SHAPE OF SATURATED OPTOACOUSTIC ABSORPTION LINE FOR VIBRATIONAL-ROTATIONAL TRANSITIONS OF MOLECULES

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Simple analytical expressions are derived for the time dependent population of the upper vibrational state of a molecule excited by a square pulse of resonance laser radiation with arbitrary intensity. Taking into account vibrational relaxation for truncated and infinite systems of levels made it possible to extend the range of applicability of the formulas to the case of wide pulses. It is shown that if the relative-population factor of the rotational levels combining with the field is much larger than the ratio of the rotational and vibrational relaxation times, then saturation of absorption on a vibrational transition is achieved much more easily with wide pulses than short pulses.

The method of laser optoacoustic spectroscopy (LOAS) has undergone significant development in the last ten years.[1–3] The application of this method in the spectroscopy of atmospheric gases, using pulsed ruby lasers and CO_2 lasers, enabled B.G. Ageev et al.[14] to observe definite deviations from linear absorption of light by H_2O and CO_2 molecules. The existing experimental data show that LOAS can be used to study nonstationary excitation of vibrational transitions of molecules, which processes are nonlinear in the intensity of the laser radiation.

The theory of such processes, as it would apply to the characteristics of the method, has not been adequately developed. In particular, in Refs. 5–8 the vibrational relaxation of molecules was neglected; this limits the theory to the case of narrow pulses. In Refs. 10 and 11, on the other hand, only the stationary nonlinear spectroscopy of molecules was studied. The approximation adopted in Ref. 9 in order to take into account the vibrational relaxation is suitable only for the regime of weakly saturated absorption.

In this paper we derive formulas for the shape of an optoacoustic absorption line. These formulas take into account the vibrational relaxation of molecules and are suitable for comparing with experiments in a wide range of pulse widths and intensities of laser radiation.

As follows from the instrumentational theory of the method,[1–4] the starting quantity in the calculations of the recorded spectrophone signal is the time dependence of the total population of the upper vibrational level of a molecule excited by the laser pulse. We shall derive the expressions for $N_2(t)$ in the following standard approximat ions:

1) The radiation pulse is described by a segment of a cosinusoid of width τ with a uniform spatial distribution of the intensity across the beam.

2) The balance equations in models of relaxational constants and strong vibrationally inelastic collisions can be used to describe the dynamics of excitation of a molecule. This determines the lower limit on the pulse width $\tau > (3-5)\Gamma^{-1}$, where Γ^{-1} is the lifetime of the dipole moment induced by the field on the vibrational-rotational (VR) transition under study.

3) Radiative relaxation can be neglected compared with collisional relaxation, while rotational relaxation proceeds with the same rates $\gamma = 1/\tau_{rot}$ in all states.

Vibrational relaxation can proceed according to different schemes, depending on the specific molecules and the transition. We shall focus on two simple cases: closed and open schemes with two vibrational states.

The closed scheme can be represented in the form of the ground (1) and excited (2) vibrational states with the corresponding networks of rotational levels. The laser radiation couples two rotational levels with populations n_1 and n_2, which belong to the lower and upper vibrational states, respectively. We shall assume that under equilibrium conditions only the ground vibrational state is populated before the laser pulse appears.

Under the foregoing assumptions the system of balance equations has the following form:

$$
\begin{array}{l|l}
\dot{N_2}/\gamma + \varepsilon N_2 = \frac{1}{2}\kappa\left(n_1 - n_2\right) \equiv G & N_2(0) = n_2(0) = 0 \\[2mm]
\dot{N_1}/\gamma - \varepsilon N_2 = -G & N_1(0) = 1 \\[2mm]
\dot{n_1}/\gamma + n_1 - qN_1 - \varepsilon qN_2 = -G & n_1(0) = q \\[2mm]
\dot{n_2}/\gamma + n_2 - qN_2 - \varepsilon n_2 = G &
\end{array}
\tag{1}
$$

$$
\kappa = \frac{2\sigma I}{\gamma\hbar\omega q} = \frac{I}{I_{sat}} = \frac{1}{\gamma\Gamma}\left[\frac{d_{12}E}{\hbar}\right]^2\left[1 + (\Omega/\Gamma)^2\right]^{-1};
$$

$$
\varepsilon = \gamma_{VT}/\gamma,
$$

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where ω is the frequency of the laser radiation, Ω is the detuning of the laser frequency from the frequency of the resonance VR transition, d_{12} is the matrix element of the dipole moment of the given VR transition, q is the relative population of the rotational levels studied, and is assumed to be identical for both vibrational states, E and I is the intensity of the electric field and the intensity of the laser radiation, σ is the cross section for absorption of light on a given VR transition, I_{sat} is the intensity of saturation of absorption, $\gamma_{VT} = 1/\tau_{VT}$ is the rate of vibrational-translational relaxation, and ε is the ratio of the rotational and vibrational relaxation times. The quantity $\kappa = \kappa(\Omega)$ is the saturation parameter of an individual VR transition and depends on the detuning of the frequency.

The exact solution of Eq. (1) is

$$N_2(t) = \frac{1}{2} q\kappa F(t),\qquad(2)$$

$$F(t) =$$

$$= \begin{cases} (1 + \varepsilon)/\prod_{i=1}^{3} s_i - \sum_{i=1}^{3}(1 + \varepsilon - s_i)(1 - s_i)(p_i/s_i) \\ \qquad \times e^{-s_i \gamma t}/\prod_{i=1}^{3} p_i, \quad 0 \le t \le \tau, \\ F(\tau)\exp\left[-\gamma_{VT}(t - \tau)\right], \quad t \ge \tau, \end{cases}$$

$$p_1 = s_2 - s_3, \quad p_2 = s_1 - p_3, \quad p_3 = s_1 - s_2,$$

where s_i, $i = 1-3$, are the roots, taken with a minus sign, of the characteristic equation

$$s^3 + as^2 + bs + c = 0;\qquad(3)$$

$$a = 2 + \kappa + 2\varepsilon; \quad b = 1 + 3\varepsilon + \varepsilon^2 +$$

$$+ \kappa\left[1 + \frac{3}{2}\varepsilon + q - \frac{1}{2}\varepsilon q\right];$$

$$c = \varepsilon + \varepsilon^2 + \kappa\left[\varepsilon + q + \frac{1}{2}\varepsilon^2 - \frac{1}{2}\varepsilon^2 q\right].$$

For $\gamma t \le 1$ the expression (2) for $F(t \le \tau)$ can be represented with a relative error $\le 4\%$ in the form

$$F(t) = \gamma t + \frac{1}{2}(\gamma t)^2\left(2 + \varepsilon - s_1 - s_2\right) + \frac{1}{6}(\gamma t)^3 \times$$

$$\times (1 + \varepsilon - s_1)(1 - s_1)(s_1^2 p_1 - s_2^2 p_2 + s_3^2 p_3)/(p_1 p_2 p_3).$$
$$(4)$$

It follows from Eqs. (4) and (2) that for pulse widths τ less than the rotational relaxation time τ_{rot}, taking into account only the main term in the expansion of $F(t)$ (4) $N_2(\Omega) \simeq 1/2 q\kappa(\Omega)\gamma t$, i.e., the absorption line contour is completely determined by the dependence $\kappa(\Omega)$ and there is not enough time for the vibrational transition to be saturated even with high radiation intensities $I > I_{sat}$.

Using the smallness of ε, $q \ll 1$,[1-4] we can obtain the following approximate solutions of the cubic equation (3):

$$\begin{cases} s_1 = \varepsilon + \kappa q; \\ s_2 = 1 + \frac{1}{2}(\kappa + \varepsilon - Q) - \frac{1}{2}\kappa q - \frac{1}{4}(\kappa - \varepsilon)Q; \\ s_3 = 1 + \frac{1}{2}(\kappa + \varepsilon + Q) - \frac{1}{2}\kappa q + \frac{1}{4}(\kappa - \varepsilon)Q; \\ \qquad\qquad q \ll 1, \ 0 \le \kappa \sim \varepsilon; \\ \qquad Q = \sqrt{\kappa^2 + \varepsilon^2}; \end{cases}$$
$$(5)$$

$$\begin{cases} s_1 = \varepsilon + q\dfrac{\kappa}{1+\kappa} - \dfrac{\varepsilon^2}{1+\kappa} - \dfrac{1}{2}\varepsilon q\dfrac{\kappa^2}{(1+\kappa)^2} + \\ \qquad + q^2\dfrac{\kappa^2}{(1+\kappa)^3}; \\ s_2 = 1 + \dfrac{1}{2}\varepsilon + \dfrac{3}{4}\dfrac{\varepsilon^2}{\kappa}; \\ s_3 = 1 + \kappa + \dfrac{1}{2}\varepsilon - q\dfrac{\kappa}{1+\kappa} - \dfrac{1}{4}\varepsilon^2\dfrac{3-\kappa}{\kappa(1+\kappa)} \\ \qquad + \dfrac{1}{2}\varepsilon q\dfrac{\kappa^2}{(1+\kappa)^2} - q^2\dfrac{\kappa^2}{(1+\kappa)^3}, \ \varepsilon, \ \varepsilon^2/q \ll \kappa \end{cases}$$
$$(6)$$

Substituting Eq. (6) into Eq. (2) we obtain

$$N_2(t) = \begin{cases} \frac{1}{2}r\dfrac{\kappa}{1+\kappa(1+r)}\left[1 - \exp\left(-\dfrac{1+\kappa(1+r)}{1+\kappa}\times\right.\right. \\ \qquad\left.\left. \times \gamma_{VT}t\right) + O(\varepsilon, q)\right], \quad 0 \le t \le \tau; \\ N_2(\tau)\exp\left[-\gamma_{VT}(t - \tau)\right], \ t \ge \tau; \ r \equiv q/\varepsilon. \end{cases}$$
$$(7)$$

In the case when Eqs. (5) are applicable, the formula for $N_2(t)$ follows from the expression Eq. (7), if terms $\sim \kappa$ are neglected in Eq. (7) compared with unity.

In analyzing the characteristics of saturation in the line wings the fact that the formula (7) is valid for frequency detunings Ω determined by the relation

$$\Omega^2 \ll \Omega_m \equiv \Gamma^2\kappa_0/\max(\varepsilon, \ \varepsilon^2/q); \quad \kappa_0 \equiv \kappa(0).\qquad(8)$$

must be taken into account. In the case $\Omega \ge \Omega_m$ Eq. (5) and the corresponding modification Eq. (7), stipulated above, must be used.

Considering the solution (7) at the times

$$\tau_{rot} < t \ll t_s \equiv 1/(\gamma_{VT} + q\gamma) = \tau_{VT}/(1 + r),\qquad(9)$$

we obtain from Eq. (7)

$$N_2(t) \simeq \frac{1}{2}q\gamma t\dfrac{\kappa}{1+\kappa} = \frac{1}{2}q\gamma t\kappa_0\Gamma^2/[\Gamma^2(1 + \kappa_0) + \Omega^2]^{-1},$$
$$t \le \tau.\qquad(10)$$

The frequency dependence of $N_2(\Omega)$ (10) is identical to the Karplus-Schwinger line shape[12] for

saturated absorption on a two-level transition. The saturation parameter κ_0 in this case, is determined by the characteristics of an individual VR transition, i.e., by the quantities I, d_{12}, Γ, and γ (1).

In the case $t \gg t_s$ the expression (7) reduces to the stationary limit

$$N_2(t) = \frac{1}{2} r \frac{\kappa}{1 + \kappa(1 + r)} , \quad t_s \ll t \leq \tau. \quad (11)$$

The shape of the absorption line once again acquires the Karplus-Schwinger form, but with a saturation parameter that is $1 + r$ times larger than κ_0. Therefore, in the case of slow vibrational relaxation, when $r \gg 1$, saturation of the vibrational transition is achieved with the help of pulses with width $\tau \geq t_s$ at significantly lower intensities than for narrower pulses. In this case, the quantity $\gamma_{VT}/q \ll \gamma$ appears in the saturation parameter instead of the rotational relaxation constant γ.

We note that the characteristic time t_s (9), which controls the transition to the limiting cases (10) and (11), can be much shorter than the vibrational relaxation time, if the vibrational relaxation is much slower than the rotational relaxation. This is certainly the case if $\gamma_{VT} \ll \gamma q$, $\varepsilon \ll q(r \ll 1)$. This circumstance, as well as possibly the significant difference between the saturation parameters for narrow and wide pulses, must be taken into account, in particular, when determining the population factor of VR transitions of molecules by the method, proposed in Ref. 6, of saturation of absorption with laser radiation.

The open scheme of levels differs from the closed one by the fact that the vibrational states 1 and 2 of interest lie next to one another and the population is constantly being redistributed between them owing to collisions, which equilibrate the system. We shall also assume that the lower state 1 is not the ground state.

The system of balance equations for the populations under the indicated conditions, and using the previous notation, has the form

$$\dot{N}_2/\gamma + \varepsilon\left(N_2 - N_2^0\right) = \frac{1}{2}\kappa\left(n_1 - n_2\right) \equiv G \quad \bigg| \quad N_1(0) = N_1^0$$
$$\dot{N}_1/\gamma - \varepsilon\left(N_1 - N_1^0\right) = -G \quad \bigg| \quad N_2(0) = N_2^0$$
$$\dot{n}_1/\gamma + (1 + \varepsilon)n_1 - q\left(N_1 - \varepsilon N_1^0\right) = -G \quad \bigg| \quad n_1(0) = qN_1^0$$
$$\dot{n}_2/\gamma + (1 + \varepsilon)n_2 - q\left(N_2 - \varepsilon N_2^0\right) = G \quad \bigg| \quad n_2(0) = qN_2^0$$
$$(12)$$

where $N_{1,2}^0$ are the equilibrium values of the populations of the vibrational states 1 and 2. The exact solution of this system is

$$\Delta N_2(t) \equiv N_2(t) - N_2^0 = \frac{1}{2}\left(N_1^0 - N_2^0\right)q\kappa F(t),$$

$$F(t) = \begin{cases} \dfrac{1 + \varepsilon}{s_1 s_2} - \dfrac{1 + \varepsilon - s_1}{s_1\left(s_2 - s_1\right)} e^{-s_1 \gamma t} + \dfrac{1 + \varepsilon - s_2}{s_2\left(s_2 - s_1\right)} \\ \quad \times e^{-s_2 \gamma t}, \quad 0 \leq t \leq \tau, \\ \\ F(\tau) \exp\left[-\gamma_{VT}(t - \tau)\right], \quad t \geq \tau; \end{cases}$$
$$(13)$$

$$s_{1,2} = \frac{1}{2} b \mp \sqrt{b^2/4 - c},$$

$$b = 1 + \kappa + 2\varepsilon, \quad c = \varepsilon + \varepsilon^2 + \kappa(\varepsilon + q).$$

The expansion of the exponential in Eq. (13) for $\gamma t \ll 1$ gives

$$F(t) \simeq \gamma t + \frac{1}{2}(\gamma t)^2\left(1 + \varepsilon - s_1 - s_2\right), \, 0 \leq t \leq \tau.$$
$$(14)$$

Calculation of $s_{1,2}$, which are the roots of the quadratic characteristic equation, using the facts that ε, $q \ll 1$ and substituting them into the expression for $F(t)$ Eq. (13), gives a formula for $\Delta N_2(t)$, whose accuracy is the same as that of Eq. (7) up to terms of order $O(\varepsilon, q)$. Thus the formulas (7)−(11) and the results following from them regarding the character of the saturation also remain valid for the open system of two vibrational states. The *a priori* not obvious fact that the main characteristics of the saturation VR transitions of molecules do not depend on the vibrational relaxation scheme indicates that the saturation mechanism is determined primarily by the existence of two relaxation channels − fast (rotational relaxation) and slow (vibrational relaxation).

The situation studied above is characterized by Lorentzian (collisional) line broadening. At low pressures of the broadening gases, however, Doppler broadening, when γ_{VT}, γ, $\Gamma \lesssim k \bar{\upsilon}$, where k is the wave number of the radiation and $\bar{\upsilon}$ is the average thermal velocity of the absorbing molecule, predominates. The formulas (2), (4), (7), (10), (11), (13), and (14) must be averaged over the velocities υ. This averaging is performed by replacing in $\kappa(\Omega)$ the frequency detuning Ω by $\Omega - k \upsilon$ and integrating over υ from $-\infty$ to $+\infty$ the expressions $N_2(\upsilon)$ and $\Delta N_2(\upsilon)$ multiplied by Maxwell's velocity distribution $W_M(\upsilon) = \exp[-(\upsilon/\bar{\upsilon})^2]/\sqrt{\pi}\,\bar{\upsilon}$.

Next, we shall derive a formula for the recorded spectraphone signal. As is well known,[1–4] the electric signal of the spectraphone is proportional to the maximum pressure increment ΔP produced when the energy of excitation of the molecules by the laser pulse is converted into heat. The time dependence $\Delta P (t)$ is described by the equation[13,3,8]

$$\frac{d\Delta P}{dt} = \frac{2}{3}\hbar\omega\gamma_{VT}N(t) + \gamma_T\Delta P, \quad (15)$$

where $\gamma_T = 1/\tau_T$ is the thermal relaxation rate of the spectraphone and $N(t)$ is the density of excited molecules, determined by the expressions for $N_2(t)$ and $\Delta N_2(t)$. We shall represent $N(t)$ in the form

$$N(t) = \frac{1}{2}\, nq\kappa F(t),$$

$$F(t) = \begin{cases} k_0 - \sum_{i=1}^{m} k_i \, \exp(-s_i \gamma t), & 0 \le t \le \tau \\ F(\tau)\, \exp[-\gamma_{VT}(t - \tau)], & t \ge \tau, \end{cases}$$

(16)

where n is the density of absorbing molecules in the ground state in the case of the closed scheme of levels and the difference of the populations of the molecules in the vibrational states 1 and 2 for the open scheme in equilibrium; the quantities m, k_1, s_1, $I = 0 - m$ are determined by the formulas (2), (5), (6), and (13). After this, we find the maximum value of the solution (15) ΔP_{max}:

$$\Delta P_{max} = \alpha(1 - \beta)A(\beta A/B)^{\frac{1}{1-\beta}} ;$$

(17)

$$\alpha = \frac{1}{3}\, \hbar\omega nq; \quad \beta = \gamma_T/\gamma_{VT};$$

$$B = F(\tau)/(1 - \beta); \quad A = B + \tilde{F}(\tau);$$

$$\tilde{F}(\tau) = \gamma_{VT} \int_0^{\tau} F(t)\, e^{\gamma_T t}\, dt = k_0\left[e^{\gamma_T t} - 1\right]/\beta -$$

$$- \varepsilon \sum_{i=1}^{m} \frac{k_i}{s_i - \beta\varepsilon} \left\{ 1 - \exp\left[- (s_i\gamma - \gamma_T)\tau\right] \right\} .$$

For $\beta \ll 1$ the expression (17) for ΔP_{max} can be represented approximately as

$$\Delta P_{max} \simeq \alpha\kappa A[1 + \beta\, \ln(A\beta/Be)].$$

(18)

Next, we shall make some numerical estimates of τ_T, ε and q. As follows from Ref. 3,

$$\tau_T \simeq 0.174\rho R^2 C_v/K,$$

(19)

where ρ is the density of the gas being excited, R is the radius of the spectraphone cell, C_v is the heat capacity of the gas at constant volume, and K is the thermal conductivity of the gas. Substituting into Eq. (19) the tabulated values of C_y and K, for $T = 273$ K, $R = 0.5$ cm, and broadening by air we have $\tau_T = 0.16$ s · atm^{-1} · P, where P is the gas pressure. Taking as the characteristic values for the absorbing gas $\gamma_{VT} \simeq 10^{-8}$ s^{-1} · atm^{-1} · P,[4] we obtain $\beta \simeq 1.6 \cdot 10^{-7}$ at $P = 1$ atm and $\beta = 1$ at

$P = 4 \cdot 10^{-4}$ atm = 0.3 Torr. Since, as mentioned above, the balance equations are applicable for $\tau \gtrsim (3-5)\, \Gamma^{-1}$, setting $\Gamma \simeq 2\pi \cdot 0.1$ cm^{-1} · atm^{-1} · P, we obtain $\tau \gtrsim 2 \cdot 10^{-10}$ s · atm$/P$, i.e., the equality $\beta = 1$ is achieved for $\tau \ge 0.5\, 10^{-6}$ s. For narrower pulses, for example, $\tau = 10^{-8}$ s, the $\beta \lesssim 0.5\, 10^{-2}$ for P $\gtrsim 15$ Torr. Thus, in many cases, the formula (18), retaining only the first term in it, can be used for the spectraphone signal.

For most molecules under atmospheric conditions $\gamma \sim 10^9$ s^{-1}. From here, for the value of γ_{VT} given above, we have the typical values $\varepsilon \cong 10^{-3}$.

For linear molecules the parameter q is given by the expression (see, for example, Ref. 14):

$$q = \frac{Bhc(2J + 1)}{k_B T} \exp\left[- BhcJ(J + 1)/k_B T\right].$$

(20)

Here J is the rotational moment of the molecule, k_B is Boltzmann's constant, and B is the rotational constant. For example, for the laser transition 10°0–00°1 CO_2, $\lambda = 10.6$ μm, for $J = 20$, $B = 0.39$ cm^{-1}, (Ref. 15) and $T = 293$ K Eq. (20) gives $q \simeq 3.5 \cdot 10^{-2}$. Since γ_{VT}^{-1} ($CO_2 \simeq 1 \cdot 10^{-5}$ s · atm$/P$, (Ref. 16) we obtain $r = q/\varepsilon \simeq 3.5 \cdot 10^2 \gg 1$. The last inequality means that this transition in CO_2 is approximately two orders of magnitude easier to saturate with pulses longer than $t_s = \gamma_{VT}/(1 + r) \simeq 3 \cdot 10^{-8}$ s$/P$ atm) than with significantly narrower pulses.

An analogous estimate of q for the transition $4_{-3}(000)–5_{-4}(103)$ H_2O, $\lambda = 694.38$ nm, is based on the formula[17]

$$q = \frac{g_i}{Z} \exp(- E_1/k_B T), \quad g_i = 2 - (-1)^{\tau_i},$$

(21)

$$Z = 2\left[\pi\left(k_B T/hc\right)^3/(ABC)\right]^{1/2} \exp\left[hc(BC)^{1/2}/4k_B T\right],$$

where τ_1 is the quantum number of an asymmetric top, referring to the ground state, $E_1 = 224.838$ cm^{-1} (Ref. 18) is the energy of the lower level $4_{-3}(000)$, $A = 27.88$ cm^{-1}, $B = 14.52$ cm^{-1} and $C = 9.28$ cm^{-1} (Ref. 18) are the rotational constants of the H_2O molecule. For $T = 293$ K the factor $q = 5.8 \cdot 10^{-3}$. Data on the vibrational relaxation rate of the state 103 of H_2O exist only for pure water vapor with no buffer gases.[19] According to Ref. 19 $\gamma_{VT} \simeq 4.2 \cdot 10^{-8}$ s·atm$/P$. Assuming that in the atmosphere the relaxation rate of the state 103 is not less than 1% of the rate in pure water vapor[4] and using the value $\tau_{rot} \simeq 10^{-9}$ s · atm$/P$, we obtain $\varepsilon \gtrsim 4 \cdot 10^{-3}$ and $r \le 1$. Therefore, in this situation there is no order of magnitude difference, like in the case of CO_2, in the saturation parameters of the transition under study for $\tau > t_s$ and $\tau < t_s$.

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