in the limiting cases of strong deorientation (a) and complete absence of deorientation (b):

$$K(o, o') = \begin{cases} 1/4\pi & \text{(a)} \\ \delta(o - o') & \text{(b)}, \end{cases} \qquad (2)$$

The approximate analytical solutions of (1) for the models of the kernel and for the range of pulse widths studied are

$$2\langle N_2\rangle = \begin{cases} 1 - \left(1 - \langle K_s\rangle\right)\exp\left(-\langle K_s\rangle\gamma\tau\right), & \text{(a)} \\ 1 - \left\langle\left(1 - K_s\right)\exp\left(-K_s\gamma\tau\right)\right\rangle, & \text{(b)} \end{cases} \qquad (3)$$

$$K_s = q\kappa/(1 + \kappa);$$

$$q^{-1}\langle K_s\rangle = \begin{cases} 1 - \dfrac{1}{\sqrt\kappa}\arctan\sqrt\kappa, \\ \Delta\cdot\sigma = \pm1 \text{ or } \Delta = \sigma = 0, \\ 1 - \dfrac{1}{\sqrt\kappa\sqrt{2 + \kappa}}\ln\dfrac{\sqrt{2 + \kappa} + \sqrt\kappa}{\sqrt{2 + \kappa} - \sqrt\kappa}, \\ \Delta = \pm1,\ \sigma = 0 \text{ or } \Delta = 0,\ \sigma = \pm1. \end{cases}$$

The brackets in Eqs. (3) denote orientational averaging. The numerical calculations showed that the error of the approximation (3) does not exceed 1% for $\tau \geq 10\tau_{rot}$. As $\tau \to 0$ and for $q \ll 1$ the expression for $\langle N_2\rangle$ (3) is identical to the formulas derived in Refs. 10 and 11 for the stationary case, but in a different relaxation model, in which rotational and vibrational relaxation are not distinguished. The contour of the absorption line, in this case, is determined by the dependence $\langle K_s(\Omega)\rangle$.

Figures 1–4 show the results of numerical calculations performed using the formulas (3), which represent the behavior of the shape, the half-width δ, and the maximum amplitude $N_{\max} \equiv \langle N_2(\Omega = 0)\rangle$ of the absorption line contour as a function of the saturation parameter κ_0, the pulsewidth τ, the polarization of the light (linear or circular), and the presence or absence of deorientation. The half-width δ for circular polarization for absorption in the P and R branches (linear for the Q branch) is 4 … 7% smaller than the half-width in the case of linear polarization (circular for the Q branch), corresponding to the same values of the parameters κ_0 and τ, and are not presented in Fig. 2 in view of the insignificance of the difference.

From analysis of the data presented in Figs. 1–4 the following conclusions, characterizing the nonstationary saturation on vibrational transitions of the molecules, can be drawn:

1. The lineshape for the values of the parameters κ_0, τ, and q studied here differs from the Lorentzian lineshape by not more than 3 ... 5%, and in addition the differences are 1.5 ... 2 times larger in the presence of collisional deorientation of the molecules.

2. The half-width of the line δ increases as the square root of the saturation parameter κ_0, and all the more rapidly the larger the pulse width τ and the relative population factor q of the VR levels, are. The formula

$$\delta = \frac{1}{4}\gamma(7 + 2q\gamma\tau)\cdot\sqrt{1 + \kappa_0}, \qquad \gamma\tau \geq 10. \tag{4}$$

is an approximation for δ for the model of strong deorienting collisions for absorption of linearly polarized radiation in the P and R branches.

3. The absorption of linearly polarized radiation in the P and R branches is always higher than in the case of circularly polarized radiation and vice versa in the Q branch. The maximum relative difference η in the absorption of linearly and circularly polarized radiation is observed with $\kappa_0 = 1$ ... 5 and is equal to about 20%. It decreases as the pulsewidth increases in the presence of deorientation and increases insignificantly in the absence of deorientation.

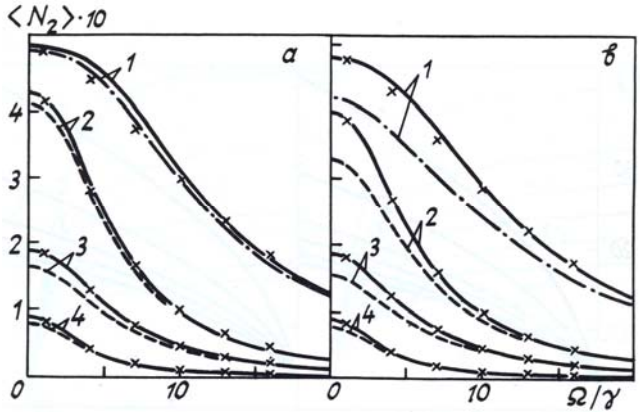

FIG. 1. Contour of a saturated-absorption Line $\langle N_2(\Omega)\rangle$ (3) in the model of strong deorienting collisions (a) and in the absence of deorientation (b); the solid curves correspond to linear polarization in the P and R branches (circular polarization in the Q branch) and the dashed lines correspond to circular polarization in the P and R branches (linear polarization in the Q branch); $\gamma\tau$ = 400 (curves 1, 2), 40 (3, 4); κ_0 = 5 (1, 3), 1 (2, 4); q = 0.02; ××— the Lorentzian contour fit to the curves with linear polarization in P and R branches according to the maximum and half-width at half-height.

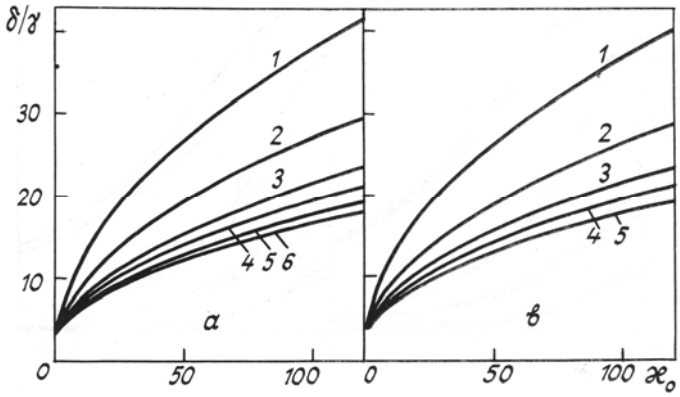

FIG. 2. Half-width of the contour at half-height δ as a function of the saturation parameter κ_0 for linear polarization in the P and R branches with pulsewidths $\gamma\tau$ = 200 (curve 1), 100 (2), 50 (3), 30 (4), and 10 (5) in the case of strong deorienting collisions (a) and in the absence of deorientation (b); the curve 6 (a) represents the half-width of the contour $\langle K_s(\Omega)\rangle$ (3) in the relaxation model of Refs. 10 and 11 for linearly polarized, continuous-wave radiation in the P and R branches; q = 0.02.

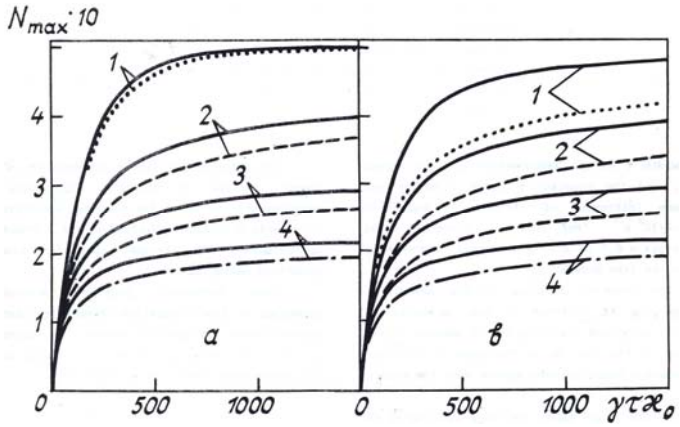

FIG. 3. The absorption at line center $N_{max} = \langle N_2(\Omega = 0)\rangle$ as a function of the product $\gamma\tau\kappa_0$ proportional to the pulse energy, for strong deorienting collisions (a) and in the absence of collisional deorientation (b); the solid lines correspond to linear polarization in the P and R branches (circular polarization in the Q branches); the dashed line is for circular polarization in the P and R branches (linear polarization in the Q branch); $\gamma\tau = 1000$ (curve 1), 100 (2), 50 (3), 30 (4); $q = 0.02$.

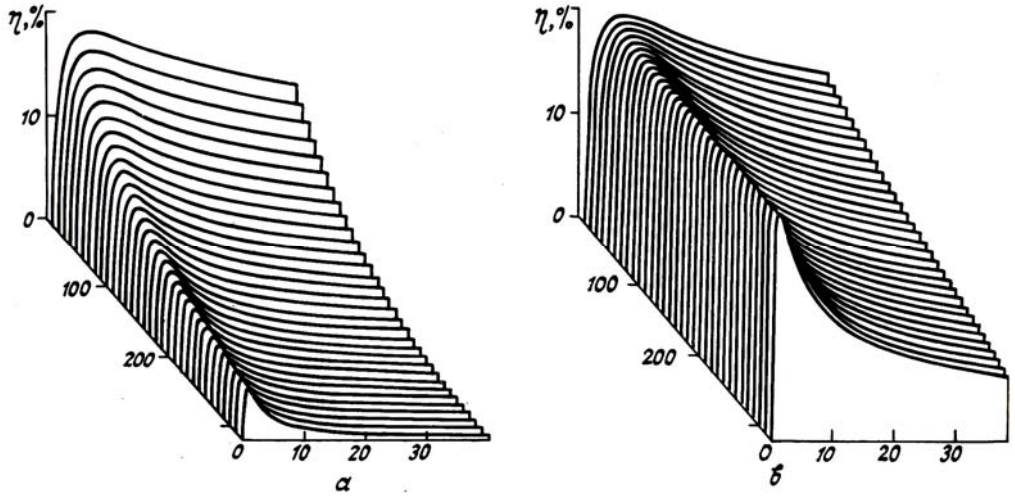

FIG. 4. The relative difference η (in %) of the magnitude of the absorption at line center for linear and circular polarization in the P and R branches (vice versa in the Q branch) as a function of the pulsewidth τ and the saturation parameter κ_0: a) model of strong deorienting collisions, b) absence of deorientation; $q = 0.02$.

4. In accordance with Sec. 3, the degree of saturation of a vibrational transition, which is a measure of how close $N_{\max}$ is to the limiting value $\langle N_2\rangle = 1/2$, is larger for absorption of linearly polarized radiation in the P and R branches (circularly polarized radiation in the Q branch) than for absorption of circularly polarized radiation (linearly polarized in the Q branch). The difference in the degrees of saturation decreases as the pulsewidth increases and the deorientation appears.

We shall compare the qualitative features of the manifestations of saturation, including the polarization dependence of the lineshape, following from the mechanism studied, with what are presently the only experiments[12,2] performed with the help of the LOAS method. The approximations, adopted in the calculations performed, correspond to the conditions of these experiments. The absence of field-induced line broadening in the measurements is completely explained by the small value of the saturation parameter, according to estimates based on the data of Ref. 19 concerning the line strength and the collisional broadening parameters, constituting $\kappa_0 \simeq 2 \cdot 10^{-4}$. We shall estimate the value of the product $q\gamma\tau$, which, according to Eq. (4), can also affect the linewidth. The factor q for the transition studied was calculated in Ref. 6 and is equal to $q = 5.8 \cdot 10^{-3}$. The pulsewidth τ in the measurements did not exceed 50 ns, and the constant γ under a buffer gas pressure (nitrogen) of 270 torr is equal to $\gamma \simeq 3.0 \cdot 10^8$ s^{-1} (Ref. 20). Therefore the product $q\gamma\tau \simeq 8.7 \cdot 10^{-2} \ll 1$ and cannot appreciably affect the line broadening.

The observed decrease in the absorption accompanying an increase in the intensity of linearly polarized radiation in the absence of any changes in the contour in the case of circular polarization qualitatively agrees with the result of Sec. 4.

On the other hand, the very low degree of saturation of absorption, realized in the experiment, practically completely nullifies the polarization dependence of the line contour caused by the mechanism under study. For the same reason, the dipping of the contour, associated with saturation of absorption, also should not be observed.

In addition, a strong consequence of the theory (result 3) directly contradicts the measurements, in which the recorded absorption of circularly polarized radiation in the P branch was approximately 25% stronger than for linearly polarized radiation.

Thus different physical mechanisms, appearing at lower radiation intensities than the nonstationary saturation effect in molecular systems, must obviously be used to explain all of the experimental facts as a whole.[12,2]

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